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AN EXPERIMENTAL STUDY OF TRANSITION METAL HALIDES, DIRECTED
TOWARDS THE TEST OF A STEREOCHEMICAL THEORY

by

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This thesis contains no material previously submitted for a degree or diploma in any University, and, to the best of my knowledge, contains no material previously published or written by any other person, except where due reference is made.

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SUMMARY

This work is an attempt to test a stereochemical theory based on interatomic-core repulsion as applied to molybdenum and tungsten in oxidation states 2, 2.5, 3 and 4. The theory is most powerful as a predictive tool when applied to binary and ternary staphylonuclear compounds, hence an exhaustive preparative survey was undertaken to find new compounds of these types with novel structures. The results of this survey follow.

Several new halogenomolybdate (II) and halogenomolybdate (2.5) compounds were prepared. Analytical evidence, as well as physical properties of these complexes (magnetic susceptibility, spectroscopy, X-ray powder diffraction and molecular weight determination), shows that the previously assigned structure for the halogenomolybdates (II), based on the trimeric $\text{Mo}_3\text{Cl}_{13}^{3-}$ unit, is in agreement with this present work. For chloromolybdates (2.5) a structure of the $\text{W}_2\text{Cl}_9^{3-}$ type seems more likely than the originally proposed $\text{Mo}_4\text{Cl}_{16}^{6-}$ unit in the light of spectral and X-ray data. This is in agreement with theoretical prediction.

Attempts to prepare new staphylonuclear complexes of tungsten in low oxidation states were unsuccessful. It was hoped that a study of compounds containing the $\text{W}_6\text{Cl}_8^{4+}$ and $\text{W}_6\text{Br}_8^{4+}$ units might lead to such a discovery.

The chemistry and structure of compounds containing the $W_6Cl_8^{4+}$ unit was found to be closely analogous to that of the $Mo_6Cl_8^{4+}$ unit except for the former's lesser stability under all conditions. Some adducts of "tungsten dibromide" were prepared and formulated as $W_6Br_8 \cdot Br_4 \cdot 2L$, but with many coordinating ligands tried, compounds with $W:Br$ ratios < 2 were prepared. This is rationalized by proposing substitution of the peripheral bromines by ligand. In this study no compounds were found containing anything but the $W_6X_8^{4+}$ unit.

The iodides W_6I_{12} and W_6I_{14} are reported.

Disproportionation of molybdenum and tungsten tetrahalides has been investigated as a new preparative method for ternary staphylonuclear complexes. The properties and structures of $M_3Mo_2X_9$, $M_2Mo_2X_8$, $M_3W_2X_9$ and $W_2Cl_4(CH_3O)_4(CH_3OH)_2$ etc. prepared in this study have been investigated and the results agree with theoretical prediction. Proposed structures for the tetrahalides are also discussed.

The theory predicts that the compound $MoCl_4[(C_6H_5)_3AsO]_4$ cannot exist. The report of this has been examined and it was found that under the same experimental conditions the product is not of reproducible composition and, indeed, is not a molybdenum (IV) adduct at all. Attempts to prepare this complex by other methods have failed, the only product that appears is the bis adduct.

An account of the development of the theory and nomenclature for staphylonuclear compounds now in use is given by way of introduction.

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CHAPTER 1. INTRODUCTION

The principal aim of this research is to test a theory whose model is based on intercore repulsion. Since it was first developed for use with complexes containing metal-metal bonds, the testing of the theory has been carried out in this area with one exception (see Chapter 2).

The novel bonding characteristics and properties of compounds containing direct metal-metal bonds has stimulated great interest in these compounds over the last decade, and several excellent reviews^{1,2,3,4} which discuss in detail these types of complexes have appeared recently. No attempt will be made in this thesis to elaborate on these, other than by short introduction to the individual chapters.

At this time the terms "staphylonuclear" and "metal cluster" are both used to describe these compounds. In this work "staphylonuclear" will be used, and a staphylonuclear compound is defined as one containing a finite group of metal atoms which have significant interaction between each other.

Conventional stereochemical theories are unable to predict and explain the existence of staphylonuclear compounds. They rely on the classification of compounds into groups depending on bond type, (i.e. covalent, ionic or metallic) to make any stereochemical prediction. Therefore the existence of compounds containing both "ionic" metal-halogen and "metallic" metal-metal bonds is incompatible according to these theories.

It seems reasonable that a theory of stereochemistry could be formulated by consideration of atomic nuclei without reference to bond type. Such a theory would be applicable to all chemistry, rather than for small areas as do conventional theories. Such a theory has been developed by Sheldon,³ but is, as yet, unpublished. A short summary of its derivation follows.

A THEORY OF COORDINATION NUMBER BASED ON
INTERATOMIC CORE REPULSION

INTRODUCTION

(1) Significance of Pauling Electronegativity

Pauling⁶ has stated that each element's physical and chemical properties can be correlated by a parameter, χ , which is related to the bond energies (D) for elements A and B by

$$D_{AB} - \frac{1}{2} (D_{AA} + D_{BB}) = \Delta = (\chi_A - \chi_B)^2 \quad \dots (1)$$

Since D is in electron volts χ has the dimensions of $(\text{energy})^{\frac{1}{2}}$

The usual physical interpretation of χ is the ability of an atom to attract bonding electrons (i.e. negative charge). An equally plausible interpretation is the ability of an atom to repel positive charge i.e. neighbouring atomic cores. The second interpretation is chosen because it accounts for the origin of equation (1) (the

first interpretation does not), the properties of χ , and allows stereochemical predictions to be made.

(ii) Evaluation of χ

To enable wide use of this concept to be made it is essential to be able to calculate χ for those elements whose single bond dissociation energies are not known.

Using Cottrell and Sutton's⁷ relationship, ($C_{AB} = \frac{1}{2} (C_{AA} + C_{BB})$; $C =$ electronic binding energy) it may be derived that

$$\chi_A = Z_{NA}^* / 2r_A^{\frac{1}{2}} \quad \dots(2)$$

where Z_{NA}^* is the effective positive charge experienced by another positive charge at distance r_A .

It has been found that this equation, when modified to

$$\chi = k \frac{Z^*}{n^{\frac{1}{2}}} \quad \dots(3)$$

where n^* is the Slater effective quantum number, $k = 1.48eV^{\frac{1}{2}}$ and

Z^* is the effective nuclear charge

gives χ values in good agreement with empirical values and can be used to determine χ values for elements whose single bond dissociation energies are not known.

(111) The Relationship Between Internuclear Repulsion and Coordination Number (CN)

Because all elements do not adopt a close packed array (i.e. high CN) in the elemental state, there must exist a restraint that permits only low CN in some cases (e.g. N_2). It is proposed that this restraint is internuclear repulsion and therefore is a function of χ .

The theory has developed by assuming that $2\chi_A\chi_B$ is a measure of the effective internuclear repulsion energy (EIE) for AB, provided that the AB distance is normal. If A displays a stable CN of n towards B and towards itself of m , then the total EIE of the coordination sphere of A in AB_n or elemental A is $2n\chi_A\chi_B$ or $2m\chi_A^2$ respectively. It was found that this value is approximately constant for all elements with $2n\chi_A\chi_B \sim 40\text{eV}$ and this therefore becomes a useful equation for predicting CN

THE MODEL

The molecule will be viewed as a continuum of valence electrons surrounding the atomic cores, with EIE providing the restraint to complete coalescence of the atoms. The model assumes that the coordination sphere EIE is constant for most atoms, but since it is not measurable, values must be chosen on an ad hoc basis, however only a few choices need be made to correlate a large field of chemistry.

The model assumes

(i) EIE for an AB contact is $2\alpha_{AB} \chi_A \chi_B$ where α_{AB} corrects for the disparity of the bonding radii of A and B - this can be calculated, but it has been found that its inclusion does not significantly affect the results, thus it is neglected.

(ii) The equation for an actual compound is

$$2m\chi_A^2 + 2n\chi_A\chi_B + 2p\chi_A\chi_C + \dots = H_A \dots (6)$$

where m, n, p etc. are the CN of A with respect to A atoms, B atoms, C atoms, etc.

(iii) χ values are either calculated (equation 1) or obtained experimentally - the actual values, of course, depend on valence state.

(iv) χ is a function of interatomic distance because of its dependence on Z^{\oplus} . Thus χ values are only appropriate to the contact radii displayed in the measured systems.

PREDICTIVE ABILITY

(i) Binary Halides

It is found that H_A (equation 4) is a characteristic constant for a particular class of compounds. The following values chosen for halides are examples of the ad hoc choices for H_A .

Compound type	H_A
transition metal chlorides	66 [†]
" " bromides	60.5
" " iodides	52

Equation 4 for binary halides becomes $2nx_M^2 + 2nx_MX_X = H_A$ and on substituting H_A values for the class of compounds under consideration, and fixing either n or n_x values for the unknown CN can be computed. It becomes immediately obvious that several combinations of CN may be possible for any one chemical constitution. As an example Table 1.1 shows the CN predicted for the molybdenum chlorides. As can be seen the theory accounts for a number of molybdenum-chlorine structures.

Observations and Predictions

- (1) The existence of $MoCl_6$ is marginal - if prepared it should be unstable. A short and unauthenticated note on its existence has been published.⁹
- (2) $MoCl_5$ contains no metal-metal interaction - crystal structure determination has verified this.¹⁰
- (3) $MoCl_4$ consists of chains of $MoCl_6$ octahedra with some interaction

[†] The value chosen here is not the same as that reported⁸ in a recent publication because the theory has since been modified.

TABLE 1.1

COORDINATION NUMBERS IN MOLYBDENUM CHLORIDES

PREDICTED BY THEORY

Chloride	Mo valence state	χ_{Mo}	Mo-Mo CN (n)	Cl:Mo CN (n)
MoCl ₆	6	1.76	~ .1	(6)
MoCl ₅	5	1.70	.3	(6)
MoCl ₄	~ 4.5 ^a	~ 1.67	~ .5	(6)
MoCl ₄	6		1.7	(5)
MoCl ₃	6	1.63	.8	(6)
MoCl ₃	6		2.7	(5)
MoCl ₂	6	1.50	2.0	(6)
MoCl ₂	6		4.2	(5)

^a this value is chosen because some d electrons are used in metal-metal bonding (lower magnetic susceptibility than expected for 2 unpaired electrons)

between molybdenum atoms (see Chapter 7) - this is consistent with one possibility of the theory.

(4) MoCl_3 has a layer structure with $n = 6$ and $m = 1$ ¹¹ - as predicted.

(5) Molybdenum (II) chloride has $n = 5$ and $m = 4$ which corresponds to $[\text{Mo}_6\text{Cl}_9]\text{Cl}_4$ as the theory predicts.

Alternative structures are predicted for some oxidation states and whether or not these can be prepared will be an interesting test of the theory.

(ii) Ternary Halides

For $\text{A}_a\text{MX}_{x+a}$ equation 4 becomes

$$a^2 n_{\text{AA}} X_A^2 + a^2 n_{\text{AX}} X_A X_X + 2n_{\text{MX}} X_M^2 + 2n_{\text{MX}} X_M X_X + a^2 n_{\text{MA}} X_M X_A = a^2 N_{\text{AX}} + N_{\text{MX}}$$

For the ternary staphylonuclear halides of potassium, rubidium and caesium the following assumptions must be made.

- (a) $N_{\text{AX}} = N_{\text{MX}}$
- (b) no AA or AM contacts
- (c) $n_{\text{AX}} = 12$

Thus $2^4 X_A X_X + 2n_{\text{MX}} X_M X_X + 2n_{\text{MX}} X_M^2 = (a + 1)N_{\text{MX}}$ must be solved as for binary halides.

Using this equation quite a remarkable agreement between predicted and observed alkali metal halocomplexes of the $Re_3X_{9+x}^{x+}$ type has been obtained, but owing to the difficulty in implementing this equation, (x values for cations are unreliable) a more favoured approach now seems to be an extension of the predictions for binary compounds to ternary compounds.

CONCLUSIONS

This theory can, and does, predict Q_N in transition metal (and other) compounds, but at the present time is limited to "normal" bond lengths at room temperature, because of our lack of knowledge of the variation of x with distance and temperature.

It must be stressed that the theory predicts only Q_N and not structure. Knowing the Q_N the structure must be assigned from the geometrical possibilities which fit the Q_N - usually this is unambiguous.

NOMENCLATURE FOR STAPHYLONUCLEAR COMPOUNDS

Since many staphylonuclear compounds may have one type of ligand (e.g. chloride) in several different structural situations i.e. terminal, doubly bridging or triply bridging some means whereby these can be distinguished is necessary. Such a system has been

proposed¹² and although it can be rather tedious it seems the best way of dealing with these compounds.

Triply bridging groups are prefixed by μ_3 ; doubly bridging groups by μ_2 ; and terminal groups are referred to without prefix. The oxidation state of the metal is placed in brackets after the metal.

As examples of the use of this system the following (all encountered in this thesis) are named.

- $K_2Re_2Cl_8$ - Potassium octachlorodirhenate (III)
 $Rb_3W_2Br_9$ - Rubidium hexabromotri- μ_2 -bromoditungstate (III)
 $Cs_3Mo_2Cl_8$ - Caesium pentachlorotri- μ_2 -chlorodimolybdate (2.5)
 $(NH_4)_7Mo_3Cl_{13}$ - Ammonium nonachloro- μ_3 -chlorotri- μ_2 -chlorotrimolybdate (II)
 $[(C_2H_5)_4N]_2[W_6Cl_8]Cl_6$ - Tetraethylammonium hexachloroocta- μ_3 -chlorohexatungstate (II)

Since this is such a cumbersome system to use, these names were abbreviated at all times when no confusion was possible. The following are examples of the abbreviations used.

- $Re_2Cl_8^{2-}$ - chlororhenate (III) or chlorodirhenate (III)
 $Mo_3Cl_{13}^{7-}$ - chloromolybdate (II) or chlorotrimolybdate (II)
 $W_6Br_8^{4+}$ - bromotungsten (II)
 $[W_6Cl_8]I_4$ - chlorotungsten (II) iodide
 $Mo_2Cl_8^{3-}$ - chloromolybdate (2.5)
 $Mo_2Cl_9^{3-}$ - chloromolybdate (III) - with the specification that

it is dimeric if necessary.

$(H_2O)_2[W_6Br_8]Br_6 \cdot 6H_2O$ - bromotungsten (VI) bromoacid or simply
bromoacid if no confusion arises.

ABBREVIATIONS USED

en	- ethylenediamine
dien	- diethylenetriamine
trien	- triethylenetetramine
tetraen	- tetraethylenepentamine
φ or C ₆ H ₅	- phenyl
dipyr	- 2,2'-dipyridyl
phen	- 1,10-phenanthroline
Pr	- propyl
Et	- ethyl
pyr	- pyridine

CHAPTER 2. ON THE NONEXISTENCE OF $\text{MoCl}_4[(\text{C}_6\text{H}_5)_3\text{AsO}]_4$

INTRODUCTION

The claim of Horner and Tyree (HT) of having prepared $\text{MoCl}_4[(\text{C}_6\text{H}_5)_3\text{AsO}]_4$ (I) has been investigated in order to test the theory (Chap. 1), as it predicts that molybdenum IV cannot be surrounded by eight highly electronegative groups ^{within a neutral complex}.

HT state¹³ that a red carbon tetrachloride solution of "molybdenum tetrachloride" (termed this for the present) was decolourised when poured into a six- to eight-fold excess of triphenylarsine oxide in carbon tetrachloride. A flocculent white precipitate immediately formed, but on addition of further "molybdenum tetrachloride" solution, the precipitate became tinged with green. Since the precipitate was diamagnetic and resistant to oxidation no molybdenum oxidation state was reported. In spite of their alarmingly erratic analytical figures which show that the $(\text{C}_6\text{H}_5)_3\text{AsO}/\text{Mo}$ ratio is nearer 3.6 than 4.0 as required by I, HT still formulated their product as I.

It is of interest to note that in another work HT found¹⁴ that excess triphenylphosphine oxide, triphenylarsine oxide and dimethylsulphoxide all oxidise molybdenum V chloride (the first gives an adduct of MoO_2Cl_2 and the others give complexes of MoOCl_3). Also in their paper in which they report I they found that excess

triphenylphosphine oxide and dimethyl sulphoxide oxidise their "molybdenum tetrachloride". They report no attempt to show that triphenylarsine oxide does not oxidise the "tetrachloride", even though they observed the formation of green colours (usually indicative of molybdenum V halo-oxo compounds) on addition of "top notch" "molybdenum tetrachloride" solution.

Accordingly this present study has taken the form of: (1) determining the nature of the "molybdenum tetrachloride" (used by HT) - triphenylarsine oxide reaction, (2) establishing the composition of the "molybdenum tetrachloride" used by HT, (3) attempting the synthesis of I by more reliable means.

RESULTS AND DISCUSSION

Products of the Reaction of "Molybdenum Tetrachloride" with Triphenylarsine Oxide.

The above reaction was carried out eleven times using different samples of "tetrachloride" (prepared as described by HT) using the same conditions as HT.

A variety of products was obtained, a few of which resemble the materials reported by HT. These experimental results are summarised together with the published results of HT in Table 2.1. Even discounting the coloured or initially oily products, the solute materials from reactions 8-11 do not have reproducible analysis.

TABLE 2.1

REACTION PRODUCTS OF "MOLYBDENUM TETRACHLORIDE" AND MASS TRIPHENYLARSINE OXIDE

Reaction	Nature of initial products	Treatment before analysis	Mp, °C	Infrared absorption bands, 800-900 cm ⁻¹	Analyses, %				
					C	H	As	Cl	Mo
1	(a) White finely divided ppt, plus colorless crystals on standing	...	171	823 858 898	58.9	4.5	20.4	9.7	0.3
	(b) Green oil	Re-pptd from acetone with ether	171	
2	Pale green oil	Vacuum drying	150	47.4	3.4	14.2	19.4	6.0
3	Pale green oil
4	Red-brown oil	Vacuum drying	...	848 873 ...	54.3	4.3	18.8	6.1	6.8
5	Red-brown oil
6	Very pale green solid	None	148	828 845 898	54.5	4.1	17.7	8.2	2.7
7	Very pale green solid	None	...	843 868 894	52.2	4.1	17.7	7.9	4.3
8	Gray-white solid	None	158	845 865 891	55.5	4.2	19.2	9.45	5.4
9	Gray-white solid	None	150	844 867 893	49.7	3.9	16.0	15.0	7.4
10	White solid	None	...	849 876 ...	52.5	4.2	18.3	9.9	7.2
11	White solid	None	120-150	8.0	..
HT	White solid	None	161-163	848 878 900	53.5	3.81	..	9.42	6.24
HT								9.93	6.81
HT								9.45	6.88
HT								9.18	
	Calculated for (C ₆ H ₅) ₃ As(OH)Cl		171 (lit.)	823 858	60.3	4.5	21.0	9.8	0.0
	Calculated for MoCl ₄ ·[(C ₆ H ₅) ₃ AsO] ₄				56.7	4.0	19.7	9.3	6.3

Moreover reaction 1 provides evidence that $(C_6H_5)_3As(OH)Cl$ may be a prominent constituent of all these products. Fraction (a) had a very similar melting point and infra-red absorption spectrum to an authentic sample of $(C_6H_5)_3As(OH)Cl$ prepared by the reaction of triphenylarsine oxide and hydrogen chloride.

The exact nature of the precipitated products cannot be elucidated from the analytical data but they are probably mixtures of $MoO_2Cl_2[(C_6H_5)_3AsO]_2$ and/or $MoOCl_4(C_6H_5)_3AsO$ together with $(C_6H_5)_3As(OH)Cl$. Nevertheless it can be stated that these results are similar to those of HT in all important particulars.

Tyree has said¹⁵ that they attempted the reaction nineteen times and succeeded in obtaining a white solid only four times. In the other preparations green oils were obtained and HT attributed these failures to the impurity of the molybdenum tetrachloride.

At this stage the important conclusion to be drawn is that the molybdenum halide used in this work was the same as the "molybdenum tetrachloride" used by HT, since the results obtained are sufficiently similar to theirs.

The Nature of the "Molybdenum Tetrachloride"

Attempts to determine the oxidation state of molybdenum in the products failed due to interference by the triphenylarsine oxide. Thus a demonstration of the oxidation of the "tetrachloride" by triphenylarsine oxide was attempted. During this work it was found

that (i) the "tetrachloride" used by HT contains molybdenum in oxidation state 5.5, despite a resemblance to MoCl_4 in composition, (ii) carbon tetrachloride solutions of the "tetrachloride" displayed infra-red absorption bands at 909, 961, 988 and 1008 cm^{-1} - characteristic of Mo-O linkages, (iii) authentic molybdenum (IV) chloride was completely insoluble in carbon tetrachloride¹⁶ - this was confirmed by repeating the preparation of Larsen and Moore, although the product obviously contained some of the carbonaceous impurity found by these workers.

It is noteworthy that MoCl_5 , MoOCl_4 , and MoO_2Cl_2 are all soluble in carbon tetrachloride, the first two giving red solutions. Also it is unprecedented that a tetrahalide of a lower transition element would be soluble in nonpolar solvents.

Tyree and his associates have reported two original methods for the preparation of molybdenum tetrachloride^{17,18} and used both sources of the tetrachloride in the synthesis of I. These methods are:

- (i) the chlorination of molybdenum (IV) oxide in refluxing hexachlorobutadiene
- (ii) the action of carbon tetrachloride on molybdenum (IV) oxide in sealed ampoules at 250-300°C.

It seems remarkable that these methods could give pure molybdenum (IV) chloride, free from pentachloride and oxychlorides, since the enthalpies of formation of MoOCl_4 (154), MoO_2Cl_2 (173) and MoCl_5 (126) are all greater than that of MoCl_4 (114) kcal. mol^{-1} .¹⁹

Method (i) is not now considered reliable by Tyree¹³ as it appears to yield a mixture of "tetrachloride" and pentachloride. The product from method (ii) contains unchanged molybdenum (IV) oxide^{13,19} and so a variation of the method - passing carbon tetrachloride vapour at 100°C over molybdenum (IV) oxide - has been recommended.¹⁹ The product then is a mixture of chlorides and oxychlorides, and only by subliming these off can a residue of pure molybdenum (IV) chloride be obtained.

It is significant that Tyree and his associates reported no molybdenum oxidation numbers for chlorides prepared by methods (i) or (ii). For selected samples, i.e. "for a good preparation",¹⁴ the total molybdenum plus chloride content was always significantly less than that required for molybdenum (IV) chloride - see Table 2.2.

TABLE 2.2

ANALYTICAL DATA FOR "MOLYBDENUM TETRACHLORIDE"

Preparative method	% Cl	% Mo	Ratio Mo:Cl	Deficiency from 100%	Ref.
$\text{MoO}_2\text{-Cl}_2\text{-C}_4\text{Cl}_6$	59.78	39.24	1:4.12	0.98	14
$\text{MoO}_2\text{-CCl}_4$	58.31, 58.73	39.67, 40.17	1:3.98 1:3.96	1.56	14
$\text{MoO}_2\text{-CCl}_4$	57.6	39.0	1:4.00	3.4	19

It has been observed by HT and in this study that some molybdenum (IV) oxide remained unaffected after its reaction with

carbon tetrachloride, thus, if ratios of Mo:Cl of 1:4 are obtained by analysis of the reaction products, then the ratio of Mo:Cl in the chlorine-containing products must be greater than 1:4 (since some of the molybdenum is in the oxide). Even if all of the molybdenum (IV) oxide is consumed, some oxygen must be present. It is suggested that the "tetrachloride" prepared by HT and in this study is largely a mixture of MoCl_5 and MoO_2Cl_2 (or MoOCl_4). For example a 70-30% mixture of the first two would have an analytical composition of $\text{MoCl}_{4.1} \text{O}_{0.8}$ giving an apparently satisfactory Cl:Mo ratio for molybdenum (IV) chloride, but being 4% deficient in molybdenum and chlorine and having a molybdenum oxidation number of 5.3.

The possibility of there being some molybdenum (IV) chloride present in some of the preparations by method (ii) is not ruled out, but if formed it is very unlikely to be soluble in carbon tetrachloride.¹⁶ Thus the carbon tetrachloride extracts of such preparations, used by HT to synthesise I, contained only molybdenum pentachloride and oxychlorides. The distinctive red colour of such solutions was principally due to molybdenum (V) chloride.

The Reaction of Molybdenum (V) Chloride with Excess Triphenylarsine Oxide

The reaction was carried out in the same manner as the HT synthesis of I, save for the replacement of the "tetrachloride" by authentic molybdenum (V) chloride. The red carbon tetrachloride

solution was decolourised and a pure white, flocculent precipitate was immediately formed. The appearance of the reaction differed in no way from that reported by HT (including the green colour if too much molybdenum pentachloride was added), or from reactions 10 and 11 (Table 2.1), except that the precipitate had a much cleaner appearance. These observations lead to the rejection of the explanation given by HT^{13,15} for the numerous failures of their synthesis of I to give pure white solids. They suggested that the purity of the tetrachloride is critical and that the yield of pure white precipitate with the arsine oxide was indicative that the requisitely pure molybdenum (IV) chloride was being used.

The reaction products from molybdenum (V) chloride using HT's experimental procedure are shown in Table 2.3, and it can be seen that these differ very little from the materials reported by them (by comparing Tables 2.3 and 2.1). Furthermore a similar reaction using excess triphenylphosphine oxide proceeds with slow decolourisation and the eventual formation of a yellow precipitate of $\text{MoO}_2\text{Cl}_2[(\text{C}_6\text{H}_5)_3\text{PO}]_2$. These results are identical with those of HT using their "tetrachloride" and excess triphenylphosphine oxide.¹³

The Reaction of Authentic Molybdenum (IV) Chloride with Triphenylarsine Oxide - An Attempt to Synthesise I

Powles, et al have reported²⁰ a number of authentic molybdenum (IV) adducts together with appropriate oxidation numbers

TABLE 2.3

REACTION PRODUCTS OF MOLYBDENUM (V) CHLORIDE AND EXCESS

TRIPHENYLARSINE OXIDE

Reaction no.	Nature of product	Mp, °C	Infrared absorption bands, cm^{-1}			Analyses, %				
			C	H	As	Cl	Mo			
1	White solid	120				8.8	
2	White solid	120	840	870	897	54.2	4.6	17.3	7.8	6.55
3	White solid	162	848	866	883	54.46	3.96	21.5	9.1	8.45

TABLE 2.4

QUANTITATIVE INFRARED SPECTROSCOPY OF MOLYBDENUM (IV) ARSINE

OXIDE SOLUTIONS IN CHLOROFORM

Molar ratio (R)	Conc., $\text{M} \times 10^3$		Optical density (888 cm^{-1})		Concn of arsine oxide, M		
	Mo(IV) [A]	Arsine oxide	Obsd	Correc-tion ^a	Free	Com-bined [B]	B/A
0.91	7.5	6.85	0.07	-0.05	0.4	6.4	0.85
1.9	6.75	13.0	0.42	-0.22	4.0	9.0	1.3
3.0	6.1	18.5	0.57	-0.25	6.6	11.9	1.95
4.3	5.5	23.5	0.74	-0.28	9.7	13.8	2.5
5.2	2.75	14.2	0.41	0 ^b	8.6	5.6	2.0
8.2	2.5	20.2	0.65	0 ^b	14.7	5.5	2.2
10.6	1.8	18.5	0.67	0 ^b	15.3	3.2	1.8

^a Contribution from adduct to be deducted.

^b Small and difficult to estimate.

and magnetic moments. They are of the form MoCl_4L_2 , prepared by a replacement reaction in chloroform solution:



(L = n-propylcyanide).

This method of adduct preparation overcomes the insolubility of molybdenum (IV) chloride in non-polar solvents. We have attempted to prepare I by Fowles' method in order to confirm the prediction that I does not exist.

It is recognised that merely unsuccessful efforts to precipitate I from solution are not conclusive evidence as to its nonexistence - it must be shown that it cannot possibly appear from such solutions.

In this study no molybdenum tetrachloride-triphenylarsine oxide adduct at all could be prepared using the method of Fowles. Both dilute and concentrated solutions of $\text{MoCl}_4 \cdot 2n\text{-C}_3\text{H}_7\text{CN}$ gave no precipitate when a slight stoichiometric excess of triphenylarsine oxide was added. On addition of excess triphenylarsine oxide to these solutions nothing visibly occurred in the dilute system, but in the concentrated one the solutions turned green and yielded green precipitates containing molybdenum (V) (identified by visible spectroscopy). On the other hand, triphenylphosphine oxide produces no significant oxidation of the molybdenum (IV) and gave a very low yield of a yellow precipitate - too

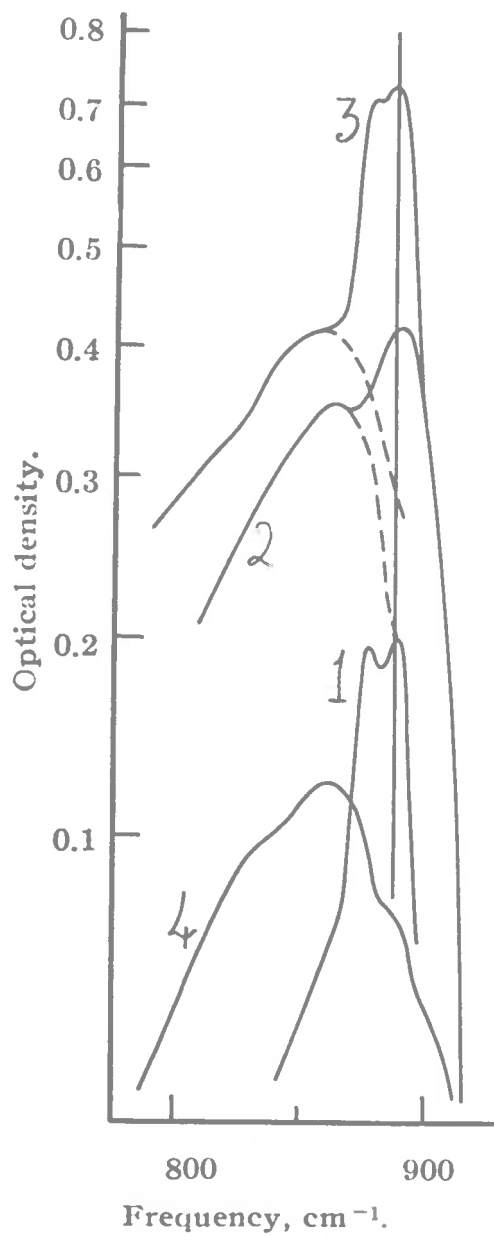
small for proper identification - but it is presumably the 2:1 adduct $\text{MoCl}_4 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$, previously reported²⁰ by Fowles et al. It seems significant that although 2:1 adducts of molybdenum (IV) with triphenylphosphine, triphenylarsine and triphenylphosphine oxide were reported, no mention²⁰ was made of a triphenylarsine oxide adduct.

Dilute $\text{MoCl}_4 \cdot 2n\text{-C}_3\text{H}_7\text{CN} - (\text{C}_6\text{H}_5)_3\text{AsO}$ chloroform solutions have been examined over a range of triphenylarsine oxide: molybdenum ratios (R) by quantitative infra-red spectroscopy.

Triphenylarsine oxide displays doublet (see Figure 2.1) at 876 and 888 cm^{-1} which obeys Beer's Law, ϵ_{888} (888 cm^{-1}) = 300. Mixtures of low R displayed a broad band which had a maximum at 860 cm^{-1} , which is assigned to triphenylarsine oxide coordinated to molybdenum. In the experimental runs the doublet and broad bands appeared together, with relative intensities dependent on R (Figure 2.1). It is possible to estimate the molarities of free and combined triphenylarsine oxide from these spectra if some judgement is exercised in resolving the two overlapping bands. However, it was found that the final conclusions were not affected by independent resolutions. The results remain at all times approximate since slow oxidation of the molybdenum (IV) and consumption of triphenylarsine oxide occurred, even in dilute solution.

The results of this investigation are shown in Table 2.4. The ratio of coordinated triphenylarsine oxide to molybdenum (B/A) never exceeded 2.0 by a significant amount, even with large excesses

FIGURE 2.1



Infrared absorption spectra of triphenylarsine oxide and mixtures with bis(propyl cyanide)molybdenum (IV) chloride: 1, triphenylarsine oxide; 2, molybdenum (IV)-arsine oxide mixture, 0.0075 M-0.0068 M; 3, molybdenum (IV)-arsine oxide mixture 0.0068 M-0.0130 M; 4, molybdenum (IV)-arsine oxide mixture, 0.0054 M-0.023 M.

of triphenylarsine oxide. These results show evidence for the formation of the adduct $\text{MoCl}_4 \cdot 2(\text{C}_6\text{H}_5)_3\text{AsO}$ which is entirely plausible in view of the existence of similar MoCl_4L_2 complexes previously reported.

If a tetrakis (triphenylarsine oxide) adduct was present in these chloroform solutions, it must now be supposed that it is present in a low concentration and in equilibrium with the observed bis(triphenylarsine oxide) adduct. This is equivalent to saying that the tetrakis adduct is dissociated by chloroform, which in all normal circumstances is certainly never coordinating, and therefore the tetrakis adduct is quite unstable. The possibility of a stable tetrakis adduct at high concentrations of triphenylarsine oxide is also ruled out by the rapid oxidation occurring which would, just conceivably, result from a species of high coordination number breaking down to yield triphenylarsine and oxidised molybdenum (IV).

CONCLUSIONS

We must conclude from the overwhelming weight of evidence that a stable tetrakis (triphenylarsine oxide) adduct of molybdenum (IV) does not exist i.e. the nonexistence of I has been proved.

As must be reasonably obvious the nonexistence of I is not in itself an important chemical fact, but demonstrates the inability of conventional valence theories to detect curious and hence possibly mistaken, structures in chemistry. It is to this end that the

stereochemical theory proposed by Sheldon⁵ (see Chapter 1) assumes importance, as it first predicted that such an adduct as proposed by HT could not exist in the following manner.

The total internuclear energy of a molybdenum atom (M_{110}) surrounded by chloride and oxygen ligands cannot be specified exactly, but is probably in the range 66-72 eV, which is appropriate for most transition metal chlorides and oxides. On solving equation 4, Chapter 1 it is found to be impossible that molybdenum could be surrounded for eight such highly electronegative ligands, unless some of the Mo-Cl or Mo-O bonds are unusually long, but if these bonds did become much longer the term "eight coordinate molybdenum (IV)" would not have such significance. All of the molybdenum (IV) tetrachloride adducts with oxygen donors reported so far appear to be six coordinate as fits the theory.

EXPERIMENTAL

Preparation and Purification of Reagents

Analytical Reagent grade carbon tetrachloride was used after 20% of its volume was distilled off to remove moisture.

Triphenylarsine oxide was prepared from triphenylarsine by hydrogen peroxide oxidation²¹ and recrystallised from benzene.

The molybdenum pentachloride used was Climax Molybdenum Corp. material, carefully resublimed in a working vacuum before use.

Molybdenum (IV) oxide was prepared by the method of Brauer.²²

~~The product of~~ The reaction of molybdenum (IV) oxide and carbon tetrachloride was carried out as described in reference (18). The bomb used was a modified Autoclave Engineers, Inc. 300 ml stirred autoclave. The "molybdenum tetrachloride" was obtained as red-black needles, soluble in carbon tetrachloride. The ampoules were opened carefully, the product washed well with dry degassed carbon tetrachloride, and immediately dissolved in dry degassed carbon tetrachloride ready for reaction - except when the sample was being analysed. Analyses for four independent preparations (1) Cl, 62.0%; Mo, 38.9%; (2) Cl, 56.5%; Mo oxidation no., 5.6 (assuming 39% Mo); (3) Mo oxidation no., 5.4; (4) Mo oxidation no., 5.6 (The last two results are from assays on carbon tetrachloride solutions of the product.)

Molybdenum (IV) chloride was prepared by the reduction of molybdenum (V) chloride by refluxing benzene.¹⁶ As found by the previous workers the product contained a considerable quantity of carbonaceous by-product. The black powder was completely insoluble in carbon tetrachloride. Analysis: Calc. for Cl_4Mo : Cl, 59.6; Mo, 40.3; Mo oxidation no. 4.0. Found: Cl, 54.4; Mo, 37.4; Cl/Mo = 4.0; Mo oxidation no. = 4.1.

Bis(n-propyl cyanide)molybdenum (IV) chloride appeared as red-brown needles from a solution of molybdenum pentachloride in n-propyl cyanide after standing in a sealed tube for 24 hrs.²⁰

Analysis: Calc. for $C_8H_{14}Cl_4Mo$: Cl, 37.8; Mo, 25.5; Mo oxidation no., 4.0. Found: Cl, 37.3; Mo, 24.6; Mo oxidation no., 3.9.

Preparation of Complexes

Where necessary all oxygen and moisture were excluded by use of a dry-box.

When preparing triphenylarsine oxide complexes with "molybdenum tetrachloride" and molybdenum (V) chloride it was found more convenient to make up the "tetrachloride" solution in the storage flask of an automatic filling burette, fitted so that the solution was kept under oxygen free dry nitrogen at all times. The required amount was then run into triphenylarsine oxide solution. When determining oxidation numbers and molybdenum content of this solution, aliquots were run into acidified ferric sulphate or tared crucibles respectively (the crucibles were then heated to 520°C and the molybdenum weighed as the trioxide).

The triphenylphosphine oxide adduct with molybdenum (V) chloride was prepared by slow addition of the chloride in carbon tetrachloride to the phosphine oxide, in carbon tetrachloride. The yellow complex which formed slowly was filtered off, washed with

carbon tetrachloride, and dried in vacuum. *Analysis:* Calc. for $\text{MoO}_2\text{Cl}_2[(\text{C}_6\text{H}_5)_3\text{PO}]_2$: C, 57.2; H, 4.2; Cl, 9.4; P, 8.2. Found: C, 57.2; H, 4.2; Cl, 10.0; P, 9.3.

The preparation of the molybdenum (IV) chloro adduct of triphenylphosphine oxide (and the attempted preparation of the corresponding triphenylarsine oxide adduct) was carried out as suggested by Fowles et al.²⁰

Techniques

The infra-red spectroscopy was carried out in a Perkin-Elmer model 21 double beam spectrophotometer, using NaCl optics, with matched NaCl window cells of 0.13 cm path length.

When arsenic was present the molybdenum was analysed by X-ray emission techniques, by the Australian Mineral Development Labs., S. Australia.

Other analyses were carried out by standard techniques - see Appendix 1.

CHAPTER 3. PREPARATION AND PROPERTIES OF CHLOROTRIMOLYBDATES (II)

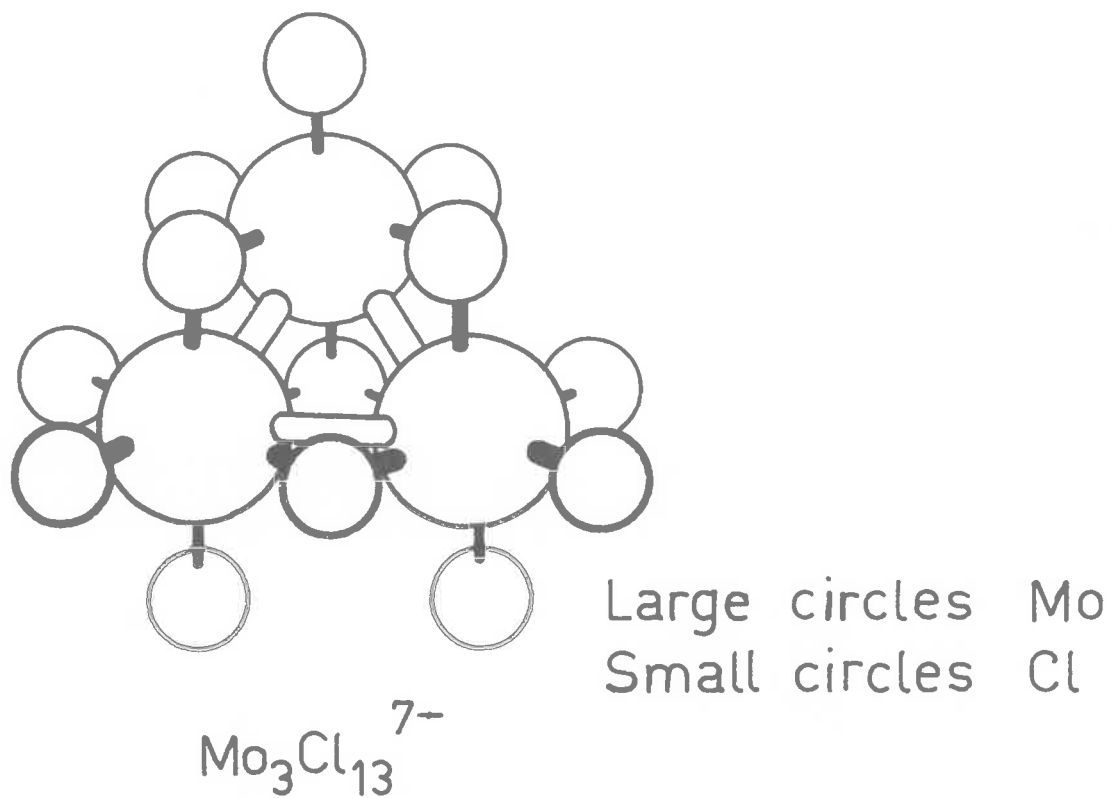
INTRODUCTION

The theory (Chapter I) for binary halides predicts that if a molybdenum (II) atom is coordinated to six chloride ligands, two molybdenum-molybdenum bonds should result. If this is extended to a ternary molybdenum (II) complex, a structure which accommodates these coordination number requirements is the $\text{Mo}_3\text{Cl}_{13}^{7-}$ species. This is based on the Hb_3Cl_8 structure²³ (see Figure 3.1). It has been proposed^{24,25} that this is the structure adopted by compounds precipitated from solutions of molybdenum (II) acetate in hydrochloric acid by alkali metal cations.

Because molybdenum diacetate is dimeric this formulation poses a conceptual difficulty. How do the dimers become trimers in solution? To determine whether or not the complexes are trimers, single crystal X-ray diffraction studies seem to be the ideal method. However the complexes do not crystallize from the reaction mixtures in sufficient size, and cannot be recrystallized due to their instability in solution, thus chemical and physical properties of the compounds, as well as analytical data, must be relied upon for structural assignment.

It was to this end that the preparation of a large number of similar molybdenum (II) compounds was embarked upon. It was hoped that their compositions and properties might help verify the structure.

FIGURE 3.1



Organic cations were used in an attempt to prepare compounds that would be soluble in solvents suitable for molecular weight and conductivity measurements.

It was also hoped to test the theory by the preparation of new types of compounds. Some rather novel compounds prepared to this end are discussed at the end of the chapter.

RESULTS AND DISCUSSION

I. COMPOUNDS WITH MOLYBDENUM:CHLORINE RATIOS OF APPROXIMATELY 1:6

(1) Compounds Prepared and their Properties

The cations which were found to yield precipitates of chlorotrimolybdenum (II) species from molybdenum-diacetate-hydrochloric acid solutions were ethylenediammonium, bisethylenetriammonium, trisethylenetetrammonium, tetraethylenepentammonium, pyridinium, anilinium, hexaminechromium (III) trisethylenediamminechromium (III) and thallium (I). In addition a quinolinium complex can be formed at high quinolinium hydrochloride concentrations by addition of the hydrochloride to concentrated solutions of ammonium chlorotrimolybdate (II) in dilute hydrochloric acid. Precipitation of the complexes over as large a range of [cation]:[molybdenum (II) acetate] ratios as possible was attempted, because it has often been observed that the product obtained is a function of this ratio.²⁵ In this work the range was limited in the case of the amine hydrochlorides and

thallium (I) chloride due to their insolubility in hydrochloric acid. For the anilinium salt high concentrations of the hydrochloride produced such rapid precipitation that acetate particles were occluded in the complex.

Purification of these chloromolybdates (II) is difficult due to inability to recrystallise them; thus the criterion adopted for sample homogeneity and purity is the reproducible analyses of several preparations.

The analytical results (displayed in Table 3.1) show that this cation survey has produced stapylonuclear anions varying in constitution between $\text{Mo}_3\text{Cl}_{11}^{5-}$ and $\text{Mo}_3\text{Cl}_{15}^{9-}$. Quite often analyses were irrational or erratic indicating compounds containing mixtures of the above species. For example the anilinium complex appears to be a mixture of $(\text{C}_6\text{H}_5\text{NH}_2)_3\text{Mo}_3\text{Cl}_{12}$ and $(\text{C}_6\text{H}_5\text{NH}_2)_6(\text{H}_2\text{O})\text{Mo}_3\text{Cl}_{13}$. Many organic cations other than those reported in Table 3.1 produced red-violet precipitates from molybdenum (II) solutions, but these were not investigated further.

The visible spectra of all the compounds listed in Table 3.1 and of $(\text{NH}_4)_7\text{Mo}_3\text{Cl}_{13}\text{H}_2\text{O}^{24}$ are essentially identical in 3M hydrochloric acid solutions, having a peak at 19.1 mK (which obeys Beer's Law);
 $\epsilon_{\text{max}} = 2,000$

The compounds are unstable in hydrochloric acid, the rate of decomposition being proportional to the acid concentration; thus all spectra must be extrapolated to zero time.

TABLE 3.1

ANALYTICAL DATA FOR CHLOROTRIMOLYBDATES (II)

Compound	Yield	C	H	N	Cl	Tl or Cr	Mo	Cl/Mo	Oxidation number	Colour
$(enH_2)_3(H_2O)_2Mo_3Cl_{13}H_2O$ ²	~70%	-	-	-	47.4		28.8	4.45	1.9	
		7.1	3.6	8.5	45.9		-	-	-	
		7.6	3.7	8.5	46.8		-	-	-	
		-	-	-	46.8		29.2	4.5	-	violet
		-	-	-	47.0		29.0	4.4	1.9	
		77.5	3.7	8.5	46.8		29.0	4.4	1.9	
<i>Required</i>		7.6	3.7	8.5	46.8		29.1	4.33	2.0	
$(bisen)_3Mo_3Cl_{15}$	70-80%	-	-	-	47.5		24.8	5.2	1.85	
		-	-	-	47.0		24.9	5.1	1.8	
		13.3	4.4	10.6	47.5		-	-	-	violet
		13.0	4.4	10.8	47.7		-	-	-	
	<i>Required</i>		12.88	4.3	11.1	46.8		25.3	5.0	2.0

cont'd

$(\text{trisnH}_4)_2\text{Mo}_3\text{Cl}_{14}$	70-80%	-	-	-	45.5	27.5	4.45	1.8	
		-	-	-	46.0	27.2	4.59	2.0	
		12.5	4.0	9.1	46.2	-	-	-	violate
		13.0	4.0	9.0	46.2	27.1	4.6	1.9	
<i>Required</i>		15.3	4.0	10.3	46.9	26.8	4.67	2.0	
$(\text{pyrH})_5\text{Mo}_3\text{Cl}_{11}(\text{C}_3\text{H}_6\text{O})_2$	~80%	-	-	-	35.4	25.0	3.85	- ^a	
		30.8	3.6	5.9	32.4	23.8	3.7	-	red
		31.5	3.7	5.9	32.9	24.0	3.7	-	
	<i>Required</i>		31.3	3.6 ¹	5.86	33.7	24.1	3.67	2.0
Anilinium Salt	70-80%	-	-	-	34.0	22.6	4.1	2.1	
	Probably a mixture of	-	-	-	32.2	22.1	4.0	2.0	
		30.6	3.8	6.3	34.6	22.6	4.15	2.1	red-violet
		-	-	-	34.8	22.6	4.15	-	
		33.5	3.8	6.4	34.3	22.4	4.15	2.1	
$(\text{C}_6\text{H}_5\text{NH}_2)_3\text{Mo}_3\text{Cl}_{13}$		33.8	3.8	6.6	33.4	22.6	4.0	2.0	
and $(\text{C}_6\text{H}_5\text{NH}_2)_3(\text{H}_2\text{O})\text{Mo}_3\text{Cl}_{13}$		32.5	3.8	6.3	34.6	21.7	4.33	2.0	

cont'd

(tetraamH₅)⁵⁺ salt

Analyses not rational but several preparations show Mo/Cl = 5.0 - therefore contains

red



~80%

36.0	3.62	5.47	31.1	22.1	3.8	2.05
36.0	3.64	5.47	30.7	21.4	3.9	-

red-violet

Required

36.0	3.27	4.85	31.2	21.2	4.0	2.0
------	------	------	------	------	-----	-----



~20%

22.8	58.0	19.7 ^c	3.2	-
23.4	56.3	-	-	-
23.5	55.5	-	-	-
23.3	57.2	16.0	3.85	2.05
23.4	55.9	16.5	3.8	2.05
23.4	55.8	16.8	4.0	2.0

blue

Required



~90%

-	-	-	32.0	17.2	5.0	2.3
14.8	5.5	15.6	30.3	16.5	5.0	-
-	-	-	31.0	16.7	5.0	2.1
-	-	-	35.8	18.7	5.15	2.15

pink

cont'd

		-	-	-	31.4	16.6	5.1	2.3	
		14.2	5.5	15.9	30.3	16.5	5.0	2.1	
<i>Required for 2H₂O</i>		13.5	5.2	15.7	32.8	17.7	5.0	2.0	
$[\text{Cr}(\text{NH}_3)_6]_3\text{Mo}_3\text{Cl}_{15}\cdot 2\text{H}_2\text{O}^{\text{d}}$	~80%	-	-	-	35.9	20.9	4.7	-	
		4.6	4.6	17.2	39.1	20.9	5.05	2.1	
		-	-	-	39.2	20.9	5.05	2.05	Pink
		4.7	17.3	37.0	10.4	20.6	4.85	2.3	
<i>Required for 6H₂O</i>		6.8	18.1	38.2	11.2	20.7	5.0	2.0	

a - no satisfactory determination possible

b - can be formulated as a dimer $(\text{NH}_3)_3(\text{H}_2\text{O})\text{Mo}_2\text{Cl}_8\cdot 2\text{H}_2\text{O}$

c - Tl interferes with molybdenum determination

d - these complexes are isomorphous with the corresponding $\text{Co}(\text{en})_3^{3+}$ complex

i.e. $[\text{Co}(\text{en})_3]_3\text{Mo}_3\text{Cl}_{15}\cdot 6\text{H}_2\text{O}^{25}$

In general the complexes were insoluble in organic solvents, with the exception of the anilinium complex which is soluble in, and relatively stable in aniline, but since the compound could not be prepared in an analytically pure form, and aniline not being a good solvent for molecular weight determination, it was thought to be unprofitable to pursue this attempt to find the degree of polymerisation in the solution phase.

The magnetic susceptibilities of all the compounds prepared, measured at room temperature, showed small positive or negative values which yield μ_{eff} values of 1.0-1.9 BM per trimer.

Powder diffraction data for all the compounds reported in Table 3.1 are unique with the exception of the $\text{Cr}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{en})_3^{3+}$ salts which are isomorphous. The striking blue thallium (I) complex (contrasting with the usual red and violet colours) whose constitution approximates to $\text{Tl}_5(\text{H}_2\text{O})\text{Mo}_3\text{Cl}_{12}4\text{H}_2\text{O}$ has a powder pattern very similar to that found for rubidium and caesium chlorotrimolybdates (II).²⁵ Their formulation also approximates to that suggested for the thallium complex.

Where the formulation is as a hydrate the infra-red spectrum shows absorption appropriate for the presence of water (i.e. at ca. 1600 cm^{-1} and 3400 cm^{-1}).

(11) Chloromolybdenum (II) Species in Organic Solvents.

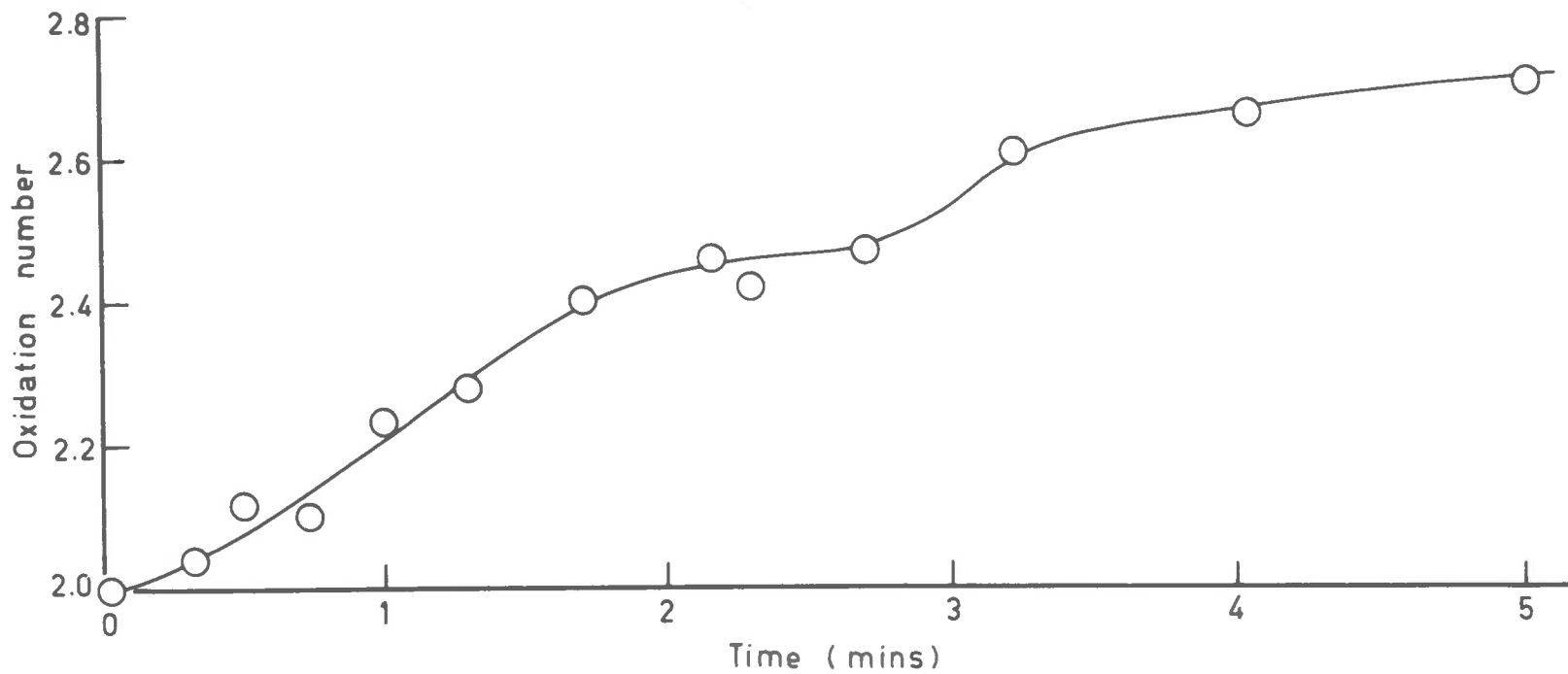
The use of non-aqueous solvents saturated with dry hydrochloric acid gas as media for the synthesis of molybdenum (II) compounds from molybdenum (II) acetate was investigated. Some brightly coloured (red-violet) complexes were formed, but all compounds found were extremely sensitive to oxidation, thus an analytical survey was not attempted.

The solvents (saturated with hydrochloric acid) which gave red-violet precipitates with caesium and potassium were acetic acid, ethanol and acetone (chloroform and other solutions gave dark coloured precipitates with the acetate alone).

To determine whether molybdenum (II) has any stability in these solutions, the rate of oxidation of the diacetate in 2.5N hydrochloric acid in acetic acid was followed, and was found to be much more rapid than that observed²⁴ in aqueous hydrochloric acid. Also, almost insignificant stabilisation of the +2.5 oxidation state was observed (see Figure 3.2) compared with the quite marked effect in the aqueous system.

It was notable that in all non-aqueous solvents the hydrochloric acid concentration required to bring about relatively rapid solution of the acetate was markedly less than for water. The only explanation for this is the slightly enhanced solubility of the diacetate in such solvents.

FIGURE 3-2. Oxidation Number of Molybdenum II Acetate in 2.5 M Hydrochloric Acid at 28°C.



(iii) Evidence for the Trimeric Formulation

(a) Analytical

Several of the products have analyses unequivocally supporting the trimeric formulation.- $(enH_2)_3(Mo_3Cl_{13} \cdot 2H_2O)$, $(triaenH_4)_2Mo_3Cl_{14}$, $(pyrH)_5Mo_3Cl_{11} \cdot (C_3H_6O)_2$ and $Tl_3(Mo_3Cl_{12} \cdot 4H_2O)$. The compositions of the others were equivocal - supporting equally well a dimeric or trimeric formulation. The appearance of ligand deficient anions in some cases is not unexpected since this phenomenon is well established in the Re_3^{n-} series of compounds.²⁶

It is necessary to postulate that the crystal lattice can accommodate extra chloride when these must be present to fulfil stoichiometric requirements.

(b) Spectra and Magnetic Susceptibilities

In hydrochloric acid the spectra of the chloromolybdates (II) are identical at any particular hydrochloric acid concentration (but with ϵ_{max} varying from 800-2400 with concentration), suggesting that if any of the staphylo-nuclear anions are formulated as trimers then all must be (in solution). The spectra obtained are also identical with those found for the alkali metal chloromolybdates (II),²⁷ suggesting that all chloromolybdates (II) prepared by the dissolution of molybdenum diacetate in hydrochloric acid are trimers.

Additional evidence that the anions are trimers, some of them being ligand deficient comes from the work of van Bronswyk,²⁷

who studied the effect of potassium chloride disc formation pressure on extinction coefficients, when investigating quantitative solid state spectroscopy of the $\text{Mo}_3\text{Cl}_{12}^{6-}$ and $\text{Mo}_3\text{Cl}_{13}^{7-}$ anions. In $(\text{NH}_4)_7\text{Mo}_3\text{Cl}_{13}\cdot 2\text{H}_2\text{O}$ ϵ for the peak at 18.4 m μ , was 2600 and independent of disc formation pressure, while for $\text{K}_6\text{Mo}_3\text{Cl}_{12}$ the extinction coefficient at 18.4 m μ , rose from 1000 at low discing pressures to 2300 with increasing pressure. Since there is a similar range of extinction coefficient in both solid and solution the equilibrium



is suggested in both cases. In very dilute acid (< 0.1M) it appears that $\text{Mo}_3\text{Cl}_{12}^{6-} \rightleftharpoons \text{Mo}_3\text{Cl}_{11}^{5-} + \text{Cl}^-$ occurs.²⁷

The low magnetic susceptibilities encountered are consistent with extensive metal-metal interaction, as implied by the trimeric formulation.

(c) Halide Exchange

The proposed structure (Figure 3.1) of the $\text{Mo}_3\text{Cl}_{13}^{7-}$ species has one μ_3 , three μ_2 and nine terminal chlorides. It appears to be a general rule in staphylonuclear chemistry that terminal groups exchange much more rapidly than bridging groups (with $\text{W}_2\text{Cl}_9^{3-}$ being the exception - here all the chlorides are kinetically equivalent).²⁸ Van Bronswyk²⁷ has found that nine of the thirteen chlorides exchange rapidly with $^{36}\text{Cl}^-$ - this is the expected result for the $\text{Mo}_3\text{Cl}_{13}^{7-}$ unit.

II. COMPOUNDS OF LOW MOLYBDENUM:CHLORIDE RATIOS

(1) Complexes and their Properties

A novel series of molybdenum (II) compounds has been prepared using the ligands 1,10-phenanthroline and 2,2'-dipyridyl. Tables 3.2, 3.3 and 3.4 show the results of an analytical survey. The preparation of these complexes can be effected in either of two ways.

(1) From 12M hydrochloric acid solutions unsaturated with molybdenum (II) species (ex. molybdenum diacetate), complexes could be precipitated out by the addition of ethanol. If no ethanol was added only molybdenum (2.5) species came out of solution (see Chapter 4).

(2) From 4N hydrochloric acid solutions saturated with molybdenum (II) species, (solution saturated with $(\text{NH}_4)_2\text{Mo}_2\text{Cl}_{13}\cdot 2\text{H}_2\text{O}$) complexes came out on addition of ligand.

The complexes thus prepared are extremely sensitive to atmospheric oxidation, some being pyrophoric on exposure to air. This property, coupled with their insolubility in all solvents except warm dimethylsulphoxide and dimethylformamide, (and even when prepared solutions were extremely unstable) hampered any investigation of their properties.

Due to their mode of preparation and inability to recrystallise these compounds, the analytical figures from preparation to preparation

TABLE 3.2

ANALYTICAL DATA FOR PRODUCTS OBTAINED FROM THE REACTION OF MOLYB-
BDENUM (II) ACETATE WITH 1:10-PHENANTHROLINE IN 12M HYDROCHLORIC
ACID, USING ETHANOL AS PRECIPITANT

Preparative Ratio moles acetate: moles phen.	Mo	Cl	C	H	N	Oxidation equivs.	Oxidation no.	Cl/Mo
1:8	26.0	22.2				10.3	2.2 ^a	2.31
1:4	26.5	22.0				10.5	2.2 ^a	2.24
1:2	30.1	21.8						1.96
1:2	31.0	22.9						2.00
1:1	30.1	21.9						1.97
1:1		21.9	37.5	2.8	11.4	11.3		
1:1	28.2	21.5				11.0	2.2 ^a	2.06
1:5	26.6	23.5				10.4	2.2	2.39
1:2		21.0				13.3		
1:2	31.0	22.0						1.92
1:2	31.5	22.9	31.4	2.8	5.6	13.1	2.0	1.96
1:2	29.0	21.0	32.4	3.04	5.32	11.9	2.1	1.96
<i>Required for</i>								
$Mo_3Cl_6(phen)_2 \cdot 4H_2O$	30.8	22.8	30.9	2.5	0.0		2.0	2.00

a - These oxidation numbers are high due to incomplete solution of the complex in acidified ferric sulphate solution.

TABLE 3.3

ANALYTICAL DATA FOR PRODUCTS OBTAINED BY ADDITION OF 1:10-PHENANTHROLINE TO AMMONIUM

CHLOROPOLYDATE (II) IN 4M HYDROCHLORIC ACID

Preparative Ratio		Mo	Cl	C	H	N	Oxidation	Oxidation	Cl/Mo	C/Mo	C/N	H/Mo
Moles $(NH_4)_2Mo_3Cl_{13}$	moles phen						equivs.	no.				
1:20		25.8	21.9	37.7	2.84	7.01	10.7	2.02	2.29	11.7	6.3	1.86
1:10		28.7	22.9	35.4	2.89	6.83	11.4	2.18	2.16	9.4	6.1	1.63
1:10			21.8	36.3	2.87	6.76						
1:5		28.5	23.4	36.5	2.82	6.76	11.8	2.1	2.22	10.2	6.3	1.63
1:1.5		32.9	25.1	30.0	2.65	5.27	13.5	2.06	2.08	7.3	6.6	1.1
1:1.5		32.8	24.9	26.4	2.60	3.74	13.6	2.00	2.04	6.4	8.2	.70
<i>Required for</i>												
$(H_2O)Mo_3Cl_7(phen)_3 \cdot 2H_2O$		35.5	21.9	38.1	2.74	7.43		2.0	1/233			
<i>Required for</i>												
$[Mo_3Cl_{13}(phen)_3] \cdot 12H_2O$		32.8	34.2	24.6	2.7	4.8		2.0	1/2.0			

TABLE 3.4

ANALYTICAL DATA FOR PRODUCTS OBTAINED BY ADDITION OF 2,2'-DI-
PYRIDYL TO AMMONIUM CHLOROMOLYBDATE (VI) IN 6M HYDROCHLORIC

ACID

Preparative Ratio moles $(NH_4)_2Mo_2Cl_{12}$ moles dipyr.	Mo	Cl	C	H	N	Oxidation equivs.	Oxidation no.	Cl/Mo
1:20	29.1	23.1						2.15
1:2	32.7	25.1	26.7	2.83	5.45	13.2	2.1	2.08
1:2	32.0	23.7	29.7	3.24	5.94	12.3	2.3	2.00
1:1	35.1	26.2	24.0	2.59	5.52	15.1	1.9	2.02
Required for $(Mo_2Cl_8)_2(dipyr)_3 \cdot$ $9H_2O$	35.3	26.1	22.1	2.48	5.18		3.0	2.00

vary appreciably, but for both ligands the following features are recognisable.

(1) Rather surprisingly the two methods of preparation appear to yield similar types of products.

(2) From high [ligand]:[molybdenum (II)] ratios the molybdenum:chloride ratio approaches 1:2.33 and in the phenanthroline case (the one most fully investigated), the gray-blue solid approximates to $(H_2O)Mo_3Cl_7(phen)_3 \cdot 2H_2O$ (or $(phen)Mo_3Cl_7(phen)_2 \cdot 3H_2O$).

(3) From low [ligand]:[molybdenum (II)] ratios the deep blue solids obtained always have molybdenum:chloride ratios near 1:2.00. However analyses are variable and the only definite compounds that seem to appear are $Mo_3Cl_6(phen)_2 \cdot 4H_2O$ and $[Mo_3Cl_6]_2(ligand)_3 \cdot nH_2O$.

(4) The analytical data show a continuous variation of amount of ligand coordinated to the Mo_3 unit. This variation is between 1.5 and 3.0.

The infra-red spectra of all the phenanthroline adducts were found to be essentially the same with bands at 1520 (s), 1435 (s), 1348 (w), 1227 (w), 1152 (m), 1113 (w), 1040 (w,br), 850 (s), 723 (s) cm^{-1} . All the dipyriddy adducts also had similar spectra with bands at 1607 (s), 1500 (w), 1456 (s), 1322 (m), 1252 (w), 1178 (m), 1165 (m), 1080 (w,br), 1030 (m,br), 870 (w,br), 776 (s), 731 (s) cm^{-1} . On careful exposure to air the spectra remained unchanged with the exception of a new band at $972cm^{-1}$ due to Mo=O stretch. These band positions agree with those reported²⁹ for phenanthroline and dipyriddy adducts.

Strong bands at 1508 cm^{-1} (for phenanthroline) and 1537 cm^{-1} (for bipyridyl) were missing - Schilt and Taylor²⁹ have found bands in these positions for the protonated ligand. These results suggest that a proton is the cation when molybdenum:chlorine ratios greater than 1:2.00 are encountered. Bands appropriate for the presence of water are also found in the infra-red.

In the visible region, mulls show a single peak which varies in position from 17.7-18.1 μ . Solution spectra cannot be recorded due to the insolubility of the compounds. This peak position agrees well with that found for previously encountered chloromolybdates (II), but many other staphylonuclear anions also absorb in this region, (including some dimers).

The adducts are all diamagnetic and show a small residual paramagnetism.

(ii) Formulation

The fact that all of the physical and chemical properties of these adducts are similar suggests a basic structural unit, common for all of these compounds.

An isomeric form of the well known hexameric $(\text{Mo}_6\text{Cl}_8\text{Cl}_4)_n$, first prepared by Stephenson, Bannister and Wilkinson,³⁰ has been reinvestigated by Anderson³¹ and is now thought to have a CdCl_2 -type layer structure. This structure allows Mo_3 groups to form while still retaining octahedral coordination of chloride about molybdenum.

This structure has the coordination number requirements of one theoretical possibility for molybdenum (II) chloride (see Table 1.1).

It is now suggested that the unstable adducts prepared here are addition compounds of this new form of molybdenum (II) chloride i.e. they contain triangles of metal-metal bonded molybdenum atoms. The reason for the variable amount of ligand coordinated remains obscure. Where a low Mo_3 :ligand ratio is encountered edge-sharing of the Mo_3 units must occur via chlorine and/or ligand bridging. Both phenanthroline and dipyridyl are well able to bridge between units since the N-N distances are 3.2 Å and 3.3 Å respectively (calculated from known C-C and C-N bond lengths reported³² for similar systems).

The magnetic susceptibility is consistent with extensive metal-metal interaction as implied by the formulation.

The experimental data does not really preclude the possibility of these compounds being dimeric again with bridging ligands and a very short Mo-Mo bond. A bridged structure similar to the one that might occur has been found for molybdenum (II) acetate,³¹ where the Mo-Mo distance is 2.11 Å, compared with the "normal" Mo-Mo distance of 2.7 Å.

CONCLUSIONS

For the compounds reported in Table 3.1 the only structure able to accommodate all three lines of evidence is the trimeric formulation, with the structure based on the Mo_3Cl_9 type, as first

proposed by Anderson and Sheldon.²⁴ Sometimes the species is halogen deficient and sometimes halogen "rich". Unfortunately the most powerful evidence comes from solution studies, and although solid state spectroscopy supports this formulation, the structure in the actual crystal will be unequivocally known only when and if X-ray diffraction studies become possible. As was pointed out in the introduction the formulation of these compounds as trimers is supported by theory.

From reaction mixtures using 1:10-phenanthroline and 2,2'-dipyridyl the solids obtained appear to almost always be mixtures, but some compounds appear to be gemine. Although it seems most likely that these must be trimeric with ligands bridged symmetrically about a triangle of molybdenum atoms, the possibility of them being dimeric, again with bridging ligands and a very short metal-metal bond, cannot be ruled out.

The fact that many of the molybdenum (II) complexes consistently appear to adopt a trimeric structure means that in solution some molybdenum diacetate must break up into chloromolybdenum (II) monomers. Therefore in solution there must be an equilibrium between monomers, dimers and trimers.

EXPERIMENTAL

The amines were used as supplied from Koch-Light.

Molybdenum diacetate was prepared using the modifications of the method of Hannister and Wilkinson³⁴ as suggested by Anderson and Sheldon.²⁴

To prepare the amine, chromium, and thallium complexes molybdenum diacetate (1 gm) was shaken with 50 ml of a saturated solution of the cation in 12M hydrochloric acid for 1 hr at room temperature. The brightly coloured complexes were filtered off, washed with 12M hydrochloric acid and acetone and then dried in vacuum.

The thallium complex could only be prepared in very low yield because of the extremely low solubility of thallium chloride in hydrochloric acid. Attempts to prepare the complex by mixing thallium chloride and $(\text{NH}_4)_7\text{Mo}_3\text{Cl}_{13}\cdot 2\text{H}_2\text{O}$ solutions in 1M hydrochloric acid were not successful.

The anilinium complex was prepared by shaking aniline (2 gm), molybdenum acetate (1 gm) and hydrochloric acid (50 ml). The product was worked up as above.

Using the above method no product was obtained when pyridine was used, therefore the following procedure was adopted. Pyridine (10 gm) was dissolved in 12M hydrochloric acid (50 ml). This was shaken with finely ground molybdenum (II) acetate (1 gm) in a stoppered filter tube for 30 seconds. This solution was quickly filtered into 150 ml of acetone and the red complex collected as above.

Quinolinium chloromolybdenum (II) complexes could not be prepared by shaking cation solutions with diacetate, as only higher oxidation states of molybdenum appeared; thus the complex was prepared by mixing 2M hydrochloric acid solutions of the hydrochloride and $(\text{NH}_4)_7\text{Mo}_3\text{Cl}_{13}\cdot\text{H}_2\text{O}$. The violet precipitate so formed was worked up as above.

For the determination of change of oxidation number of solutions of molybdenum (II) acetate in 2.5M hydrochloric acid in acetic acid, finely crushed acetate (approx. 0.2 gm) was reacted for different times with 5 ml of the acid. The reaction was quenched by the addition of 0.1M acidified ferric sulphate solution, and the oxidation number of the molybdenum determined by titration of this solution with standard ceric sulphate using N-phenylanthranilic acid as indicator.

1:10-Phenanthroline and 2,2'-dipyridyl complexes:

Using molybdenum (II) acetate as the source of molybdenum (II) they were prepared in an analogous manner to the pyridinium complex, but care was taken to exclude oxygen. The finely divided blue complexes were collected by centrifugation.

Using $(\text{NH}_4)_7\text{Mo}_3\text{Cl}_{13}\cdot\text{H}_2\text{O}$ as the source of molybdenum (II), this complex (1 gm) was dissolved in 2M hydrochloric acid and the ligand in 2M acid added. The complex, which precipitated immediately, was collected by centrifugation and washed with 2M hydrochloric acid and then ethanol, and dried in vacuum.

For all operations (analyses, etc.) involving the phenanthroline and dipyridyl complexes, oxygen was rigorously excluded by use of a glove box, which was continually flushed with dry oxygen-free nitrogen.

The procedure used for all routine operations and analytical methods is outlined in Appendix I.

CHAPTER 4. PREPARATION, PROPERTIES AND STRUCTURE OF SOME COMPLEXES
CONTAINING THE CHLOROMOLYBDENUM (2.5) AND (III) ANIONS

INTRODUCTION

Other workers in this laboratory have shown²⁴ that dissolution of molybdenum (II) acetate in 12M hydrochloric acid yields, after preliminary oxidation, a stable molybdenum oxidation state of +2.5. From such solutions a caesium salt, formulated as $\text{Cs}_6\text{Mo}_4\text{Cl}_{16}$ was precipitated.²⁴

This present work is an extension of the study of molybdenum (2.5) chloro complexes - the preparation of new molybdenum (2.5) complexes being undertaken in the hope that -

- (i) similar compounds, but of differing stoichiometry might be prepared, and that these might help in structural assignment
- (ii) compounds could be prepared that would be soluble in solvents suitable for the determination of conductivity and molecular weight, thus providing a basis for testing the above formulation.

For convenience this Chapter is divided into two sections. The first being a study of the above mentioned molybdenum (2.5) complexes, and the second a study of a rather unusual molybdenum (III) complex prepared under conditions that usually yield molybdenum (2.5) species.

PART I. RESULTS AND DISCUSSION

Compounds prepared

Table 4.1 lists the results of this cation survey. It was found that two methods of preparation for these complexes are available. If no molybdenum (II) complex forms they can be prepared by the reaction of a 12M hydrochloric acid solution of the cation with molybdenum (II) acetate; or they can be prepared by the addition of cation to an already aged molybdenum diacetate-hydrochloric acid solution.

In addition to the complexes listed several other compounds of similar colour, and reaction with alkali, were prepared using tetraphenylarsonium, dipyridylum, and similar large organic cations.

Until it became known that these complexes could be recrystallised, the criterion adopted for sample homogeneity and purity was the reproducible analysis of several preparations. Eventually recrystallisation of $[(C_6H_5)_3PH]_2(H_3O)Mo_2Cl_8 \cdot 2H_2O$ was successful, the products giving analyses as good, or better, than the original products, thus showing that the compound is not a mixture, and that the complex is unchanged on recrystallisation.

Table 4.1 shows that oxidation numbers for unrecrystallised samples of this complex were high. This was not due to oxidation of the solid, but to the coprecipitation of oxidation products during the preparation, as the oxidation number of the complex, undried, in a hydrochloric acid slurry, was also found to be high. This phenomenon accounts for some of the poor analyses obtained.

TABLE 4.1

ANALYTICAL DATA FOR CHLOROMOLYBDATES (2.5)

Compound	Cation:Mo:Cl ₂ ratio	Mo	Cl	C	H	F	N	Oxid ^a No.
$(C_3PH)_2(H_3O)Mo_2Cl_8 \cdot 2H_2O$	Equimolar	18.4	27.1	41.1	3.80	6.0		2.7
		18.2	26.7					2.7
mustard-yellow		18.1	26.7					2.6
yield ~90%		19.3	26.9					2.8
		18.1	26.4	42.0	4.3	5.9		2.7
	Recrystallised	18.3	26.7			6.2		2.5
	"	17.9	26.9	41.1	3.8	6.0		2.5
	"	18.2	26.8	41.1	4.0	6.2		2.5
Required		18.8	26.8	40.8	3.7	6.1		2.5
$(C_3PH)_3Mo_2Cl_8$	10:1	15.2	22.7					2.5
		16.8	22.4					2.5
Light-yellow								2.5
yield ~90%								2.5
Required		16.8	22.4					2.5
$(phen)_2 \cdot 1.5 Mo_2Cl_8 \cdot 2H_2O$	1:1	24.1	35.5					2.6 ^a
		24.6	36.4	27.9	2.8		5.5	2.7 ^a
chocolate brown								2.6 ^a
yield ~80%			35.3					2.7 ^a
Required		24.4	36.2	27.5	2.4		6.8	2.6

a - poor end point

Properties

Of the chloromolybdenum (2.5) complexes obtained $[(C_6H_5)_3PH]_2(H_3O)Mo_2Cl_8 \cdot 2H_2O$ was chosen for further study.

This compound, in common with the other chloromolybdates (2.5), was stable indefinitely in vacuum, but in air, over a period of a few weeks decomposed to a dark-green oil.

In alkali, in common with chloromolybdenum (II) compounds it decomposed rapidly to a black precipitate (presumably a hydroxymolybdenum (2.5) species) and a colourless solution containing all of the chloride.

The complex is relatively stable in boiling 12N hydrochloric acid, and can be recrystallised from this, but with appreciable initial decomposition. It is also soluble in polar organic solvents, but in all of these tried it decomposed slowly in solution, thus making conductivity and molecular weight data difficult to obtain.

In vacuum the complex starts to lose weight and darken at 100°C, and melts to a black tar at 145°C with a weight loss of 5.3%. For the reaction



the weight loss is 5.2%.

Figures 4.1 and 4.2 show weight and oxidation number changes with time, under varying conditions, for the complex. These show that increase in both oxidation number and weight, occurs much more rapidly in the atmosphere (moist) than in dry oxygen. Although

FIGURE 4.1. Weight Changes on Storage Under Varying Conditions for $(\phi_3PH)_4(H_3O)_2 Mo_4Cl_{16}.4H_2O$.

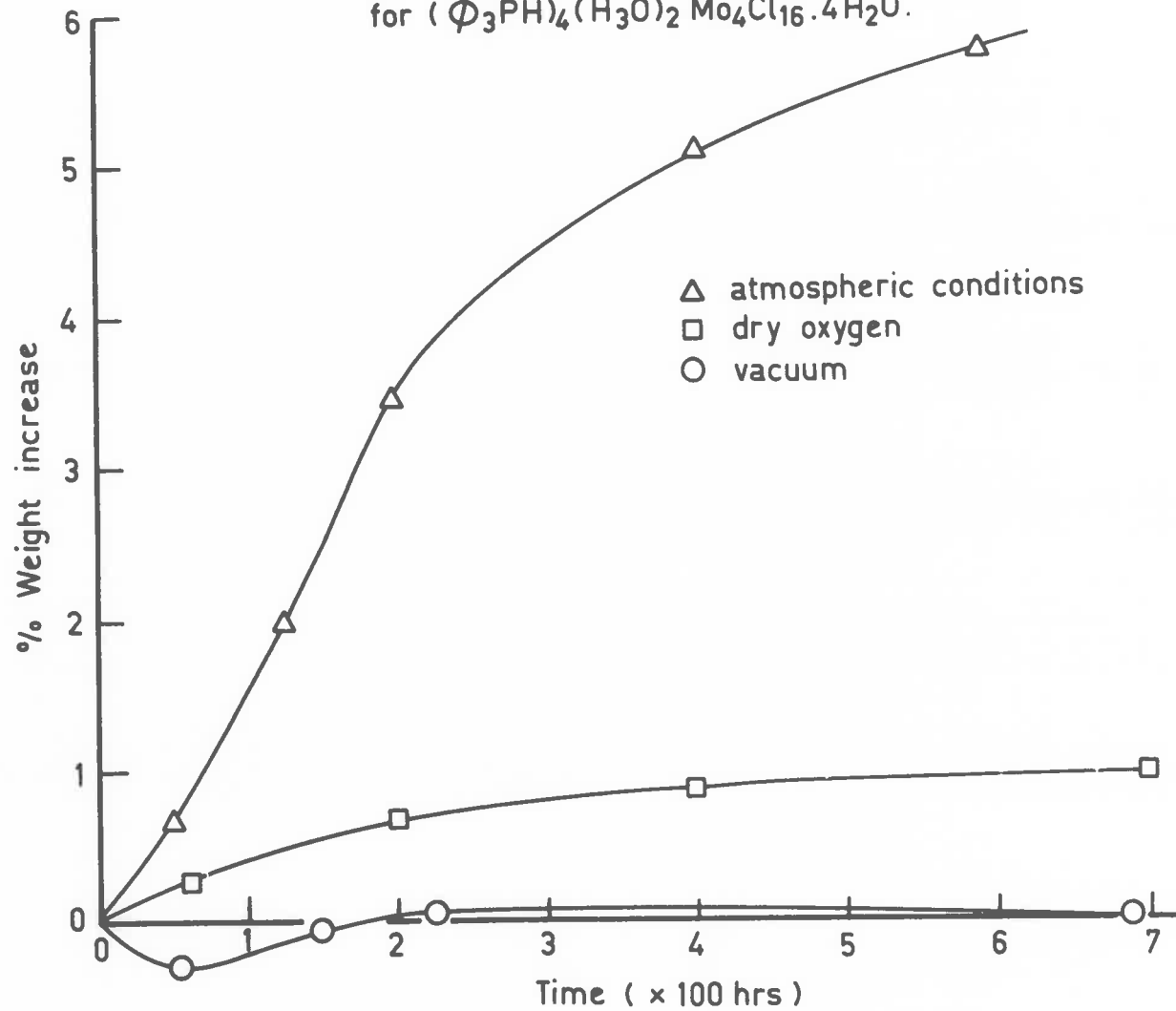
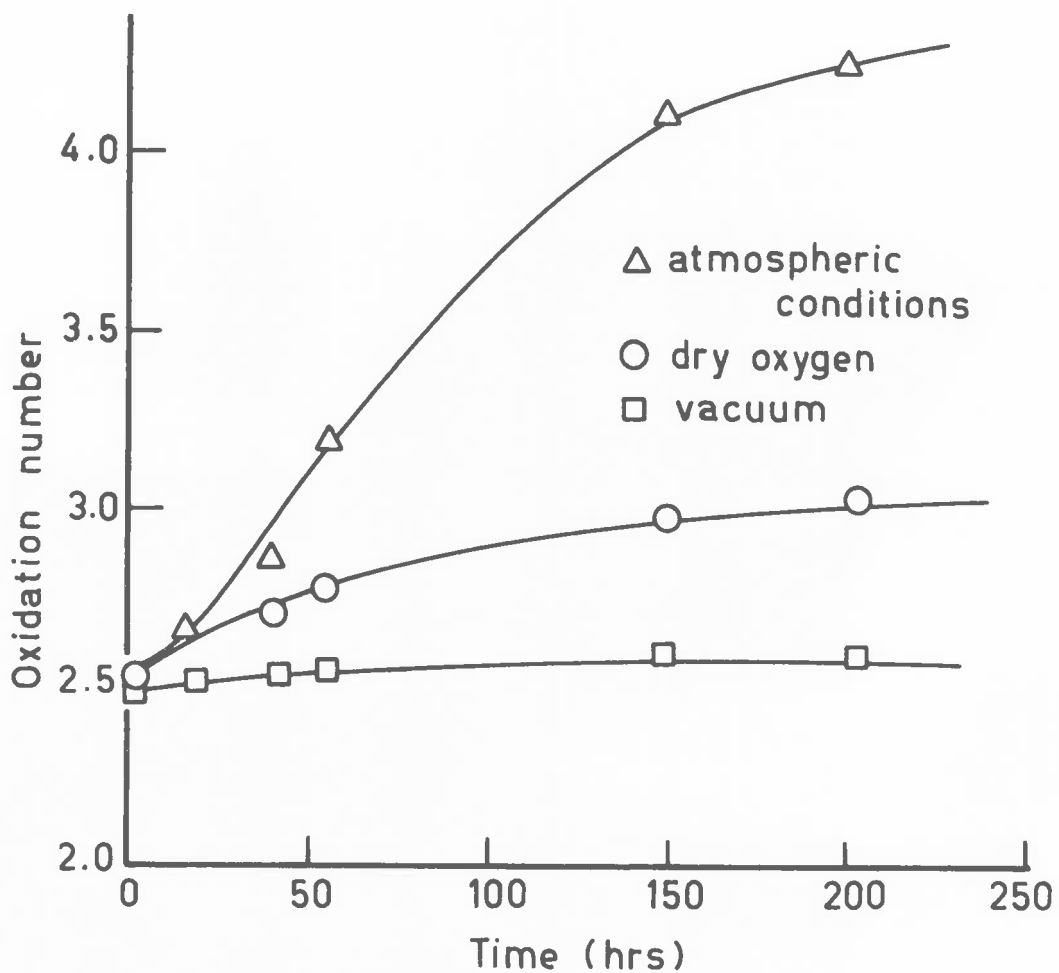


FIGURE 4.2. Change of Oxidation Number on Storage Under Varying Conditions for $[(C_6H_5)_3PH]_2(H_3O)Mo_2Cl_8 \cdot 2H_2O$



this was not a complete study, these results suggest that the first step in the breakdown of the metal cluster is nucleophilic attack by water, followed by breakdown of the metal cluster, and oxygen uptake (oxidation) of the fragments. The above reactions are not light stimulated, as they were carried out both in daylight and in dark conditions without significant change in rate. A similar, although light stimulated, decomposition has been observed²⁵ for the solid state decomposition of the molybdenum (II) complex $(Coen)_3Mo_3Cl_{15} \cdot 6H_2O$. A quantitative explanation, giving a reaction appropriate for the weight change (6.0%) cannot be made.

The infra-red spectrum possesses as well as the bands expected for triphenylphosphonium, peaks at approximately 3400, 1585 and 1615 cm^{-1} - indicating the presence of water.

Structures

(a) Spectroscopic, Solution and Magnetic Evidence

Tables 4.2 and 4.3 - a comparison of the mull and solution spectra respectively, of the chloromolybdate (2.5) compounds - provides good evidence that the staphylonuclear anion has the same structure as the previously reported³¹ alkali metal chloromolybdates (2.3), since the mull spectra are very similar, and the spectra in hydrochloric acid are identical.

The variation of the spectra with hydrochloric acid concentration has been investigated²⁷ in the range 0.05-12M. In this hydrochloric acid concentration range the following are observed -

TABLE 4.2

NULL SPECTRA OF CHLOROMOLYBDENUM (2,5) SPECIES

$(\text{C}_6\text{H}_5\text{PH})_2(\text{H}_3\text{O})\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$	23.1 kK	19.4 kK (sh)	13.0 kK
$(\text{C}_6\text{H}_5\text{PH})_3\text{Mo}_2\text{Cl}_8$	23.3 kK	19.0 kK	13.2 kK
$(\text{phenH}_2)_{1.5}\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$	24.4 kK	18.7 kK	(v. broad)
$\text{Rh}_3\text{Mo}_2\text{Cl}_8$	22.5 kK	19.4 kK (sh)	14.5 kK

TABLE 4.3

SOLUTION SPECTRA OF CHLOROMOLYBDENUM (2,5) SPECIES IN

12M HYDROCHLORIC ACID

$\text{Ca}_3\text{Mo}_2\text{Cl}_8^{27}$		$[(\text{C}_6\text{H}_5)_3\text{PH}]_2(\text{H}_3\text{O})\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$	
$\nu(\text{kK})$	ϵ_{max}	$\nu(\text{kK})$	ϵ_{max}
47.4	$4 \cdot 10^4$	triphenylphosphine obscures spectrum	
42.0	$6 \cdot 10^4$		
23.6	$3.6 \cdot 10^3$	23.6	$3.6 \cdot 10^3$
19.4	270	19.3	240
13.2	220	13.1	270

(i) In 12M hydrochloric acid the spectrum is very similar to that reported for $K_3Mo_2Cl_9$ ³⁵ i.e. this suggests that the solid contains ligand deficient $Mo_2Cl_9^{4-}$ with the reaction $Mo_2Cl_9^{3-} + Cl^- \rightarrow Mo_2Cl_9^{4-}$ occurring on solution.²⁷

(ii) In 0.1M-8M acid the initially yellow solutions evolve a gas (presumably hydrogen) and take on a pink hue at a rate inversely proportional to acid concentration. It has been suggested²⁷ that this corresponds to the reaction $2H_3O^+ + 2Mo_2Cl_9^{4-} \rightarrow 2Mo_2Cl_9^{3-} + 2H_2O + H_2$, but the spectrum found is not in agreement with that found in this work (see Chapter 7) for $Mo_2Cl_9^{3-}$. It is not unreasonable that oxidation of the cluster should occur, since this is a well known phenomenon in other metal clusters. In this work this reaction was investigated to determine whether or not $Mo_2Cl_9^{3-}$ was produced. Addition of caesium chloride to dilute chloromolybdenum (2.5) solutions did, indeed, result in the precipitation of $Cs_3Mo_2Cl_9$ (identified by powder photography), but since the spectrum found above does not correspond to that of $Mo_2Cl_9^{3-}$ some monomeric molybdenum (III) and molybdenum (V) species must be produced simultaneously. This is the first example in molybdenum chemistry where a staphylonuclear complex has been oxidised with retention of the staphylonucleus.

In an attempt to correlate the observed spectra with oxidation number changes in solution, 1 and 8M hydrochloric acid solutions were investigated oxidimetricaly by van Bronswyk.²⁷ (Unfortunately the

caesium chloromolybdate used was not sufficiently soluble in 12M hydrochloric acid for a study at this concentration to be made.) He found that solutions of chloromolybdates (2.5) nearly always gave oxidation numbers of +3.0 except in ice cold solutions, where initial values of 2.7, increasing rapidly to 3.0, were observed. These results seem paradoxical when an attempt is made to correlate the spectral results with them, but the paradox is solved if the following hypotheses are made.

Oxidation numbers are determined by quenching with aqueous ferric solution, followed by ceric titration i.e. in low chloride concentration, and it is known (see spectral results) that the rate of oxidation of chloromolybdates (2.5) is fairly rapid in low chloride concentration. Hence the initial spectra in 1-2M hydrochloric acid are considerably different to that in 12M hydrochloric acid, it is now suggested that in 1-2M acid, the structure of the chloromolybdates (2.5) is such that the unit is oxidised to molybdenum (III), by water, before the ferric can react with it. It is also suggested that could the oxidation number be determined in 12M acid it would be 2.5, as is the oxidation number of the solid chloromolybdates (2.5) determined by dissolution of the solid in ferric solutions i.e. this second type of chloromolybdenum (2.5) species does not react so rapidly with water, allowing time for the ferric to react.

If the hypothesis is correct, it provides rather elegant confirmation that the structure of chloromolybdates (2.5) is similar in solid and 12M acid, but different from those in 0.1-2M acid. It

seems that the $\text{Mo}_2\text{Cl}_9^{4-}$ species must become aquated in low [hydrochloric acid] for it to become unstable. It has been noticed³⁶ that $\text{Mo}_6\text{Cl}_8^{4+}$ becomes less stable when oxygen donor ligands replace chlorides.

Other explanations may be possible, but the above seems to have most appeal.

Molecular weight and conductivity data were, as expected, difficult to obtain reproducibly. Nitrobenzene was chosen as the solvent. To see if decomposition of the complex occurred on solution, attempts were made to recover the complex unchanged from solution, but oils always resulted. However the spectrum of the complex showed little change up to 5 mins after dissolution.

Molecular weights in the range 290-330 were obtained by depression of the freezing point. For a tetrameric formulation of the complex (7 ions) the molecular weight expected is 302; for a dimeric formulation (4 ions) molecular weight expected is 264.

The molar conductance at infinite dilution is approximately $190 \text{ ohm}^{-1} \text{ cm}^2 \text{ moles}^{-1}$, assuming either a dimer or tetramer and is therefore useless in determining the degree of polymerisation of the staphylonuclear anion.

$[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{H}_3\text{O})\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ is diamagnetic at room temperature, $\chi_m = 3.83 \cdot 10^{-4}$ C.G.S. units. This corresponds to a μ_{eff} value of 0.4 BM per molybdenum atom, which is consistent with considerable metal-metal interaction.

(b) Powder Diffraction Data

Table 4.4 shows a comparison of the d-spacings of $K_3W_2Cl_9$ (as reported by Brosse³⁷), $Rb_3W_2Cl_9$ (prepared in this work), $Rb_3Mo_2Cl_9$, $Rb_3Mo_2Cl_8$, and $Cs_3Mo_2Cl_8$. From the table it may be readily gleaned that the d-spacings of caesium and rubidium chloromolybdates (2.5), especially the latter, are very similar to those found for $Rb_3W_2Cl_9$, suggesting that the above complexes are isostructural. Since it seemed possible that the $Mo_2Cl_8^{3-}$ structure might be similar to that reported for $Mo_2Cl_8^{2-}$ ³⁸ and $Tc_2Cl_8^{3-}$,³⁹ the d-spacings for $K_2Mo_2Cl_8 \cdot 2H_2O$ and $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ were calculated using the reported^{38,39} unit cell data. In Table 4.4 an attempt has been made to match these values with those of rubidium and caesium chloromolybdates (2.5). As can be seen there is very little similarity for d-spacings greater than 3.0 (some fit for values less than this is observed, because of the large number of possible d-spacings in this area to choose from).

Since $Cs_2Mo_2Cl_8$ is isomorphous with $Rb_3W_2Cl_9$ (Chapter 7), the oxidation of molybdenum (2.5) species to give dimeric molybdenum species (see earlier) occurs with retention of structure, as well as of staphylnuclear.

CONCLUSIONS

Several new chloromolybdates (2.5) have been prepared, but all were of similar stoichiometry, thus the analytical figures above do not aid structural assignment.

TABLE 4.4

COMPARISON OF POWDER DIFFRACTION DATA OF SOME CHLOROMOLYBDATES (2.5) WITH THAT OF SOME POSSIBLY

ISOSTRUCTURAL COMPLEXES

$K_3W_2Cl_9$ ³⁷		$K_3W_2Cl_9$ ^a		$Rb_3W_2Cl_9$ ^b		$Ca_3Mo_2Cl_8$ ^c		$Rb_3Mo_2Cl_8$ ^c		$(NH_4)_3Te_2Cl_8 \cdot 2H_2O$ ^{d39}	$K_2Re_2Cl_8 \cdot 2H_2O$ ^{d38}
d	int	d	int	d	int	d	int	d	int	d	
		8.29	4	8.34	8	8.56	m	8.26	7	8.40	7.19
		7.89	8	-						6.74	6.81
		6.17	2	6.28	2	6.40	m	6.10	2	6.32	5.97
		5.79	10	5.89	9	6.02	m	5.75	8	5.64	
		4.91	1	-		5.12	m			5.15	4.31
										4.68	
4.06	w	4.01	2	4.14	3	4.24	m	4.08	6	3.94	3.96
3.59	s	3.57	6	3.63	8	3.70	vs	3.55	9	3.76	3.80
3.39	vw	3.36	1	3.46	3	3.56	w	3.42	1	3.53	3.60
3.28	m	3.26	4	3.32	4	3.41	vw	3.27	2	3.37	3.41
3.11	vw	3.09	1					3.09	1	3.04	2.99
3.05	w	3.02	2								
2.99	w	2.96	2								
2.90	w	-									
2.87	vs	2.85	8	2.93	10	3.02	vs	2.91	10	2.93	2.91
						2.86	w	2.75	3	2.80	2.83
2.69	m	2.68	7	2.74	7	2.79	vs	2.69	10	2.67	2.70
2.48	m	2.46	7	2.51	7	2.57	vs	2.48	8	2.51	2.55
2.46	m	-									
2.35	vw	-									
2.32	s	2.30	6	2.35	4			2.31	4	2.34	2.40
2.23	vw	-									
2.24	m	2.23	6	2.28	5	2.34	m	2.26	6		
2.17	m	2.16	8	2.21	6			2.21	4		
2.15	m	2.15	8	2.19	2	2.23	m	2.16	4		

cont'd

1
1

2.07	w	2.07	2	2.09	1	2.12	n	2.12	1
2.04	w	2.03	2	2.07	2			2.06	3
2.02	vw	2.01	2	2.03	1				
2.01	vw	2.00	2					2.00	1
1.94		-							
1.92	w	1.92	a	1.97	6	2.03	m	1.96	6
1.90	m	1.89	5	1.92	5	1.98	n	1.91	6
1.86	m	1.83	7	1.89	6	1.94	m	1.83	6

a - prepared by tin reduction⁴⁴

b - prepared by disproportionation of WCl_6 (see Chapter 8)

c - powder photographs taken and measured by I.R. Anderson³¹

d - d-spacings chosen from all those possible (calculated from cell constants),
in an attempt to match them with the others

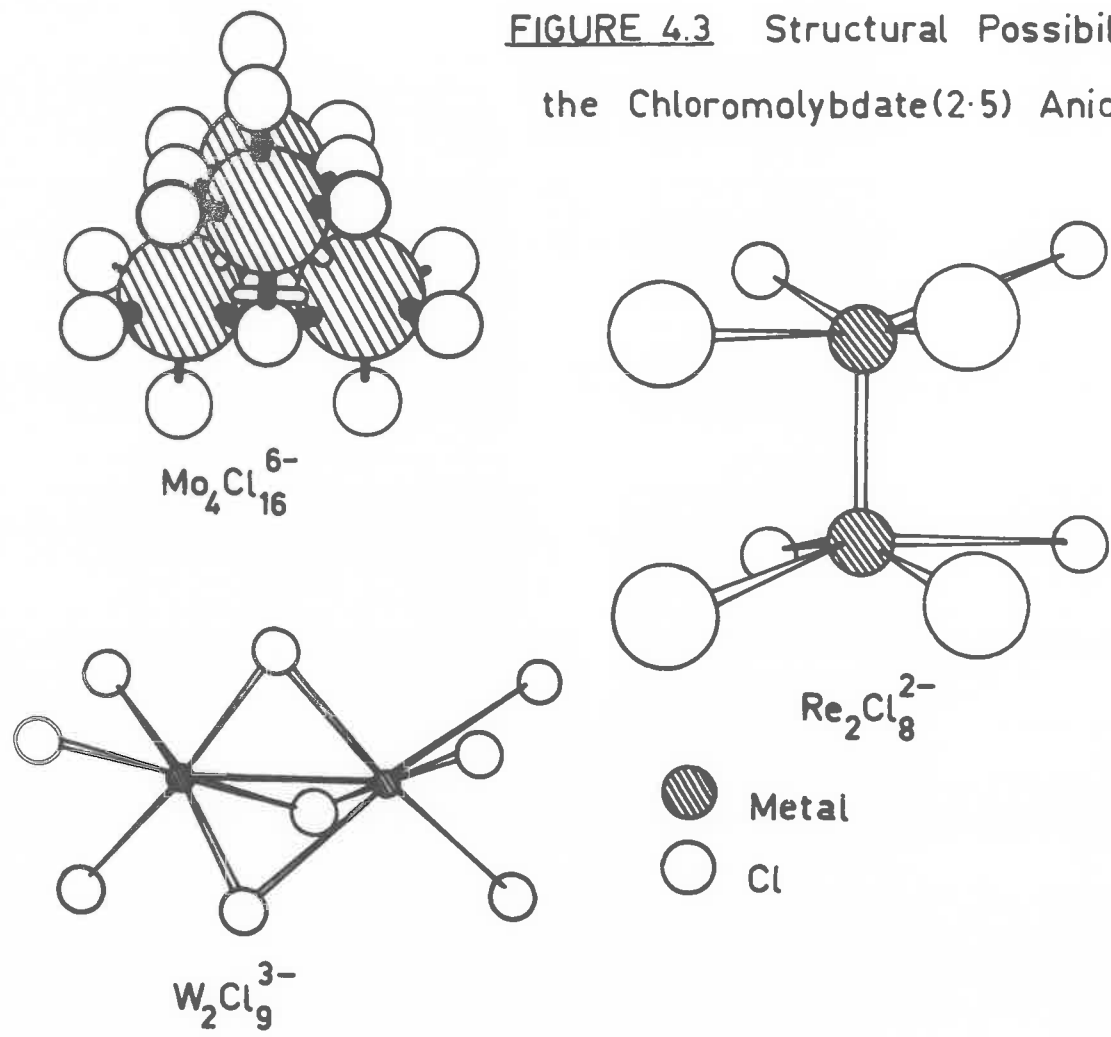
The three most likely possibilities for the structure are shown in Figure 4.3. These are -

- (I) The $\text{Mo}_4\text{Cl}_{16}$ structure proposed by Anderson and Sheldon.²⁴
- (II) The $\text{W}_2\text{Cl}_9^{3-}$ ⁴⁰ structure - face shared WCl_6 octahedra, with a ligand deficiency.
- (III) The $\text{Re}_2\text{Cl}_8^{2-}$ ³⁸ and $\text{Te}_2\text{Cl}_8^{2-}$ ³⁹ type structures (these are essentially the same).

The evidence presented by the different physico-chemical results for the different structures, is as follows.

- (a) The observed magnetic susceptibility supports, if anything, the tetrameric formulation since the dimer would be expected to have one unpaired electron, (c.f. $(\text{NH}_4)_3\text{Te}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ whose magnetic moment is consistent with one unpaired electron³⁹), while a tetramer with considerable metal-metal interaction should show small positive or negative susceptibility since it has no unpaired electrons.
- (b) Spectral evidence is not conclusive but points to a dimer.
- (c) Molecular weight evidence supports the tetrameric formulation.
- (d) Conductivity is not sensitive enough to distinguish between the possibilities.
- (e) A preliminary crystallographic study carried out by Sheldon⁴¹ on $[(\text{C}_6\text{H}_5)_3\text{P}]_2(\text{H}_3\text{O})\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$, seems to rule out the possibility of the structural unit being a tetramer.

FIGURE 4.3 Structural Possibilities for the Chloromolybdate(2·5) Anion.



(f) Powder diffraction data leans heavily in favour of the $W_2Cl_9^{3-}$ type structure.

From the above, the indirect evidence ((a) and (c)) supports the tetrameric formulation, but the more direct evidence ((b), (e) and (f)), thus the more powerful, strongly supports a ligand deficient $W_2Cl_9^{3-}$ structure.

The theory predicts that if the structure is dimeric there will be an extremely short molybdenum-molybdenum distance (2.1-2.2 Å). Complete elucidation of the structure will therefore prove a useful test of the theory.

PART II. INTRODUCTION

In almost all cases shaking of molybdenum (II) acetate with 12M hydrochloric acid and cation yields either molybdenum (II) or (2.5) species - as is expected from the oxidation number changes observed²⁶ for the acetate in 12M hydrochloric acid. However with quinolinium as cation an unusual complex is formed.

RESULTS AND DISCUSSION

The products obtainable from molybdenum (II) solutions using quinolinium as cation are of at least three types.

(1) The $Mo_3Cl_{13}^{7-}$ type, prepared by addition of quinolinium hydrochloride to a high concentration of molybdenum (II) chloro species in solution (see Chapter 3).

(ii) Very unstable, yellow-brown complexes prepared by shaking equimolar quantities of molybdenum (II) acetate and quinoline in 1M hydrochloric acid.

(iii) A molybdenum (III) complex which separates out when using high [quinolinium]:[acetate] ratios. This is formulated as



It is interesting to note that quinolinium has a quite marked effect on the rate of oxidation of molybdenum (II) - hydrochloric acid solutions, since precipitation of this molybdenum (III) complex commences almost immediately from what oxidation number studies²⁴ show normally to be a molybdenum (II) solution. It seems that molybdenum (II) chloro species must be precursors for the formation of this complex, as it cannot be prepared by addition of cation to a molybdenum (2.5) solution.

An Investigation of $(\text{QnH})_3(\text{H}_3\text{O})_2\text{Mo}_3\text{Cl}_{14}\cdot 4\text{H}_2\text{O}$

A microscopic investigation of the complex showed that it was definitely not a mixture of two crystal types - the crystals all being brick-red hexagonal plates.

Kouřil³⁵ has found that the "compound" $\text{K}_5\text{V}_3\text{Cl}_{14}$ is a mixture of $\text{K}_3\text{V}_2\text{Cl}_9$ and $\text{K}_2\text{V}(\text{OH})\text{Cl}_5$, and during a study of this system, two distinct crystal types were found on microscopic investigation. However Cotton and Lippard⁶² have isolated compounds with the general

formula $\text{M}_2\text{Re}_4\text{Br}_{15}$ and subsequent structural analysis has shown that the crystals were all of the same type, with the unit cell containing four M_2ReBr_6 and four Re_3Br_9 species i.e. this is an intracrystalline effect.

It is suggested here that a similar situation exists in the above compound i.e. crystals have within them, equal mixtures of the dimeric $(\text{QnH})_2(\text{H}_3\text{O})\text{Mo}_2\text{Cl}_9$ and monomeric $(\text{QnH})(\text{H}_3\text{O})\text{MoCl}_5 \cdot \text{H}_2\text{O}$.

Unfortunately the magnetic susceptibility does not fit well with this hypothesis as assuming one paramagnetic molybdenum per formula unit, it is found

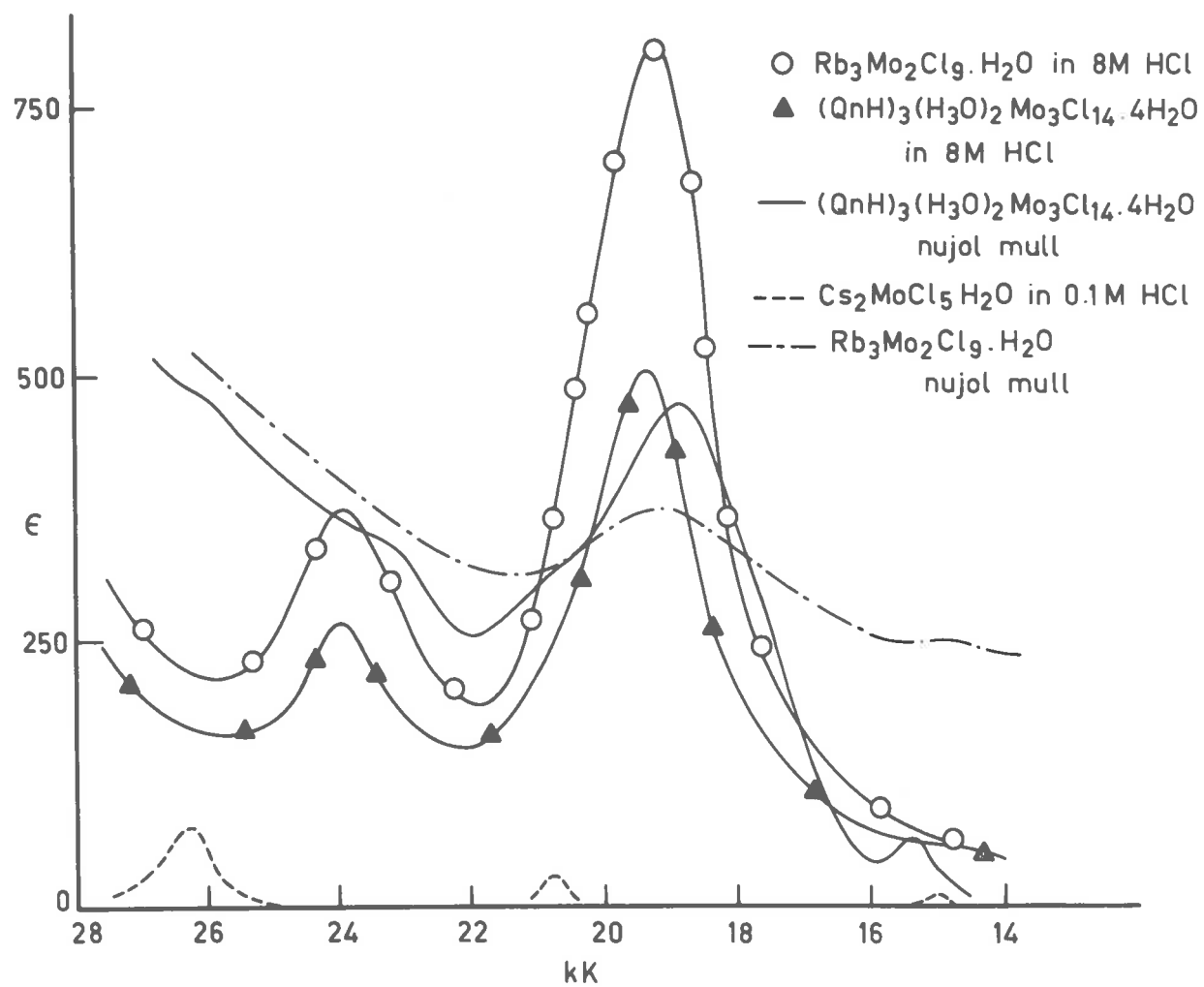
$\mu_{\text{eff}} = 1.6 \text{ BM}$, which is well below the value of 3.78 BM ^{reported} found for

$(\text{NH}_4)_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$.⁴³ Thus one can only assume that there is considerable magnetic interaction between monomer and dimer. Unfortunately Cotton and Lippard⁶² do not report any magnetic data for comparison with this result.

The visible solution and null spectra of the complex are compared with the spectra of $\text{Rb}_3\text{Mo}_2\text{Cl}_9 \cdot \text{H}_2\text{O}$ and $\text{Cs}_2\text{MoCl}_5 \cdot \text{H}_2\text{O}$. Figure 4.4 shows that the spectrum of the quinolinium complex is, indeed, a superimposition of the spectra of $\text{Mo}_2\text{Cl}_9^{3-}$ and $\text{MoCl}_5 \cdot \text{H}_2\text{O}^{2-}$ as is required by the proposed formulation.

This hypothesis is also supported by the fact that dissolution of the quinolinium chloromolybdenum (III) complex in 8M hydrochloric acid, followed by addition of caesium chloride results in the complex $\text{Cs}_3\text{Mo}_2\text{Cl}_9$ (identified by powder photography). The powder diffraction

FIGURE 4.4. Comparison of the Visible Spectra of Some Chloromolybdenum (III) Compounds.



data of the complex when compared with that of $(\text{QnH})_3\text{Mo}_2\text{Cl}_9$, showed no correlation with that of $(\text{QnH})_3(\text{H}_3\text{O})_2\text{Mo}_3\text{Cl}_{14}\cdot 4\text{H}_2\text{O}$, thus precluding the possibility that this complex is a mixture of two crystal types, as was found for $\text{K}_3\text{W}_3\text{Cl}_{14}$.

CONCLUSIONS

Analytical, visual, X-ray and spectroscopic data all provide evidence for the formulation of $(\text{QnH})_3(\text{H}_3\text{O})_2\text{Mo}_3\text{Cl}_{14}\cdot 4\text{H}_2\text{O}$ as containing an intracrystalline mixture of the two different molybdenum (III) chloroanions $\text{Mo}_2\text{Cl}_9^{2-}$ and $\text{MoCl}_5\text{H}_2\text{O}^{2-}$ in equal proportions.

EXPERIMENTAL

The molybdenum (2.5) chloro complexes were prepared by shaking approximately equimolar quantities of cation and molybdenum (II) acetate in 12N hydrochloric acid for 1.5 hrs., followed by filtration, washing with 12N hydrochloric acid and vacuum drying.

The complex $[(\text{C}_6\text{H}_5)_3\text{PH}]_3\text{Mo}_2\text{Cl}_8$ was prepared in the above manner, but by using a ten-fold excess of cation.

$(\text{QnH})_3(\text{H}_3\text{O})_2\text{Mo}_3\text{Cl}_{14}\cdot 4\text{H}_2\text{O}$ was prepared as above using a 10-20 fold excess of quinoline.

Analysis: Calculated for $\text{C}_{27}\text{H}_{38}\text{Cl}_{14}\text{Mo}_3\text{N}_3\text{O}_6$: C, 25.2; H, 3.0; Cl, 38.6; Mo, 22.4; N, 3.3; molybdenum oxidation number 3.0. Found: C, 25.6; H, 3.1; Cl, 38.5; Mo, 22.5; N, 3.3; molybdenum oxidation number, 2.95. (Values very near these were found for three separate preparations.)

Molecular weight was found by the depression of freezing point in redistilled nitrobenzene.

For analytical and other techniques see Appendix I.

CHAPTER 3. STAPHYLONUCLEAR TUNGSTEN CHLORO COMPLEXES

INTRODUCTION

An important theoretical and practical issue is the existence and structure of tungsten (II) compounds other than those derived from tungsten "dihalides". An extensive preparative survey was undertaken in an attempt to find such low valent tungsten compounds.

A study of tungsten (II) compounds derived from tungsten "dichloride" was undertaken in order to fully investigate its properties. Some previous workers have reported^{45,46,47} a few properties of these compounds, but these reports were rather sketchy and made forty years ago. After this work had been completed, a report⁴⁸ appeared on the preparation of a few complexes containing the $W_6Cl_8^{4+}$ unit, as part of a spectroscopic survey. During the early work both molybdenum and tungsten "dichloride" derivatives were formulated as trimers, but since that time Brosset's⁵⁰ crystallographic work has shown that the molybdenum compounds contain the $Mo_6Cl_8^{4+}$ unit, and Sheldon⁵¹ has prepared many derivatives of this unit.

~~besides~~ This work establishing^{ed} a similarity between the structural unit in tungsten (II) and molybdenum (II) chlorides. It ^{then} was hoped that oxidation of ~~the tungsten structural unit~~ might occur with retention of structure, and in this way new complexes ^{be} prepared. Or that ~~the~~ ^{with the} breakdown of the ^{Tungsten} metal cluster, complexes containing a new staphylo-nuclear unit might arise. Oxidation of metal clusters with

retention of structure has been observed^{52,53,54,55} in staphylonuclear niobium and tantalum (2.33) halo complexes, as well as in this work (Chapter 4).

RESULTS AND DISCUSSION

Attempts to Prepare New Staphylonuclear Complexes of Tungsten in Low Oxidation States

The precursor for the preparation of the new molybdenum (II) staphylonuclear halo complexes, is the readily obtainable molybdenum (II) acetate, (prepared by the reaction of molybdenum hexacarbonyl, diglyme[†] and acetic acid³⁴) but using a wide range of conditions and substituted acetic acids, the synthesis of the corresponding tungsten acetate could not be effected; in each case the end product was a tungsten blue.

In the hope that low valent tungsten chloro-acetates (useful as precursors) might form, three methods of preparation of these were tried.

(i) Reflux of tungsten hexacarbonyl, diglyme, acetic acid and tetraethylammonium chloride or dry hydrochloric acid.

(ii) Reflux of $(C_2H_5)_4N.W(CO)_5Cl$ with diglyme and acetic acid.

[†] diethyleneglycol dimethyl ether

(iii) The reaction (usually in a sealed tube) of acetic acid with tungsten (II) chloride.

Method (iii) at first seemed to show most promise. The products obtained were deep brown, but of variable analyses and insoluble in hydrochloric acid, and therefore of no use as a starting material for chlorotungsten compounds. Methods (i) and (ii) gave only tungsten blue.

The methods which proved successful in the preparation of the Na_2Cl_9 ^{2- 56} and Tc_2Cl_8 ^{3- 57} units i.e. reduction with hypophosphorous acid, hydrogen under high pressure, or hydroxylamine, of high valent hydrochloric acid solutions, also proved unsuccessful in the preparation of low valent tungsten species.

It was found that the previously reported⁵⁸ $(\text{C}_2\text{H}_5)_4\text{NW}(\text{CO})_5\text{Cl}$ was insoluble in aqueous hydrochloric acid, but on oxidation of this to the tungsten (II) state[†] by chlorine in chloroform, followed by immediate extraction with hydrochloric acid, yielded brightly-coloured solutions, but only higher valent tungsten chloro complexes could be precipitated out with caesium chloride.

[†] A report⁵⁹ that $(\text{C}_2\text{H}_5)_4\text{N.W}(\text{CO})_4\text{Cl}_3$ could not be isolated has been made, this was confirmed, but there did not appear to be any marked oxidation of the chloroform solution before addition of the hydrochloric acid.

Properties of Tungsten (II) Chloride

The tungsten (II) chloride is soluble in, and can be crystallised from, hydrochloric acid to yield the "chloroacid" $((H_3O)_2[W_6Cl_8]Cl_6 \cdot 6H_2O)$, of similar constitution to that reported³¹ for the molybdenum system. Lindner⁴⁶ has previously reported a compound of this constitution, but formulated it as a trimer.

Lindner also reported⁴⁶ that on crystallisation of the chloroacid from hydrobromic acid, he obtained a compound whose analyses fit the formula $(H_3O)_2W_6Cl_6Br_3 \cdot 6H_2O$ (he formulated it as a trimer). Since this is a rather unexpected result in the light of the known chemistry of chloromolybdenum (II), Lindner's work was repeated. The results of digestion of tungsten chloroacid with 8.5M hydrobromic acid at 90°C, are displayed in Table S.1.

Since the most highly brominated compound obtained in this work (after digestion for 18 hours) was $(H_3O)_2W_6Cl_{7.25}Br_{6.75} \cdot 6H_2O$, it seems difficult to believe that Lindner could have obtained the compound he reported by simple crystallisation. van Bronevyk²⁷ has found that when the chloroacid is subjected to high temperature hydrobromic acid until equilibrium is reached, complete bromo-substitution occurs - but this takes three days at 150°C in a sealed tube!

Crystallisation of the chloroacid from hydroiodic acid yields the expected complex $(H_3O)_2[W_6Cl_8]I_6 \cdot 6H_2O$. In this case longer digestion does not give rise to marked substitution by iodide in the

TABLE 5.1

RESULT OF DIGESTION OF $(\text{H}_3\text{O})_2[\text{W}_6\text{Cl}_6]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ IN 8.5M HYDROBROMIC

ACID FOR VARYING TIMES

Time (hrs)	% Cl	% Br	Cl:Br
0	14.1	24.3	1:1.76 ^a
	14.0	24.7	1:1.78
1	13.5	25.3	1:1.83
7.5	13.0	24.4	1:1.83
18.0	12.5	26.0	1:1.93 ^b

a - corresponds to $(\text{H}_3\text{O})_2[\text{W}_6\text{Cl}_6]\text{Br}_6 \cdot 6\text{H}_2\text{O}$

(calc. Cl = 14.1%; Br = 23.9%)

b - corresponds to $(\text{H}_3\text{O})_2[\text{W}_6\text{Cl}_{7.25}\text{Br}_{.75}]\text{Br}_6 \cdot 6\text{H}_2\text{O}$

(calc. Cl = 12.6%; Br = 26.3%)

$W_6Cl_8^{4+}$ core, but appreciable decomposition occurs. (van Bronsweyk²⁷ reports that under extreme conditions the $[W_6Cl_3I_3]^{4+}$ unit is attained.)

In order to test that the chloroacid has the formulation $(H_3O)_2[W_6Cl_8]Cl_6 \cdot 6H_2O$ rather than that of an oxidised derivative e.g. $(H_3O)_2[W_6Cl_8]Cl_6 \cdot nH_2O$ determination of the free acid was attempted.

Since the chloroacid is unstable in neutral or basic aqueous solutions, the free acid content was determined by titration with base into an ethanolic solution of the acid. In all cases a little too much alkali was consumed, and, at the same time, a dark-coloured precipitate was formed rather than the expected yellow $[W_6Cl_8]Cl_4 \cdot nH_2O$ e.g. titration of 0.1967 gm of chloroacid in ethanol with standard (0.100N) aqueous caustic soda gave an end point of 2.22 ml (calculated for $(H_3O)_2[W_6Cl_8]Cl_6 \cdot 6H_2O$, 2.35 ml) which is in reasonable agreement with that expected. The high titre value must be due to some alkali being consumed by the reaction of alkali with the $W_6Cl_8^{4+}$ unit, since compounds formed by hydroxyl attack are dark coloured.

Comparison of the powder photographs of $(H_3O)_2[W_6Cl_8]Cl_6 \cdot 6H_2O$, $(H_3O)_2[W_6Cl_8]Cl_6 \cdot 6H_2O$ and $(H_3O)_2[W_6Cl_8]Br_6 \cdot 6H_2O$ show that the first two are isomorphous, but, surprisingly, the bromo acid has a different powder pattern. Clark et al⁴⁸ report that all three are isomorphous.

The anhydrous chlorotungsten (II) halides can be prepared by heating the corresponding acids at 200°C in vacuum. The solids obtained in this manner are amorphous. As can be seen from Table 5.2, the colour changes on exposure to air and heating are very similar to those witnessed for their molybdenum analogues.⁵⁷ At higher

TABLE 3.2

VARIATION OF COLOUR WITH TEMPERATURE FOR CHLOROTUNGSTEN (II)

HALIDES

	In vacuum at 25°C	After exposure to air	In vacuum at 200°C
$W_6Cl_8 \cdot Cl_4$	yellow	light yellow	orange
$W_6Cl_8 \cdot Br_4$	yellow	yellow	medium brown
$W_6Cl_8 \cdot I_4$	chocolate brown	light brown	deep brown

temperatures (>300°C) the normally thermochroic $W_6Cl_8 \cdot Cl_4$ becomes irreversibly darkened, and the chloride content and weight drops (calculated weight loss for $(H_2O)_2W_6Cl_8 \cdot Cl_6 \cdot 6H_2O \xrightarrow{\Delta} W_6Cl_8 \cdot Cl_4$ is 11.7%, found 13.8%). Comparison of this temperature with the temperature at which $Mo_6Cl_8 \cdot Cl_4$ starts to decompose, (>600°C) reflects the general trend that chlorotungsten compounds are less stable than their molybdenum analogues under most conditions.

Since there appeared to be a chemical change in moist air, (Table 3.2) the weight change (assumed to be due to the uptake of water) of the anhydrous halides in moist air was investigated. A fairly rapid weight increase was observed at first, followed by a slow loss in weight, which, presumably, corresponds to the loss of hydrohalic acid in accordance with the partial hydrolysis.



as was observed⁵¹ in the molybdenum system. The hydration numbers of the halides were obtained from the weight increase with time graph⁵¹ (Figure 5.1) and were found to be

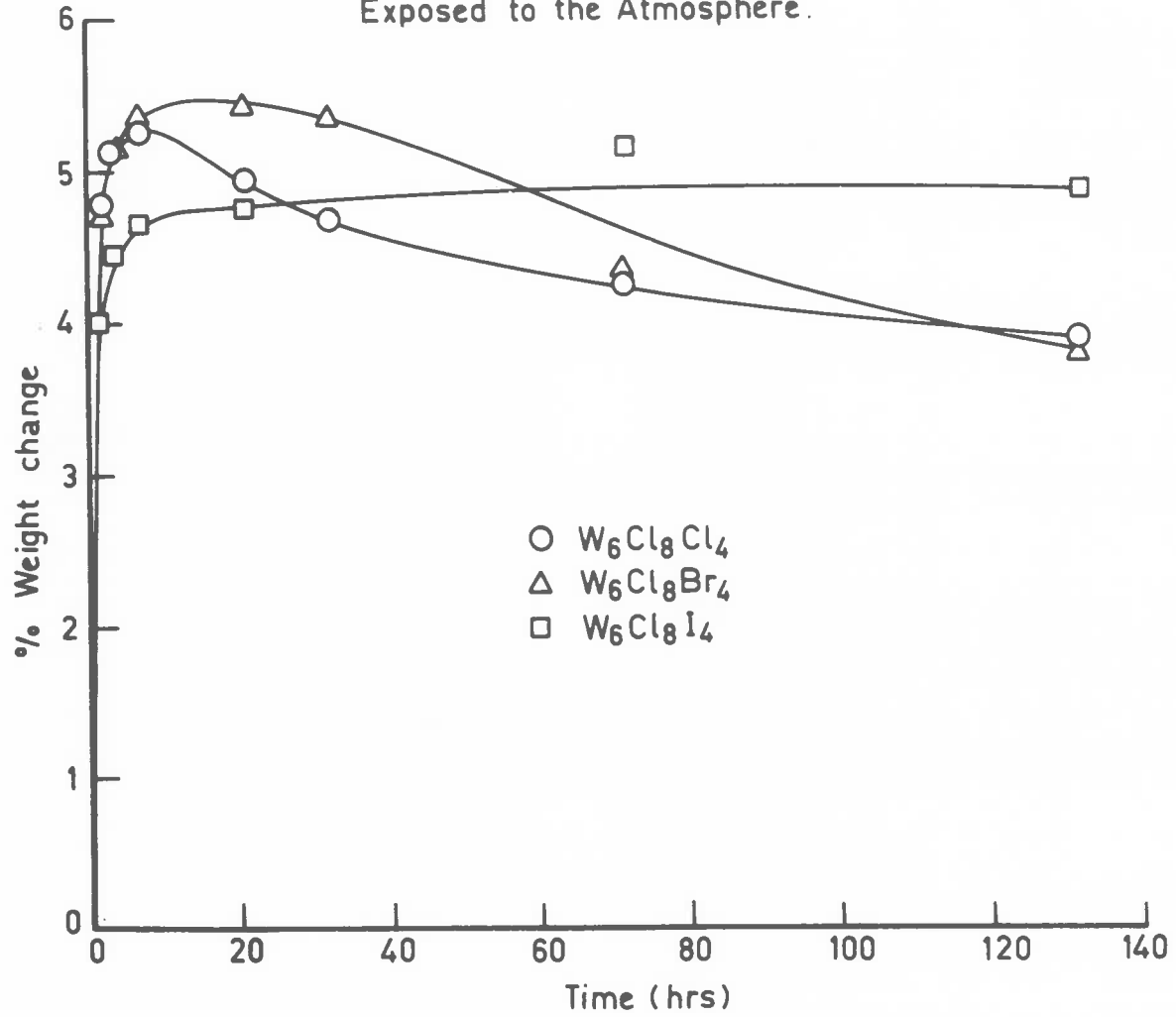


Since the reaction took place in the solid state these may not correspond to maximum hydration numbers.

Complexes Containing the $\text{W}_6\text{Cl}_8^{4+}$ Species

The complexes $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{W}_6\text{Cl}_8\text{Cl}_6$, $[(\text{C}_2\text{H}_5)_4\text{N}]_3(\text{H}_3\text{O})$, $[\text{W}_6\text{Cl}_8]_2\text{Cl}_{12} \cdot 3\text{H}_2\text{O}$, $\text{Cs}_3(\text{H}_3\text{O})[\text{W}_6\text{Cl}_8]_2\text{Cl}_{12} \cdot 3\text{H}_2\text{O}$ and $\text{W}_6\text{Cl}_8\text{Cl}_4 \cdot 2\text{DMSO}$ were prepared,⁴⁵ the X-ray powder patterns of the first two being identical with their molybdenum analogues.⁶⁰ Clark et al⁴⁸ have reported the preparation of $[(\text{W}_6\text{Cl}_8)\text{Cl}_2(\text{o-phen})_2]\text{Cl}_2$ and $[(\text{W}_6\text{Cl}_8)\text{Cl}_2(\text{diars})_2]\text{Cl}_2$ while Lindner⁴⁶ has reported the preparation of some rather unexpectedly formulated pyridinium salts and pyridine adducts. It is noteworthy that in both chlorotungsten (II) and chloromolybdenum (II) chemistry the $\text{M}_6\text{Cl}_8^{4+}$ species prefers octahedral coordination about it, and many of these complexes can be regarded as relatively simple octahedral complexes, MX_6 , where $\text{M} = \text{W}_6\text{Cl}_8^{4+}$, this provides a rather simple basis for the seemingly complex behaviour of these staphylonuclear complexes.

FIGURE 5-1. Weight Changes for the Anhydrous Halides When Exposed to the Atmosphere.



Properties of the $W_6Cl_8^{4+}$ Unit

Complexes containing this unit are quite stable in acid solution; however some substitution of the species may occur, but there is retention of structure. However, in neutral or basic solutions, this species is very unstable, and in water tungsten (VI) compounds have been reported⁴⁵ to yield dark coloured precipitates. In the light of the known chemistry of the $Mo_6Cl_8^{4+}$ species it is possible that the product is one of two types,

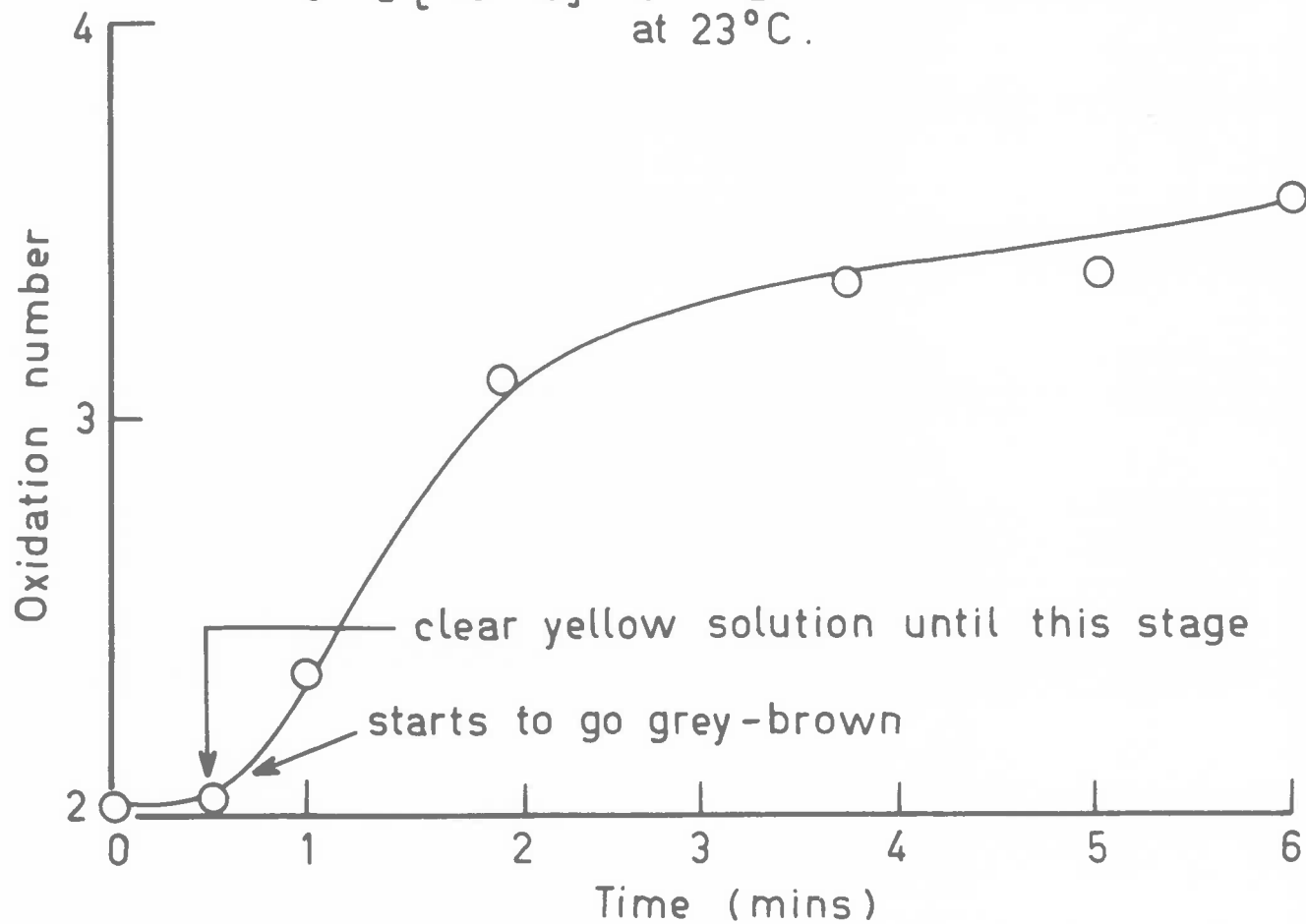
(i) oxidation products - possibly hydrated tungsten (III) and (IV) oxides

(ii) compounds of the type $[W_6Cl_{8-n}(OH)_n]Cl_x(OH)_{4-x} \cdot yH_2O$ formed by nucleophilic attack by water on the unit. In the molybdenum system these compounds are brown-black,^{36,60} and are formed by alkaline attack on $Mo_6Cl_8^{4+}$.

Since the oxidation number of the product in (ii) is 2.0, determination of the oxidation number of tungsten after varying exposures of $W_6Cl_8^{4+}$ to water will determine which path the reaction takes. The result of such a study is shown in Figure 5.2. It can be seen that the oxidation number rises quite rapidly suggesting that reaction (i) is the predominant one.

Reaction of compounds containing $W_6Cl_8^{4+}$ occurs extremely rapidly with dilute alkali. Hydrogen is evolved and complete breakdown of the unit occurs, with there never being any sign of the yellow complex, $[W_6Cl_8](OH)_6^{2-}$, whose molybdenum analogue is readily prepared.⁵¹

FIGURE 5.2. Variation of Oxidation Number of Tungsten in $(\text{H}_3\text{O})_2[\text{W}_6\text{Cl}_8]\text{Cl}_6 \cdot 6\text{H}_2\text{O}$ Reacted With Water at 23°C .



The above reactions again emphasize the lesser stability of the $W_6Cl_8^{4+}$ species as compared with $Mo_6Cl_8^{4+}$ under most conditions.

An Attempt to Substitute Chloride in $W_6Cl_8^{4+}$

When compounds containing the $Mo_6Cl_8^{4+}$ unit are dissolved in alkali and allowed to stand, the initially clear yellow solutions precipitate a dark brown solid of the composition $[Mo_6Cl_{8-n}(OH)_n](OH)_4 \cdot xH_2O$. Compounds containing a species of the composition $[Mo_6Cl_{8-n}(OH)_n]^{4+}$ can then be prepared⁶⁰ by addition of hydrobromic acid to the alkaline reaction mixture.

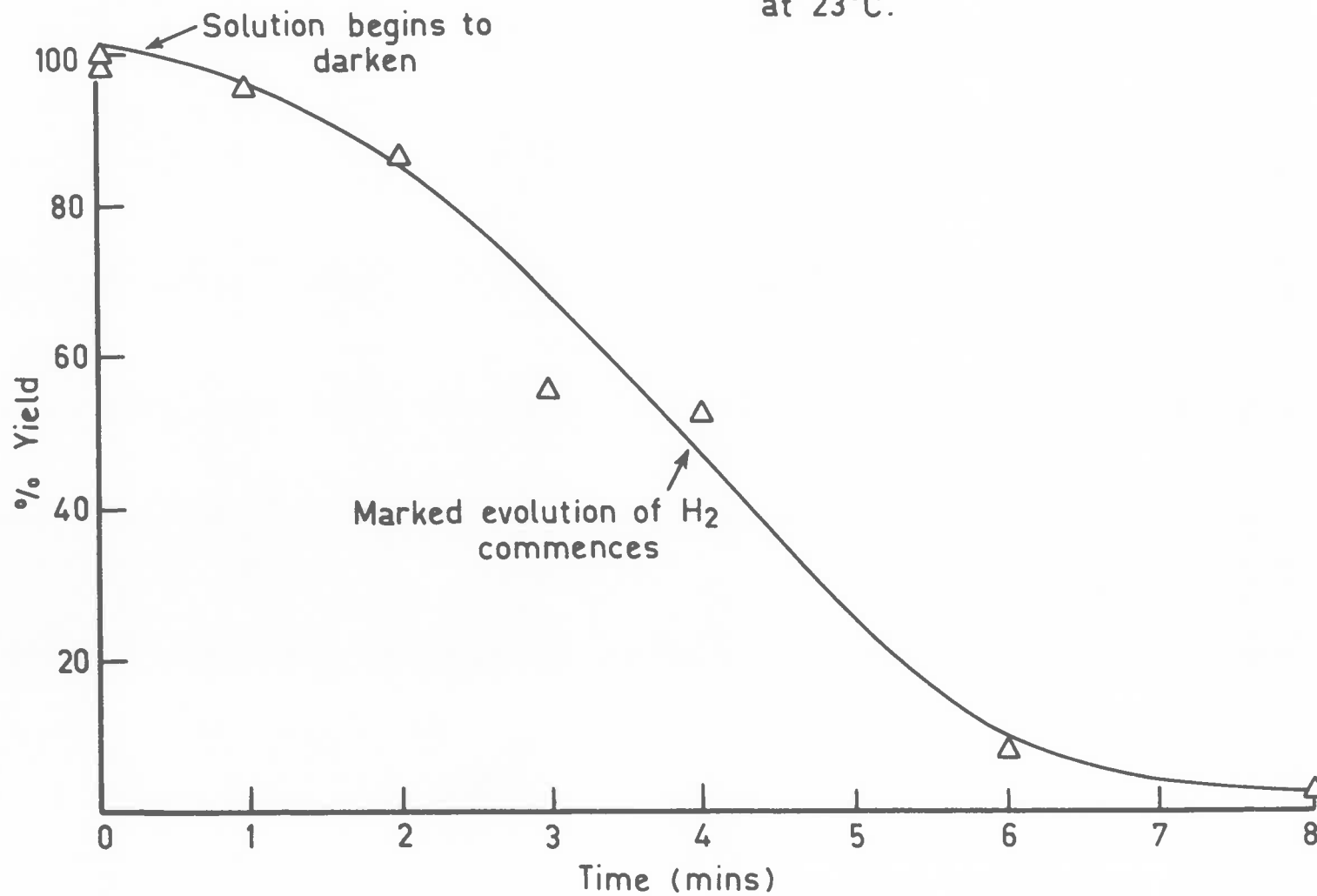
Attempts to carry out this reaction scheme using aqueous caustic soda or ammonia as the alkali proved abortive, as complete break up and oxidation of the staphylonuclear unit occurred instantaneously, with substantial evolution of hydrogen.

However when the chloro acid is dissolved in ethanol and a small amount of aqueous ammonia added, a deep brown precipitate is formed, with only slight evolution of hydrogen. Workup of this yields tetraethylammonium salts which are not significantly bromo (or hydroxyl) substituted. Attempts to bring about substitution by longer exposures to alkali, result only in a non substituted product, but with a marked drop in yield (Figure 5.3). These results suggest that substitution of one hydroxyl into $W_6Cl_8^{4+}$ brings about complete breakdown of the structure.



etc.

FIGURE 5.3 Variation of Yield of $[W_6Cl_8]Cl_6^{2-}$ on Exposure to Base at 23°C.



Spectroscopy

The spectrum of the chloro acid in hydrochloric acid was found (as expected) to be independent of acid concentration (0.1-8.0M). Beer's law was obeyed over a 20-fold concentration range up to 40 kK. The peak observed at 47.8-49.1 kK varies in both position and extinction coefficient with change in complex concentration. In ethanol Beer's law was obeyed over a 20-fold concentration range over the entire spectral range investigated. Figure 5.4 shows that the spectrum is virtually independent of solvent, and is quite similar to that reported⁵¹ for compounds containing the $Mo_6Cl_8^{4+}$ species.

On long standing, 0.1M hydrochloric acid and ethanolic solutions of the chloro acid deposit ^{ed} yellow solids - these are possibly the compounds $[W_6Cl_8]Cl_4 \cdot nH_2O$ and/or $[W_6Cl_8]Cl_3(OH) \cdot nH_2O$ resulting from partial hydrolysis of $[W_6Cl_8]Cl_6^{2-}$.

The shape of the spectrum of the $W_6Cl_8 \cdot Cl_6^{2-}$ ion in solution suggests that a number of bands are hidden, thus the spectrum was resolved into the minimum number of gaussian peaks, in order to detect these bands. Using extrapolated results of the molecular orbital energy calculations of Cotton and Haas⁶¹ together with a p value of 6.0, it can be seen (Table 5.3) that there is rather striking agreement between the experimentally determined, and the calculated peak positions assuming a valence state ionisation potential of 39.0 for tungsten (II). It is reasonable to suppose that the band observed at 43.4 kK is due to metal-chloride charge transfer since it has a high extinction coefficient (a similar band is found in $[Mo_6Cl_8]Cl_6^{2-}$ ²⁸).

FIGURE 5-4 Ultra-violet Spectrum of

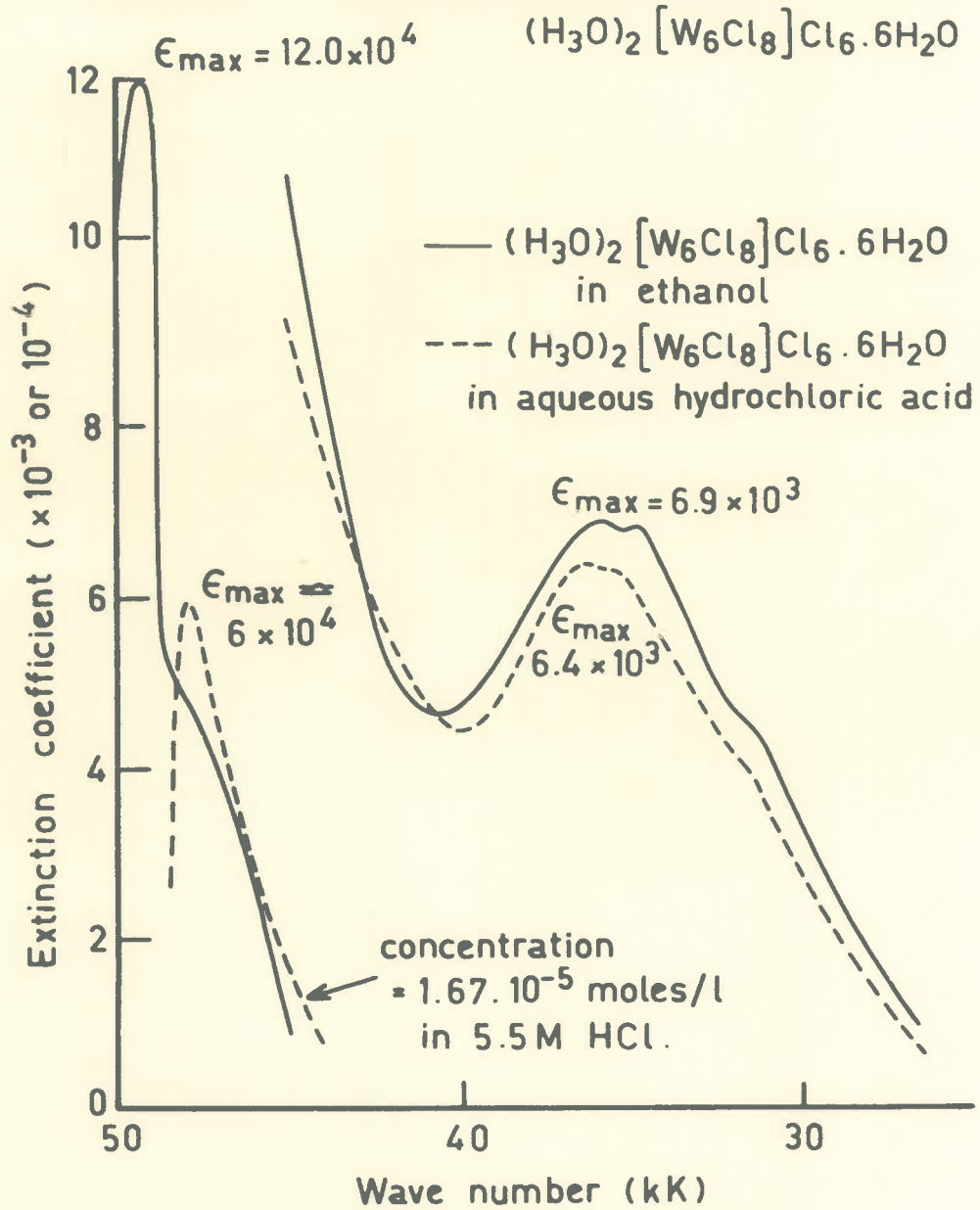


TABLE 5.3

COMPARISON OF PREDICTED AND EXPERIMENTAL PEAK POSITIONS FOR



ν observed (kK)	ν calculated (kK)	Assignment
49.7	52	$T_{2g} \rightarrow T_{1u}$ or $T_{1u} \rightarrow A_{2g}$
48.0	50	$E_g \rightarrow T_{1u}$
43.4	charge transfer ^a	
36.3	36	$T_{1u} \leftarrow T_{2g}$
32.4	31	$T_{1u} \leftarrow E_g$
	25	$T_{2u} \rightarrow T_{2g}$

a - see text

The spectrum below 30 kK is seemingly featureless and resolution proved unsatisfactory.

It is concluded that the octahedronuclear models chosen by Cotton and Haas are strikingly successful for $\text{W}_6\text{Cl}_8^{4+}$, $\text{Mo}_6\text{Cl}_8^{4+}$ 27 and $\text{Nb}_6\text{Cl}_{12}^{2+}$ 62 species, as in all cases they provide an intelligible basis for the unusual structure, and account for the rather complex ultraviolet and visible spectra.

Attempts to Oxidise the $\text{W}_6\text{Cl}_8^{4+}$ Species

Attempts were made to produce, by oxidation, species such as $\text{W}_6\text{Cl}_8^{6+}$. The following were tried -

(i) Bubbling oxygen through an ethanolic solution of the chloro acid for several weeks. After this time the tungsten species was precipitated out with tetraethylammonium, but only the unoxidised $[(C_2H_5)_4N]_2W_6Cl_8 \cdot Cl_6$ resulted (Analysis: Calculated, Cl, 26.8; Found, Cl, 26.7).

(ii) Oxidation of hydrochloric acid solutions of the chloro acid using ferric and ceric. With these oxidants, it appeared that once oxidation of the cluster commenced, only tungsten (V) and tungsten blue resulted.

CONCLUSIONS

No new staphylo-nuclear compounds of tungsten in low oxidation states could be prepared.

An investigation of the chemistry of the previously reported tungsten (II) chloride, showed that it also contains an $W_6X_8^{4+}$ unit, as does its molybdenum analogue, and that complexes obtained may be regarded as octahedral MX_6 , where $M = W_6X_8^{4+}$. The chemistry of the $W_6Cl_8^{4+}$ species is very similar to that found for $Mo_6Cl_8^{4+}$ except for its greater instability under almost all conditions.

No oxidised $W_6Cl_8^{4+}$ species could be prepared.

EXPERIMENTAL

Tungsten hexachloride used was supplied by Alfa Inorganics. The material used was resublimed in a dynamic vacuum before use. All

operations involving this substance were carried out under dry nitrogen.

Several methods were tried for the preparation of dihydroxonium^{ox} hexachloroocta- μ_3 -chlorohexatungsten (II) (i.e. chlorotungsten chloroacid).

(i) Reaction of tungsten hexachloride with sodium amalgam with subsequent extraction with ethanol,⁴⁵ but this method gave low yields and was often dangerous.

(ii) Reaction of tungsten hexachloride with aluminium powder,⁴⁷ silicon dioxide being present as a moderator. This was carried out in an open tube under nitrogen. Yields were of the order of 10%. Greatly improved yields were obtained by carrying out the reaction in a sealed tube.

In a typical run tungsten hexachloride (10 gm), silicon dioxide, dried at 300°C, (10 gm) and aluminium powder (1.1 gm) were sealed in a pyrex tube under vacuum. The end of the tube containing the reactants was heated to the softening point of glass for 5 minutes, and cooled.

The product was extracted with 6N hydrochloric acid. Yield 30-40%.

(iii) High pressure and temperature reduction of tungsten hexachloride with hydrogen in an autoclave, but the reported⁶³ high yields could not be reproduced.

(iv) The heating of tungsten hexachloride and aluminium foil in a sealed tube in a controlled temperature gradient, followed by disproportionation of the tungsten (IV) chloride so formed at 450-500°C.⁶⁴ The chloroacid was obtained by crystallisation of the "dichloride" from 6N hydrochloric acid. Yield 45%.

From all preparations the chloro acid was obtained as light yellow needles, after air drying. Continued exposure to air resulted in loss of hydrochloric acid and water.

Analysis: Calculated for $\text{Cl}_{14}\text{H}_{18}\text{O}_2\text{W}_6$; Cl, 28.4%; tungsten oxidation number, 2.6. Found: Cl, 28.3%; oxidation number, 2.6.

$(\text{C}_2\text{H}_5)_4\text{N} \cdot \text{W}(\text{CO})_5\text{Cl}$ was prepared by the method of Abel et al.⁵⁸

A solution of this in chloroform was oxidised to the +2 state, by addition of the required amount of chlorine in chloroform.

Attempted isolation of $(\text{C}_2\text{H}_5)_4\text{N} \cdot \text{W}(\text{CO})_4\text{Cl}_3$ using the method of Ganorkar and Stiddard⁵⁹ was unsuccessful.

The reductions attempted to prepare low valent tungsten solutions were carried out as previously reported^{56,57} on tungsten (VI), dissolved in saturated aqueous hydrochloric acid.

Chlorotungsten (II) Complexes

$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{W}_6\text{Cl}_8 \cdot \text{Cl}_6$ was prepared by the addition of tetraethylammonium chloride to a solution of the chloro acid in ethanol, followed by washing and drying in vacuum. Yield 90%.

Analysis: Calculated for $\text{C}_{16}\text{H}_{40}\text{Cl}_{14}\text{N}_2\text{W}_6$; C, 10.3; H, 2.4; Cl, 26.8; N, 1.5. Found: C, 10.3; H, 2.4; Cl, 26.6; N, 1.5.

$[(\text{C}_2\text{H}_5)_4\text{N}]_3(\text{H}_3\text{O})[\text{W}_6\text{Cl}_8]_2\text{Cl}_{12} \cdot 3\text{H}_2\text{O}$ and $\text{Cs}_3(\text{H}_3\text{O})[\text{W}_6\text{Cl}_8]_2\text{Cl}_{12} \cdot 3\text{H}_2\text{O}$ were prepared by the addition of excess caesium chloride or tetraethylammonium chloride in 6M hydrochloric acid, to a solution of

chloro acid in 6M hydrochloric acid, followed by collection and recrystallisation from 6M hydrochloric acid. Yields 95% and 85% respectively.

Analysis: Calculated for $Cu_3Cl_{28}H_9O_4W_{12}$: Cl, 27.1; W, 60.4.

Found: Cl, 27.0; W, 60.4.

Calculated for $C_{24}H_{69}Cl_{28}H_3O_4W_{12}$: Cl, 27.1; W, 60.4. Found: Cl, 27.4; W, 60.5.

$W_6Cl_8 \cdot Cl_4 \cdot 2DMSO$ was prepared by the slow addition of dimethyl sulphoxide to an ethanolic solution of chloro acid.

Analysis: Calculated for $C_4H_{12}Cl_{12}O_2W_6$: Cl, 25.3; W, 65.5.

Found: Cl, 25.0; W, 65.3.

$(H_3O)_2[W_6Cl_8]Br_6 \cdot 6H_2O$ and $(H_3O)_2[W_6Cl_8]I_6 \cdot 6H_2O$ were prepared by recrystallisation of the chloro acid from the appropriate hydrohalic acid, with a minimum of boiling.

Analysis: Calculated for $Br_6Cl_8H_{18}O_6W_6$: Br, ^{23.8}~~24.9~~; Cl, 14.1. Found: Br, 24.0; Cl, 14.1.

Calculated for $Cl_8H_{18}I_6O_6W_6$: Cl, 12.4; I, 33.1. Found: Cl, 12.5; I, 32.7.

The anhydrous halides were prepared by heating the parent acids at 200°C in vacuum.

Analysis: Calculated for $Cl_{12}W_6$: Cl, 27.8. Found: Cl, 27.5.

Calculated for $Br_4Cl_8W_6$: Br, 18.7; Cl, 16.6. Found: Br, 19.0; Cl, 16.4.

Calculated for $\text{Cl}_8\text{I}_4\text{W}_6$: Cl, 15.0; I, 26.8. Found: Cl, 14.8;
I, 26.7.

Reaction of Chloro acid with ammonia.

A weighed quantity of the chloro acid (0.2 gm) was dissolved in oxygen free absolute ethanol in a centrifuge tube. Concentrated ammonia ($d = 0.88$, 1 ml) was added, and the tube flushed with nitrogen. This was stoppered and shaken for varying times. Excess 0.5N hydrobromic acid was added rapidly and the reaction mixture centrifuged. Tetraethylammonium chloride was added, and the precipitate collected and recrystallised from 6N hydrochloric acid. The yield was determined by weighing the crude tetraethylammonium salt.

The spectrum of $[\text{W}_6\text{Cl}_8]\text{Cl}_6^{2-}$ in ethanol was resolved by the method of Chatt et al.⁶⁵

Analytical and other techniques used in this Chapter are discussed in Appendix I.

CHAPTER 6. PREPARATION AND PROPERTIES OF TUNGSTEN (II)

BROMIDE AND IODIDE

INTRODUCTION

The study of these two halides is part of a study of tungsten in low valence states in solution, commenced in the previous Chapter.

This work was carried out to study the chemistry and properties of the staphylonuclei in each case, to ascertain whether or not the basic structure is similar to that found for the other molybdenum (II) and tungsten (II) halides i.e. the $W_6X_8^{4+}$ unit; and to look for new staphylonuclear species which might be formed during the reactions of these "dihalides".

A few reports on the preparation of tungsten (II) bromide have appeared in the literature,^{65,66,67} but very few properties have been reported. McCarley has found⁶⁴ that it is resistant to attack by alkali. Emelius and Gutmann report⁶⁷ that it is unattacked by hot acids except nitric, and is stable in vacuum to 600°C, and according to Murray⁶⁸ anhydrous tungsten (II) bromide increases in weight on exposure to the atmosphere, the weight increase corresponding to the uptake of two water molecules. The addition compound $[W_6Br_8]Br_4 \cdot 2C_2H_5OH$ is also reported.

Studies on the tungsten-iodide system have been limited to tungsten (II) iodide - reported in 1872,⁶⁶ and the triiodide, prepared by the reaction of tungsten hexacarbonyl with iodine.⁶⁹

RESULTS AND DISCUSSION

Tungsten (II) bromide was obtained as a deep green solid. A study of its chemistry was hampered by its extremely low solubility in all solvents, except hot dimethyl formamide and dimethyl sulphoxide.

The bromide is very slightly soluble in refluxing 8M hydrobromic acid, and from hot solutions a very few orange needles came out. Bromide only figures showed this to be $(\text{H}_2\text{O})_2[\text{W}_6\text{Br}_8]\text{Br}_6 \cdot 6\text{H}_2\text{O}$. The powder diffraction pattern was very similar to that found for the corresponding chloro acid, suggesting that the bromide contains the now familiar $\text{W}_6\text{X}_8^{4+}$ unit. Soxhlet extraction, using hydrobromic or hydrochloric acid, cannot be employed to prepare useful quantities of $\text{W}_6\text{Br}_8^{4+}$ -containing compounds because the bromide is slowly decomposed by the boiling acids.

The standard technique for obtaining a convenient source of $\text{Mo}_6\text{Br}_8^{4+}$, is to dissolve the crude molybdenum (II) bromide in hot dilute alkali and precipitate $[\text{Mo}_6\text{Br}_8](\text{OH})_4 \cdot n\text{H}_2\text{O}$ by slightly acidifying.⁷⁰ The bromide used in this work is slightly soluble in hot 0.1M caustic soda solution, forming a deep yellow solution. Orange-yellow compounds could be precipitated out on acidification, but the compounds prepared always had tungsten:bromide ratios less than that required for $[\text{W}_6\text{Br}_8](\text{OH})_4 \cdot n\text{H}_2\text{O}$ suggesting that attack of $\text{W}_6\text{Br}_8^{4+}$ occurs, with the formation of $[\text{W}_6\text{Br}_{8-n}(\text{OH})_n](\text{OH})_4 \cdot n\text{H}_2\text{O}$.

Preparation of Adducts Using Soxhlet Extraction

Because of the difficulty in preparing compounds containing the $\text{W}_6\text{Br}_8^{4+}$ species in reasonable quantities by the above methods,

hot soxhlet extraction using coordinating solvents was attempted.

Acetonitrile, ethanol, ether, pyridine and acetone were used. All gave yellow-coloured solutions after long extraction time, but in only two cases could compounds of the expected constitution be isolated - these being $[W_6Br_8]Br_4 \cdot 2H_2O$ and the previously reported $[W_6Br_8]Br_4 \cdot 2C_2H_5OH$ - both obtained by extraction of the bromide with ethanol. In all other cases (and, indeed, in some of the ethanol runs) the tungsten:bromide ratio was less than the required 1:1 for a bis-adduct. The results of extraction with varying solvents are displayed in Table 6.1. It appears that with pyridine, even though a yellow solution is formed, considerable breakdown of the $W_6Br_8^{4+}$ unit occurs. All of the adducts obtained were orange-yellow with spectra similar to that found for $Mo_6Br_8^{4+}$ -containing compounds.

Since recrystallisation of the adducts is difficult tetraethylammonium salts of the adducts were prepared from the extraction mother liquors. Recrystallisation of these was possible, but their constitution was still variable (see Table 6.2), and the only way in which the analyses can be rationalised is to postulate substitution of cyanide or ethoxide for a peripheral bromide in $[W_6Br_8]Br_4 \cdot 2L$. This is supported by the following reaction scheme. A tetraethylammonium salt with the constitution $C_{14.1} H_{41} N_{1.2} W_6 Br_{12.3}$ was heated to 80°C in vacuum and yielded $C_{11.4} H_{41} N_{1.1} W_6 Br_{12.5}$. These products correspond to the reaction scheme



TABLE 6.1

ANALYTICAL DATA FOR TUNGSTEN (VI) BROMIDE COMPLEXES PREPARED

BY SOXHLET EXTRACTION

Solvent	% W	% Br	% Resid	Formulation if all of % Resid is Solvent (=S)
acetonitrile	50.5	42.0	7.5	W_6Br_8 11.6 ^S 4 ^a
	48.9	42.6	8.5	W_6Br_8 12 ^S 4.7
	54.9	37.8	7.3	W_6Br_8 9.4 ^S 3.6
	50.1	41.1	8.8	U_6Br_8 11.3 ^S 4.7
pyridine	40.2	36.6	23.2	U_6Br_8 12.4 ^S 8.1
	41.8	40.9	17.3	U_6Br_8 13.5 ^S 5.8
ethanol	51.3	44.0	4.7	W_6Br_8 12.1 ^S 2.2
	52.8	44.1	3.1	W_6Br_8 11.6 ^S 1.4
	51.0	44.2	4.8	W_6Br_8 12 ^S 2.2
Calculated for $[W_6Br_8]Br_4 \cdot 2C_2H_5OH$	51.2	44.4		
Water	52.6	45.2		
	53.2	44.3		
	51.7	43.8		
Calculated for $[U_6Br_8]Br_4 \cdot 2H_2O$	52.6	45.6		

a - These can be formulated approximately as $(W_6Br_8) \cdot Br_2 (CH_3CH_2)_4 Br_2$, as well as $W_6Br_8 \cdot Br_4 \cdot 2C_2H_5OH$ plus excess solvent in the lattice. The last is the formulation preferred, because of the similarity of their powder photographs with those of $W_6Br_8 \cdot Br_4 \cdot 2C_2H_5OH$.

TABLE 6.3

ANALYTICAL DATA FOR TETRAETHYLAMMONIUM BROMOTUNGSTEN

BROMIDE COMPLEXES

Solvent	C	H	N	W	Br	Br/W	
				46.0	41.4	2.07	
	5.9	1.7	.7	46.3	41.2	2.04	
Ethanol *	5.8	1.7	.7	46.8	42.4	2.08	heated to 80°C
	5.2	2.0	1.2		41.1		heated to 80°C
				44.0	42.1	2.20	
Acetonitrile				45.7	42.5	2.14	
					42.6		
	3.3	.8	1.4	46.4	42.1	2.09	
Acetone				44.8	41.0	2.10	
Pyridine	7.7	1.4	1.2	53.8	30.7	1.26	

* for formulation of some of these see text

Recrystallisation of these salts from concentrated lithium chloride or bromide in ethanol did not alter the analysis i.e. the peripheral groups must be bound much more tightly than in $[\text{Mo}_6\text{Cl}_8]\text{Cl}_6^{2-}$ as in this type of complex the peripheral chlorines all exchange within two minutes at 25°C.⁷¹

The infra-red spectrum of the acetonitrile-tungsten (II) bromide adducts shows absorption maxima at 2352 and 2287 cm^{-1} . Carsichael and Edwards⁷² have found that the acetonitrile complex $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4 \cdot 2\text{CH}_3\text{CN}$ shows C≡N stretch at 2278 cm^{-1} . It is suggested here that the peak at 2287 cm^{-1} corresponds to conventionally coordinated acetonitrile, while the peak at 2352 cm^{-1} corresponds to the stretch absorption peak of the cyanide which has replaced a peripheral bromide.

The powder diffraction data of the adducts show that they are isomorphous (as are the tetraethylammonium salts from acetonitrile, ethanol and acetone extracted solutions). Table 6.3 gives a comparison of the d spacings of the ethanol and acetonitrile adducts.

From analytical, spectral and structural evidence it must be concluded that bromide in $[\text{W}_6\text{Br}_8]\text{Br}_4 \cdot 2\text{L}$ is replaced by a solvent fragment by nucleophilic attack, and it seems more likely that peripheral bromide, rather than a bridging one of $\text{W}_6\text{Br}_8^{4+}$, is replaced, since it is well known that the halogens in $\text{Mo}_6\text{X}_8^{4+}$ are inert.⁷¹

TABLE 6.3

COMPARISON OF d SPACINGS OF ETHANOL AND ACETONITRILE COMPLEXES

<u>CH₃CN Complex</u>		<u>C₂H₅OH Complex</u>	
d-spacing	Intensity	d-spacing	Intensity
9.45	m		
9.04	m		
8.69	vw		Diffuse
7.89	m		
6.59	m(br)	6.53	m(br)
2.94	vw	2.96	w
2.51	w	2.52	m
2.14	w	2.11	m
2.11	m		
2.01	w		
1.98	w		
1.95	w		
1.90	vs	1.90	vs
1.86	s	1.86	s
1.74	w(br)	1.74	w
1.65	m(br)	1.65	m(br)
1.20	m(br)	1.19	m(br)

Difficulty with the above hypothesis arises when low tungsten:bromide ratios are encountered in dimethyl sulphoxide and dimethyl formamide complexes. Table 6.4 displays the analytical data for many such adducts, but again substitution of bromide must occur.

The following are presented as evidence for the occurrence of this phenomena.

(1) The ultraviolet spectra of all of the different types of adducts prepared, including the tetraethylammonium salts, in dimethyl sulphoxide and dimethyl formamide, show identical profile and extinction coefficient (varying between 10.7 and $11.7 \cdot 10^3$ with the majority of values at $11.3 \cdot 10^3$ at $290-295$ m μ). The spectra of these complexes in $0.1M$ caustic soda have extinction coefficient of $8.0 \cdot 10^3$ at $295-300$ m μ . It is interesting to note that after relatively short times of standing (less than three hours at room temperature), the spectra change markedly, with a new peak appearing at 312 m μ , and slow disappearance of the peak at ~ 305 m μ . This behaviour is markedly similar to that observed for $[\text{Mo}_6\text{I}_8](\text{OH})_6^{2-}$ in $0.1M$ caustic soda, where it has been observed⁷⁰ that a new band appears on long standing of this complex in alkali. The new peak was tentatively assigned as being due to the $[\text{Mo}_6\text{I}_{8-n}(\text{OH})_n](\text{OH})_6^{2-}$ species. If in this work the peak at 312 m μ is assigned to the $[\text{W}_6\text{Br}_{8-n}(\text{OH})_n](\text{OH})_6^{2-}$ species this now explains why attempts to prepare $\text{W}_6\text{Br}_8^{4+}$ -containing compounds from alkali always result in compounds having bromide content too low for the expected $[\text{W}_6\text{Br}_9](\text{OH})_4 \cdot n\text{H}_2\text{O}$.

TABLE 6.4

ANALYTICAL DATA FOR DIMETHYL SULPHOXIDE AND DIMETHYL FORMAMIDE COMPLEXES OF TUNGSTEN (VI) BROMIDE

Solvent	X W	X Br	X Rest	Formulation if all of X Rest is solvent (-S)	Calculated for	
					X W	X Br
	49.5	41.7	8.8	$W_6Br_{11.6}S_{2.7}$	50.4	42.2
	50.2	40.5	9.3	$W_6Br_{11.1}S_{2.6}$	50.6	40.6
Dimethyl	50.6	41.1	8.3	$W_6Br_{11.2}S_{2.5}$	50.6	41.1
Formamide a	50.3	38.7	11.0	$W_6Br_{10.6}S_{3.3}^*$	52.2	C, 4.9; H, 1.0; N, 2.2
b	52.0	35.0	13.0	$W_6Br_{9.3}S_{3.8}$	52.3	35.2
c	53.5	32.4	14.1	$W_6Br_{8.3}S_{4.0}$	53.2	31.9
d	61.0	18.9	20.1	$W_6Br_{4.3}S_{5.0}$	57.1	17.8
	-	39.1	-			
					Calculated for	
					X W	X Br
Dimethyl	-	33.2	-			
Sulphoxide	-	39.0	-			
	48.9	35.8	15.3	$W_6Br_{10.1}S_{4.4}^{**}$	49.4	36.2

	48.4	38.2	13.4	W ₆ Br ^{10.9} S ^{4.3}	48.8	38.5		
	50.9	37.0	12.1	W ₆ Br ^{10.0} S ^{3.4}	49.5	35.8	51.4	37.2
Dimethyl	49.8	39.5	10.7	W ₆ Br ^{10.9} S ^{3.1}	48.8	38.5		
Sulphoxide e	49.5	33.7	16.8	W ₆ Br ^{9.4} S ^{4.8}	49.9	34.0		
f	53.0	28.0	19.0	W ₆ Br ^{7.3} S ^{5.1}	51.6	27.2	53.4	28.3
g	54.3	20.4	25.3	W ₆ Br ^{5.2} S ^{6.6}	53.4	20.1	55.4	20.9

a,b,c,d - were samples taken from a refluxing solution of the adduct in DMF at increasing times

e,f,g - similarly collected, but from DMSO solvent

* Found: C, 5.2; H, 1.5; N, 1.8

** Found: C, 3.9; H, 0.9; S, 6.2

These spectra compare favourably with those of complexes containing the $W_6Br_8^{4+}$ species,⁷⁰ and $W_6Cl_8^{4+}$ species (Chapter 5). A comparison of these spectra is shown graphically (Figure 6.1).

(ii) There is no significant change in the room temperature magnetic susceptibility of the dimethyl sulphoxide adduct when the tungsten:bromide ratio drops from 1.52 to 1.70. The μ_{eff} value for the W_6 unit changes from .54 to .70 BM. This suggests that there is no breakdown and oxidation of $[W_6Br_8]^{4+}$

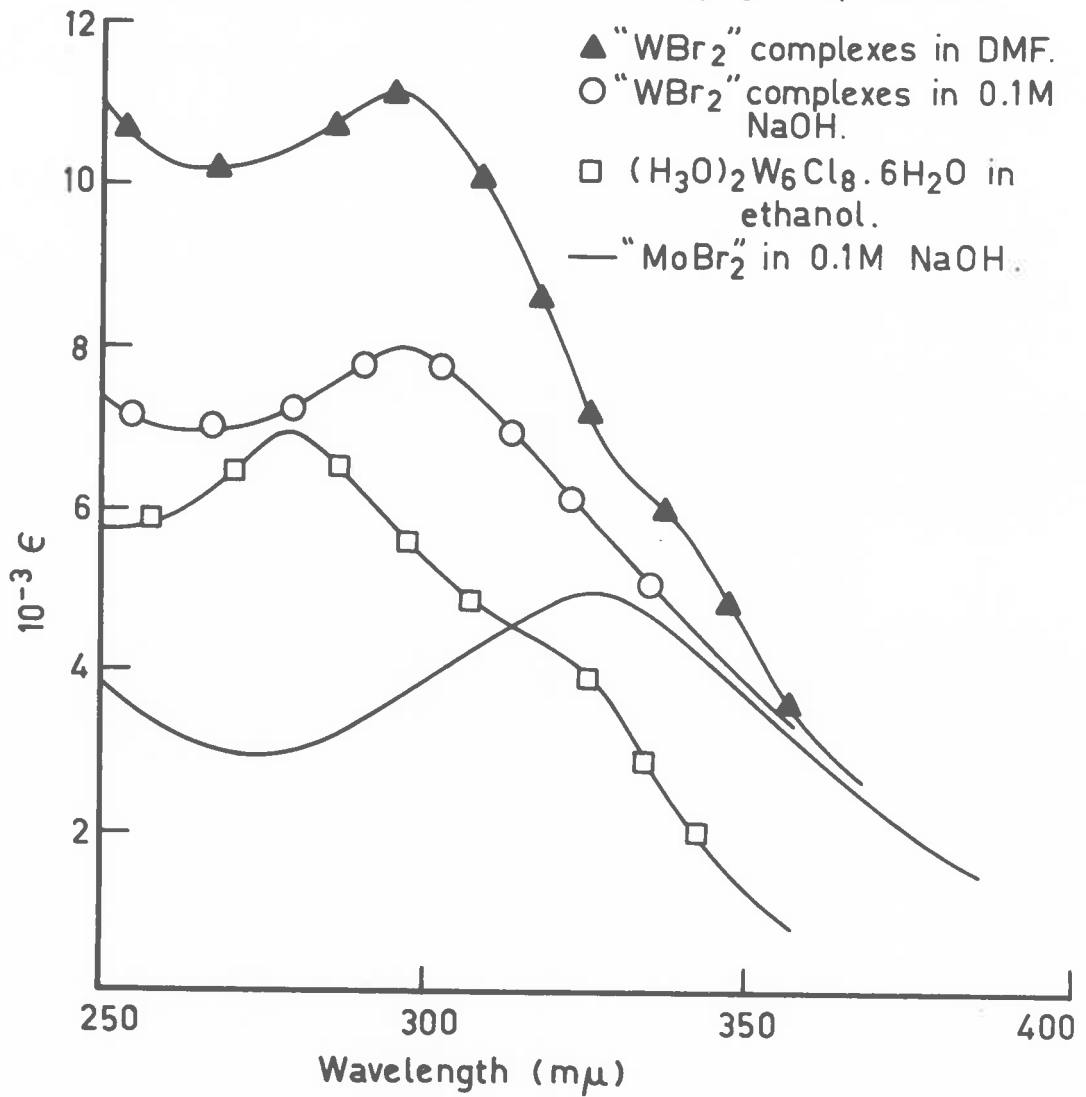
(iii) The number of oxidation equivalents consumed by dimethyl formamide adducts remains unchanged after long times of digestion with dimethyl formamide i.e. increased replacement of bromide.

(iv) As time of digestion of the bromide with these solvents increased, the yield of complex, obtained by precipitation with ethanol, dropped away markedly, until, at composition $W_6Br_{4-5}L_x$, it was negligible. Therefore, either decomposition of the W_6 unit commenced at this point, or the degree of substitution by organic material reached such a level, that the complex became soluble in the ethanol.

The Nature of the Substituting Group

The compounds with lowest tungsten:bromide ratios when formulated as $W_6Br_xL_y$ (where y represents the number of complete solvent molecules if only tungsten, bromide and solvent comprise the complex), show $x+y < p$ ($p = 14$ for DMF, and usually 15 for DMSO) while

FIGURE 6.1 Comparison of $M_6X_8^{4+}$ Spectra.



compounds early in the runs (i.e. $N:Br \sim 2$) show $x+y \sim p$. These results suggest that substitution by a solvent fragment occurs.

For example, with dimethyl sulphoxide, either the solvent or dimethyl sulphide may attack $(W_6Br_8Br_4)_n$, to leave $-O-SCH_3$ or $-SCH_3$ coordinated with $W_6Br_8^{8+}$, with the loss of methyl bromide. The second of these is feasible since dimethyl sulphide is present in hot dimethyl sulphoxide.⁷³

Since methyl bromide is a product of both of these reaction schemes, these possibilities were tested by running the mass spectrograph of the volatile products from the reflux of dimethyl sulphoxide and tungsten (II) bromide. Peaks were found at 94 and 96 mass numbers - indicative of the presence of methyl bromide.

Table 6.4 shows that there is reasonable agreement between observed and calculated composition, if it is assumed that $-N(CH_3)_2$ is substituted for bromide, when the solvent is dimethyl formamide. With dimethyl sulphoxide as solvent, the situation is not quite as clear cut. It appears, in some cases, that extra solvent may be incorporated in the crystal lattice, and is only removed on long vacuum drying. The analytical data obtained cannot distinguish between CH_3S- and CH_3SO- as the incoming groups.

Although the above possibilities seem rather bizarre, the replacement of cyanide and hydroxyl for bromide is well known in organic systems.

It is rather interesting to note that for the previously reported⁷⁴ adducts $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4(\text{DMF})_2$ and $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4(\text{DMSO})_2$, the authors do not report any chloride analyses. In this work it was found that dissolution of molybdenum (II) chloride in dimethyl sulphoxide and subsequent precipitation of the adduct with alcohol yielded compounds significantly low in chloride. However the alternative method reported⁷⁴ (i.e. dissolution of the chloride in ethanol followed by precipitation with dimethyl sulphoxide) gave correct chloride analyses. It now seems reasonable to suppose that a similar reaction to that observed above is occurring here. Also in the tungsten (II) chloride work (Chapter 3), it was found that the only successful method for preparing dimethyl sulphoxide adducts was to add ligand to an ethanolic solution of the chloride.

Except in the case of the acetonitrile adducts infrared spectra were of no value in determining the actual group taking part in the substitution.

Because less violent conditions are needed to dissolve the adducts in 0.1M caustic soda solution than are required for the crude bromide, it was hoped that $[\text{W}_6\text{Br}_8](\text{OH})_4\text{nH}_2\text{O}$ could be obtained. However, dissolution of $\text{W}_6\text{Br}_{10}(\text{DMSO})_{3,4}$ in hot 0.1M caustic soda, followed by precipitation, yielded a compound with a tungsten:bromide ratio of 6:6 (rather than 6:8 as is required for $[\text{W}_6\text{Br}_8](\text{OH})_4\text{nH}_2\text{O}$), thus with a strong nucleophile like hydroxyl, some attack of $\text{W}_6\text{Br}_8^{4+}$ still occurs (cf. earlier).

Iodides

During a high temperature decomposition study of tungsten (III) iodide it was found that at least two tungsten-iodine phases exist, i.e. W_6I_{14} and WI_2 . The former was prepared at 400°C, but on raising the temperature to 500°C decomposition to WI_2 occurs. At temperatures higher than 600°C, lighter brown compounds with tungsten:iodide ratios less than 2.0 were found, but these were not investigated further.

Attempts to prepare adducts of these by extracting with ethanol proved unsuccessful, yielding amorphous orange compounds, obviously greatly decomposed and oxidised. The iodides were slightly soluble in boiling 0.1N caustic soda solution, but with appreciable attendant decomposition. Bright yellow compounds in extremely low yield and of variable composition could be precipitated out. The iodides are soluble in hot dimethyl sulphoxide and dimethyl formamide, but little could be precipitated out on addition of alcohol.

On heating molybdenum (III) iodide in a similar manner no Mo_6I_{14} (or any other phase) was observed. At temperatures above 400°C all that could be obtained was molybdenum (II) iodide.

The powder diffraction data for the tungsten iodides is shown in Table 6.5. Since there is no correlation between the d-spacings for the two iodides it must be concluded that these are discrete compounds (i.e. W_6I_{14} is not W_6I_{12} plus trapped molecular iodine).

TABLE 6.5

POWDER DIFFRACTION DATA^a FOR W_6I_{12} AND W_6I_{14}

W_6I_{12}		W_6I_{14}	
d spacing	Intensity	d spacing	Intensity
6.55	s	6.48	vw
3.90	w	5.03	vw
3.50	w	3.87	w
3.46	m	3.81	vw
3.23	s(br)	3.70	vw
3.06	w	3.63	vw
2.93	vs	3.53	m
2.82	sv	3.43	m
2.66	m	3.23	s
2.63	w	3.21	s
2.59	w	3.17	s
2.45	s	3.12	v
2.43	w	3.05	m
2.40	vw	3.0	vw
2.34	v	2.68	v
2.30	vs	2.65	w
2.24	m	2.58	s
2.18	m	2.52	w
2.16	m	2.48	m
2.14	m	2.44	m
2.01	vw	2.38	s
2.00	s	2.30	m
1.97	m	2.26	w
1.88	vs	2.20	w
1.79	m(br)	2.15	m
		2.13	w
		2.08	vw
		2.06	m
		2.03	m
		1.97	m(br)
		1.95	m(br)
		1.92	w
		1.88	m(br)

a - d spacings obtained from Guinier photographs

The powder diffraction data for W_6I_{14} shows no similarity with that reported⁷⁵ for Ta_6I_{14} , thus it seems unlikely that W_6I_{14} has the $W_6I_{12}^{2+}$ unit as the basis for its structure. It seems more feasible that this iodide contains an oxidised $Mo_6X_8^{4+}$ structure i.e. $W_6I_8^{6+}$ with octahedral coordination of the other iodides about this group. In support of this formulation Siepmann and Schafer have reported⁷⁶ a tungsten-bromine phase corresponding to W_6Br_{14} , which has a different spectrum in ethanol and powder photograph from that of W_6Br_{12} . On standing an ethanolic solution of W_6Br_{14} gave the same spectrum as W_6Br_{12} , suggesting that reduction had occurred. Unfortunately they did not give any powder diffraction data for comparison.

CONCLUSIONS

Although adducts obtained from tungsten (II) bromide are rarely the expected $[W_6Br_8]Br_4 \cdot 2L$, it was found that for all ligands tried, the adducts, although of unusual constitution, all contain the $W_6X_8^{4+}$ species, in common with the other molybdenum (II) and tungsten (II) halo complexes.

In this survey no low valent tungsten compounds containing other than that $W_6Br_8^{4+}$ species were obtained.

The $W_6Br_8^{4+}$ species is more susceptible to nucleophilic attack than the $Mo_6Cl_8^{4+}$ and $Mo_6Br_8^{4+}$ species, but on attack by hydroxyl, although some substitution takes place, complete breakdown does not occur as in the $W_6Cl_8^{4+}$ species.



The iodide W_6I_{14} , probably containing the $W_6I_8^{6+}$ species, was prepared.

EXPERIMENTAL

Tungsten (V) bromide was prepared by subliming tungsten (VI) bromide in vacuum. The higher bromide being prepared by the reaction of bromine on tungsten hexacarbonyl.

Tungsten (II) bromide was prepared from the pentabromide by aluminium reduction and disproportionation.⁶⁴

Analysis: Calculated for Br_2W : Br, 46.5. Found: Br, 46.3, 46.9. It was necessary to fuse the complex with caustic soda before bromide analysis.

Solvents used were of analytical reagent quality and used as supplied.

Attempts to prepare $[W_6Br_8](OH)_4 \cdot nH_2O$ were made using finely crushed bromide and 0.1M caustic soda solution, containing a few drops of hydrogen peroxide (to suppress autocatalysed alkaline decomposition) at 90°C, followed by precipitation of the yellow complexes with ammonium nitrate solution.

The bromoacid was prepared in minute yield by solution of the crude bromide in refluxing 8.5M HBr followed by rapid cooling to prevent decomposition.

Analysis: Calculated for $(H_3O)_2[W_6Br_8]Br_6 \cdot 6H_2O$: Br, 47.3. Found: Br, 47.3.

Adducts except those of dimethyl sulphoxide and dimethyl formamide were prepared by hot soxhlet extraction of finely crushed bromide.

The yellow solids which collected in the solvent flask were collected. The tetraethylammonium salts were prepared from the extraction mother liquors by addition of tetraethylammonium chloride, followed by recrystallisation from the same solvent.

The aquo complex was prepared by the addition of water to an ethanol extract mother liquor.

All of the adducts were obtained in very low yield (<10%).

Dimethylsulphoxide and dimethyl formamide adducts were prepared by solution of tungsten (II) bromide in hot solvent, followed by filtration and precipitation with alcohol. Yield ~60%, but drops on increased digestion time.

Oxidation numbers were determined by dissolution of the complex in a known amount of alkaline dichromate. Excess ferrous was added and this was titrated against standard ceric sulphate solution using N-phenylanthranilic acid as indicator. Values obtained gave oxidation numbers consistently 2.3 (also on $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4(\text{DHF})_2$ - used as a standard).

For the mass spectrum, nitrogen was slowly bubbled through a refluxing solution of tungsten (II) bromide in dimethyl sulphoxide, and the products coming off were collected in a U-tube cooled with liquid air. The spectrum was recorded using an Hitachi-Perkin Elmer double focus machine, model RMB-6D.

Tungsten (III) iodide was prepared by the reaction of tungsten hexacarbonyl with iodine in a sealed tube.⁶⁹ Molybdenum (III) iodide was prepared in a similar manner. These were sealed in pyrex tubes under vacuum and heated for two days at varying temperatures.

Analysis: Calculated for $I_{14}W_6$: I, 61.6; W, 38.4. Found: I, 61.9; W, 37.9.

Calculated for $I_{12}W_6$: I, 58.0. Found: I, 58.4, 58.5.

Soxhlet extraction of this was carried out as above, but greatly decomposed products were obtained. For example from W_6I_{14} an orange solid of the composition C, 3.0; H, 1.2; I, 11.3; W, 62.0, was obtained.

Guinier photographs of W_6I_{12} and W_6I_{14} were kindly recorded by Dr. P. Smith of the University of Tasmania. Potassium chloride was used as the internal standard.

CHAPTER 7. DISPROPORTIONATION OF METAL TETRAHALIDES IN SOLUTION
AS A PREPARATIVE METHOD FOR STAPHYLONUCLEAR COMPLEXES. I.

In the search for new staphylonuclear complexes useful in testing the stereochemical theory, it became obvious that a new preparative route was needed to allow the preparation of different types of complexes.

Excluding all carbonyls, the most widely used methods for the preparation of halostaphylonuclear compounds are -

(a) Binary Halides

(i) Reduction of highest halides, e.g. by using sodium amalgam⁴⁵ or hydrogen.⁶³

(ii) The disproportionation of higher halides by heating (usually tetra- or trihalide). The higher halide being prepared from the highest halide by reduction (usually with aluminium in a temperature gradient)



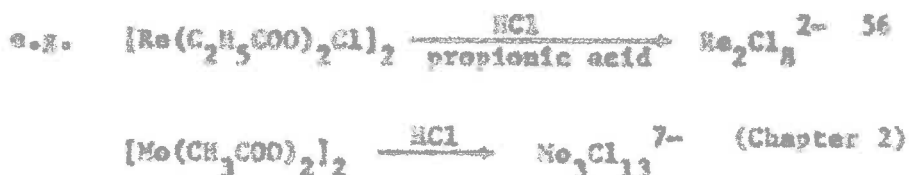
(b) Ternary Halides

(1) Solution of a binary staphylonuclear halide in hydrohalic acid, followed by precipitation with a cation

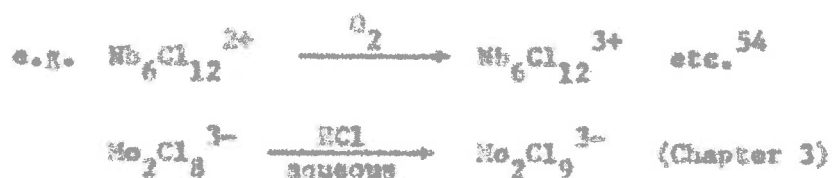


(ii) The reduction of solutions containing higher valent metal with powerful reducing agents. e.g. hypophosphorous acid, amalgam, hydrogen under pressure etc. In this manner $\text{W}_2\text{Cl}_9^{3-}$,⁷⁷ $\text{Re}_2\text{Cl}_8^{2-}$,⁵⁶ and $\text{Te}_2\text{Cl}_8^{3-}$ ⁵⁷ have been prepared.

(iii) The reaction of a compound already containing a metal-metal bond with hydrohalic acid.



(iv) Oxidation (or possibly reduction) of known staphylonuclear compounds to form new, but usually structurally related ones.



Shortly after the commencement of this work Cotton et al published⁷⁸ the results of a study on the disproportionation of β -rhenium (IV) chloride, in oxygen donor solvents. They found in all cases, that either of the staphylonuclear anions $\text{Re}_2\text{Cl}_8^{2-}$ or $\text{Re}_2\text{Cl}_9^{2-}$ were formed, together with rhenium (V) species. Their results, and the results of this work, show that the solution disproportionation of some metal (IV) halides appears to be a good general method for the preparation of staphylonuclear anions.

SOLUTION STUDIES ON MOLYBDENUM (IV) CHLORIDE

INTRODUCTION

To this time the chemistry of molybdenum (III) halogen systems has been dominated by the mononuclear species MoX_6^{3-} and $\text{MoX}_5\text{H}_2\text{O}^{2-}$, which can be prepared relatively easily by reduction of molybdenum (VI) solutions. Dimeric species $\text{Mo}_2\text{X}_6(\text{bipy})_3$ have also been reported.⁷⁹ All of these species show normal magnetic behaviour consistent with a d^3 configuration (μ_{eff} per Mo = 3.6-3.9 BM), suggesting no metal-metal interaction. Some thio-bridging molybdenum (III) compounds with low magnetic susceptibilities, therefore with some metal-metal interaction, have been reported.⁸⁰

Although molybdenum (III) chloride¹¹ and bromide⁸¹ contain molybdenum-molybdenum bonds, their insolubility in both polar and nonpolar solvents renders them useless as starting materials for the preparation of staphylonuclear molybdenum (III) compounds.

In the literature within the past few years there have been several mentions made of compounds containing the $\text{Mo}_2\text{X}_9^{3-}$ unit, but with the exception of one paper,⁸² no preparative methods have been reported. In this case the $\text{Mo}_2\text{X}_9^{3-}$ unit was prepared by the reaction of H_2MoX_6 with liquid ammonia, but no studies were made on the complexes, and analyses were poor.⁸²

As a result of a mechanistic study, it has been suggested⁸³ that molybdenum (IV) in solution disproportionates into molybdenum (III) and (V), but as no molybdenum (IV) was ever isolated, the evidence is circumstantial.

Several adducts of the type MoCl_4L_2 have been reported^{16,20} as having been prepared from molybdenum (IV) chloride. They were all prepared using suspensions, or non oxygen donor solvents. No studies have been reported on the solution properties of molybdenum (IV) chloride in oxygen donor solvents.

The structure of molybdenum (IV) chloride is important in that it may have an influence on the structure of the complexes that can be prepared from it. Colton and Martin, using magnetic evidence, have proposed⁸⁴ that the structure is based on triangles of molybdenum atoms, but they do not quote their source of tetrachloride. Larson and Moore¹⁶ have prepared a form of molybdenum (IV) chloride having a magnetic susceptibility of 0.93 EM per molybdenum, but make little comment as to its structure. Schafer et al have recently reported⁸⁵ a form of molybdenum (IV) chloride which shows normal paramagnetic behaviour for two unpaired electrons (μ_{eff} per Mo = 2.12 EM). It consists of edge-shared MoCl_6 octahedra together with isolated MoCl_6 octahedra. As the magnetic moment suggests there is very little interaction between the molybdenum atoms (Mo-Mo distance = 3.50 Å).

Schafer's tetrachloride shows an interesting comparison with the tetrachlorides of the neighbouring elements. McCarley and his group have found that niobium (IV),⁸⁶ tantalum (IV)⁸⁷ and tungsten (IV)⁸⁴ chlorides are all diamagnetic and isostructural, while technetium (IV) chloride is paramagnetic⁸⁸ and shows no metal-metal bonding.⁸⁹

RESULTS AND DISCUSSION

A portion of this work may overlap with that of other workers. This is because I was unaware of the existence of their work. There have been no papers in the open literature on the subject.

(1) Properties of Molybdenum (IV) Chloride

The very different magnetic properties of the tetrachlorides, prepared by Larson and Moore,¹⁶ and Schafer et al.,⁸⁵ combined with their differing powder diffraction lines (see later), suggest that these tetrachlorides have different structures, the former having considerable molybdenum-molybdenum interaction. Thus for convenience the former will be designated α - and the latter β -molybdenum (IV) chloride.

It has been found that α -molybdenum (IV) chloride is, in agreement with Larson and Moore,¹⁶ insoluble in all non-oxygen donor solvents tried, with the exception of pyridine and, to some extent, acetonitrile. It is soluble, with reaction, in anhydrous acetic acid, all aqueous solvents, methanol, ethanol, acetone, dimethyl formamide and dimethyl sulphoxide. These solution properties verify that it is not a mixture of molybdenum (V) and (III) chlorides, as molybdenum pentachloride is soluble in non-polar solvents; also the tetrachloride is completely soluble in oxygen donor solvents (with the exception of a small amount of carbonaceous material - a byproduct of the preparation), while molybdenum (III) chloride is not.

This work has shown that α -molybdenum (IV) chloride is unstable in oxygen donor solvents and undergoes the disproportionation reaction



No evidence was observed for the stabilisation of the +4 state at any time.

To test whether or not disproportionation takes place before the addition of cations, the spectrum of α -molybdenum (IV) chloride in 4M hydrochloric acid, acetone and methanol were recorded (see Figure 7.1). When these are compared with the spectra of molybdenum (III) dimers, (Figure 7.2), it can be seen that the characteristic peaks of molybdenum (III) (dimeric) are present. The peak at 515 m μ shows the expected extinction coefficient in hydrochloric acid, (i.e. one quarter of that observed for $\text{Mo}_2\text{Cl}_9^{3-}$ since $4\text{MoCl}_4 + \text{Mo}_2\text{Cl}_9^{3-}$) but the peak at 415 m μ has a greater extinction coefficient than expected for molybdenum (III), due to the contribution of molybdenum (V). These results show that α -molybdenum (IV) chloride disproportionates immediately on solution.

This observed disproportionation is of interest because dimeric molybdenum (III) species are formed in solution i.e. this is a preparative route for the formation of staphylonuclear complexes.

Larson and Moore reported¹⁶ the complex $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$, claimed to be 7-coordinate. Analysis obtained in this work is consistent with the unusual formulation. To determine if disproportionation is dependent on the form of molybdenum (IV), both the above complex and

FIGURE 7.1. Visible Spectra of α - MoCl_4 in Varying Solvents.

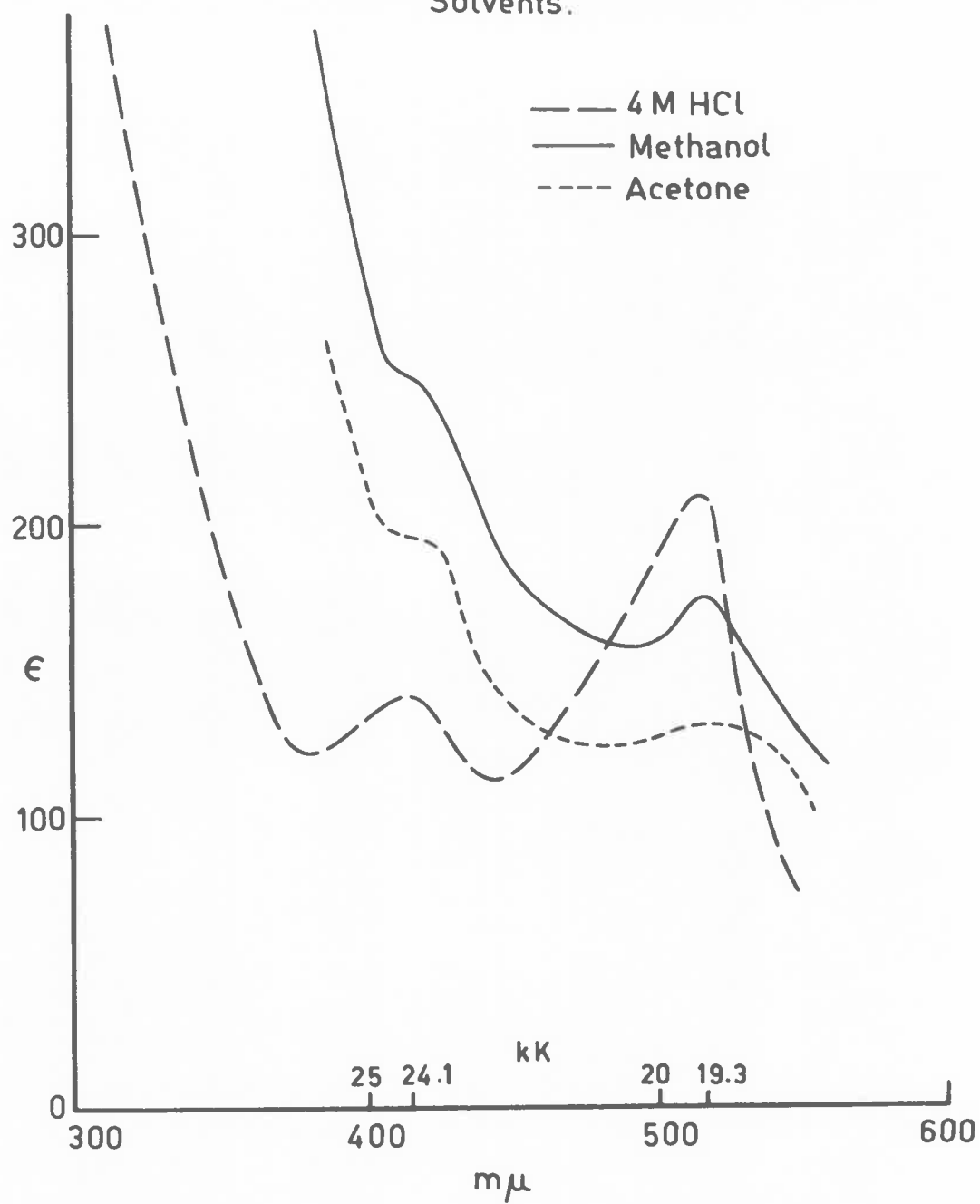
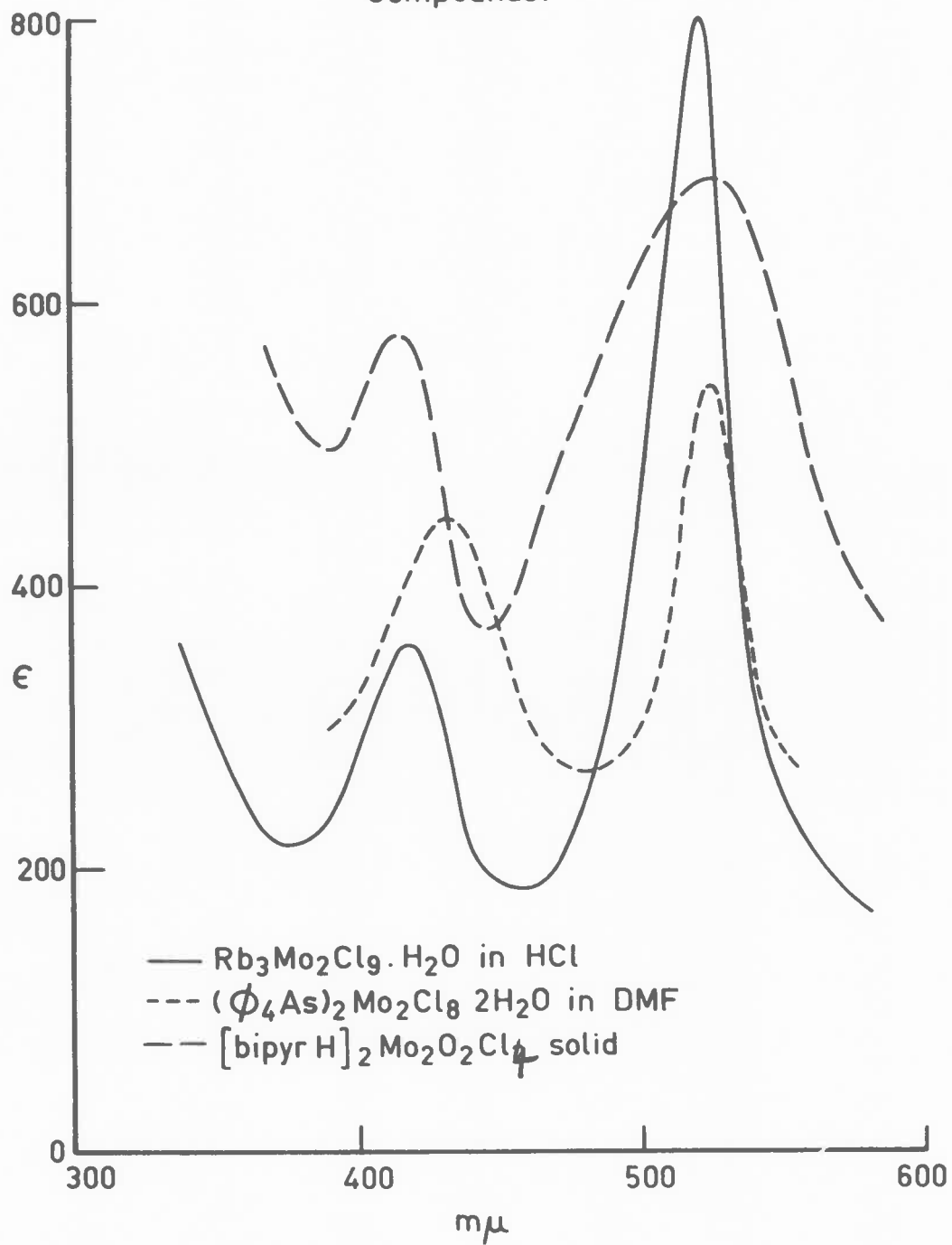


FIGURE 7-2. Visible Spectra of Chloromolybdate (III) Compounds.



and $\text{MoCl}_4 \cdot 2\text{CH}_3\text{CN}$ were reacted with methanol and dilute hydrochloric acid. In both cases, yellow-green solutions were formed and a gas evolved. No molybdenum (III) species could be precipitated out of these solutions. This shows that, indeed, the form of molybdenum (IV) is important, and the reaction of β -molybdenum (IV) chloride with oxygen donor solvents will be interesting, as this will determine the importance of the metal-metal bond in the disproportionation.

(ii) Compounds Obtained and their Formulation

Using aqueous hydrochloric acid as solvent, complexes containing the $\text{Mo}_2\text{Cl}_9^{3-}$ species were prepared, using the cations ammonium, rubidium and caesium. These were all isomorphous. Only green molybdenum (V) complexes could be obtained from aqueous solutions when using organic cations i.e. tetra(*n*-butyl)ammonium, tetraethylammonium and tetraphenylammonium - these were not investigated further. Both the rubidium and caesium chloromolybdates (III) showed a small positive room temperature magnetic susceptibility (χ_m (corr) = $9.10 \cdot 10^{-4}$ CGS units in both cases - this corresponds to $\mu_{\text{eff}} = 1.0$ BM per molybdenum). This implies considerable molybdenum-molybdenum interaction. In a recent review, Lewis,² quoting unpublished results, reports that the $\text{Mo}_2\text{Cl}_9^{3-}$ species, (preparative method not quoted), was diamagnetic.

A very significant property of the α -molybdenum (IV) chloride is its ability to always yield $\text{Mo}_2\text{Cl}_9^{3-}$, irrespective of solvent, with rubidium and caesium as cations.

Table 7.1 displays the results of digestion of α -molybdenum (IV) chloride with widely varying solvents. Immediately after digestion

TABLE 7.1

DIGESTION OF α-MOLYBDENUM (IV) CHLORIDE WITH AQUEOUS SOLVENTS.-
MOLYBDENUM (III) BEING PRECIPITATED OUT WITH RUBIDIUM OR CALCIUM

Cation	Solvent	% Mo	% Cl	Other halogen	
Rb ⁺	12M HCl	24.2	40.4	-	
	1M HCl	24.9	40.2	-	
	0.1M HCl	24.5	40.1	-	Powder
	Water	24.4	39.7	-	photographs
	8.5M HBr	24.6	37.4	6.0	identical
	1M HNO ₃	24.2	39.6	-	
	4M CH ₃ COOH	25.4	39.7	-	
	7M HI		40.1	2.9	
<i>Calculated for Rb₄Mo₂Cl₈H₂O</i>		26.4	40.7		
Ca ⁺	12M HCl	21.2	35.2	-	Powder
	8M HBr		33.5	3.0	photographs
	7M HI		32.4	4.9	identical
	<i>Calculated for Ca₅Mo₂Cl₉</i>		21.1	35.1	

the complexes were precipitated out with cation.

From methanolic solutions of α -molybdenum (IV) chloride, complexes of the type $M_2Mo_2Cl_8 \cdot 2H_2O$ (where M = tetraphenylarsonium or tetraethylammonium) and $A_3Mo_2Cl_9$ (A = pyridinium or caesium), were prepared. For the pyridinium complex the band positions obtained in the infra-red were 3220 w, 3160 w, 3080 s, 1638 w, 1612 s, 1535 s, 1412 s, 1370 w, 1325 w, 1240 v, 1202 s, 1165 s, 1050 w, 1032 w, 985 s, 864 s, 742 s, 672 s, which are in agreement with those obtained⁵⁰ for pyridinium salts.

If the methanol contained greater than 20% of aqueous 12M hydrochloric acid, only molybdenum (V) species (e.g. $(C_6H_5)_4As.MoOCl_4 \cdot 2H_2O$) could be precipitated out.

These molybdenum (III) salts again showed small positive susceptibility, indicative of considerable metal-metal interaction. Although these complexes were found to be rather unstable in most solvents, some stability of $[(C_6H_5)_4As]_2Mo_2Cl_8 \cdot 2H_2O$ was observed in dimethyl formamide, thus allowing conductivity measurements to be recorded. At 25°C the molar conductance of the complex was approximately $390 \text{ ohms}^{-1} \text{ cm}^{-2} \text{ moles}^{-1}$. This compares favourably with the value of $400 \text{ ohms}^{-1} \text{ cm}^2 \text{ moles}^{-1}$ obtained for the 2:1 electrolyte $[(C_6H_5)_4As]_2Cr_2O_7$ in the same solvent.

Methanolic solutions of the tetrachloride, as well as molybdenum (III) species, also yielded the yellow-green molybdenum (V) complex $(C_6H_5)_4As.MoOCl_4 \cdot 2H_2O$.

From acetone solutions of α -molybdenum (IV) chloride, a compound with the rather surprising constitution, $(\text{dipyridyl})_2\text{Mo}_2\text{Cl}_4\text{O}_2$, could be obtained. Since it could only be prepared in very low yield, insufficient quantity was obtained for magnetic susceptibility measurement. Thus this formulation is made only on the basis of analytical data and the null spectrum (Figure 7.2), which is very similar to spectra of other molybdenum (III) dimeric species. Oxidation number and solution spectra could not be obtained, because of the extreme insolubility of the complex in all solvents. The infra-red showed a peak at 966 cm^{-1} - presumably due to Mo-O stretch.

All attempts to prepare adducts of the type $\text{Mo}_2\text{Cl}_6\text{L}_3$ were unsuccessful using acetone or methanol as solvent, and the ligands urea, thiourea, triphenylphosphine (and oxide), triphenylarsine (and oxide), 2,2'-bipyridyl, and pyridine, although in several runs addition of pyridine to methanol solutions of α -molybdenum (IV) chloride, yielded products of variable composition but containing molybdenum in oxidation state 3.0 and having molybdenum:chlorine ratios between 1:3.0 and 1:4.5, suggesting that some adduct may be formed, together with $(\text{C}_5\text{H}_5\text{NH})_3\text{Mo}_2\text{Cl}_9$. From acetone the products always had oxidation number greater than 3.0 and showed molybdenum-oxygen stretch in the infra-red.

(iii) Properties and Structure of the Complexes

The alkali metal chloromolybdates (III) appear to be indefinitely stable in air. The complexes with organic cations

deteriorate slowly in air, but are indefinitely stable in vacuum.

Using the $\text{Re}_2\text{Cl}_8^{2-}$ species or δ -rhenium (IV) chloride several acetato rhenium (III) complexes have been prepared,⁷⁸ by reflux of glacial acetic acid with the chloro compounds. Attempts to prepare similar acetato complexes from $\text{Mo}_2\text{Cl}_9^{3-}$, $\text{Mo}_2\text{Cl}_8^{2-}$ and α -molybdenum (IV) chloride, resulted only in green molybdenum (V) solutions.

When α -molybdenum (IV) chloride was dissolved in dilute nitric acid and the released chloride titrated rapidly, 48-49% (3 titres) of the total chloride came off. For the reaction



44% of the chloride would be released, but since the end point was very difficult to determine, (even when the reaction mixture was freezing ammonium nitrate solution), the value obtained was within experimental error. Unfortunately the titration of labile chlorine in $\text{Mo}_2\text{Cl}_9^{3-}$ could not be performed successfully.

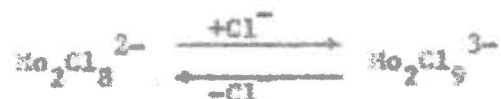
The lack of substitution by other halides (see section (ii)), and incomplete chloride release from the tetrachloride shows that $\text{Mo}_2\text{Cl}_9^{3-}$ has at least one of the properties of $\text{W}_2\text{Cl}_9^{3-}$ i.e. slow substitution of the chlorides.²⁸

There are two feasible possibilities for the structure of the anion viz. a ligand deficient $\text{M}_2\text{X}_{10}^{4-}$ species (two edge-shared octahedra), or the $\text{M}_2\text{X}_9^{3-}$ structure, as has been reported⁴⁰ for the $\text{W}_2\text{Cl}_9^{3-}$ unit. van Brouswyk has shown²⁷ that several ligand deficient

complexes based on the $\text{Mo}_3\text{Cl}_{13}^{7-}$ unit, when investigated using quantitative disc spectroscopy, show extinction coefficient dependence on the potassium chloride disc formation pressure. This technique when applied here showed that there was no pressure dependence on the peak at 19.0 mK. When this is coupled with the fact that the solution spectrum of the $\text{Mo}_2\text{Cl}_9^{3-}$ species is chloride independent, it seems that the species is not ligand deficient.

Figure 7.2 shows the visible spectrum of $\text{Re}_3\text{Mo}_2\text{Cl}_9\text{H}_2\text{O}$ in aqueous hydrochloric acid for the acid concentration range 0-8M. Both peaks obey Beer's law over the whole acid concentration range. In addition to the peaks shown in Figure 7.2, two peaks occur in the ultraviolet region at 40.8 and 34.9 mK ($\epsilon_{\text{max}} 1.54 \cdot 10^4$ and $1.02 \cdot 10^4$ respectively in 1M hydrochloric acid).

The compounds containing the $\text{Mo}_2\text{Cl}_8^{2-}$ anion are formulated as ligand deficient $\text{Mo}_2\text{Cl}_9^{3-}$, rather than being isostructural with $\text{Re}_2\text{Cl}_8^{2-}$.³⁸ The spectrum in dimethyl formamide shows peaks at 432 m μ and 524 m μ of lower extinction coefficient than $\text{Mo}_2\text{Cl}_9^{3-}$ (Figure 7.2), but on addition of aqueous 12M hydrochloric acid to the solvent, the spectrum becomes markedly similar to that of $\text{Mo}_2\text{Cl}_9^{3-}$ in hydrochloric acid. ϵ_{max} for the ca 520 m μ peak in solvent containing 10% aqueous 12M hydrochloric acid is 790 (cf. 800 for $\text{Mo}_2\text{Cl}_9^{3-}$) - suggesting the equilibrium



in solution.

In order to test the ligand deficiency in the solid state, attempts were made to test the dependence of extinction coefficient on potassium chlorida disc formation pressure, but neither of the $\text{Mo}_2\text{Cl}_8^{2-}$ salts prepared in this work would disperse properly in the discs.

Since the compounds are unstable in solution, (especially in hydrochloric acid), all of the spectra were extrapolated to zero time, when calculating extinction coefficients. This instability in solution was exemplified when recrystallisation of $\text{Rb}_3\text{Mo}_2\text{Cl}_9\text{H}_2\text{O}$ was attempted from 6M hydrochloric acid in the absence of oxygen, as all that could be obtained was the monomeric species $\text{Rb}_2\text{MoCl}_5\text{H}_2\text{O}$, (identified by powder photograph).

Table 7.2 gives a comparison of the powder diffraction data for $\text{K}_3\text{W}_2\text{Cl}_9$, $\text{Rb}_3\text{W}_2\text{Cl}_9$ and $\text{Rb}_3\text{Mo}_2\text{Cl}_9\text{H}_2\text{O}$. The extremely good correlation of the d spacings of the complexes strongly suggests that $\text{Mo}_2\text{Cl}_9^{2-}$ is isostructural with the $\text{W}_2\text{Cl}_9^{3-}$ unit and not a ligand deficient M_2X_{10} structure.

The rubidium salt is formulated as a monohydrate as there is a reversible weight loss, corresponding to the loss of one water molecule, on heating to 80°C in vacuum. It is suggested here, that the water molecules occupy vacant octahedral holes in the close-packed lattice (molybdenum atoms only fill two thirds of the available sites).

(iv) On the Structure of α -Molybdenum (IV) Chloride

It would seem reasonable that the α -molybdenum (IV) chloride structure should contain an Mo_2Cl_9 unit, (or one that easily gives rise

TABLE 7.2

COMPARISON OF X-RAY POWDER DIFFRACTION DATA FOR MOLYBDENUM (III)
AND TUNGSTEN (III) TERNARY HALIDES

$K_2W_2Cl_9^a$		$K_2W_2Cl_9^b$		$Rb_3Mo_2Cl_9 \cdot H_2O$		$Rb_3V_2Cl_9^c$	
d	int	d	int	d	int	d	int
				8.75	m		
		8.29	m	8.30	m	8.34	s
		7.89	s	-		-	
		6.17	w	6.27	w	6.20	w
		-		6.10	m	-	
		5.79	vs	5.89	m	5.89	s
		4.91	vw	5.73	s	-	
4.06	w	4.01	w	4.14	w	4.14	w
3.59	s	3.57	m	3.60		3.63	s
3.39	vw	3.36	vw	3.54	s	3.46	w
3.28	m	3.26	m	3.38	w	3.32	m
3.11	vw	3.09	vw	-		-	
3.05	w	3.02	w	-		-	
2.99	w	2.96	w	2.97	s	-	
2.90	w	-		-		-	
2.87	vw	2.85	s	2.89	s	2.93	vs
				2.82	w		
				2.73	w		
2.69	u	2.68	s	2.70	vs	2.74	s
2.48	m	2.48	s	2.51	vw	2.51	s
2.46	u	-		2.49	vw	-	
2.35	vw	-		2.30	m	2.35	m
2.32	s	2.30	m	2.28	s	2.28	m
2.25	vw	-		2.23	vw	-	
2.24	m	2.23	m	-			
2.17	m	2.16	s	-		2.21	m

cont'd

2.15	s	2.15	s	2.15	v	2.19	w
2.07	w	2.07	w	2.08	vw	2.09	vw
2.04	w	2.03	v	2.05	m	2.07	w
2.02	vw	2.01	w	-	-	2.03	vw
2.01	vw	2.00	w	2.00	m	-	-
1.94	-	-	-	-	-	-	-
1.92	v	1.92	m	1.92	s	1.97	m
1.90	m	1.89	m	1.91	s	1.92	m
1.86	m	1.85	s	1.87	w	1.89	m
1.79	w	-	-	1.78	vs	1.80	s

a - data from reference 37.

b - prepared by the method of Heints.⁷⁷

c - prepared by the disproportionation of tungsten (IV) chloride (Chapter 8).

to this), since the $\text{Mo}_2\text{Cl}_9^{3-}$ unit is retained intact regardless of solvent (section (ii)). Such a structure has been reported⁹¹ for β -rhenium (IV) chloride (pairs of face-shared ReCl_6 octahedra joined by chlorine bridges). Cotton and his group find⁷⁸ that in some circumstances this, on solvolysis, yields $\text{Re}_2\text{Cl}_9^{2-}$ (they assign a structure based on $\text{Re}_2\text{Cl}_9^{2-}$ to it, but it seems more reasonable to assign a $\text{W}_2\text{Cl}_9^{3-}$ -type structure to it, as this explains its origin).

Using the cell constants reported⁹¹ for β -rhenium (IV) chloride, the d spacings were calculated and compared with those observed for α -molybdenum chloride. Table 7.3 shows that there is little similarity between the two. Unfortunately a comparison of actual powder photographs was not possible, as one has never been recorded for the rhenium chloride.⁹² However, comparison of the powder diffraction data for tungsten⁸⁴ (IV) and niobium⁸⁶ (IV) chlorides, together with that of α -molybdenum (IV) chloride (Table 7.3), shows that all three are isomorphous. Therefore α -molybdenum (IV) chloride, surprisingly, has the structure reported⁹³ for niobium (IV) chloride i.e. MoCl_6 octahedra joined by edges, with pairs of molybdenum atoms displaced towards each other.

It is interesting to note that an isomer of rhenium (IV) chloride which is isomorphous with α -molybdenum (IV) chloride has been prepared,⁹⁴ and it was found that this gives the same solvolysis products as the β -form. The mechanism whereby $\alpha\text{-MoCl}_4 + \text{Mo}_2\text{Cl}_9^{3-}$ and α or $\beta\text{-ReCl}_4 + \text{Re}_2\text{Cl}_9^{2-}$ remains a mystery.

TABLE 7.3

COMPARISON OF X-RAY DIFFRACTION DATA FOR METAL TETRACHLORIDES

<u>NbCl₄⁸⁶</u>		<u>MoCl₄⁸</u>		<u>WCl₄⁶⁴</u>		<u>α-ReCl₄⁹⁴</u>		<u>β-ReCl₄^{a 91}</u>	
d	int	d	int	d	int	d	int	d	int
6.02	10	6.00	n	5.97	vvs	5.84	vs	6.08	
		5.75	n					5.57	
		5.30	w			5.27	v	5.00	
4.43	9	4.41	n	4.43	vvs	4.36	n	4.46	
4.09	8	4.04	n	4.02	vvs	4.00	n	4.04	
3.43	2							3.40	
		3.28	n	3.23	vs	3.21	vw	3.33	
2.95	3			3.03	vw			3.04	
		2.86	w	2.85	vw	2.82	vw	2.84	
2.71	8	2.72	vw	2.77	w			2.75	
2.61	9	2.63	vs	2.62	vs	2.59	vs	2.68	
2.57	5	2.59	n	2.58	n	2.53	vs	2.53	
		2.54	n	2.54	w			2.52	
2.22	7	2.20	n	2.23	n	2.18	n	2.23	
2.17	2			2.18	vw			2.18	
2.14	3	2.12	w	2.13	vw			2.14	
		2.10	n	2.10	w	2.08	n	2.10	
2.03	7	2.01	n	2.02	n	1.99	n		

a - The data shown here is chosen from all the possible calculated d spacings, in an attempt to obtain a correlation. Since a large number of d spacings less than 3.0 are obtained, a fit for d < 3.0 is inevitable.

Table 7.4 gives a comparison of the powder diffraction data for the molybdenum (IV) chloride, used in this work, and the chlorides prepared by Schafer,⁸⁵ and by Couch and Brenner.⁹⁵ A marked correlation is observed between the d spacings of the last two, suggesting the not surprising result that the similar reactions



both give β -molybdenum (IV) chloride, while the very different method, viz. refluxing the pentachloride with benzene, yields a different (the α -) form.

(v) Theory

The theory for $A_3\text{Mo}_2\text{Cl}_9$ (A = Rb or Cs), predicts that for a molybdenum-chlorine coordination number of six, there will be 1.5 metal-metal contacts i.e. there should be two longer than "normal" metal-metal bonds or one shorter than "normal" (i.e. 2.5\AA rather than $2.6-2.8\text{\AA}$). Determination of the Mo-Mo distance in these compounds will be a useful test of the theory, as it also predicts that the Mo-Mo distance will vary with alkali metal.

CONCLUSIONS

Two forms (α and β) of molybdenum (IV) chloride exist, one having considerable metal-metal interaction, the other not. The

TABLE 7.4

X-RAY DIFFRACTION DATA FOR ISOMERS OF MOLYBDENUM (IV) CHLORIDE

$\alpha\text{-MoCl}_4$		$\beta\text{-MoCl}_4^{85}$		MoCl_4^{95}	
d	int	d	int	d	int
				6.85	w
6.00	s			6.52	w
5.75	s	5.83	m	5.85	vs
5.30	w			5.36	w
		5.23	w	5.26	w
				5.16	w
		4.78	w	4.79	w
4.41	s			4.42	w
4.04	m			4.14	w
3.28	m	3.13	w	3.14	vw
				3.11	w
				3.04	vw
2.86	w	2.92	w	2.93	w
2.72	vw	2.68	vs	2.70	s
2.63	vs			2.65	w
2.59	s	2.56	w	2.56	vw
2.54	m			2.44	vw
2.20	m	2.17	w		
2.12	w	2.14	w		
2.10	m	2.10	m	2.11	m
2.01	s	1.95	w	1.96	w
				1.94	w
		1.75	m	1.75	m

existence of the α -form is compatible with theory, but the theory cannot explain the existence of the β -form. The α -form undergoes disproportionation in oxygen donor solvents to yield species having structures based on that of the $\text{W}_2\text{Cl}_9^{3-}$ unit.

EXPERIMENTAL

α -Molybdenum (IV) chloride was prepared by the method of Larson and Moore¹⁶ (see Chapter 2).

Reaction of α - MoCl_4 with hydrochloric acid

Eg. α - MoCl_4 (2.4 gm) was dissolved in 12M hydrochloric acid (20 ml), and the carbonaceous byproducts centrifuged off. Excess rubidium chloride (1.2 gm) in hydrochloric acid was added with stirring. Brick red crystals came out of solution. These were filtered off and washed with 12M hydrochloric acid, acetone and dried in vacuum.

Yield = .65 gm (42%). (Theoretical yield, 50%).

Analysis:

Found	% Cl	% Mo	% Rb	Oxidation No.	Ratio Mo:Cl
	40.2	23.8		3.04	1:4.55
	40.2	24.1		3.06	1:4.51
	40.4	24.2	33.2	3.03	1:4.51
	40.4				

Calculated for $\text{Rb}_3\text{Mo}_2\text{Cl}_9\text{H}_2\text{O}$

	40.7	24.4	32.7	3.00	1:4.50
--	------	------	------	------	--------

On heating 0.0768 gm of the complex in vacuum to 100°C for 48 hr., the weight dropped to 0.0751 gm. On exposure to moist air the weight increased slowly to the original. The weight loss corresponds to the loss of one molecule of water.

The ammonium (yield 14%) and cesium (yield 45%) complexes were prepared in an analogous manner.

Analysis: Calculated for $H_{12}N_3Cl_9Mo_2$: H, 2.12; N, 7.43; Cl, 56.4; Mo, 33.9; oxidation number 3.00. Found: H, 2.53; N, 7.00; Cl, 56.5; Mo, 33.3; oxidation number 3.00.

Analysis: Calculated for $Cs_3Cl_9Mo_2$: Cs, 43.8; Cl, 35.1; Mo, 21.1; oxidation number, 3.00. Found: Cs, 41.7; Cl, 35.2; Mo, 21.2; oxidation number 3.05. Slowly increases in weight on exposure to air - possibly due to uptake of water.

Reaction of $\alpha\text{-MoCl}_4$ with Methanol

$\alpha\text{-MoCl}_4$ (~1 gm) was dissolved in methanol (20 ml) and the solution centrifuged. Excess tetraphenylarsonium chloride in methanol was added. A mixture of red and yellow-green needles came out of solution. These were collected and washed well with acetone since the yellow-green crystals were soluble and the red ones not. The brick-red needles were dried in vacuum. Yield ~60%.

Analysis:

	C	H	As	Cl	Mo	Oxidation No.	As:Cl
Found	44.7	3.8	11.6	21.7			1:3.95
	44.8	4.1	11.6	21.7	15.0	2.8 ^a	1:3.95
				21.6			

Calculated for $[(C_5H_5)_4As]_2Mo_2Cl_8 \cdot 2H_2O$

45.1	3.5	11.6	22.2	15.0	3.0	1:4.00
------	-----	------	------	------	-----	--------

a - poor end point since determined by prior solution of the complex in dimethyl formamide before oxidation number determination.

The yellow-green crystals were collected by evaporation of the acetone to a small volume.

Analysis: Calculated for $C_{24}H_{24}AsCl_4MoO_4$ (i.e. $(C_5H_5)_4AsMoOCl_4 \cdot H_2O$):
 C, 44.9; H, 3.36; As, 11.4; Cl, 21.7. Found: C, 44.4; H, 3.74;
 As, 11.4; Cl, 21.3.

The tetraethylammonium (yield ~25%) and pyridinium (yield ~10%) salts were prepared in the same manner as the above molybdenum (III) salt - the coprecipitated molybdenum (V) species being removed by acetone washing. These were obtained as pale pink microcrystalline solids.

Analysis:

	C	H	N	Mo	Cl	Oxidation No.	Mo:Cl
Found	27.9	6.1	3.9	25.1	37.0	3.1	1:3.98
				24.0	35.5	3.2	1:4.00
				24.5	36.6	3.1	1:4.04
	29.2	6.2	3.7	23.4	35.0		1:4.04

Calculated for $[(C_5H_5)_3Mo_2Cl_9 \cdot 3CH_3OH]$

	37.0	6.0	3.5	24.0	35.0	3.0	1:4.00
--	------	-----	-----	------	------	-----	--------

Analysis: Calculated for $C_{15}H_{20}Cl_9Mo_2H_3O$ (i.e. $(C_5H_5NH)_3Mo_2Cl_9 \cdot H_2O$):
Cl, 41.6; Mo, 24.9; oxidation number, 3.00. Found: Cl, 42.2;
Mo, 24.7; oxidation number, 3.05.

Attempts were made to prepare molybdenum (III) adducts by addition of ligands in methanol to a methanolic solution of α -molybdenum (IV) chloride. In most cases nothing came out, but with pyridine pink solids came out. These were analysed many times, but composition was not reproducible. They appeared to be intermediates between the pyridinium salt (above) and adducts, as Mo:Cl ratios varied between 1:3.3 and 1:4.2, even though the molybdenum oxidation number was 3.00.

With some other ligands i.e. 2,2'-dipyridyl and ethylene diamine solids came out that were obviously mixtures of molybdenum (III) and molybdenum (V) species. These could not be separated thus the investigation went no further.

Reaction of α - MoCl_4 with Acetone

2,2'-Dipyridyl in acetone was added dropwise to a solution of tetrachloride in acetone. A red-purple oil resulted. This was washed with dimethyl formamide until the washings were colourless. The violet solid (in very low yield) was then washed with acetone and dried in vacuum.

Analysis: Calculated for $\text{C}_{20}\text{H}_{20}\text{Cl}_4\text{Mo}_2\text{N}_4\text{O}_2$ (i.e. $(\text{bipyridyl})_2\text{Mo}_2\text{Cl}_4\text{O}_2$): C, 35.4; H, 2.34; Cl, 20.9; Mo, 28.3; N, 8.25. Found (I) C, 34.9; H, 2.81; Cl, 20.5; Mo, 28.1; N, 7.99. (II) C, 35.4; H, 2.80; Cl, 19.4; N, 7.80. It was not possible to determine oxidation number.

The infra-red spectrum of the complex shows Mo=O stretch at 955 cm^{-1} .

Attempts to prepare other adducts using acetone solutions resulted in molybdenum (III)-molybdenum (V) mixtures, or nothing at all.

Preparation of $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$ ¹⁶

Pyridine (dried over calcium hydride) (25 ml) was degassed and distilled into a vessel containing 1.238 gm of α -molybdenum (IV) chloride. This was shaken for 24 hrs. During this time the solution became golden brown, and crystals began to deposit. The excess pyridine was removed under vacuum. Weight = 2.412 gm (calculated weight for $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$ = $2.4\frac{7}{4}$ gm).

Preparation of $\text{MoCl}_4 \cdot 2\text{CH}_3\text{CN}$

Prepared in a similar manner to the n-propyl cyanide adduct reported by Allen et al.²⁰ i.e. a solution of molybdenum pentachloride (Al_2Cl_6 - used as supplied) in redistilled acetonitrile, was allowed to stand for two days before the collection of the brown crystals formed.

Analysis: Calculated for $\text{C}_4\text{H}_6\text{Cl}_4\text{MoN}_2$: Cl, 44.4; molybdenum oxidation no., 4.00. Found: Cl, 43.9; molybdenum oxidation no., 3.96 (assuming 30.0% Mo).

Both $\text{MoCl}_4 \cdot 3\text{C}_2\text{H}_5\text{NH}_2$ and $\text{MoCl}_4 \cdot 2\text{CH}_3\text{CN}$ were dissolved in hydrochloric acid and methanol, but green solutions resulted, and only molybdenum (V) species could be precipitated out.

For analytical methods and other techniques used see Appendix I.

Brown and McCann* have just published a note on a new preparation of α -molybdenum (IV) chloride. They used reduction of molybdenum (V) chloride with tetrachloroethylene, rather than benzene, and obtained a cleaner product. They also found that their product, Larson and Moore's¹⁶ and tungsten tetrachloride were isomorphous, and of different structure to that reported by Shafer.⁸⁵

* Brown, T.M. and McCann, E.L., *Inorg.Chem.*, 7, 1227, (1968).

CHAPTER 8. DISPROPORTIONATION OF METAL TETRAHALIDES IN SOLUTION
AS A PREPARATIVE METHOD FOR STAPHYLONUCLEAR COMPLEXES. II.

INTRODUCTION

The method developed in the previous Chapter is now extended to other tetrahalides. Each of the tetrahalides investigated is discussed separately. This work makes no claim to be a thorough investigation of the tetrahalides, but merely a skeletal survey of the type, and few properties, of some of the complexes produced.

Because the phenomenon of disproportionation is, in itself, an interesting one (it is confined to a very small area of the periodic table), this study has also been directed towards the development of a model explaining the occurrence of disproportionation. This is discussed near the end of the chapter.

RESULTS AND DISCUSSION

(1) Molybdenum (IV) Bromide

(a) *Compounds Prepared*

This halide undergoes similar disproportionation, in oxygen donor solvents, to that observed for molybdenum (IV) chloride. The complexes $\text{Rb}_3\text{Mo}_2\text{Br}_9 \cdot \text{H}_2\text{O}$ and $\text{Cs}_3\text{Mo}_2\text{Br}_9$ were isolated from hydrobromic acid solvent. Comparison of their powder diffraction photographs with those of other $\text{M}_2\text{X}_9^{\text{III}}$ species prepared in this work, showed them to be isomorphous with $\text{W}_2\text{Cl}_9^{\text{III}}$ -containing compounds.

The room temperature specific susceptibility of $Rb_3Mo_2Br_9 \cdot H_2O$ is $11.6 \cdot 10^{-4}$ CGS units, which yields a ν_{eff} value of 1.2 BM per molybdenum. This low moment, now a common occurrence in these complexes, is indicative of considerable metal-metal interaction.

Again marked independence of complex formed on solvent was observed. Table 8.1 displays the results of digestion of the bromide with hydrohalic acids, prior to precipitation with rubidium or caesium.

TABLE 8.1

ANALYTICAL DATA FOR RUBIDIUM AND CAESIUM COMPLEXES PREPARED FROM MOLYBDENUM (IV) BROMIDE IN AQUEOUS ACIDS

<u>Acid</u>	<u>Rubidium Complexes</u>		<u>Caesium Complexes</u>	
	% Br	% other halogen	% Br	% other halogen
12N HCl	59.0	1.7	53.5	1.0
8N HBr	60.6	-	54.8	-
8N HI	54.7	7.1	42.8	14.4
<i>Calculated for $Rb_3Mo_2Br_9 \cdot H_2O$</i>			<i>Calculated for $Cs_3Mo_2Br_9$</i>	
	60.6		54.8	

Using ethanol or methanol as solvent, together with varying cations, a range of complexes was prepared, with Mo:Br ratios varying between 1:4.3 (for a caesium complex) and 1:1.5 (for some tetraphenyl-arsonium complexes).

The analytical data for the complexes prepared are shown in Table 8.2. The compounds came rapidly out of solution and, as before, could not be recrystallised. Thus the variability of analyses observed is not unexpected. The ligand deficient complexes $[(C_2H_5)_4N]_{1.75}Mo_2Br_{7.75}$ and $[(CH_3)_4N]_2Mo_2Br_8 \cdot 2CH_3OH$ seem to best fit the analytical figures. No reasonable formulation can be given for the tetraphenylarsonium salt, unless the molybdenum is in a fractional oxidation state. Unfortunately the complex is too insoluble to allow oxidation number determination, but the complex is free from contamination by molybdenum (V) (no Mo=O in the infra-red).

In common with α -molybdenum (IV) chloride, no adducts of the type $Mo_2Br_6L_3$ could be prepared, even though a wide variety of ligands was tried. Addition of pyridine to the bromide in methanol yielded $(C_5H_5NH)_2Mo_2Br_8 \cdot CH_3OH$.

(c) Spectroscopy

The spectrum of $Mo_2Br_9^{3-}$ (Figure 8.1) was similar to that of $Mo_2Cl_9^{3-}$ and independent of hydrobromic acid concentration.

Both the tetraethyl- and tetramethylammonium complexes show dependence on the concentration of hydrobromic acid in dimethyl formamide, suggesting that they are ligand deficient H_2X_9 species. The spectrum of the tetraphenylarsonium complex changes little on increasing the concentration of aqueous hydrobromic acid in dimethyl formamide (Figure 8.1). This may be evidence that the molybdenum has a fractional oxidation state, and the structure is not based on that of $H_2X_9^{3-}$.

FIGURE 8-1. Comparison of the Spectra of Some Bromomolybdate (III) Complexes in Solution.

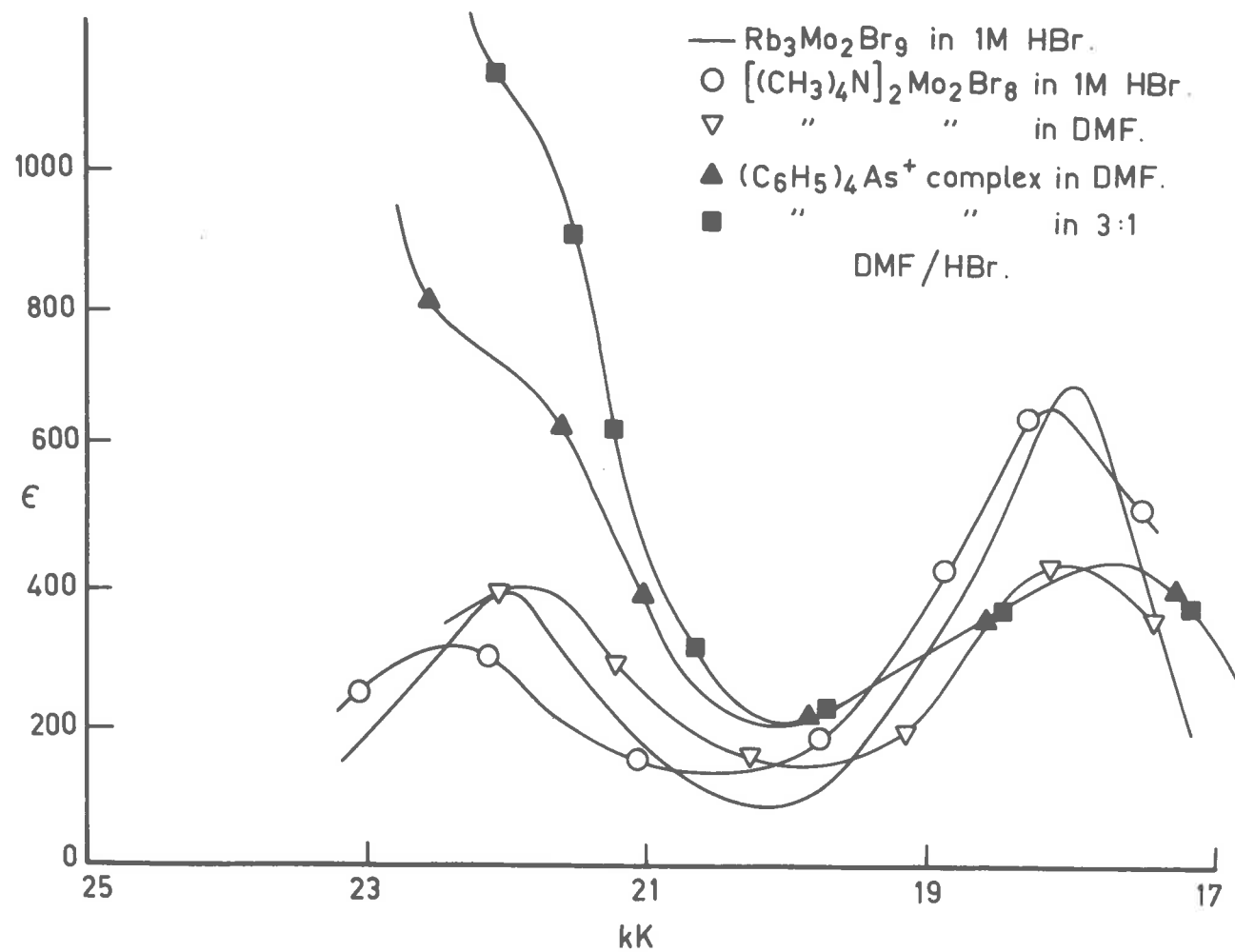


TABLE 8.2

ANALYTICAL DATA FOR COMPLEXES PRECIPITATED FROM METHANOL-

MOLYBDENUM (IV) BROMIDE SOLUTIONS

<u>Cation</u>	<u>% Br</u>	<u>% Mo</u>	<u>% N or As</u>	<u>% C</u>	<u>% H</u>	<u>Br/As</u>	<u>Br/Mo</u>	<u>Oxid^a No.</u>
Tetraphenylarsonium	40.8							
	41.8	14.6	8.5	32.9	2.9	4.6	3.42	- ^a
	40.5	13.4					3.63	-
	41.1							
	40.8							
	41.5							
	41.7		8.1	32.4	2.5	4.8		
	40.5	13.9	8.8	34.9	2.9	4.3	3.50	-
	39.4		3.2	34.9	3.0	4.5		
Tetraethylammonium	58.7	18.2						2.9
	57.8	18.7	2.0	16.7	3.5			
	58.4	18.2	1.6	16.3	3.5			2.8
	58.3	18.9	2.1	18.1	4.0			3.0
	58.8		2.5	16.6	3.6			
<i>Required for</i> $[(C_2H_5)_4N]_2MoBr_8 \cdot 7.75 H_2O$	58.7	18.8	3.4	16.5	3.4			3.0
Tetraethylammonium	63.0	19.1	3.0	11.5	3.2			3.0
	62.6	19.3	2.9	11.2	3.0			3.0
	62.5		2.6	12.4	3.0			
	62.0							
<i>Required for</i> $[(C_2H_5)_4N]_2MoBr_8 \cdot 8.5 H_2O$	63.8	19.0	2.8	11.8	3.2			3.0

^a - determination not possible

(11) Tungsten (IV) Chloride

(a) *Aqueous Solvents*

Using hydrohalic acids as a solvent for the chloride and precipitating with rubidium or caesium, complexes containing the well known $W_2Cl_9^{3-}$ unit were obtained. These were isomorphous with $K_3W_2Cl_9$ ³⁷ (powder photography).

(b) *Alcoholic Solvents*

A very different reaction occurred between alcohols and the tetrachloride than was observed in any of the other tetrahalides investigated. The following products were obtained on refluxing tungsten (IV) chloride with the parent alcohols. - $W_2Cl_4(CH_3O)_4(CH_3OH)_2$, $W_2Cl_4(C_2H_5O)_4(C_2H_5OH)_2$, $W_2Cl_4(C_3H_7O)_4(C_3H_7OH)_2$ (with both n- and iso-propyl alcohols), and $W_2Cl_4(n-C_4H_9O)_4(n-C_4H_9OH)_2$.

These are formulated as tungsten (IV) edge-shared species on the basis of the following evidence.

(i) Analytical - analytical data shows that in all cases there are five groups per tungsten.

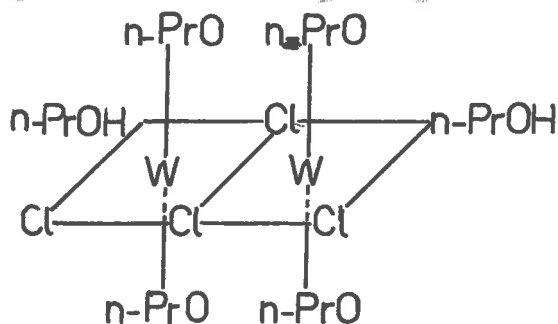
(ii) On heating the methanol derivative in vacuum at 100°C, no weight change was observed, suggesting that none of the methanol is present as loosely bound solvent.

(iii) In benzene the molecular weight of the n-propanol adduct is 860 (calculated for a dimer, 868).

(iv) The green solids are diamagnetic ($10^6 \chi \sim 0$ CGS) suggesting at least dimers, with considerable interaction between the metal atoms.

(v) Since these compounds are completely unaffected by aqueous media, their oxidation numbers could not be obtained to check the formulation as tungsten (IV) complexes. However in many cases the yields were >50%, thus ruling out the possibility of disproportionation to tungsten (III) and (V).

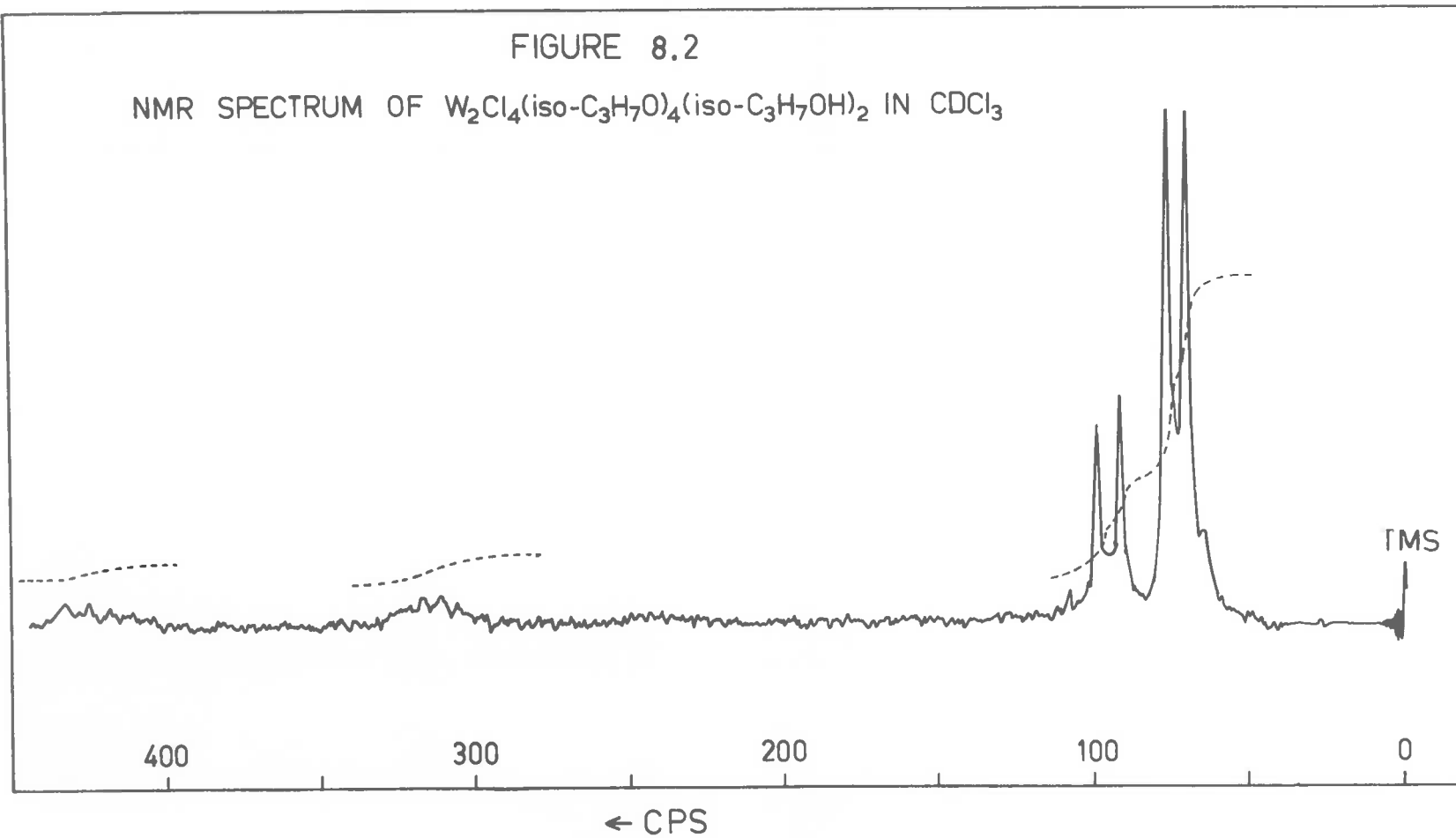
(vi) The N.M.R. spectra of the isopropanol (Figure 3.2) and n-propanol complexes show two sets of proton peaks in the ratio 2:1, indicating four and two alcoholic groups in two different environments. Using a similar argument to Klajnot's,⁹⁶ there are four possible structural possibilities, with the following being the most likely.



In 1911 a report⁹⁷ gave the preparation of a green complex, formulated as $W_2Cl_4(C_2H_5O)_6$, prepared by the electrolysis of tungsten hexachloride - ethanol solutions. Klajnot⁹⁶ has since found a red compound of the above constitution, and suggests that the green complex contains tungsten (IV). This work agrees with his conclusions, and the green complex is now formulated as $W_2Cl_4(C_2H_5O)_4(C_2H_5OH)_2$ i.e. the same as prepared in this study.

FIGURE 8.2

NMR SPECTRUM OF $W_2Cl_4(iso-C_3H_7O)_4(iso-C_3H_7OH)_2$ IN $CDCl_3$



These green compounds are all soluble to some extent in polar organic solvents, (solubility increasing with alcohol chain length), but are completely insoluble in aqueous solvents.

Attempts to crystallise $W_2Cl_4(CH_3O)_4(CH_3OH)_2$ from n-propanol, yielded only the n-propanol derivative, and not $W_2Cl_4(CH_3O)_4(n-C_3H_7OH)_2$ as hoped. Similarly crystallisation of the n-propanol derivative from methanol, yielded only the methanol derivative.

Properties of $W_2Cl_4(n-C_3H_7O)_4(n-C_3H_7OH)_2$

Attempts were made to prepare adducts of the type $W_2Cl_4(n-C_3H_7O)_4L_2$ using pyridine, hydrazine, 2,2'-dipyridyl and triphenylphosphine. With the latter two, yellow-green, air-sensitive oils were produced, and with hydrazine, yellow-brown solids of non reproducible analysis, and containing no chloride, were formed. However, with pyridine, as Table 8.3 shows, adducts of the above type may be formed.

TABLE 8.3

ANALYTICAL DATA FOR $W_2Cl_4(n-C_3H_7O)_4(n-C_3H_7OH)_2$ -PYRIDINE COMPLEXES

	<u>% W</u>	<u>% Cl</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>W/C</u>
		15.7	24.1	4.3	0.6	
	40.7	16.0	28.8	5.2	1.3	10.8
Found	42.0	16.2	28.0	5.2	1.2	10.2
	42.1	15.1	24.0	4.7	1.2	8.8
	40.8	14.9	25.6	4.9	-	9.6
Calculated for $W_2Cl_4(n-C_3H_7O)_4(pyr)_2$	40.8	15.7	29.2	4.3	3.1	11.0

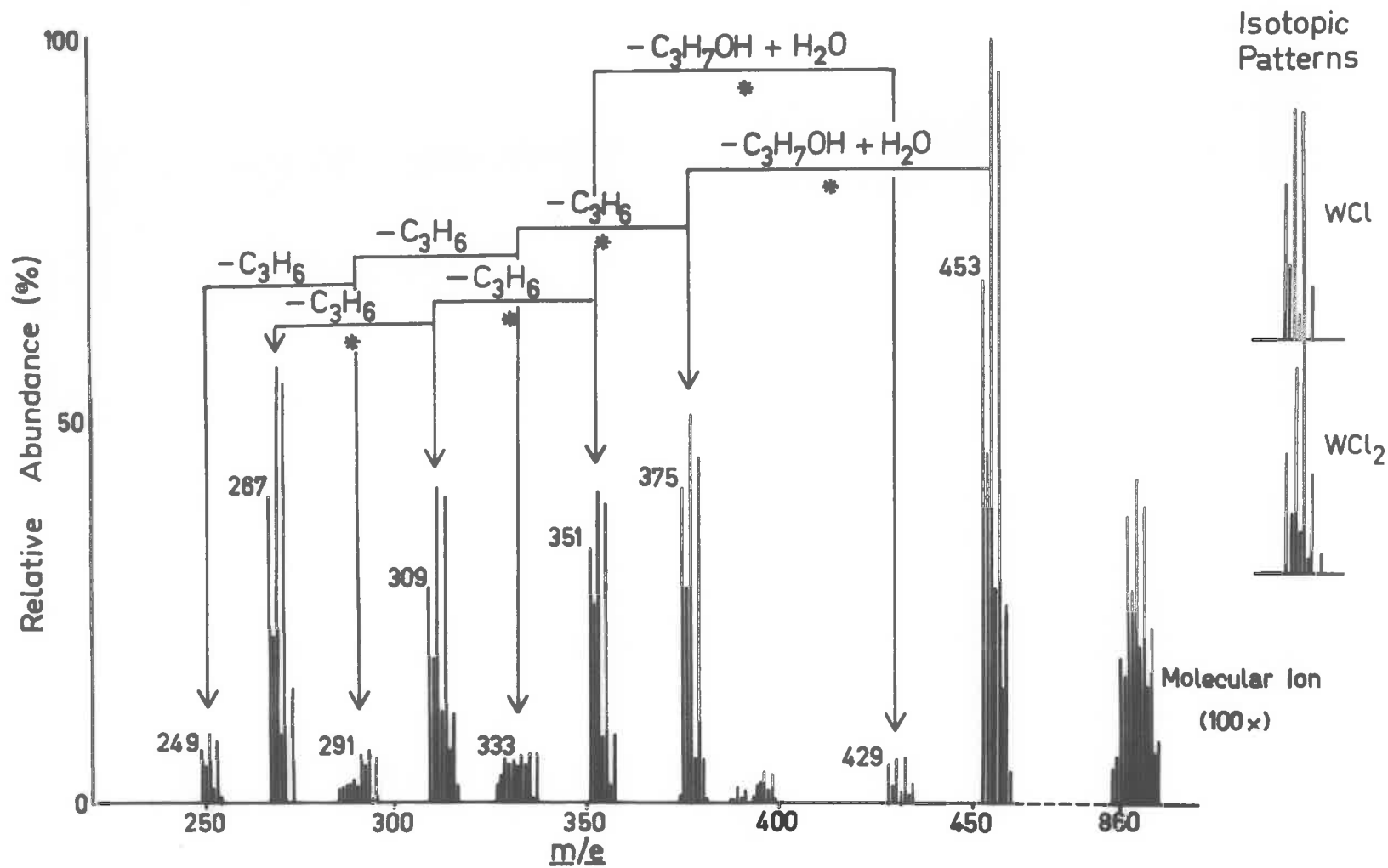
On addition of chlorine to a solution of the complex in chloroform, the initially green solution became deep red. Red platelets came out of solution - presumably the complex $W_2Cl_4(n-C_3H_7O)_6$ (c.f. the previously reported³⁶ red $W_2Cl_4(C_2H_5O)_6$).

This complex, in common with the other alcohol derivatives, on reaction with *not* acetic acid, gave bright red colours. Nothing could be precipitated from these solutions.

The visible and ultra-violet spectrum of the complex is essentially the same in carbon tetrachloride, benzene, cyclohexane, acetone and acetone/hydrochloric acid. Peaks (all obeying Beer's Law) were observed at 13.3 m μ ($\epsilon = 200$), 23.2 m μ ($\epsilon = 3460$), 39.9 m μ (at $\epsilon \sim 19,000$), 43.8 m μ ($\epsilon = 27,000$). The visible spectrum of the pyridine adduct is not significantly different from the above, thus ruling out visible spectroscopy as a method for determining the number of pyridines coordinated.

The mass spectrum of the complex, and the fragmentation pattern are shown in Figure 8.3. However, using this evidence, the highly probable symmetrical dimer seems impossible, unless rearrangement occurs after fragmentation, since the two major fragments cannot arise from such a structure. These two fragments are $(n-C_3H_7O)_4WCl^+$ and $(n-C_3H_7O)_3WCl_2^+$. The peak intensity patterns observed for these agree with those calculated for WCl and WCl_2 groups, using the elemental isotopes and their abundance.

FIGURE 8.3: Mass Spectrum of $W_2Cl_4(n-C_3H_7O)_4(n-C_3H_7OH)_2$



(111) Tungsten (IV) Bromide

(a) *Aqueous Solvents*

Hydrobromic and hydrochloric acids react exothermically with the bromide, producing red-orange solutions, together with considerable quantities of tungsten blue. From these solutions $[(\text{CH}_3)_4\text{N}]_3\text{W}_2\text{Br}_9$ and $\text{Hb}_3\text{W}_2\text{Br}_9$ were prepared, the latter complex being isomorphous with its chloro equivalent.

These are both red-orange solids, which on warming with dilute hydrobromic acid, decompose to a black precipitate, with considerable evolution of hydrogen.

(b) *Non-aqueous Solvents*

With both methanol and ethanol green solutions were obtained. From these, using tetramethyl- and tetraethylammonium, yellow-green solids were precipitated. These were not of reproducible composition, and the tungsten oxidation number was approximately 4.7. This indicates that the solids were almost certainly mixtures of W (III) and W (V) complexes. Unfortunately these could not be separated as could their molybdenum analogues.

CONCLUSIONS

Molybdenum and tungsten (IV) bromides disproportionate in both aqueous and alcoholic media to yield, on precipitation, complexes containing units whose structure is based on that of the $\text{W}_2\text{Cl}_9^{3-}$ unit.

Tungsten (IV) chloride yields the expected complexes in aqueous media, but in alcohols yields tungsten (IV) complexes i.e. disproportionation does not occur.

A MODEL FOR THE PREDICTION OF HYDROLYTIC DISPROPORTIONATION

Table 8.4 lists the binary chlorides and bromides whose metal-metal CM (n) lies between zero and one in some bonding circumstances. These values are calculated using equation 4 (page 6), using the appropriate N_A value, and a metal-halogen CM of six (i.e. $n = 6$).

A range of n values is obtained since non bonding d electrons shield the nucleus, affecting χ , and the number of these may vary for a particular oxidation state, depending upon the number of d electrons involved in metal-metal interaction.

The halides in Table 8.4 are listed in 3 classes -

- A - n cannot be less than 0.5 (no matter how many d electrons are used in bonding)
- B - n values encompass 0.4 or 0.5
- C - n values are always lower than 0.4

It is now proposed that hydrolytic disproportionation will occur if a compound belongs to class B, provided that there are oxidation states available (i.e. known) for the products of disproportionation. Table 8.4 displays whether or not this phenomenon is known to occur, and its result. Quite good agreement between predicted and observed behaviour is obtained.

TABLE 8.4

BINARY CHLORIDES AND BROMIDES WHERE $l > m$ (calc) > 0 WHEN $n = 6$,
AND FOR WHICH RELATED HIGHER AND LOWER HALOCOMPLEXES EXIST

A			B			C		
<u>Halide</u>	<u>$n(\text{calc})$</u>	<u>Disprop^a</u>	<u>Halide</u>	<u>$n(\text{calc})$</u>	<u>Disprop^a</u>	<u>Halide</u>	<u>$n(\text{Calc})$</u>	<u>Disprop^a</u>
MoCl ₃	0.8-2.5	No	VBr ₃	0.4-1.4	?	YcCl ₆	-0.7-0.3	No
VCl ₃	0.7-1.8	No	NbBr ₄	0.4-0.8	?			
NbCl ₄	0.7-1.1	? ^b	WBr ₄	0.2-1.0	Yes			
MoBr ₃	0.5-2.0	?	ReCl ₄	0.2-0.9	Yes			
WCl ₄	0.5-1.3	Yes ^a	OsCl ₃	-0.1-2.1	?			
			MoCl ₄	-0.1-0.7	Yes			
			MoBr ₄	-0.3-0.4	Yes			
			ReBr ₄	-0.4-0.6	No ^c			

a - Borderline case since it disproportionates in aqueous solvents, but not in alcohols.

b - NbCl₄ gives bright blue solutions with hydrochloric acid. In this work a preliminary study showed that blue complexes can be precipitated from these solutions with rubidium and cesium, but their extreme reactivity with air makes handling and analysis difficult.

c - The preparation of ReBr₄ using aqueous hydrobromic acid and per-rhenic acid, has been reported (98), but only one rhenium analysis, (and no other data) was cited, making this result extremely doubtful. Moreover it is unprecedented that a lower bromide could be prepared by such a method.

For single metal-metal contacts, there is a correlation between the calculated n value ("bond order") and bond lengths, in cases where these have been measured. Thus $n = 1.0$ corresponds to a metal-metal separation of $\sim 2.7 \text{ \AA}$, and a value of 0.5 corresponds to $\sim 3.0 \text{ \AA}$ etc. Therefore it appears that when the metal-metal bond length is $\sim 3.0 \text{ \AA}$ due to internuclear repulsion requirements, this corresponds to an unstable situation, and will readily give rise to two oxidation states, where the internuclear repulsion requirements allow complete separation (higher oxidation state), or complete bond formation (lower oxidation state) i.e. disproportionation will occur.

EXPERIMENTAL

Molybdenum (IV) bromide was prepared by the reaction of molybdenum hexacarbonyl with excess bromine.⁹⁹

Analysis: Calculated for Br_4Mo : Br, 76.9; Mo, 23.1. Found: Br, 75.8; Mo, 24.2.

Tungsten (IV) chloride and bromide were prepared by the aluminium reduction of resublimed hexachloride and pentabromide respectively.⁶⁴

Analysis: Calculated for Cl_4W : Cl, 43.5; Found: Cl, 43.1, 43.7.

From aqueous and methanolic solutions, molybdenum (III) bromo complexes were prepared from the tetrabromide in an identical manner to that used in the previous chapter for the preparation of molybdenum (III) chloro complexes. Yields 35-40%.

Analysis: Calculated for $\text{Rb}_3\text{Mo}_2\text{Br}_9 \cdot \text{H}_2\text{O}$: Br, 60.6; Mo, 16.2; oxidation no., 3.0. Found: Br, 61.0; Mo, 16.6; oxidation no., 2.9.

Analysis: Calculated for $\text{Cs}_3\text{Mo}_2\text{Br}_9$: Br, 54.9; oxidation no., 3.0. Found: Br, 54.8; 54.6; oxidation no. 2.9.

Although the complexes prepared using organic cations were air sensitive, oxidation had little effect if the operations were carried out quickly in the atmosphere. Yields ~30%.

The pyridine complex was prepared by the slow addition of pyridine to the tetrabromide in methanol. The pink complex was collected, and washed with acetone until the washings were colourless, and then dried in vacuum.

Analysis: Calculated for $(\text{C}_5\text{H}_5\text{NN})_2\text{Mo}_2\text{Br}_8 \cdot \text{CH}_3\text{OH}$: C, 12.9; H, 1.6; N, 2.7; Br, 62.5; Mo, 18.8; oxidation no., 3.0. Found: C, 13.5; H, 1.6; N, 3.0; Br, 62.7; Mo, 19.8; oxidation no., 3.0.

Complexes containing the $\text{W}_2\text{Cl}_9^{3-}$ unit were prepared from aqueous tungsten (IV) chloride solution in the same manner as the corresponding molybdenum compounds.

Analysis: Calculated for $\text{Rb}_3\text{W}_2\text{Cl}_9$: Cl, 33.9. Found: Cl, 33.5.

Calculated for $\text{Cs}_3\text{W}_2\text{Cl}_9$: Cl, 29.4. Found: Cl, 29.6.

Notes: Yields were calculated from total Mo(IV) thus, if disproportionation occurs, the theoretical yield is 50%.

The alcoholic complexes were prepared by refluxing tungsten (IV) chloride (0.5 gm) with the alcohol (10 ml) for five minutes. This deep green solution was filtered hot, and then allowed to cool. The green crystals were filtered off, washed with the alcohol, and then dried in vacuum. The analytical data are displayed in Table 8.5.

TABLE 8.5

ANALYTICAL DATA FOR TUNGSTEN (IV) CHLORIDE - ALCOHOL COMPLEXES

<u>Alcohol</u>	<u>C</u>	<u>H</u>	<u>Cl</u>	<u>W</u>	<u>Cl/W</u>	<u>Yield</u>
Methanol	10.6	3.1	20.6	53.5	2.00	65%
	10.3	3.0	20.5	52.8	2.01	70%
<i>Calculated for</i> $W_2Cl_4(CH_3O)_4(CH_3OH)_2$	10.3	3.1	20.4	52.8	2.00	
n-Propanol			16.7	43.5	1.98	
	25.0	5.2	16.6	44.2	1.95	~50%
	25.5	5.2	16.5	-		
<i>Calculated for</i> $W_2Cl_4(n-C_3H_7O)_4(n-C_3H_7OH)_2$	25.0	5.1	16.4	42.6	2.00	
iso-Propanol	24.9	5.3	16.6	43.8	1.97	45%
<i>Calculated for</i> $W_2Cl_4(iso-C_3H_7O)_4(iso-C_3H_7OH)_2$	25.0	5.1	16.4	42.6	2.00	
n-Butanol	30.1	5.9	15.1	40.3	1.94	30%
<i>Calculated for</i> $W_2Cl_4(n-C_4H_9O)_4(n-C_4H_9OH)_2$	30.3	5.9	15.0	38.8	2.00	

The pyridine - $W_2Cl_4(n-C_3H_7O)_4(C_3H_7OH)_2$ adducts were prepared in either of 2 ways.

(i) Slow addition of a stoichiometric amount of pyridine to a solution of the complex in chloroform, followed by precipitation of the complex with petroleum ether.

(ii) Careful addition of the required quantity of pyridine, to a saturated solution of the complex in carbon tetrachloride. On cooling, fine yellow-green needles separated out. These were collected and dried in vacuum.

Compounds containing the $W_2Br_9^{3-}$ unit were prepared, in low yield, in an analogous method to that used in preparing $Mo_2Cl_9^{3-}$ compounds, but using tungsten (IV) bromide.

Analysis: Calculated for $[(CH_3)_4N]_3W_2Br_9$: Br, 55.0; W, 28.1; oxidation no., 3.0. Found: Br, 55.1; W, 27.8. Br, 54.5; W, 28.4; oxidation no., 2.9.

Calculated for $Nb_3W_2Br_9$: Br, 53.5. Found: Br, 52.8.

Tungsten (IV) bromide, in methanol, gave green solutions. Yellow-green solids were precipitated out of these on addition of organic cations. Determination of tungsten content, together with the number of oxidation equivalents consumed, yielded oxidation numbers varying between 4.3 and 4.7, in all cases. Attempts to separate the tungsten (III) and tungsten (V) complexes by washing with acetone was not effective for separation, because both W(III) and W(V) complexes were soluble in it.

The molecular weight of the α -propanol complex was determined in benzene, using vapour phase osmometry with a Macrolab instrument.

NMR spectra were recorded in deuterio-chloroform with tetramethylsilane as the internal calibrant, using a Varian DP-60 instrument.

The mass spectrum of $W_2Cl_4(C_3H_7O)_4(C_3H_7OH)_2$ was kindly recorded by Dr. E. Sternhell of Sydney University on an MS-9 machine. The author also wishes to thank Dr. J.M. Bowie for his help with the interpretation of the spectrum.

For analytical and other techniques, see Appendix I.

APPENDIX I

ANALYTICAL METHODS

For most analyses the compounds were decomposed by hot alkaline peroxide, and the resulting clear solutions simmered to remove excess peroxide. For some tungsten (VI) bromide compounds, fusion with caustic soda was required to bring about complete decomposition.

Using such solution (acidified) halogens were determined potentiometrically with standard silver nitrate. When two halogens were present barium nitrate (~0.2 gm) was added to improve the end point.

Molybdenum was determined by the lead molybdate method,^{100a} or, if some elements present interfered, using *o*-benzoinoxime.^{100a} However, if only halogen and organic material were present, the complex was heated in a weighed crucible to 525°C with nitric and sulphuric acids, and weighed as the trioxide.

Thallium was determined as thallic chromate,^{100b} and chromium volumetrically.^{100c}

Tungsten was determined by heating the complex in a stream of hydrogen at 600°C, and weighing as the metal,⁶⁴ or by heating the complex at 700°C with sulphuric and nitric acids, and weighing as the trioxide.

Oxidation numbers were determined by dissolving the compound in excess acidified ferric ammonium sulphate solution (hot, under nitrogen, if necessary), followed by titration with standard potassium permanganate. Bromide interfered if present, therefore, it was precipitated out by addition of a slight excess of silver carbonate, before titration.

Carbon, hydrogen, nitrogen, sulphur, and arsenic were determined by microanalysis (Australian Micro-analytical Service, Melbourne).

TECHNIQUES

Air reactive compounds were handled in a glove box, continually flushed with oxygen-free dry (silica gel) nitrogen.

Infra-red spectra (usually of nujol or hexachlorobutadiene mulls) were recorded using a Perkin Elmer model 21 double beam instrument.

Visible and ultraviolet spectra were recorded on either a Unicam SP700 or SP800 spectrophotometer. The solvents used were degassed and/or redistilled if necessary. The extinction coefficients for unstable compounds were found by extrapolating measured values to zero time.

Magnetic susceptibilities were determined using a conventional Goffy balance, employing an electromagnet. Tubes were calibrated using

mercury tetrathiocyanatocobaltate (II). The small magnetic forces observed in most cases, render the susceptibility values approximate.

Powder photographs were obtained using CuK_α radiation with a Philips camera (PW1024, 114.83 mm radius). Samples were mounted on glass fibres or in 0.5 mm quartz capillaries.

d-Spacings were calculated from cell data using a computer program developed by Dr. H.R. Snow of this Department.

APPENDIX II

PUBLICATIONS

The work in Chapters 2 and 3 has been published as follows.

Allison, G.R. and Sheldon, J.C., *Inorg.Chem.*, **6**, 1493, (1967).

Allison, G.R., Anderson, I.R., and Sheldon, J.C., *Aust.J.Chem.*,
20, 869, (1967).

The results discussed in Chapter 4 are in preparation for print, and it is intended that the work in Chapters 5 and 6 will be combined in one paper.

A short note and a paper encompassing the results obtained in Chapters 7 and 8, are in preparation for print.

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(a) p. 507. (b) p. 547. (c) p. 311.

APPENDIX III

A COMPARISON OF STEREOCHEMICAL THEORIES

To be useful a theory must do more than rationalise known phenomena - it must have some predictive value.

As previously mentioned, (page 1) conventional stereochemical theories relying on classification of bond type are rendered useless in staphylonuclear compounds where ionic and metallic bonding supposedly coexist.

The adjusted Crystal Field theory can make no predictions because of the presence of non polar $m - m$ bonds in these structures.

The Valence Bond approach (i.e. electrons are considered as localised in two-centre bonds) is still a widely accepted basis for the description of stereochemistry in transition metal complexes. It asserts that the various stereochemistries encountered result from the interaction, and hybrid formation, of the $(n-1)d$, ns and np metal orbitals. However this theory is devoid of any predictive ability.

Although this model can explain the structures of

some staphylonuclear compounds (e.g. for $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Re}_3\text{X}_{12}^{3-}$ ($\text{X} = \text{Cl}, \text{Br}$)¹⁰¹ sp^2d and d^3sp^3 hybridisation can explain the observed structures), real difficulty is encountered when non integral valence occurs, (e.g. $\text{Nb}_6\text{Cl}_{12}^{2+}$) as canonical forms have now to be postulated.

Of the traditional theories, the Molecular Orbital(MO) approach is probably the best predictive tool; its main drawback is the complexity of computation in all but the simplest cases. However, using very approximate methods, Cotton and Haas⁶¹ have been able to calculate energy level diagrams for some staphylonuclear units. Although these diagrams can be used to explain the spectra reasonably well (see page 79), few predictions as to the existence and structure of new compounds can be made, and when made they are at the best a well informed guess, based on a variable such as the overall charge on the ion⁶¹. Kettle¹⁰² has suggested that several new octahedral staphylonuclear compounds might exist on the basis of a forty electron model, but as yet none of these have been authenticated.

Very qualitative predictions as to whether a particular element might form staphylonuclear compounds can be made by consideration of its position in the periodic table, and oxidation number, but no stereochemistry can be predicted in this manner.

Sheldon's theory (Chapter 1) relies on an entirely new approach to stereochemistry. He postulates that the position of atoms in a structure is controlled by inter-nuclear repulsion. Since this can be calculated, roughly quantitative predictions can be made.

Stereochemical predictions made by this theory have previously been outlined (pp. 5-9, 23-24, 28, 63, 121, 123, 138-140). In each case a comparison of predicted and observed phenomena is mentioned.

CONCLUSIONS

Comparison of 'old' and new theories is difficult because few predictions made by them lie on common ground. The older theories being mainly concerned with prediction and explanation of electronic properties, and in its present form Sheldon's theory can make no spectral or magnetic predictions.

One of the few common predictions pertains to the existence of $\text{Mo}_3\text{Cl}_{12}^{6-}$. The Sheldon theory supports the existence of this, while, using a MO argument, Cotton and Haas⁶¹ claim that it would not exist. Work described in this thesis supports the existence of this unit.

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