EXPERIMENTAL STUDIES IN THE ISOMERISM AND STRUCTURAL VARIATIONS IN MOLYBDENUM AND RHENIUM HALO-COMPOUNDS

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 and belief, contains no material previously published or written by another person, except where due reference is made in the text.

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Abstract

The question of isomerism and structural variations in molybdenum and rhenium halo-compounds has been examined. These compounds provide an experimental test of a new theory of stereochemistry. Three predictions of this theory have been investigated.

(1) Trimeric staphylonuclear ternary halides of molybdenum(II) exist as an alternative form to the usual hexamers.

(2) Molybdenum(II) chloride exists in two isomeric forms.

(3) α-$ReCl_4$ does not adopt a Re_3Cl_2-type structure, but is more likely to be dimeric with octahedral metal-chlorine coordination and one Re-Re bond.

Prediction (1) has been largely confirmed by the preparation of several halogenomolybdates(II) of the types $Mo_3Cl_{13}^{7-}$, $Mo_3Br_{13}^{7-}$, $Mo_3Cl_{12}^{6-}$ and $Mo_3Br_{11}^{5-}$. The trimeric formulation, initially suggested by this preparative study, has been subsequently supported by spectroscopic and kinetic studies by another worker.

The reaction of dry hydrogen chloride with molybdenum(II) acetate produced β-$MoCl_2$. It is tentatively proposed that its structure is a distorted $CdCl_2$-type.

The preparation of α-$ReCl_4$ from the reflux of thionyl chloride with hydrated rhenium dioxide has been re-examined. The method did not give pure α-$ReCl_4$. Little evidence was found to support a trimeric formulation, but the preparative, chemical and X-ray powder diffraction studies indicate that α-$ReCl_4$ adopts a $NbCl_4$-like structure.

A thorough study of the solution chemistry of molybdenum(II) acetate in 12 M hydrochloric acid revealed a relatively stable species in solution, with oxidation number of 2.5. A number of halogenomolybdates(2.5) have been isolated, and formulated as $A_3Mo_2X_8$ (As, Rb, Cs; X = Cl, Br). Spectroscopic and X-ray diffraction studies indicate that these compounds adopt a ligand deficient W_2Cl_9-type structure.

The preparation of β-$ReCl_4$ by the chlorination of hydrated rhenium dioxide with carbon tetrachloride at high temperature and pressure in a steel bomb has been studied. The β-$ReCl_4$ produced is not pure but the method provides a useful starting point for the synthesis of new derivatives unique to $ReCl_4$.

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Chapter 1. The Prediction of Binary and Ternary Staphylonuclear Halides

Introduction

The chemistry of staphylonuclear compounds has developed extensively within the past decade, from a position where only a few examples were known and which were regarded as isolated and rather special, to the present position where metal-to-metal (m-m) bonding has been claimed in some oxidation state for nearly every transition element.

These compounds have already been the subject of at least three excellent reviews(1,2,3). Thus it is not felt necessary to give a detailed and comprehensive review of their chemistry in this thesis. Most of the important structure types and the general principles emerging from studies on staphylonuclear compounds have become sufficiently well documented and require no further emphasis.

While m-m bonding may occur in a large range of different types of compounds, this thesis is particularly concerned with the staphylonuclear binary and ternary halides of the transition elements. Thus this discussion is restricted to the cases in which the bonding occurs between atoms of the same element and the ligands are halogens, while recognising the relationship and relevance of other m-m bonded compounds to this topic.

The importance of the existence of staphylonuclear compounds is the challenge which they present to the conventional theories of valence. In defying these theories to explain and predict their existence, staphylonuclear compounds emphasise the need for a theory of stereochemistry able to rationalise the novel structures which have been reported.

It has become apparent that most of the staphylonuclear binary and ternary halides are formed by the earlier second and third row transition elements and in particular by the elements Nb, Ta, Mo, W and Re. In addition a low formal oxidation state appears to be favourable for the formation of m-m bonding. Despite many attempts to correlate and rationalise the increased tendency of these metals to engage in m-m bonding, no satisfactory theoretical explanation has yet been proposed.

Current stereochemical theories rely on the division of compounds into various groups depending on the bond type i.e. whether "ionic", "covalent" or "metallic", and there is not a comprehensive theory applicable in all cases. The division of bonding into these types is not useful in staphylonuclear compounds where "ionic" metal-halogen and "metallic" metal-metal bonds supposedly coexist but are incompatible. This arbitrary division of bond type is devoid of predictive ability with respect to stereochemistry.

The so called "conventional valence theory" requires numerous concepts for full discussion and all these categories refer specifically to the location and type of bond. Thus the stereochemistry, which is in fact the arrangement of atoms, has been approached from the viewpoint of bonding theories. However, the location and type of bond cannot be measured. It seems feasible that a theory of stereochemistry could be formulated on the measurable quantity, the position of the atomic nuclei, without recourse to classification of bond types. The value of such a theory to predict the occurrence of staphylonuclear compounds and suggest plausible structures for them is self evident.

A stereochemical theory, based on internuclear repulsion, rather than the manner in which electrons are shared, has been proposed by Dr. J.C. Sheldon(4) of this Department and is discussed here briefly. It will be shown later in this chapter that the compounds chosen for study provide a critical experimental test of the validity of this theory.

A Theory of Stereochemistry based on Internuclear Repulsion

(a) Reinterpretation of Pauling Electronegativity (χ)

The basis of the proposed theory is a reinterpretation of Pauling's electronegativity parameter χ. Pauling's theory of electronegativity states that each element is characterised by a largely constant parameter χ, which quantitatively correlates physical and chemical phenomena, the most important of which are single bond dissociation energies and the stereochemistries of elements and their simple compounds. Thus the fundamental and qualitative definition of χ is

$$D_{AB} - \tfrac{1}{2}(D_{AA} + D_{BB}) \equiv \Delta = (\chi_A - \chi_B)^2 \qquad \text{Eqn. (1)}^{(5)}$$

where D = single bond dissociation energy and AA, BB and AB are diatomic pairs.

The structures of the elements are related to χ in that "metallic" or "covalent" structures appear for low or high values of χ respectively. Also "ionic" structures appear for compounds in which the combining elements have a large difference in χ values.

The departure from conventional approaches is the re-interpretation of the physical significance of χ. This parameter has usually been interpreted as the ability of an atom to attract electrons. Mulliken(6) has preferred the term "electron affinity" for this type of electronegativity. An equally permissable and alternative physical interpretation of χ is the ability of an atom to repel positive charge i.e. other neighbouring atomic cores.

It is possible to compute the values of χ using the expression

$$\chi = 1.10\ n^{*2/3}/r \quad eV^{\frac{1}{2}} \qquad \text{Eqn. (2)}$$

where n^* = Slater effective quantum number

r = most probable radius.

This expression gives good agreement with the empirical values obtained from single bond dissociation energies and in the cases where this data is unavailable, provides a means by which χ values may be calculated.

(b) The Relationship Between Internuclear Repulsion and Coordination Number

Many atomic combinations (e.g. metals) can achieve a high coordination number (C.N.) while in others there exists a restraint which permits only much lower C.N. (e.g. O_2, N_2). This restraint is internuclear repulsion and thus C.N. must be a function of χ.

The quantitative relationship between C.N. and χ is developed by assuming that the function $2\chi_A\chi_B$ is a measure of the effective internuclear repulsive energy (E.I.E.) between A and B in the diatomic AB. This is providing that the distance between A and B is comparable with the sum of r_A and r_B. Thus in a compound AB_x, if atom A displays a C.N. towards B of n, and towards itself of m, then the E.I.E. of the coordination sphere of A in the compound AB_x is $2n\chi_A\chi_B$ or $2m\chi_A{}^2$ in the elemental form of A. The theory postulates that these quantities are approximately the same in all atomic combinations, a generalisation which can be shown to be true for elements spread across the Pauling electronegativity scale.

It now becomes possible to write down an equation for the total E.I.E. (N_M) of a metal in its coordination sphere in a binary halide. This equation becomes:

$$2m\chi_M^2 + 2n\alpha_{M-X}\chi_M\chi_X = N_M \qquad \text{Eqn. (3)}$$

The factor α_{M-X} is a disparity factor which includes those cases in which r_M and r_X are not comparable.

It is now proposed that N is a constant for a given system e.g. M-F = 62.5 eV, M-Cl = 55 eV, M-Br = 52 eV and M-I = 44 eV. While these values for N are chosen on an ad hoc basis, the amount of data which may be correlated makes this warranted and justified. Thus, for a binary metal chloride equation (3) becomes

$$2m\chi_M^2 + 2n\alpha_{M-Cl}\chi_M\chi_{Cl} = 55\text{ eV} \qquad \text{Eqn. (4)}$$

In the application of this equation the values of χ may be either empirical or those computed using equation (2). Care must be taken that the χ_M values refer to the appropriate valence state. The determination of the valence state of M is arbitrary since the distribution of particular electrons cannot be measured. However, the valence state of M is assumed to be as follows:

(1) The number of n s and p electrons is equal to the metal oxidation number.

(2) The remaining extra-inert-gas-core electrons are all in bonding (n-1) d orbitals.

The use of Slater's rules(7) and equation (2) gives the appropriate value of χ_M.

The theory proposes that staphylonuclear halides result from m-m, in addition to metal-halogen bonding, so that the metal is in a high valence state. The corollary to this is that if χ_M for such a high valence state is too high to permit suitable C.N. leading to staphylonuclear structures, then M will not form any, but will adopt a lower valence state producing halides with ordinary structures but without m-m bonding.

The Prediction of Staphylonuclear Binary Halides

For an assumed valence state the model suggests appropriate C.N. While the theory may suggest too many structures, it eliminates a greater number which may otherwise be regarded as feasible, and in the prediction of possible structures, the theory is subject to testing and rigorous confirmation.

The theory does not predict the structure of binary halides in itself but gives the permissible values of m and n. Plausible structures may be deduced from a consideration of the geometrical possibilities which arise from these values of m and n. Often these C.N. suggest an unambiguous structure or one for which a precedent has been reported.

Equation (3) may now be used for the correlation and prediction of the binary halides of the transition elements. Using the values n = 5 and 6, and plausible metal oxidation states, the appropriate value of X may be substituted in this equation to yield various values of m.

The theory makes the following predictions which are tested experimentally in the remaining chapters in this thesis.

(a) The Isomerism of Molybdenum(II) Chloride

The question of isomerism in transition metal binary halides has received little attention, probably due to the inability of current stereochemical theories to foreshadow this possibility. The recent claim$^{(8)}$ that $ReCl_4$ exists in two different forms reflects the need for a close re-examination of the feasibility of isomerism in transition metal binary halides.

The theory predicts that isomerism should be common among these halides and the plausible alternative forms and the elements likely to display isomerism are quite predictable. In particular, use of equation (4) for molybdenum(II) chloride yields the m:n values of 4:5 and 2:6. The 4:5 combination is satisfied by the well known $(Mo_6Cl_8)Cl_4$ form of molybdenum(II) chloride.

Equation (4) may suggest possible forms for compounds but it can not predict their relative stability. The preparation of the alternative forms may well require sophisticated experimental techniques, widely differing from those which produce the common isomers.

(b) The Nature of Rhenium(IV) Chloride

Our attention was first attracted to this halide by the proposal(9) that it was trimeric containing the Re_3Cl_{12} unit, similar to Re_3Cl_9 and $Re_3Cl_{12}^{3-}$. This proposal is at variance with the theory which will not allow a trimeric formulation when $d_{Re-Re} \approx 2.7$ Å, as required by this structure. The subsequent claim(8) of the preparation of another form of $ReCl_4$ provides a rigorous test of the theory to resolve the problem of the nature of $ReCl_4$ and other tetrahalides.

In the case of $ReCl_4$, equation (4) can be used to compute values of m for corresponding values of n. The Re_3Cl_{12}-type structure is based on a halogen-metal C.N. of 5 i.e. $n = 5$. If Re(IV) employs all available electrons in Re-Cl and Re-Re bonding as assumed(9), then $m = 1.5$ when $n = 5$. Thus the theory predicts that the trimer $(Re_3Cl_9)Cl_3$ is most unlikely where the Re_3 group is strongly bound i.e. $d_{Re-Re} \approx 2.7$ Å.

The structure of the second reported form of $ReCl_4$ was based on octahedral Re-Cl coordination i.e. $n = 6$. It is instructive to consider the case of $n = 6$ not only for $ReCl_4$ but for other transition metal tetrahalides.

If niobium(IV), molybdenum(IV), technetium(IV), tantalum(IV), tungsten(IV) and rhenium(IV) chlorides adopt an MCl_6 octahedron as a basic stereochemical unit, and these elements engage all their available electrons in m-m bonds, the m values will be 0.7, 0, 0, 1.3, 1.5 and 0 respectively. Thus it is predicted that rather long m-m bonds ($d > 2.8$ Å) will be displayed by $NbCl_4$ and WCl_4 since $m < 1$. $TaCl_4$ will display a Ta-Ta distance a little shorter than 2.8 Å since $m > 1$. These three chlorides will be diamagnetic since all available d electrons are assumed bonding.

On the other hand, it is impossible for Mo(IV) and Tc(IV), and Re(IV) to engage all their available d electrons in m-m bonding if $m = 0$ and it is therefore predicted that the chlorides of these oxidation states will display para- or antiferro-magnetism characteristic of essentially non-bonding atomic d electrons. Assuming some or all of the d electrons remain atomic then it is possible for m to adopt values in the range 0.7-0, 0.3-0, and 0.9-0 for Mo(IV), Tc(IV) and Re(IV) respectively. These theoretical predictions agree well with the observations.

Thus for $ReCl_4$ the predicted stereochemical arrangement is $m:n = 0.9:6$. This combination is satisfied by both the W_2Cl_9-type and $NbCl_4$-type structures in which the m-m distance is slightly greater than 2.8 Å. The theory cannot distinguish between the two structures and the possibility of isomerism exists.

The Prediction of Staphylonuclear Ternary Halides

The theory may be extended to include ternary halides i.e. of the type $A_a MX_{(x+a)}$, where A = alkali metal and X = halogen. The equation relating the electronegativities with C.N. now becomes

$$a2\alpha_{AX}n_{AX}\chi_A\chi_X + 2\alpha_{MX}n_{MX}\chi_M\chi_X + 2m_{MM}\chi_M^2 = N_T \qquad \text{Eqn. (5)}$$

It is altogether more difficult to apply the equation to the ternary halides due to the presence of the alkali metal in the lattice. This introduces the terms N_T, n_{AX} and χ_A for which the values are not known with certainty. These values are chosen on an ad hoc basis but as yet insufficient systems have been reported to confirm whether the values chosen are widely applicable. Using these values the equation may be solved for n_{MX} for the compound $[A_a MX_{(x+a)}]_S$ where S specifies n_{MM}. Combinations of (x+a), S and n_{MX}(calc.) are identified with known or feasible structures.

Tables 1.1 and 1.2 list the predicted staphylonuclear ternary halides of molybdenum(II) and rhenium(III), together with those which have already been reported or which have been prepared in this study.

Two very important predictions are noted:

(i) Contrary to other predictions$^{(10)}$, trimeric staphylonuclear ternary halides of molybdenum(II) are a quite feasible alternative form to the usual hexamers found for molybdenum(II).

(ii) Ligand deficient compounds are expected. While the theory

Table 1.1. Predicted Staphylonuclear Ternary Halides of Molybdenum(II)

	Cl		Br		I
	Pred.	Found	Pred.	Found	
K	$K_7Mo_3Cl_{13}$				None predicted and none found for any alkali metals
	$K_6Mo_3Cl_{12}$	$K_6Mo_3Cl_{12}$			
			$K_5Mo_3Br_{11}$		
Rb	$Rb_7Mo_3Cl_{13}$	$Rb_7Mo_3Cl_{13}\cdot H_2O$			
			$Rb_5Mo_3Br_{11}$	$Rb_5Mo_3Br_{11}$	
Cs	None	$Cs_7Mo_3Cl_{13}\cdot H_2O$	$Cs_7Mo_3Br_{13}$	$Cs_7Mo_3Br_{13}\cdot H_2O$	

Table 1.2. Predicted Staphylonuclear Ternary Halides of Rhenium(III)

Theoretical Prediction	Reported to date
$K_3Re_3Cl_{12}$ (a)	
$Rb_3Re_3Cl_{12}$	$Rb_3Re_3Cl_{12}$
	$Cs_3Re_3Cl_{12}$
$K_3Re_3Br_{12}$	
$Rb_3Re_3Br_{12}$	
$Cs_3Re_3Br_{12}$	$Cs_3Re_3Br_{12}$
$K_2Re_3Br_{11}$	
$Rb_2Re_3Br_{11}$	$Rb_2Re_3Br_{11}$
	$Cs_2Re_3Br_{11}$
	$CsRe_3Br_{10}$ (b)
$CsRe_3I_{10}$	

(a) No Re_3Cl_{11} compounds predicted.

(b) Brief reports with crystallographic parameters subsequently attributed to $Cs_2Re_3Br_{11}$.

does not predict ligand deficiencies with absolute accuracy, it does predict that ligand deficiency is more likely with bromo- and iodo-compounds than with chloro-compounds.

The preparation of the compounds described in Chapter 2 provides verification of both the above predictions of this theory of stereochemistry.

Objectives of Research and Summary

Apart from their own intrinsic interest and the contribution which they make to the understanding of the chemistry of the relatively neglected second and third row transition elements, the compounds studied have been specifically chosen. Each compound, either by its actual preparation or by its reactions, provides a critical experimental test of some particular aspect of the theory.

Chapter 2 describes the preparation of a number of staphylonuclear halogenotrimolybdates(II) whose existence is predicted by the theory. Plausible structures are assigned to these compounds in accordance with those suggested by the theory. This chapter also shows how the theory is able to cope satisfactorily with the problem of ligand deficiencies.

A problem which is just beginning to receive the attention of inorganic chemists is that of isomerism in binary transition metal halides. The nature of $ReCl_4$ has been examined in view of the recent claim that two different forms of this halide exist. As a test of the predictions of the theory, the validity of these two forms has been studied. This work is described in Chapter 3.

Chapter 4 further develops the question of isomerism in transition metal binary halides. In this instance the theory predicts that molybdenum(II) chloride should exist in an alternate form to that of the well known $(Mo_6Cl_8)Cl_4$ form and Chapter 4 describes the search for this alternate form.

The remaining chapters of this thesis describe a number of experiments associated with these major topics. A thorough study of the decomposition of molybdenum(II) acetate in hydrochloric acid and the search for other staphylonuclear halogenomolybdates in other oxidation states has been undertaken. A number of halogenomolybdates(2.5) have been prepared and the theory has been used to suggest plausible structures for them.

It has been reported$^{(8)}$ that the preparation of β-$ReCl_4$ has not been successfully repeated and an attempt has been made to prepare this halide using chlorination with CCl_4 in a steel bomb under high temperature and pressure.

Terminology

Throughout this thesis, no attempt will be made to use the systematic names of these compounds. This is done only in the interests of brevity and no ambiguity arises through the terminology used. Thus the ternary molybdenum(II) halides prepared in this study have been referred to as halogenotrimolybdates(II) to distinguish them from the hexameric molybdenum(II) compounds. All other compounds have been named as halogenomolybdates with the oxidation number of the molybdenum being placed in brackets.

The systematic names for some of the compounds prepared in this study are:

$K_6Mo_3Cl_{12}$	Potassium octachloro-μ_3-chlorotri-$\mu_2$chlorotrimolybdate(II).
$(NH_4)_7Mo_3Cl_{13}.H_2O$	Ammonium nonachloro-μ_3-chlorotri-μ_2-chlorotrimolybdate(II) monohydrate.
$Rb_5Mo_3Br_{11}$	Rubidium heptabromo-μ_3-bromotri-μ_2-bromotrimolybdate(II).
$Cs_3Mo_2Cl_8$	Caesium pentachlorotri-μ_3-chlorodimolybdate(2.5).

All other abbreviations used in this thesis are accepted common usage, e.g. En = ethylenediamine.

Chapter 2. The Chemistry of Staphylonuclear Halogenotrimolybdates(II)

Introduction

Molybdenum(II) acetate is soluble in 12 M HCl and 9 M HBr producing bright violet coloured solutions from which may be precipitated a number of compounds containing molybdenum in the oxidation state 2.0.

A large variety of precipitating cations has been used but the compounds produced by the ammonium and alkali metal cations are of particular interest and relevance. This chapter is concerned with these particular compounds and other interesting halogenotrimolybdates(II) are dealt with in Chapter 5.

Results and Discussion

1. Preparation

These compounds can only be isolated by precipitation and drying, and since they are easily solvolysed and oxidised in the moist state, the criterion of purity has been the reproducible composition of numerous samples. Moreover, since it is suspected that more than one compound may be precipitated by the added halide AX (where A is an alkali metal, ammonium etc.) e.g. $A_7Mo_3X_{13}$, $A_6Mo_3X_{12}$ and $A_5Mo_3X_{11}$, it is essential to vary the AX:Mo$(CH_3COO)_2$ ratio of the preparative mixture to detect such mixed products. The analytical and preparative data for the ammonium and alkali halogenotrimolybdates(II) are given in Tables 2.1-2.5.

Table 2.1. Analytical and Preparative Data for $K_6Mo_3Cl_{12}$

Mo %	Cl %	K %	Cl/Mo at. ratio	Mo oxidn. Number	Yield %	Method of Drying
30.1	44.7	25.5	4.0	2.0	78	Air, 20°C
29.7	45.5	-	4.1	2.0	70	Vac., Room T.
29.7	45.6	-	4.1	2.0	81	"
29.5	45.4	-	4.1	2.0	74	"
30.4[a]	45.6	-	4.0	2.0	48	"
Theory						
30.4	44.8	24.8	4.0	2.0	-	-

[a] Prepared from 5:1 excess of KCl.

Yield smaller due to large volume of HCl required.

Table 2.2. The Analytical and Preparative Data for $(NH_4)_7Mo_3Cl_{13}.H_2O$

A/Mo Prep. Ratio	Mo %	Cl %	Cl/Mo at. ratio	Mo oxidn. Number	N %	H %	Yield %	Method of Drying
5	30.2	50.9	4.5	2.0	10.8	3.7	95	Vac., Room T
5	31.5	51.7	4.4	2.0	-	-	83	Vac., 115°C, 5 hours
5	31.5	50.0	4.3	2.0	11.0	3.6	83	Air
5	31.6	51.4	4.3	2.1	11.0	3.6	88	Vac., 115°C, 2 hours
5	31.7	51.3	4.4	2.1	-	-	~100	Vac., Room T
5	32.3	51.4	4.3	2.1	-	-	~100	"
5	31.8	51.9	4.4	2.0	-	-	~100	"
5	32.0	49.5	4.2	2.1	10.8	3.5	93	"
8	31.5	51.6	4.4	2.0	-	-	86	"
10	31.9	51.5	4.3	2.0	-	-	94	"
16	31.6	50.5	4.3	2.0	-	-	88	"
Theory								
-	32.2	51.6	4.3	2.0	11.0	3.4	-	-

Table 2.3. Analytical Data for Rubidium Chloromolybdate(II)

Proposed Formula	A/Mo prep. ratio	Yield %	A %	Mo %	Cl %	Cl/Mo at. ratio	Mo oxidn. Number
$Rb_7Mo_3Cl_{13}\cdot H_2O$	2	76	36.0	24.2	35.6	4.0	2.0
	2	93	37.4	24.5	35.2	3.9	2.0
	2	86	35.4	24.9	35.4	3.95	2.1
	4	76	36.1	24.1	34.7	3.9	2.2
	8	93	-	21.7	33.1	4.1	2.0
	8	100	39.5	21.2	33.2	4.2	2.0
	16	99	44.6	20.0	32.7	4.4	2.0
	16	100	42.2	21.5	33.8	4.25	2.0
Theory							
	-	-	43.8	21.1	33.8	4.33	2.0

Table 2.4. Analytical Data for Caesium Chloromolybdate(II)

Proposed Formula	A/Mo prep. ratio	Yield %	A %	Mo %	Cl %	Cl/Mo at. ratio	Mo oxidn. Number
$Cs_7Mo_3Cl_{13}.H_2O$	2	78	45.8	21.5	30.3	3.8	2.0
	4	69	50.2	18.3	28.5	4.2	2.1
	5	84	51.3	18.7	28.0	4.0	2.1
	5	96	49.5	18.9	27.9	4.05	2.1
	8	98	52.0	18.3	27.7	4.1	2.2
	16	92	55.5	17.0	26.9	4.3	2.2
Theory	-	-	54.8	17.0	27.4	4.33	2.0

Table 2.5. Analytical Data for Rubidium and Caesium Bromomolybdates(II)

Proposed Formula	A/Mo prep. ratio	Yield %	A %	Mo %	Br %	C %	H %	Br/Mo[a] at. ratio	Mo oxidn. Number
	2	51	27.8	18.1	50.7	0.4	0.7	3.55	2.2
$Rb_5Mo_3Br_{11}$	2	55	25.3	18.1	50.6	0.7	0.6	3.6	2.05
	2	49	21.9	19.4	52.1	1.2	0.7	3.7	2.3
	2	58	22.2	18.5	51.7	0.9	0.6	3.7	2.1
<u>Theory</u>									
	-	-	26.8	18.1	55.1	0	0	3.67	2.0
	5	84	33.3	15.8	45.8	1.4	0.8	4.2	2.1
	5	80	35.5	15.7	45.2	1.6	1.0	4.4	2.2
$Cs_7Mo_3Br_{13}\cdot H_2O$	10	98	42.3	13.6	42.2	1.2	0.8	4.55	2.2
<u>Theory</u>									
	-	-	40.9	12.7	45.6	0	0.1	4.33	2.0

[a] Br/Mo at. ratio corrected for the presence of $Mo(CH_3COO)_2$

It is significant to note that, in agreement with the prediction of the theory, no iodotrimolybdates(II) have been prepared. In addition, lithium and sodium halides produce no precipitates from $MoAc_2$/hydrohalic acid solutions.

2. Formulation

The six halogenotrimolybdates(II) found in this study have been formulated as:- $K_6Mo_3Cl_{12}$, $A_7Mo_3Cl_{13}.H_2O$ (A = NH_4, Cs, Rb), $Cs_7Mo_3Br_{13}.H_2O$ and $Rb_5Mo_3Br_{11}$.

The analytical figures show that samples of the ammonium compound prepared from a wide range of $NH_4Cl:Mo(CH_3COO)_2$ concentrations gave similar analyses and it is therefore not a mixture. Such a variation in the preparative mixtures cannot be accomplished with the potassium compound, since KCl has a restricted solubility in 12 M HCl. However, this compound has a unique powder photograph relative to the other compounds produced and is unlikely to be a mixture of compounds e.g. $K_7Mo_3Cl_{13}$ and $K_5Mo_3Cl_{11}$.

The variation of the $AX:Mo(CH_3COO)_2$ ratios in the preparations of caesium and rubidium chlorotrimolybdates gave products whose composition varied in a systematic manner, accompanied by changes in powder photographs and small, but significant changes in colour. The analytical figures of the products obtained from the highest

A:Mo ratio are consistent with the $A_7Mo_3Cl_{13}$ formulation. This assignment is confirmed by these samples giving powder photographs identical with that obtained for $(NH_4)_7Mo_3Cl_{13}.H_2O$.

The formulation of ammonium, caesium and rubidium chlorotrimolybdates(II) as monohydrates is tentative. The analytical data for the ammonium compound best fits a monohydrate formulation. The rubidium and caesium compounds show infrared absorption bands ascribable to water and as all three are isomorphous it is concluded that they are monohydrates.

The rubidium and caesium bromotrimolybdates are found to contain small amounts of carbon. This is believed to arise through the insolubility of the bromotrimolybdates in HBr which causes rapid precipitation on, and occlusion of, unchanged $Mo(CH_3COO)_2$. Unfortunately, these small amounts of carbon reflect large errors in the percentage of molybdenum attributed to the bromotrimolybdate by reason of the high atomic weight of molybdenum. The Br/Mo ratios given in Table 2.5 have been corrected, assuming that the observed amounts of carbon arise from unchanged acetate. These ratios are close to 4.33 and 3.67 for the caesium and rubidium compounds, the proposed formulations thus being $Cs_7Mo_3Br_{13}.H_2O$ and $Rb_5Mo_3Br_{11}$.

Further confirmation of these formulations is gained from the powder photographs which show that the caesium compound is isomorphous with the other $A_7Mo_3Cl_{13}.H_2O$ compounds, while the rubidium compound has a unique powder photograph relative to all other compounds found in this investigation. This latter compound does not show any infrared absorption bands attributable to water.

The formulation of these compounds as trimeric has been made on the following grounds. The atomic ratios of X:Mo of 4.33 and 3.67 require that the minimal degree of polymerisation is three to produce integral atomic ratios i.e. 13/3 and 11/3 respectively. All other known halogenomolybdenum(II) compounds are hexameric, possessing the (Mo_6Cl_8) group. However, it is difficult to visualise, on geometrical grounds, how an octahedral arrangement of molybdenum atoms could accommodate 26 or 22 surrounding halogen atoms before repulsion between neighbouring halogen atoms becomes prohibitive.

In the potassium compound, with its Cl:Mo ratio of 4:1, the further possibilities of dimeric or tetrameric formulations exist. Another study(11) in these laboratories has identified the equilibrium

$$Mo_3Cl_{12}^{6-} + Cl' \rightleftarrows Mo_3Cl_{13}^{7-}$$

in solution. The close spectral similarities between the ammonium and potassium compounds and the absence of any significant differences between them, leads to the conclusion that the potassium compound is trimeric also.

Unfortunately, the halogenotrimolybdates(II) are either insoluble in, or decomposed by, all common polar and non-polar solvents, so that molecular weight and molar conductance studies cannot be undertaken. In the absence of these measurements, the ultimate resolution of the problem must come from crystal structure analysis. However, these compounds are prepared by precipitation methods and all attempts to grow larger crystals required for a crystal structure determination have been unsuccessful.

The criteria of m-m bonding are that the intermetallic distance is comparable to the distance between the metal atoms in the elemental state and that the compound must be diamagnetic or at least show reduced paramagnetism. The combined consideration of these two criteria is the only conclusive means of identifying m-m bonds. As the crystal structure data is unavailable, the claim that these compounds are m-m bonded rests on their diamagnetism.

The evidence strongly suggests that these halogenomolybdates(II) are polymeric and m-m bonded. The highly desired crystal structure determinations will provide the ultimate verification, or otherwise, of these assertions.

3. Proposed Structures

It is now possible to suggest structures for these halogenotrimolybdates. Reference to all previously reported staphylonuclear compounds shows that two structural principles appear to be generally obeyed.

(1) The halogen-metal bonding is based on octahedral coordination, although it is frequently observed that one or two halogen-metal bonds are absent, generating square pyramidal or square planar arrangements.

(2) The metal clusters are trigonal, tetrahedral or octahedral for trimeric, tetrameric and hexameric compounds respectively.

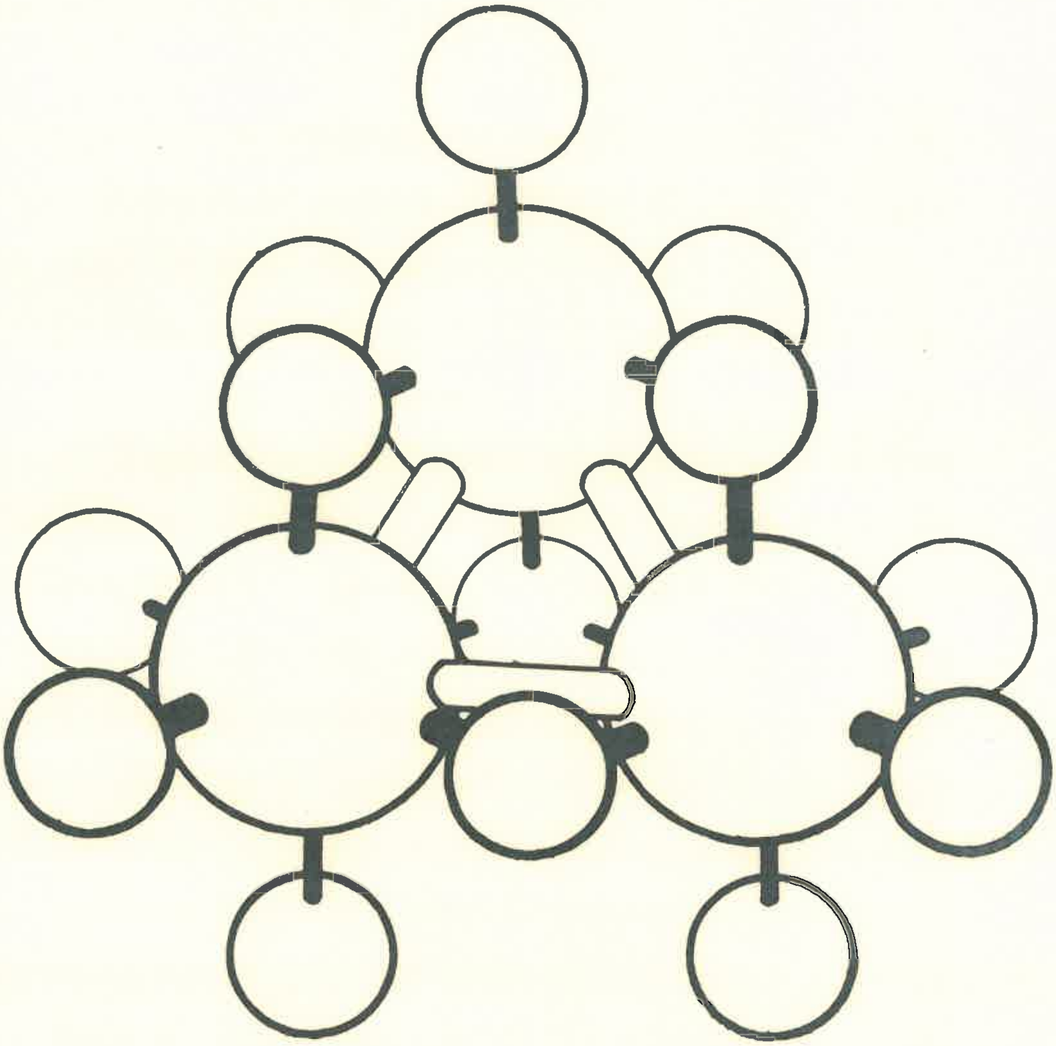
In the course of this investigation and another(12) in these laboratories, it has been found that the Mo_3X_{13} group recurs quite frequently and it is proposed that this is the basic unit.

An Mo_3X_{13} unit may be derived from the "close packing" of halogen atoms into layers (seven atoms in one layer and six in the other) which mutually "close pack" generating three octahedral locations suitable for occupation by the molybdenum atoms. This is similar to the arrangement found in $Zn_2Mo_3O_8$(13), Nb_3X_8 (X = Cl, Br, I)(14).

The structure proposed for this Mo_3X_{13} group is shown in Fig. 1.

This proposed structure fulfils the requirements of the two structural principles stated above. The structure is based on octahedral coordination of halogen around the metal atoms and consists of nine terminal halogen atoms, three μ_2 bridging halogen atoms and

The proposed structure of the Mo_3Cl_{13} group.



Large circles – Mo
Small circles – Halogen

FIG. 1.

one μ_3 bridging halogen atom.

The structures of the other halogenotrimolybdate(II) compounds may now be regarded as ligand deficient derivatives of the Mo_3X_{13} structure. Ligand absences are well established in the halogenorhenate(III) compounds and the types Re_3X_{12}, Re_3X_{11} and Re_3X_{10} are now known(15,16).

Spectroscopic crystallographic and radio-chemical exchange studies(17), reported by other workers in these laboratories, provide strong evidence that the trimeric formulation and the proposed structure are correct. The interaction of ammonium chloromolybdate(II) with acetic acid, may also be interpreted in terms of trimers.

4. The Interaction of $(NH_4)_7Mo_3Cl_{13}.H_2O$ with Acetic Acid

Cotton et al. have shown(18) the high yield interconvertibility of these compounds in the reaction

$$Re_2Cl_8^{2-} \underset{HCl}{\overset{RCOOH}{\rightleftarrows}} [Re(RCOO)_2Cl_2]$$

e.g. The reactions proceeds to the right in refluxing acetic acid to give an 85% yield in 20 minutes. It is suggested that this rapid interconvertibility is facilitated by the similarity in structure and by the rhenium being in oxidation state III in both compounds.

A similar interconversion reaction has now been found in the molybdenum(II) system:

$$Mo_2(CH_3COO)_4 \underset{CH_3COOH}{\overset{aq.\ HCl}{\rightleftarrows}} [Mo_3Cl_{13}]^{7-}$$

The forward reaction occurs in high yield (>90%) and in solution, since the acetate is entirely soluble in hydrochloric acid and the chloromolybdate(II) species must be precipitated by particular reagents. The conversion of dimeric molybdenum(II) acetate into a trimeric halogenomolybdate may well occur in solution by means of an intermediate labile monomer e.g. $[Mo(CH_3COO)_2Cl_2]^{2-}$.

The molybdenum(II) system now differs significantly from the rhenium(III) system, in that the yield of product in the reverse reaction is about 66%.

$(NH_4)_7Mo_3Cl_{13}.H_2O$ is insoluble in hot acetic acid but reacts rapidly with it and the solid changes from violet to pink. This product contains only molybdenum(II) species but is a mixture consisting of a water-soluble and a water-insoluble species. This latter species was identified by a powder photograph and analysis to be molybdenum(II) acetate.

Found: Mo = 45.5%, C = 22.1%, H = 3.1%, ox. no. = 2.0

Calc. for: Mo = 44.8%, C = 22.5%, H = 2.8%, ox. no. = 2.0

$Mo_4(CH_3COO)_2$

The yields of this acetate after 15, 30, 60 and 120 minutes refluxing of the chloromolybdate(II) in acetic acid were 60, 63, 66 and 73% respectively.

It is possible to interpret these observations by the postulated trimeric formulation of the chloromolybdate(II), and the known dimeric nature of the acetate$^{(19)}$ by proposing an Mo_3 ring cleaving reaction:

$$[Mo_3Cl_{13}]^{7-} + CH_3COOH \rightarrow Mo_2(CH_3COO)_4 + [Mo^{II}?]$$

The residual and unknown molybdenum(II) product may itself yield molybdenum(II) acetate by a subsequent and slower reaction.

The identity of the water-soluble species is not known since it can not be separated from the acetate without decomposition or hydrolysis. A partial analysis, obtained by subtracting the contribution of molybdenum(II) acetate from the total analysis of the reflux residue, yielded the following result:

Found: Mo = 24.7%, Cl = 43.5%, Cl:Mo = 4.76:1, ox. no. = 2.1

5. Properties

All of the $A_7Mo_3X_{13}.H_2O$ compounds are bright violet, $K_6Mo_3Cl_{12}$ is bright red and $Rb_5Mo_3Br_{11}$ is red-brown in colour. All are rapidly hydrolysed by water or base solutions, but may be stored conveniently in desiccators for a considerable time without serious deterioration. The compounds decompose in hydrohalic acid, in the absence of oxygen, at rates which depend on the hydrogen and halide ion concentration.

The magnetic susceptibilities were measured at room temperature and were found to be small positive or negative values which yielded μ_{eff} values of 1.0-1.9 B.M. per trimer unit. This is consistent with extensive Mo-Mo bonding as implied by the Mo_3X_{13} staphylonuclear structure. It is possible that this μ_{eff} refers not to a discrete unpaired electron but to a feeble paramagnetism from another source.

The solubility of these compounds was tested using a wide range of polar and non-polar solvents. They are generally insoluble in, or decomposed by these solvents.

6. Spectra

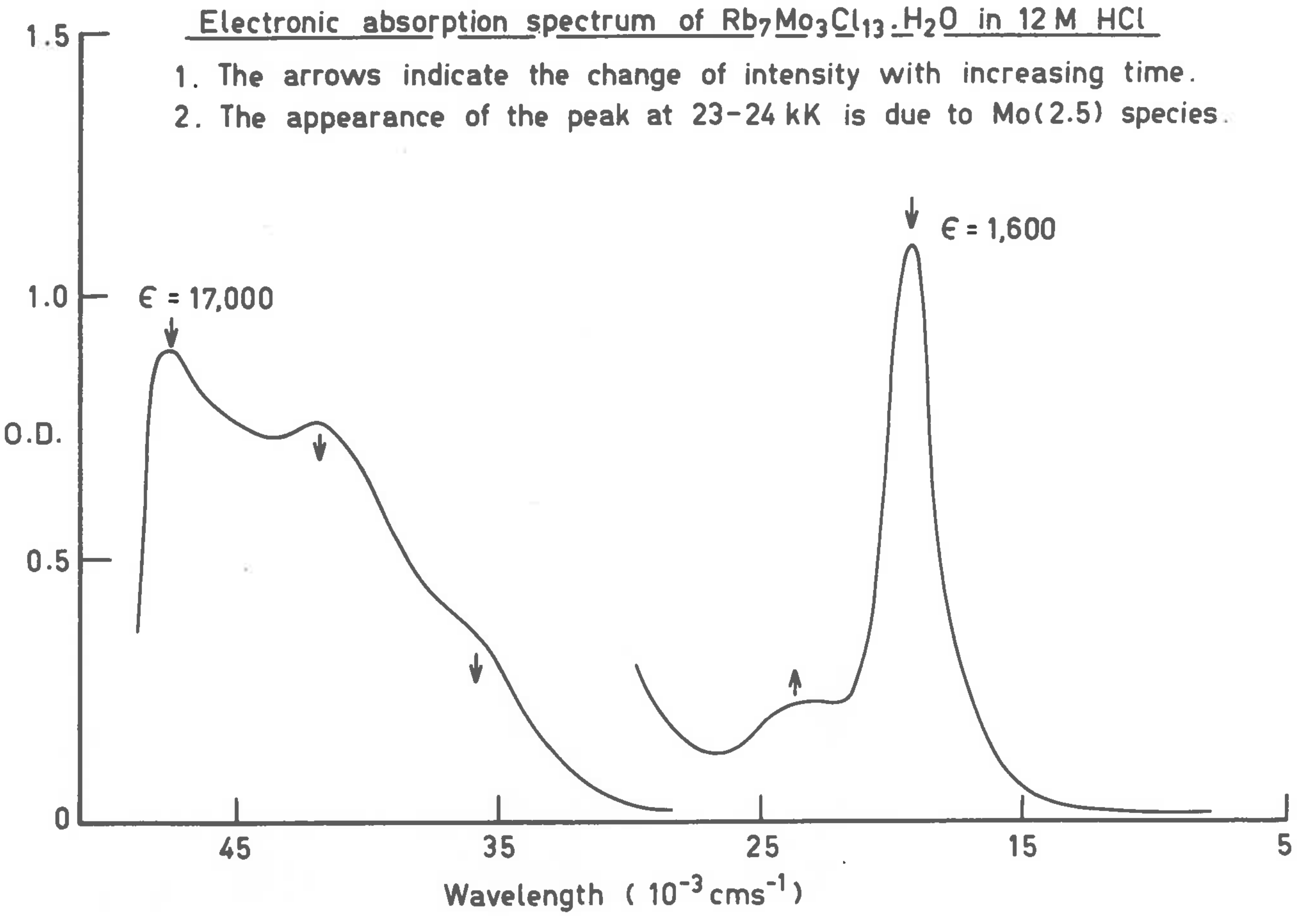
A spectroscopic investigation of $Rb_7Mo_3Cl_{13}.H_2O$ prepared from A/M ratios of 2 and 16 was undertaken to ascertain any significant difference which may throw light on the nature of these samples. The results are tabulated in Table 2.6, together with the spectrum of $Cs_7Mo_3Cl_{13}.H_2O$ for comparison.

The spectra are similar in all cases and are similar to the spectra of other halogenotrimolybdates(II) recorded in these laboratories$^{(11)}$.

Fig. 2, showing the spectrum of $Rb_7Mo_3Cl_{13}.H_2O$ (from A/M = 16) in 12 M HCl, may be regarded as representative of the spectra of

Table 2.6. Electronic Absorption Spectra of $Rb_7Mo_3Cl_{13}.H_2O$ and $Cs_7Mo_3Cl_{13}.H_2O$ in Hydrochloric Acid

Compound	A/M Prepn. Ratio	Molarity of HCl					
		1M		4M		8M	
		λ	ε	λ	ε	λ	ε
$Rb_7Mo_3Cl_{13}.H_2O$	2	19.2	1040	19.4	1600	19.25	1670
		~41.0	s	~41.0	s	41.5	19400
		48.3	8700	47.0	12000	47.6	18000
	16	19.25	1130	19.4	1450	19.4	1600
		~41.0	s	~41.0	s	42.0	17300
		47.85	10300	47.0	12900	48.2	17100
$Cs_7Mo_3Cl_{13}.H_2O$	16	-		-		19.2	2300
						41.5	20700
						47.75	20000



Electronic absorption spectrum of $Rb_7Mo_3Cl_{13}.H_2O$ in 12 M HCl

1. The arrows indicate the change of intensity with increasing time.
2. The appearance of the peak at 23-24 kK is due to Mo(2.5) species.

FIG. 2.

halogenotrimolybdates(II).

The peak at ~41 KK decreases in intensity very rapidly and disappears within 15 minutes, while a peak at 23-24 KK slowly appears, indicating the formation of molybdenum(2.5) species (see Chapter 6).

Concluding Remarks

The preparation of these halogenotrimolybdates(II) is in accord with the predictions of the theory outlined in Chapter 1. They have been formulated as trimers and are believed to contain the Mo_3X_{13} unit or to be ligand deficient derivatives of it. Some of the properties of these compounds have been investigated but their instability in solution or general insolubility in non-aqueous solvents has proved a severe restriction to a more extensive study of their chemistry.

Experimental

(a) Preparation of Halogenomolybdates(II)

Finely ground molybdenum(II) acetate(20) was shaken with 12 M HCl or 9 M HBr containing the predetermined amount of the appropriate cation necessary to give the required molar ratios of reactants, for 30 minutes at room temperature. The preparations were also attempted with 7 M hydriodic acid. The resulting precipitate was filtered, washed successively with concentrated hydrohalic acid, ethanol and ether and dried in vacuo at room temperature. In most cases the yields were > 80%.

(b) Analytical Methods

(i) Oxidation Number

A known amount of compound was dissolved in a slight excess of acidified ferric ammonium sulphate solution and titrated with standard permanganate. Silver carbonate was added before the titration to remove the bromide ions. Blank titrations were performed and the presence of chloride was shown not to interfere.

(ii) Halogens, Molybdenum and Alkali Metals

For the determination of these elements the compounds must be brought into solution in a suitable form. This was achieved by decomposing the compounds with alkaline peroxide and simmering the clear solution to remove excess peroxide. The analyses were performed by the conventional methods:

Molybdenum - gravimetrically as lead molybdate(21)

Halogen - potentiometrically with silver nitrate solution

Alkali metals - quantitative flame photometry using a Unicam SP900A flame spectrophotometer.

(iii) Carbon, Hydrogen and Nitrogen

These were determined by microanalysis by the Australian

Microanalytical Service, Melbourne.

(c) Magnetic Susceptibilities

These were determined by a conventional Gouy balance employing a permanent balance. The small magnetic forces observed render the susceptibility values approximate.

(d) Powder Photographs

Powder photographs were obtained by CuK_{α} radiation (Ni filter) with a Philips camera (PW1024, 114.83 mm. radius). The results are given in Table 2.7.

(e) Infra Red Spectra

A Perkin-Elmer Model 21 double beam I.R. spectrophotometer was used to obtain these spectra.

(f) Ultra Violet and Visible Spectra

These spectra were recorded on a Unicam SP700 Recording Spectrophotometer, using degassed hydrochloric acid and a pair of matched 1 cm. silica cells. The spectra were repeated after known intervals of time and the values of λ and ϵ were extrapolated to "zero" time.

Table 2.7. Data from X-Ray Powder Photographs, Lattice Spacings (Å)

$K_6Mo_3Cl_{12}$		$(NH_4)_7Mo_3Cl_{13}\cdot H_2O$	
7.25	v.s.	8.34	v.s.
6.15	s	6.96	v.s.
3.92	m	5.90	v.s.
3.20	m	5.22	v.s.
3.08	m	4.65	m
2.64	v.s.	4.08	w
2.53	v.s.	3.90	w
1.99	m	3.28	w
1.97	m	2.95	s
1.79	s	2.78	s
1.48	m	2.73	m
		2.62	v.s.
		2.06	m

Chapter 3. The Question of Isomerism in Rhenium(IV) Chloride

Introduction

A particularly good test of the theory outlined in Chapter 1 is the potential isomers that a transition element halide may display, since these are quite predictable, but as yet not widely reported. Of particular interest is the case of a halide in forms displaying quite different halogen:metal coordination number, since none has been reported until recently.

Two separate studies indicated that rhenium(IV) chloride adopted, firstly, a proposed trigonal cluster structure $(Re_3Cl_9)Cl_3$(9), similar to that established for $Cs_3Re_3Cl_{12}$, and secondly a dimeric form established by X-ray crystallography(22) and containing Re_2Cl_9 groups, similar to the chloro groups found in $K_3W_2Cl_9$. These two materials are referred to as the α and β forms throughout this chapter. α- and β-$ReCl_4$ are obtained respectively from refluxing thionyl chloride and hydrated rhenium dioxide and from the pyrolytic disproportionation of rhenium pentachloride. The reported Cl:Re and Re:Re coordination numbers are 5 and 2, and 6 and 1 respectively.

The proposed structures for α- and β-$ReCl_4$ are significant in being the only example of a transition element halide appearing in isomers displaying different halogen:metal coordination number. Despite the interest such isomerism arouses, the theory does not allow that the trimeric structure for $ReCl_4$, particularly containing a strongly bonding Re_3 group, is at all likely, and moreover little evidence has been put forward$^{(9)}$ to support it.

α-$ReCl_4$ is reported$^{(23)}$ to be amorphous to X-rays, so that direct refutation or confirmation of structure seems remote, and β-$ReCl_4$ appears not to have been prepared in the laboratory since its unexpected delivery from a commercial source.$^{(8)}$ The evidence supporting the trimeric structure of α-$ReCl_4$ has been re-examined, and this chapter reports an extensive series of attempted preparations of $ReCl_4$ and the light they throw on the isomerism in this chloride.

The preparative, chemical, and X-ray powder diffraction studies clearly support the more plausible $NbCl_4$-like structure for α-$ReCl_4$. Accordingly α- and β-$ReCl_4$ are quite closely related stereochemically in that both consist of pairs of $ReCl_4$ octahedra joined by a shared edge or face respectively.

Results and Discussion

1. The Products of Hydrated Rhenium Dioxide in Refluxing Thionyl Chloride

The $SOCl_2/ReO_2.2H_2O$ reaction has been carried out a total of 24 times under a variety of conditions. The results are given in Table 3.1.

Consistantly, very dark solid separated from the dark refluxing

Table 3.1. The Composition and Properties of the Product from Refluxing $SOCl_2$ and $ReO_2.nH_2O$

Preparation No.	Reflux Time (hrs)	Yield %	% Composition					Cl:Re	% Chloride Release		Solution Colour[b]			Remarks
			Cl[a]	Re	C	H	S		0.1 M NaOH	0.1 M HNO_3	6 M HCl	MeCN	Acetone	
1	6	50	28.7								r-v	r-b	g-b	$SOCl_2$ used direct from bottle
2	6	-	21.9								v	v	g	$SOCl_2$ used as recovered
3	24	31	17.2	73.8				1.22	17.0		v	r-v	g	anhydrous ReO_2 used
4	6	35	34.9	46.9				3.9			v	r-b	r-b	sealed tube 120°
5	48	-	34.1	44.5				4.0	(33.1)[c]		v	r-v	g-b	"
6	24	63	36.6	48.7	0.64	0.51	0.72	4.0	35.1	8.9	r-b	g	g-b	N_2 atmosphere
7	50	95	38.9	41.7	0.79	0.85	0	4.85	35.5	12.4	-	-	-	"
8	96	-	36.1	48.2				4.0	(30.9)[c]	17.6	r-b	r-b	g	"
9	6	50	29.3								r-b	r-b	g-b	
10	6	50	31.0								r-b	r-b	g-b	
11	96	59	27.6	62.6				2.3	27.8	23.5	v	r-b	g-b	
12	192	67	31.7	56.3				3.0	32.6		r-b	r-b	g-b	
13	384	84	31.5	55.8				3.0	32.4		g	g-b	g-b	
14	0.5	<<5	30.5								-	-	-	ratio $SOCl_2/ReO_2.nH_2O$ (vol./wt.) = 20
15	0.5	8	37.2		1.73	0.57	3.48		35.5		v	-	-	10
16	1	<5	35.1								-	-	-	20
17	1	9	35.6	49.6	1.68	0.44	2.89	3.8	35.5		v	-	-	10
18	2	<5	35.1								-	-	-	20
19	2	9	37.0	48.0	1.84	0.55	2.80	4.0	34.8		v	r-b	g	10
20	4	23	30.4	52.3	1.35	0.84	3.12	3.0	32.8		v	g-b	g	5
21	4	8	38.8	48.3	1.47	-	2.52	4.2	38.1		v	g-b	g	10
22	4	<5									-	-	-	100
23	6	20	36.2	47.5				4.0	39.3		-	-	-	20
24	8	11	37.8	47.4	2.65	0.93	2.71	4.2	35.8		v	g-b	g	10
25	8	<5									-	-	-	100
26	48	24	32.3	44.6				3.8	31.6		v	-	-	20
27	72	52	41.4	57.0				3.8	41.5		v	v[d]	g	20
28	72	49	42.8	56.0				4.0	47.5		v	v[d]	g	20

a Obtained by NaOH fusion; b v = violet, g = green, r-v = red-violet, r-b = red-brown, g-b = green-brown; c Hydrolysis with water; d Slowly soluble solution, and a majority of samples possessed a Cl:Re ratio distinctly close to 4.0 as required by $ReCl_4$. Rather notable exceptions are samples 12 and 13 which were obtained after very long reflux times and possessed a ratio of 3.0. Moreover, a number of samples at least superficially resembled the original α-$ReCl_4$ (9,23), since they are soluble in methyl cyanide and acetone giving red-brown solutions. Similar colours are found after solution in 6 M hydrochloric acid. In dilute alkali, most of the samples dissolved to give the persistent and significant red-brown colour described for α-$ReCl_4$. These colours are important since they contrast with the violet or green solutions generated by β-$ReCl_4$ in hydrochloric acid or in acetone respectively.

However, almost all these samples contained additional material to Re and Cl since their total content was usually only 85%. Moreover the samples left appreciable black residue after solution in hydrochloric acid or acetone, and selected samples contained appreciable quantities of sulphur, hydrogen and carbon (viz. Table 3.1).

It is now apparent that the reported preparation(23) of α-$ReCl_4$ is unique in the claim of forming a pure transition metal halide *in situ*, without the need of further purification, by the action of thionyl chloride on an oxide or hydroxide e.g. Bagnall and Brown(24) find that niobium, tantalum and protactinium hydroxides can react in the cold with thionyl chloride and they warn against overheating of the thionyl chloride and the impure products that would result. These workers, nonetheless purified their chlorides by sublimation. Uhlemann and Fischbach(25) find 7% sulphate in the trichloride resulting from heated chromium trioxide and thionyl chloride.

The general deficiencies of the refluxing thionyl chloride method of converting hydroxides to chlorides has been confirmed by investigating the products from seven first transition element hydroxides. The results are given in Table 3.2.

The reactions were carried out over 2, 6 and 24 hours and in nearly all cases the product was of the same composition for each hydroxide indicating complete reaction. The near to integral chlorine: metal ratio supports that reaction was complete and that the actual composition did not result from occluded hydroxide.

The results provide two surprises. Hydroxychlorides result in some cases and most samples possessed infra red absorption bands at 3600-3340 and 1645-1595 $cm.^{-1}$ indicating residual aquo-groups. Of greater relevance is the observation that the total metal, chlorine and hydroxide content is well short of 100%. It is concluded therefore that the refluxing thionyl chloride method is not at all reliable for the preparation of pure transition metal chlorides _in situ_.

Although one is predisposed to accept that thionyl chloride must remove all water, it is not certain that this is actually true.

Table 3.2. The Products of Refluxing Thionyl Chloride on First Transition Element Hydroxides

Hydroxide	Reflux time (hrs)	% Composition Cl	Metal	(Cl+M)	Cl:M
$Ni(OH)_2.nH_2O$	2	46.3	36.9	83.2	2.1
	6	44.9	35.7	80.6	2.1
	24	45.4	38.4	83.8	2.0
$Cu(OH)_2.nH_2O$	2	41.6	35.3	76.9	2.1
	6	42.7	41.7	84.4	1.8
	24	44.2	32.5	76.7	2.4
$Cr(OH)_3.nH_2O$	2	37.5	25.8		2.1
	6	39.6	26.8		2.2
	24	38.9	25.2		2.3
$Co(OH)_3.nH_2O$	2	30.3	45.5		1.1
	6	30.2	47.2		1.1
	24	31.2	45.5		1.1
$Mn(OH)_2.nH_2O$	2	25.2	41.7		0.9
	6	25.8	41.3		1.0
	24	28.4	46.8		0.9
$Fe(OH)_3.nH_2O$	2	60.3	27.1	87.4	3.5
	6	57.8	29.0	86.8	3.1
	24	57.2	29.0	86.2	3.1
$Zn(OH)_2.nH_2O$	2	36.3[a]			
	6	34.8			
	24	37.4			

[a] Reqn. by $ZnCl_2$, 52.1%

Some, but not all, of the samples of α-$ReCl_4$ possessed infra red aquo-group absorption bands. There is a qualitative report(26) that $[CrCl_2(H_2O)_4]Cl.2H_2O$ does not produce anhydrous $CrCl_3$ with refluxing $SOCl_2$.

In view of the nature of our results and conclusions, we were grateful to be informed(26) by Fergusson that his independent study of the $SOCl_2$-$ReO_2.2H_2O$ reaction led him also to conclude that it gave variable products, sometimes containing Re(III), sometimes aquo-groups, and usually low in overall rhenium and chlorine.

The important conclusions at this stage are firstly, that the reported properties of α-$ReCl_4$ are probably confused by impurities and secondly, that at least some of our preparations must contain a similar chloride of rhenium to that found by Colton and Brown. We do not contest their claim to have prepared a pure sample of $ReCl_4$, since we ourselves achieved nearly as much in samples 22 and 28 (Table 3.1), but suggest they enjoyed some good fortune in the samples chosen for analysis.

2. The Properties of α-$ReCl_4$

The most diagnostic chemical property reported for the trimeric formulation is the 25% release of chloride when α-$ReCl_4$ is dissolved in dilute alkali since this supports a reaction scheme:

$$[(Re_3Cl_9)Cl_3]^0 + 3OH^- \rightarrow [(Re_3Cl_9)(OH)_3]^0 + 3Cl^-$$

However, this striking observation did not warrant a mention in the first two papers(23,27) and appears as a post hoc justification of the trimer proposition in the third paper(9), and without quantitative support. On the other hand, early mention was made of the rather low chlorine figures obtained for samples of α-$ReCl_4$ which in our view is equally well explained by poor products of the sort we find. Our observations are that all samples gave virtually the same chloride release in cold 0.1 M hydroxide, even water, as in fused alkali. This is quite inconsistent with our samples, albeit impure, containing any quantity of trimer.

Moreover, we cannot accept the validity that a fractional release of chloride from α-$ReCl_4$ implies some structure or other, when it is also reported(23) that α-$ReCl_4$ easily hydrolyses giving rhenium dioxide (which does not appear in the above equation) and that the apparently characteristic and significant resistance to complete hydrolysis of α-$ReCl_4$ is similar to $TcCl_4$, which is now known not to possess a cluster-type structure at all.(28)

It is unprecedented for a neutral and non-electrolyte hydroxochloride, such as $[(Re_3Cl_9)(OH)_3]^0$ to be soluble in aqueous solution, and it is unprecedented for a cluster chloro-compound to require fusion with alkali for complete decomposition. Nonetheless, we observe the persistent coloured solutions that result when α-$ReCl_4$ is dissolved in aqueous alkali, but we infer these to result from colloidal rhenium hydroxide since a brown precipitate is immediately given on acidification or on long standing.

It has been pointed out(8) that the violet solutions given by β-$ReCl_4$ in hydrochloric acid or methanol, or the green solutions in acetone, provide some of the grounds for supposing that α-$ReCl_4$ is probably of a different structure since it does not give these colours. We have found that most of our samples of α-$ReCl_4$ did give, not only the same violet or green colours, but all the derivative reactions(8) of β-$ReCl_4$. These were conducted on a qualitative and test-tube basis since we are familiar at first hand with the chemistry of β-$ReCl_4$ by virtue of the partially successful synthesis of it (See also Chapter 7).

It is now concluded that there are no adequate grounds for maintaining that α-$ReCl_4$ is either a trimer or of a stereochemistry greatly different from β-$ReCl_4$.

3. The Structure of α-$ReCl_4$

Our samples of α-$ReCl_4$ have consistently given rather diffuse but discernible and extensive X-ray powder diffraction patterns, which bear an unmistakable resemblance to the patterns for niobium(IV)(29), molybdenum(IV)(30), and tungsten(IV)(31) chloride. Table 3.3 lists the d spacings and relative intensities in a comparative form for the four tetrachlorides.

Table 3.3. X-ray Powder Diffraction Data for Nb(IV), W(IV), Mo(IV) and Re(IV) Chlorides

$NbCl_4$ (29)		WCl_4 (31)		$MoCl_4$ (30)		α-$ReCl_4$	
d	Int	d	Int	d	Int	d	Int
6.02	10	5.97	v.v.s.	6.00	s	5.84	v.s.
				5.75	s		
				5.30	w	5.27	w
4.45	9	4.45	v.v.s.	4.41	s	4.36	m
4.09	8	4.02	v.v.s.	4.04	m	4.00	m
3.43	2						
		3.23	v.s.	3.28	m	3.21	v.w.
2.95	3	3.03	v.v.w.				
		2.85	v.w.	2.86	w	2.82	v.w.
2.71	8	2.77	w	2.72	v.w.		
2.61	9	2.62	v.s.	2.63	v.s.	2.59	v.s.
2.57	5	2.58	s	2.59	s	2.53	v.s.
		2.54	w	2.54	m		
2.22	7	2.23	s	2.20	m	2.18	m
2.17	2	2.18	v.v.w.				
2.14	3	2.13	v.w.	2.12	w		
		2.10	w	2.10	m	2.08	m
2.03	7	2.02	s	2.01	s	1.99	m
		1.98	v.v.w.				
1.92	1	1.93	v.v.w.				
						1.89	v.s.
1.87	4	1.86	v.v.w.			1.85	s

A brief report(32) gives the essential stereochemistry of $NbCl_4$ as consisting of pairs of octahedra joined by an edge. The niobium atoms are displaced towards each other in these pairs, but only to a distance of 3.0 Å, indicating a Nb-Nb bond of low order i.e. < 1. We have recently learned(33) from Kepert that he finds molybdenum(IV) chloride isomorphous with niobium(IV) chloride and that the former must contain a partially formed (or low order) Mo-Mo bond on the basis of magnetic susceptibility.

It is worth noting in passing that the $NbCl_4$-like structure is theoretically plausible for the above tetrachlorides, and we find the brief mention that molybdenum(IV) chloride exists in a form with Mo-Mo spacings of 3.5 Å as remarkable, and confirmation of this result is awaited with interest.

We have not measured the magnetic susceptibility of α-$ReCl_4$ with any thoroughness since we have not been able to obtain sufficient pure material. However, the room temperature susceptibility of several impure samples indicates an effective moment of 2.0 B.M. per Re atom. This at least supports the view that a partially developed, or weak, Re-Re bond occurs in α-$ReCl_4$.

Concluding Remarks

The results obtained in this study agree well with the predictions of the theory. The trimeric formulation for α-$ReCl_4$ is most unlikely and the more likely stereochemical unit involves the m:n = 1:6 type. Isomerism is thereby possible but involving closely related stereochemical arrangements, and not involving structures with different combinations of m:n values.

Experimental

(a) Thionyl Chloride

This was purified by the linseed oil-quinoline method(34) and fractionated (b.pt. 75-76°V; cf. Lit. 77°C(34)). The origin of carbon in the reaction products results from contaminated thionyl chloride, possibly from the ingredients used in purifying it. However some purification of $SOCl_2$ is essential since very poor results are obtained with crude or recovered $SOCl_2$ (viz. preps. 1 and 2, Table 3.1). Colton et al. do not state how they purified their $SOCl_2$.

(b) Hydrated Rhenium Dioxide

Preparations 1-13 employed dioxide prepared from the reduction of $KReO_4$ with zinc and hydrochloric acid. Although this material contains detectable amounts of zinc (probably as metallic fragments) the overall results were the same as in preparations 14-28, where dioxide from the aqueous hydrolysis of $ReCl_5$ was employed. The precipitated dioxide was washed with water, and acetone, and dried in vacuum at room temperature.

(c) The First Row Transition Element Hydroxides

The colloidal precipitates from the action of alkali on the appropriate chloride were washed (assisted by centrifugation for separation) and dried as for $ReO_2.2H_2O$.

(d) Analysis

The following methods of analysis were used.

(i) Chlorine - potentiometric titration with $AgNO_3$ solution.

(ii) Rhenium - determined spectrophotometrically by the α-furildioxime method(35). The optical densities required were measured on a Shimadzu Photo-electric Spectrophotometer Model QR-50.

(iii) Remaining Transition Elements - quantitative flame spectrophotometry against standard solutions.

(iv) Carbon, hydrogen, nitrogen and sulphur - commercial microanalysis as previously described.

(e) Reaction Products

These were efficiently separated from the $SOCl_2$ phase by centrifugation and decantation. The chloride products were handled under dry nitrogen and dried in vacuum.

Chapter 4. The Isomers of Molybdenum(II) Chloride

Introduction

The type of isomerism displayed by $ReCl_4$ described in Chapter 3 presents an example of a compound existing in two different forms but having the same m:n ratio, in this case 1:6. The question arises whether a compound can have isomeric forms in which the m:n values are different.

Such isomeric forms are predictable using the theory outlined in Chapter 1. One compound in which isomerism is predicted is molybdenum(II) chloride, with the expected forms having m:n values of 4:5 and 2:6.

The 4:5 isomer is the well known yellow $(Mo_6Cl_8)Cl_4$. This chapter describes the work undertaken in the search for the other isomeric form.

The Reaction of Molybdenum(II) Acetate with Dry Hydrogen Chloride

This reaction was studied by Stephenson, Bannister and Wilkinson(36) in 1964 and has been re-investigated.

The acetate was reported to react with dry hydrogen chloride at about 130°C, producing a brown material. The dark brown product obtained at around 250°C analysed for approximately 98% $MoCl_2$, but was never completely free from carbon, hydrogen and oxygen. The physical and chemical properties of this brown product were significantly different from those of the usual (Mo_6Cl_8)Cl_4. The authors believed that they had prepared a different form of molybdenum(II) chloride.

In this work the reaction was carried out as follows. Molybdenum(II) acetate was crushed and heated with dry hydrogen chloride for a short time at the desired temperature. This process was repeated successively several times. After each crushing and heating operation, the chloride content of the brown residue was determined and its infra red spectrum recorded.

Several preliminary experiments were performed before the conditions were found under which the reaction could be successfully repeated. These experiments are summarised in Table 4.1. The final products in these experiments were black (two were dark blue-black) indicating that an oxide or oxyhalide was also being formed. This black material usually formed a surface layer and as it appeared to restrict the uptake of further chlorine, those preparations giving black products were not pursued for longer heating times.

It became apparent that the presence of oxygen was causing the experimental difficulties. These were eliminated when the hydrogen chloride was allowed to flow through the apparatus for at least 60 minutes before heating commenced. The product was then brown coloured and the chloride content reached a maximum at approximately 42.5%.

The reaction has been successfully repeated at both 250°C and

Table 4.1. Preliminary Experiments of the Reaction of Dry Hydrogen Chloride with Molybdenum(II) Acetate

Sample	Temp. °C	% Chlorine after heating times (hours)											Colour of Sample
		1	2	3	4	5	6	7	8	9	12	16	
1	250				21.0	25.9			25.6	28.1	28.3	27.2	black
2	250		23.1	28.2			30.9			30.7			black
3	300			26.4	34.8								black
4*	350		34.7										blue-black
5*	350				36.0								black
6	350		11.8										blue-black
7	300		11.4			27.2	33.1	33.9					black
8	300	32.0											brown

* Acetate not crushed before heating

300°C. The rate of chlorine substitution at these temperatures is shown in Table 4.2. As the chlorine content increases, the intensities of the acetate absorption bands in the infra red decrease until no bands are present at maximum chlorine content. The carbon and hydrogen analyses also confirm the absence of acetate. The complete analytical data for the above four samples are given in Table 4.3.

It is worth noting in passing that the contaminated samples prepared in the preliminary experiments produce pure $MoCl_2$ when warmed with 12 M hydrochloric acid since the dichloride is insoluble but the oxide, oxyhalide or unreacted acetate impurity are all soluble.

Properties:- The product of the reaction is a brown powder which slowly deteriorates after long exposure to the air, turning blue-black after several weeks. It is rapidly hydrolysed by both concentrated and dilute alkali to give a black precipitate and a clear solution, but is insoluble in, and unaffected by, water. The compound is insoluble in boiling 12 M HCl and in most non-aqueous solvents. It is soluble in nitrobenzene, giving a green solution and partially soluble in hot pyridine and isoquinoline producing very air sensitive yellow and red solutions respectively.

These observations agree well with those reported(36), and are markedly different from those of $(Mo_6Cl_8)Cl_4$.

Table 4.2. Rate of Chlorine Substitution for Molybdenum(II) Acetate/Dry Hydrogen Chloride Reaction

Time of heating (hours)	% Cl			
	250°C (a)	250°C (b)	300°C (c)	300°C (d)
1	23.2	19.3	38.4	-
2	36.8	35.6	39.0	-
3	37.6	36.3	42.2	42.5
4	39.2	38.6	42.3	42.5
5	40.5	40.7		
6	41.2	41.0		
6.5	42.0	42.2		
7	42.3	42.4		
7.5	42.3	42.4		
Theory	42.5	42.5	42.5	42.5

Table 4.3. Complete Analytical Data for Products of Molybdenum(II) Acetate/Dry Hydrogen Chloride Reaction

Sample	%Cl	%Mo	Cl/Mo	%C	%H	Ox. No.
(a)	42.3	56.8	2.03	<0.2	0.87	2.1
(b)	42.4	57.4	2.00	0.22	<0.5	2.2
(c)	42.3	57.7	1.98	0.20	0.90	2.1
(d)	42.5	57.7	1.99	0.22	0.77	2.0
Reqd. for $MoCl_2$	42.5	57.5	2.00	-	-	2.0

The magnetic susceptibility was found to be 24.3×10^{-6} C.G.S. units, which corresponds to $\mu_{eff} = 0.49$ B.M. Samples of $MoCl_2$ were heated for 4 hours at 140°C in sealed tubes with 12 M HCl and with glacial acetic acid. In both cases, no apparent reaction occurred and the dichloride was recovered unchanged.

Possible Structure:- These samples give rather diffuse X-ray powder diffraction photographs (see Fig. 3) with relatively few lines, making comparison with patterns of compounds of known structures very difficult. It is tentatively proposed that the structure of this isomer is a distorted $CdCl_2$-type layer structure which allows trimeric Mo_3 groups to form while still retaining octahedral coordination of the chlorine atoms.

For convenience this isomer may be referred to as the β-form and the yellow $(Mo_6Cl_8)Cl_4$ as the α-form of molybdenum(II) chloride.

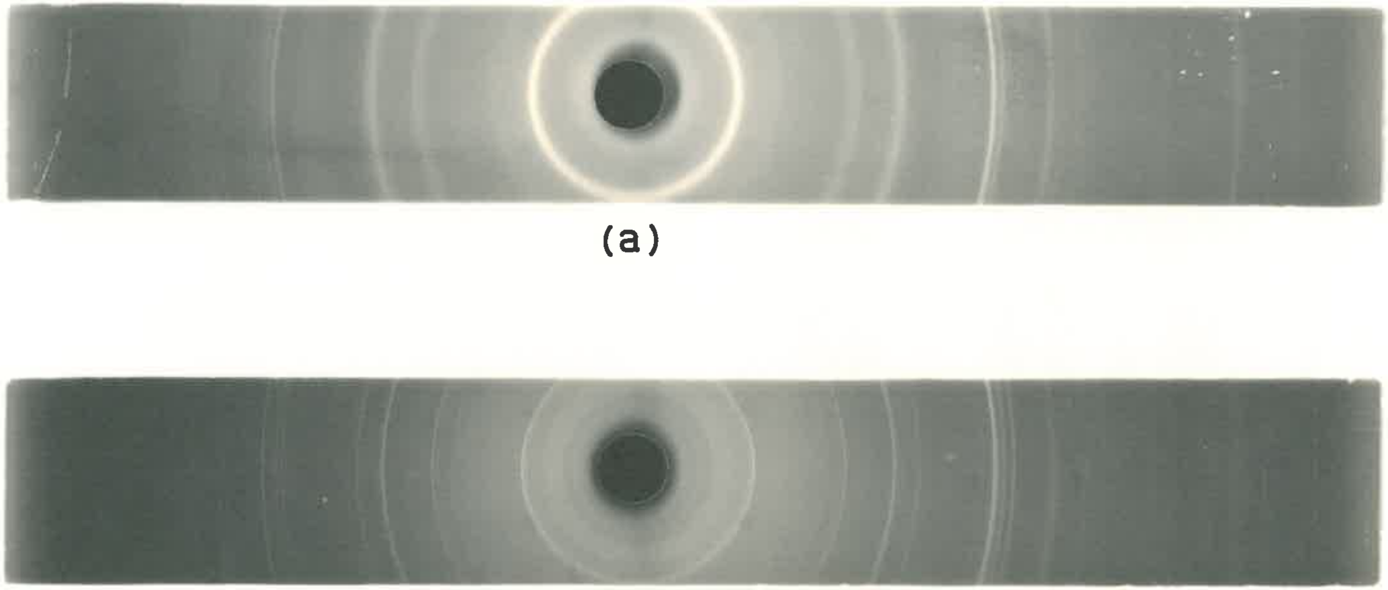
The Pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$

The pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$ bears close investigation since it is possible that heating this compound in vacuum will yield the following reaction:

$$(NH_4)_7Mo_3Cl_{13}.H_2O \rightarrow 3MoCl_2 + 7NH_4Cl + H_2O$$

This may prove a route for a new form of $MoCl_2$.

FIG. 3. X-ray Powder Photographs.



(a)

(b)

(a) β-$MoCl_2$. 20 hours exposure, Cu Kα radiation (Ni filter); Sample mounted in 0.2 mm quartz capillary.

(b) $CdCl_2$. 8 hours exposure, Cu Kα radiation (Ni filter); Sample mounted in 0.5 mm quartz capillary.

The pyrolysis has been conducted over a wide range of conditions, and it is found that NH_4Cl is evolved but the residue varies in appearance and composition yet never corresponds to $MoCl_2$. The sublimation begins at 140°C, and a sample heated at 120°-130°C for 6 hours remains unchanged.

Samples were heated for 1 hour at temperatures from 140°C to 240°C and the molybdenum oxidation number determined. The results are tabulated in Table 4.4.

Shorter heating times gave residues with oxidation number closer to 2.0 and violet in colour, while longer heating times produced darker and more oxidised residues. This is borne out by the experiments summarised in Table 4.5. It may also be seen that the pyrolyses are not very reproducible.

A series of short pyrolysis experiments yielded the results given in Table 4.6. It may be inferred from these results that the pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$ proceeds only as far as

$$(NH_4)_7Mo_3Cl_{13}.H_2O \rightarrow (NH_4)Mo_3Cl_7.H_2O + 6NH_4Cl$$

before extensive decomposition occurs although there appears to be some evidence for the stabilisation of oxidation state 2.5 in the solid state. However, $MoCl_2$ was never obtained and it must be concluded that this attempt to produce an isomeric form of molybdenum(II) chloride was therefore unsuccessful.

Table 4.4. Pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$ as a Function of Temperature

Pyrolysis	Conditions	Oxidation No.	Residue
1	120°C; 5.5 hrs	2.0	violet (appears unchanged)
2	140°C; 1 hr	2.35	violet
3	160°C; "	2.36	red-brown
4	180°C; "	2.40	brown
5	200°C; "	2.43	brown
6	220°C; "	2.46	brown-black
7	240°C; "	3.04	black

Table 4.5. Pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$ as a Function of Time

Pyrolysis	Conditions		Oxidation No.	Residue
Run I	150°C;	3/4 hr	2.19	violet
(Sample (a))	" ;	2 hrs	2.21	red-brown
	" ;	6 hrs	2.48	brown
Run II	150°C;	0.5 hr	2.14	red-violet
(Sample (b))	" ;	2 hrs	2.37	dark red
	" ;	4 hrs	2.60	brown
Run III	180°C;	3/4 hr	2.46	red-brown
	" ;	2 hrs	3.08	brown
	" ;	6 hrs	5.07	black

Table 4.6. The Products of the Pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$ in Vacuo

Pyrolysis	Conditions	% Mo	% Cl	Oxid. No.	Cl/Mo	% Mo reqd. for Mo = 2.0
1	190°C; 1 hr	-	44.5	-	-	47.2
2	" ; 2 1/4 hrs	-	44.4	-	-	39.2
3	" ; ½ hr	-	42.9	-	-	46.3
4	" ; 1½ hrs	49.8	43.4	2.18	2.35	47.6
5[a]	195°C; 2 hrs	50.2	41.2	2.03	2.22	49.8

[a] Found for pyrolysis 5: N = 2.5%; H = 1.5%

Calcd. for $MoCl_2$: Mo = 57.5%, Cl = 42.5%, N = 0%, H = 9%,
Cl/Mo = 2.0, Ox. No. = 2.0.

Calcd. for $(NH_4)Mo_3Cl_7.H_2O$: Mo = 50.4%, Cl = 43.4%, N = 2.5%,
H = 1.0%, Cl/Mo = 2.33, Ox. No. = 2.0.

Concluding Remarks

Two widely differing routes towards the preparation of an alternate form of molybdenum(II) chloride have been investigated. Although the pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$ has proved abortive, the success of the acetate/hydrogen chloride method verifies the prediction of the theory that isomerism is possible. Unfortunately the plausible structure suggested by the theory cannot be confirmed.

Molybdenum(II) chloride is only one of several transition metal binary halides for which isomerism may be expected, and the future preparation of isomers of other metal halides is awaited with interest.

Experimental

Preparation of β-$MoCl_2$

Molybdenum(II) acetate was crushed to a fine powder and dry hydrogen chloride was passed over it for at least 60 minutes before heating commenced. The sample was heated for the required time, allowed to cool in a stream of dry hydrogen chloride, and finally the apparatus was flushed out with oxygen-free nitrogen. Any remaining hydrogen chloride was removed in vacuo. The I.R. spectrum and the chlorine contents were determined and the whole procedure repeated until no further uptake of chlorine occurred. The yield of the dichloride was ~85-90%.

Molybdenum Oxidation Number in β-$MoCl_2$

β-$MoCl_2$ is only slowly soluble in acidified ferric ammonium sulphate solution. Dissolution was obtained by employing strongly acid ferric solutions and by prolonged (at least 6-8 hours) warming under N_2. The oxidation number was then determined using standard permanganate solution.

The Pyrolysis of $(NH_4)_7Mo_3Cl_{13}.H_2O$

The initial pyrolysis experiment was conducted using a sublimation apparatus. This consisted of a vessel having an outer jacket and an inner "cold finger" through which cold water was continuously circulated. A constant temperature was maintained using a Wood's metal bath, and the vessel was kept under a dynamic vacuum. After pyrolysis, the vacuum was released and nitrogen was introduced into the vessel simultaneously. The compound was handled in a dry nitrogen atmosphere. In later experiments, this sublimation vessel was replaced with a narrow glass tube which allowed electrical heating with a metal block. The ammonium chloride sublimed well along the cold sides of the tube and the remaining residue was easily separated by cutting the tube between the two deposits. The temperature of the pyrolysis and the length of heating were varied as required.

The methods of analysis of all the other elements were the same as those described in Chapter 2.

Chapter 5. Solution Studies of Molybdenum(II) Acetate in Hydrochloric Acid

The Dissolution of Molybdenum(II) Acetate in Hydrochloric Acid

This occurs slowly at room temperature with the production of bright violet-coloured solutions. Molybdenum(II) acetate was added to hydrochloric acid solutions of various strengths (e.g. 0.1, 1.0, 2.0, 4.0, 6.0, 8.0 and 12.0 M) to determine the acid strength necessary for reaction. For acid strengths below approximately 8 M, the rate of dissolution is very slow, so that hydrolysis and decomposition are too fast to allow the formation of the violet solutions. These solutions yield dark brown-black precipitates after prolonged standing.

The addition of various cations to the violet-coloured acetate/12 M HCl solution causes the precipitation of a number of chlorotrimolybdates(II). More than seventy different cations have been tried as precipitating agents in a systematic study. These represent singly, doubly and triply charged species, complex cations and organic amine hydrochlorides in HCl solution.

The species produced by the ammonium or alkali metal cations have been described previously. Other singly charged cations used were the tertiary and quaternary ammonium, phosphonium and arsonium cations and their substituted derivatives. No precipitates were obtained with these singly charged cations or with other doubly or triply charged cations.

The addition of organic amine hydrochlorides to the acetate/12 M HCl solution produces a large number of chlorotrimolybdates(II).(12)

$[Co(en)_3]_3Mo_3Cl_{15}.6H_2O$

The use of complex cations as precipitating agents has also been investigated.

This compound may be prepared by the addition of $Co\ en_3Cl_3$ to the violet solution. An alternative preparative method involves the mixing of $Co\ en_3Cl_3$ and $(NH_4)_7Mo_3Cl_{13}.H_2O$ in 2 M HCl. The analytical data for this compound is shown in Table 5.1. The presence of water has been proposed on analytical grounds. The strong absorption in the infra red spectrum due to the $Co\ en_3$ group completely obscures any possible bands due to water.

The properties of $[Co(en)_3]_3Mo_3Cl_{15}.6H_2O$ are very similar to those of the other halogenomolybdates(II). It is insoluble in non-aqueous solvents and thus no direct evidence could be gained regarding its solution phase degree of polymerisation. Its composition is equivocal and may be expressed as a dimer or trimer. Since there are no features that distinguishes this compound from the other chloromolybdates(II) it has been concluded that it must be of the same structure and contain the Mo_3Cl_{13} unit. This requires that the lattice displays extra chlorine atoms, not

Table 5.1. Analytical data for $[Co(en)_3]_3Mo_3Cl_{15}.6H_2O$

Sample	% Mo	% Cl	Cl:Mo	% Co	Mo:Co	% N	% H	% C	Ox. No.	% Yield
1	17.2	32.0	5.02	-	-	-	-	-	2.3	81
2	17.3	33.3	5.21	10.3	1.03	-	-	-	2.3	85
3	17.6	32.3	4.96	10.0	1.08	15.22	5.16	13.41	2.1	71
4	17.4	32.3	5.02	10.4	1.03	15.7	4.87	13.11	2.1	68
5	17.5	32.4	5.00	-	-	15.05	5.25	13.84	2.3	86
Theory	17.5	32.4	5.0	10.7	1	15.3	5.1	13.1	2.0	-

associated with the staphylonuclei, but present through the requirements of the multivalent group Co en_3^{3+}.

The isomorphous Cr en_3 compound has also been prepared$^{(12)}$.

The Solid State Decomposition of $[Co(en)_3]_3Mo_3Cl_{15}.6H_2O$

The $[Co(en)_3]$ compound, unlike the $[Cr(en)_3]$ compound undergoes a rapid intramolecular redox reaction whose rate is increased by light (producing bleaching) or by moisture, but not by oxygen.

Table 5.2 shows the rate of oxidation of $[Co(en)_3]_3Mo_3Cl_{15}.6H_2O$ under various conditions.

Cobalt(II) is detected in fresh and stored samples. The molybdenum oxidation numbers of the samples were determined by dissolving them in acidified ferric ammonium sulphate solution and titration with permanganate. It is assumed that the cobalt(II) products do not contribute to the titration, but remain as the $[Co(H_2O)_6]^{2+}$ complex. The oxidation number of samples stored in dark dry conditions rises over a few days from about 2.0 to various relatively stable values in the range 2.4-3.0.

The rate of oxidation and the terminal value of the oxidation number are not reproducible. The final product of oxidation in the presence of moisture is rapidly formed (within 2-3 days) and is a green material containing 31.5% Cl; 17.3% Mo (i.e. Cl:Mo = 4.9) and with oxidation number 4.9. This indicates the presence of the

Table 5.2. Change of Oxidation Number of Molybdenum in $[Co(en)_3]_3Mo_3Cl_{15}.6H_2O$ Stored in the Dark Under Various Conditions

In Vacuo		Dry Air		Dry O_2	
Days	Oxidn. No.	Days	Oxidn. No.	Days	Oxidn. No.
0	2.14	0	2.14	0	2.23
1	2.30	1	2.23	1	2.44
2	2.41	2	2.26	2	2.48
3	2.53	3	2.22	5	2.55
4	2.67	4	2.24	10	2.64
7	2.85	7	2.30	14	2.66
12	2.97	12	2.40	27	2.80
15	2.98	15	2.39		
28	2.99	28	2.40		

In Vacuo		Dry Air		Moist N_2	
Days	Oxidn. No.	Days	Oxidn. No.	Days	Oxidn. No.
0	2.27	0	2.27	0	2.36
1	2.65	1	2.47	1	4.17
2	2.73	2	2.53	3	4.77
3	2.72	3	2.60		
4	2.70	4	2.63		
6	2.76	6	2.71		
8	2.74	8	2.74		
10	2.76	10	2.78		
13	2.79	13	2.85		
18	2.82	18	2.87		
22	2.84	22	2.85		

$[Mo^{V}OCl_5]^{2-}$ group.

Magnetic Behaviour

The magnetic susceptibilities of samples 3 and 4 were determined as a function of time. The following results were obtained:

Time (hours)	$10^6\ \chi_M$ (C.G.S.)	$10^6\ \chi_M$ (C.G.S.)
2	308	202
24	686	454
48	1330	902
72	1780	1320

The χ_M values of the freshest samples correspond to μ_{eff} values of 1.7 and 1.9 B.M. per trimer unit respectively, which is consistent with considerable m-m interaction.

The Rate of Oxidation of Molybdenum(II) Acetate in 12 M Hydrochloric Acid

The violet solutions produced by molybdenum(II) acetate and 12 M HCl, and which contain only molybdenum(II) initially, are only relatively short-lived. It is worthwhile to study the oxidation of these solutions since they may afford a means of preparation of a number of species of higher oxidation number and which have not previously been reported.

On standing under nitrogen this violet solution becomes oxidised and the rate of formation of higher oxidation states increases with temperature, the presence of oxygen or molybdenum(VI) oxide. It is apparent that several molybdenum species are formed in this solution and a thorough investigation of the rate of oxidation under various conditions has been undertaken.

The apparent (average) oxidation number displayed by the molybdenum in the molybdenum(II) acetate/12 M HCl solution under various conditions is given as a function of time in Figs. 4-6.

Several interesting features of these runs may be noted:

(i) The initial rapid increase in oxidation number.

(ii) The relatively constant value at 2.5-2.7.

(iii) The increase in rate due to temperature cf. runs at 30°, 50°, 70° and 90°C under oxygen atmosphere.

(iv) The increase in rate due to oxygen cf. runs at 30°C and 70°C under nitrogen and oxygen.

(v) The non-smooth nature of curvature of the graph in which much higher oxidation numbers have been obtained, viz. runs at 70°C and 90°C under an oxygen atmosphere.

The change in oxidation number is accompanied by colour changes of the solution. The initial bright violet colour produced on mixing loses its intensity, changing rapidly to an amber-green colour corresponding to an oxidation number of approximately 2.5-2.7.

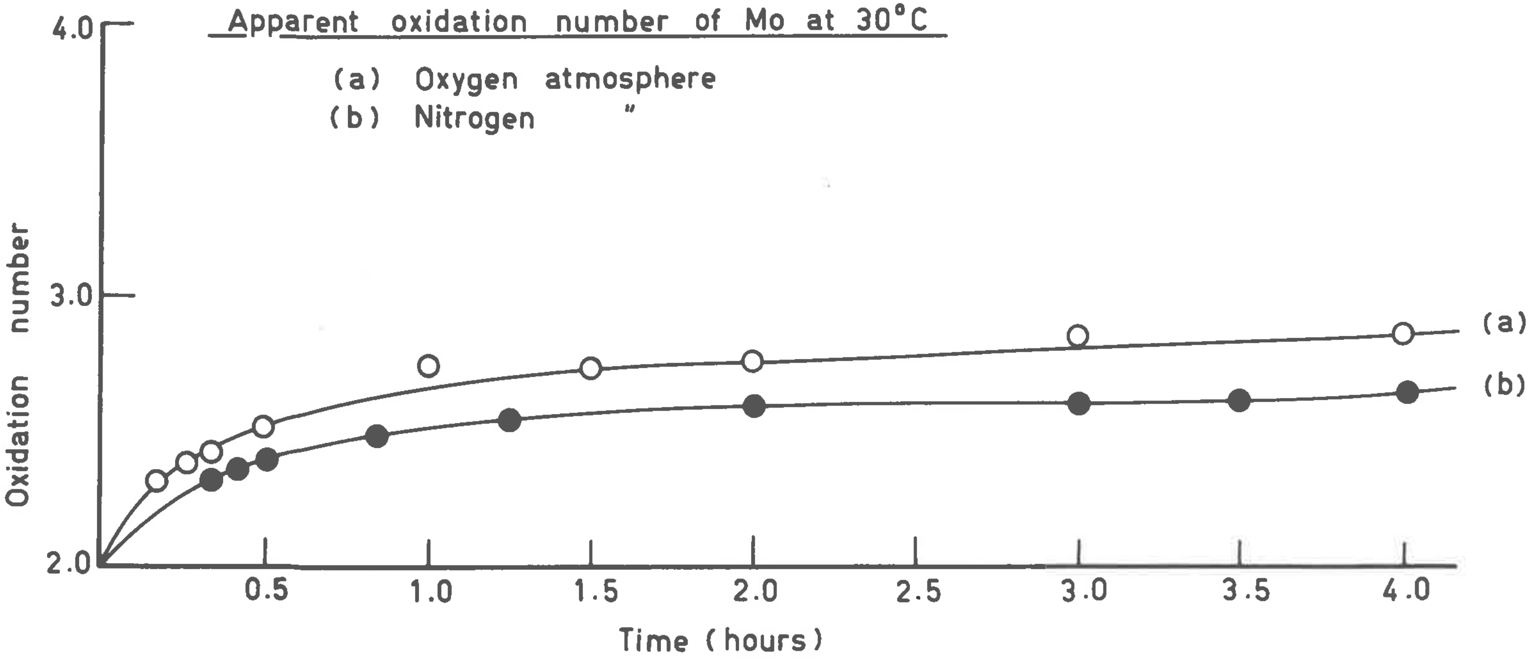

Apparent oxidation number of Mo at 30°C
(a) Oxygen atmosphere
(b) Nitrogen "
Oxidation number
4.0
3.0
2.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Time (hours)
(a)
(b)

FIG. 4.

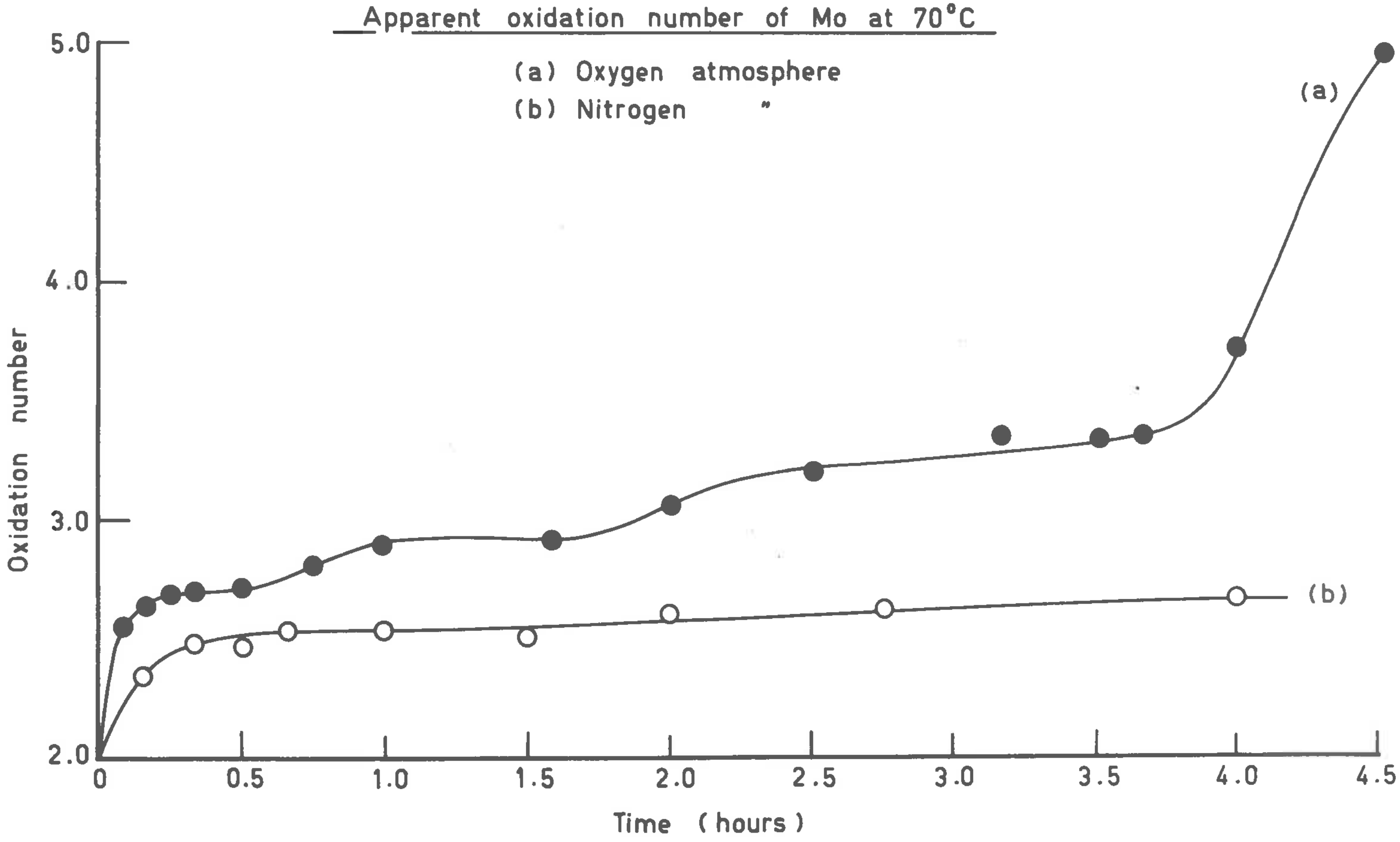

Apparent oxidation number of Mo at 70°C
(a) Oxygen atmosphere
(b) Nitrogen "
(a)
(b)
Oxidation number
5.0
4.0
3.0
2.0
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Time (hours)

FIG. 5.

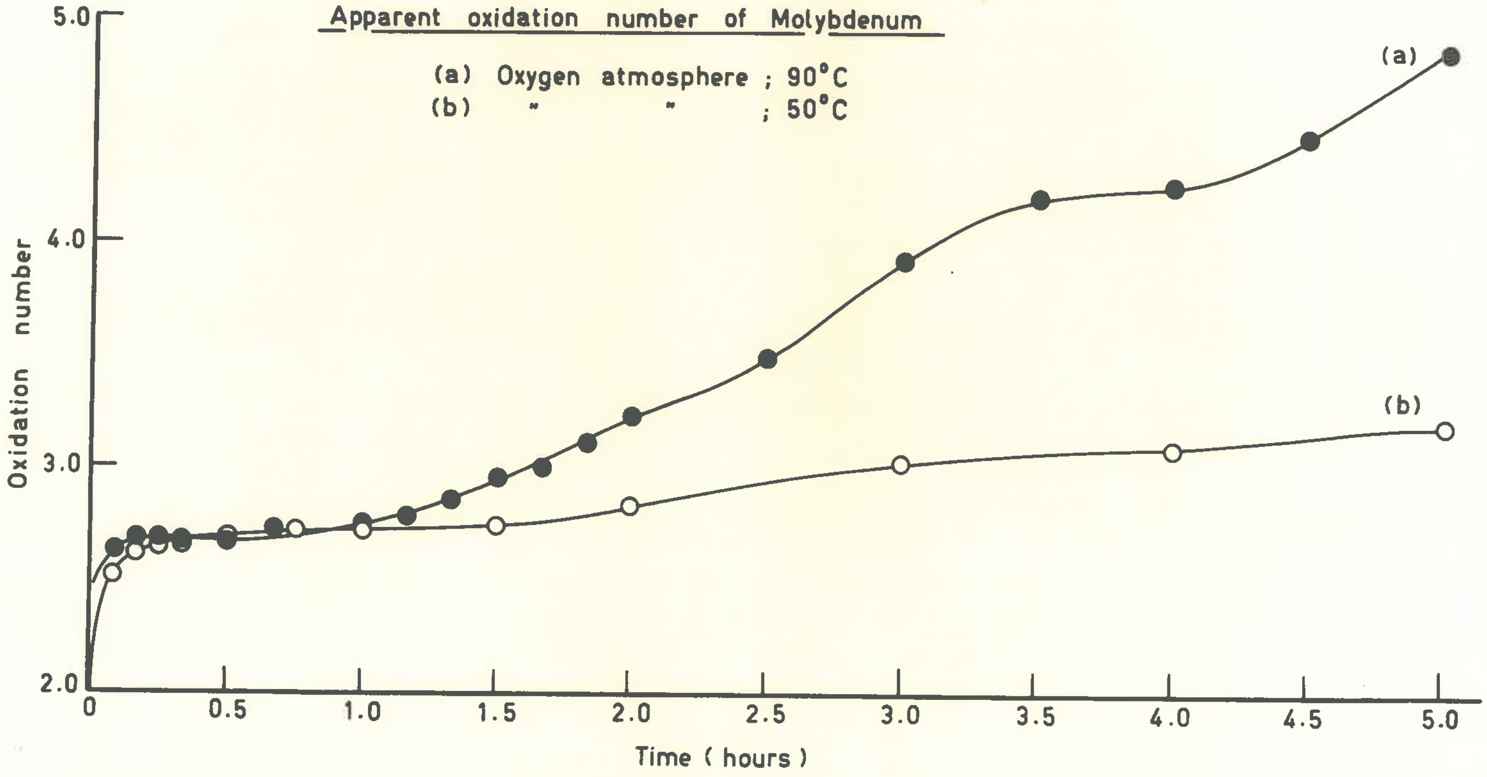

Apparent oxidation number of Molybdenum
(a) Oxygen atmosphere ; 90°C
(b) " " ; 50°C
(a)
(b)
Oxidation number
5.0
4.0
3.0
2.0
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Time (hours)

FIG. 6.

While the solution is in the vicinity of 3.0 the solution changes to a reddish colour and finally becomes emerald green corresponding to oxidation number 5.0. This solution is stable indefinitely.

From these colour changes and from the broken nature of the curves at 70°C and 90°C, it is apparent that a number of successive reaction products are formed. The first relatively level portion of the curves at oxidation numbers 2.5-2.7 is most important since it is from just these solutions that an extensive range of molybdenum(2.5) compounds may be precipitated.

While it appears that several species exist in solution at various times, solubility prevents precipitation of them all. It has been possible to precipitate molybdenum species in the oxidation states 2.0, 2.5, 3.0 and 5.0. These last two species have been obtained as $Cs_2[Mo^{III}Cl_5.H_2O]$ and $Cs_2[Mo^{V}OCl_5]$ as shown by analysis and a spectral investigation.

(a) Found: Mo = 17.1%, Cl = 31.9%, Cl/Mo = 5.05, Ox. No. = 3.0
Calcd. for: Mo = 17.2%, Cl = 31.8%, Cl/Mo = 5.0, Ox. No. = 3.0
$Cs_2[Mo^{III}Cl_5.H_2O]$

(b) Found: Mo = 17.1%, Cl = 31.7%, Cl/Mo = 5.0, Ox. No. = 5.0
Calcd. for: Mo = 17.3%, Cl = 31.9%, Cl/Mo = 5.0, Ox. No. = 5.0
$Cs_2[Mo^{V}OCl_5]$

The Electronic Absorption Spectra of $Cs_2[Mo^{III}Cl_5.H_2O]$ and $Cs_2[Mo^{V}OCl_5]$ in Hydrochloric Acid

The spectra of these two compounds were recorded since they were essential for the correlation of the spectra of other species prepared in this study and no comprehensive data had been reported previously.

(a) $Cs_2[Mo^{III}Cl_5.H_2O]$

The U.V. and visible spectrum of $Cs_2[Mo^{III}Cl_5.H_2O]$ (red-pink) was recorded in 8, 4 and 0.1 M hydrochloric acid. The results are similar to those obtained by Jörgensen(37) and are tabulated in Tables 5.3-4.

Low intensity absorption peaks (ε = 4 and 6 respectively) appear at 9.70 KK and 14.80 KK over the whole concentration range. The peak at 19.30 KK in 8 M HCl shifts to 19.80 KK in 0.1 M HCl, while a shift from 24.10 KK to 25.30 KK is observed in the next peak under the same conditions of dilution. A fourth peak at 32.00 KK in 8 M HCl shifts to 33.80 KK in 0.1 M HCl. A further peak appears at approximately 45.00 KK with a shoulder at 39.50 KK in 0.1 M HCl.

Although the spectra in 8 and 4 M HCl remain relatively constant for at least 24 hours, those obtained in 0.1 M HCl change quite rapidly. The peaks at 19.80 KK and 25.30 KK shift to shorter

Table 5.3. The Electronic Absorption Spectra of $Cs_2[Mo^{III}Cl_5.H_2O]$ in Hydrochloric Acid

Concentration	λ (KK)	ε	Literature(36)
8 M	9.70	4	9.55
	14.75	6	14.75
	19.30	31	19.75
	24.10	51	24.60
	32.30	890	-
	45.40	12,000	-
4 M	14.85	5	-
	19.65	30	
	24.35	55	
	32.70	-	
	46.85	-	

Table 5.4. Electronic Absorption Spectra of Cs$_2$[Mo^{III}Cl$_5$.H$_2$O] in 0.1 M HCl as a Function of Time

0 hours		2 hours		8 hours	
λ (KK)	ε	λ (KK)	ε	λ (KK)	ε
9.95	1	10.10	1	10.30	2
14.85	5	15.55	5	15.30	6
19.80	25	20.80	30	~21.00	31
25.30	61	26.30	70	26.90	73
33.80	745	33.65	1350	33.80	1700
~39.50	~990	38.90	1580	39.10	2000
45.00	3100	44.75	1950	45.15	3100

wavelengths and increase in intensity while the bands at 33.80 KK and 39.50 KK show a marked increase in intensity within 8 hours.

(b) $Cs_2[Mo^VOCl_5]$

The spectrum of $Cs_2[Mo^VOCl_5]$ was recorded over the following concentration range of hydrochloric acid:- 12, 8, 4, 2 and 0.1 M HCl. The solutions in 8-12 M HCl are emerald green while below 8 M the solutions are amber-coloured.

A Beer's Law plot taken at 12 M and 0.1 M HCl shows that Beer's Law is obeyed. The position and intensity of the peaks in the resulting spectra are tabulated in Table 5.5.

At each particular concentration of HCl, the spectra were recorded as a function of time and in each case remained unchanged for at least 24 hours at room temperature. The results obtained are in good agreement with those obtained by Jörgensen(37) and Simon and Souchay(38).

The spectral bands of the green complex, i.e. in the range 8-12 M HCl appear to remain unchanged in both position and intensity. On dilution with water, the peak at approximately 14.00 KK becomes very broad and less intense and is not observed below 4 M HCl. The second peak at approximately 23.00 KK exists in 8-12 M HCl but on dilution to 4 M HCl becomes a shoulder ($\epsilon \approx 125$) which disappears on further dilution. The peak at 28.00 KK ($\epsilon \approx 500$) is only observed

Table 5.5. The Electronic Absorption Spectra of $Cs_2[Mo^VOCl_5]$ in Hydrochloric Acid

Concentration	λ (KK)	ε	Previously Reported	
12 M (Green)	13.90	17		
	22.30	14		
	27.90	520	-	
	32.20	4900		
	41.20	5600		
8 M (Green)	14.00	17	14.05	(16)(37)
	22.30	15	22.50	(14)
	28.20	460	28.20	(500)
	32.30	3600	32.20	(4400)
	41.60	5200	40.70	(5500)
	47.50	10500	-	-
4 M (Amber)	14.30	3	~14.00	(6)(38)
	23.10	125	~23.00	(120)
	32.90	3500	~33.00	(2000)
	47.85	8900	-	-
2 M (Amber)	25.30	60	~25.00	(50)(38)
	~33.50	3500	~33.00	(1800)
	38.10	7000	-	-
	48.30	7900	-	-
0.1 M (Amber)	25.70	54		
	33.80	1800		
	38.70	2200	-	
	49.00	3900		

in the 8-12 M HCl range. The peak at 32.00 KK in 12 M HCl shifts to 33.80 KK in 0.1 M HCl, with an accompanying drop in intensity from ε = 4900 (12 M) to ε = 1800 (0.1 M). The remaining two peaks appear at all concentrations, are broad and intense, and appear at 38.00-40.00 KK and 48.00-49.00 KK.

Concluding Remarks

A thorough study of the molybdenum(II) acetate/12 M hydrochloric acid system has revealed that although we suspect that several species are present in solution, only molybdenum compounds in the oxidation states 2.0, 2.5, 3.0 and 5.0 can be precipitated.

We are aware that a larger number of compounds could have been prepared. However the main object of this study, was not the preparation of a large number of particular species, but rather the discovery of all the different structure types present in the system. It is unlikely that this method of preparation will yield any more different types in the solid state. However, the theory predicts that such compounds, having different structure types and fractional oxidation numbers, are possible and alternative methods of preparation must be investigated.

Experimental

(a) Preparation of $[Co(en)_3]_3Mo_3Cl_{15}.6H_2O$

A 2 M hydrochloric acid solution of Co en_3Cl_3 was quickly added to a solution of $(NH_4)_7Mo_3Cl_{13}.H_2O$ in 2 M HCl. A fine microcrystalline red precipitate formed after approximately 5 minutes. This precipitate was filtered, washed successively with cold 2 M HCl, ethanol, and ether, and dried in vacuum at room temperature. The yield was usually 70-80%. Due to its insolubility in, or decomposition by solvents, this compound could not be recrystallised.

2 M hydrochloric acid was used due to the restricted solubility of $(NH_4)_7Mo_3Cl_{13}.H_2O$ in conc. HCl. This allowed homogeneous reaction mixtures. The compound has also been prepared using other chloromolybdates(II), e.g. $K_6Mo_3Cl_{12}$ and $Cs_7Mo_3Cl_{13}.H_2O$.

The cobalt content was determined gravimetrically as tetrapyridinecobalt(II) thiocyanate(21), and all other elements by methods previously described.

(b) Determination of the Apparent Oxidation Number of Molybdenum in Molybdenum(II) acetate/12 M HCl

1.000 gms. of finely powdered molybdenum(II) acetate were dissolved in 50 ml. of 12 M HCl, previously thermostatted to the required temperature. The atmosphere above this solution was either nitrogen, air or oxygen as required. During the reaction, the reaction vessel was shaken with a mechanical stirrer or the solution agitated by a vigorous flow of oxygen or nitrogen.

At various intervals of time, aliquots of the solutions were removed, and discharged into an acidified solution of ferric ammonium sulphate. The oxidation number was then determined by "back titration" with standard permanganate solution.

Small errors due to evaporation (in a flow system) are inherent in this method, especially at higher temperatures. These may be overcome by using a closed system and effecting sampling by means of a syringe through a rubber membrane. Other errors due to volume changes of volumetric pipettes at higher temperatures are unavoidable but, fortunately, small.

Care must be taken with the initial readings to ensure complete dissolution of the acetate. This may be speeded up by introducing the acetate as a fine powder.

(c) Visible and Ultra Violet Spectra

These were recorded on a Unicam SP700 recording spectrophotometer using degassed hydrochloric acid and a pair of 1 cm. matched silica cells.

Chapter 6. Halogenomolybdates(2.5)

Introduction

In the study (Chapter 5) of the rate of oxidation of molybdenum(II) acetate in hydrochloric acid under various conditions, a relatively level part of the graphs indicated the presence of a species of some stability with an oxidation number in the range 2.5-2.7. The significance of this observation forms the basis of this chapter.

Results and Discussion

(1) Preparation

Molybdenum(II) acetate, and the halogenotrimolybdates(II) prepared from it, dissolve in concentrated hydrohalic acid to give short-lived violet solutions of molybdenum(II) which change through red to amber or brown. The addition of various precipitating cations to this oxidised solution produces yellow or mustard-coloured compounds having molybdenum in the oxidation state 2.5.

A thorough investigation of the compounds formed by the alkali metal cations and the ammonium cation has been undertaken. No compounds were produced by Li^+, Na^+, K^+ or NH_4^+ and no iodomolybdates(2.5) were formed by any cation. The compounds produced by Rb^+ and Cs^+ have been formulated as $A_3Mo_2^{2.5}X_8$ (A = Rb, Cs; X = Cl, Br).

Another investigation in these laboratories$^{(12)}$ has shown that similar compounds are produced with several other cations, e.g. tetraphenylphosphonium, tetraphenylarsonium, o-phenantholinium cations.

The preparative and analytical data for the alkali metal halogenomolybdates(2.5) are given in Tables 6.1-4.

Since halogenomolybdates of low oxidation states are difficult to handle and purify, we have adopted as the criterion for sample homogeneity and purity, the reproducible analysis of different preparations.

$Rb_3Mo_2Br_8$ could not be isolated pure. Preparative mixtures with Rb:Mo ratios >5:1 yield light brown precipitates very rapidly. The analytical data (see Table 6.4) show that these samples have a Br/Mo ratio near 4.0 and the oxidation numbers are close to 2.5. The powder photographs are very similar to those of the other halogenomolybdates(2.5). When preparative mixtures of much lower Rb:Mo ratios are used, the precipitates form slowly, and are darker brown in colour. The oxidation numbers are near 3.0 and the Br/Mo ratios are in the range 4.26-4.40. The powder photographs of these samples are very similar to those of $Rb_3Mo_2^{III}Br_9$ prepared in another study in these laboratories$^{(12)}$.

It is inferred that the rubidium bromomolybdate samples are mixtures of $Rb_3Mo_2Br_8$ and $Rb_3Mo_2^{III}Br_9$. Attempted purification by

Table 6.1. Analytical Data for Rubidium Chloromolybdate(2.5)

A/Mo	% Mo	% Cl	Cl:Mo	Oxid. No.	% Yield
3:2	25.6	38.8	4.10	2.72	82
3:2	25.4	39.4	4.18	2.63	79
3:2	25.8	39.5	4.14	2.66	85
5:1	25.6	38.4	4.05	2.48	84
10:1	25.5	38.9	4.12	2.50	80
Theory	26.2	38.8	4.00	2.50	-

Table 6.2. Analytical Data for Caesium Chloromolybdate(2.5)

A/Mo	% Mo	% Cl	Cl:Mo	Oxid. No.	% Yield	% Cs
3:2[a]	21.4	32.6	4.12	2.50	80	-
3:2	21.8	31.7	3.94	2.57	70	-
3:2	21.9	32.5	4.00	2.63	67	44.9
3:2	21.8	32.3	4.00	2.55	67	45.1
3:2	21.8	32.5	4.02	2.60	65	45.1
5:1	21.5	32.4	4.07	2.48	72	-
10:1	21.7	33.4	4.16	2.57	77	-
Theory	21.9	32.5	4.00	2.50	-	45.6

[a] Sample dried in vacuo at 50°C for 3 hours %Cl = 32.8

" " " " " 110°C " 6 " %Cl = 32.6

Table 6.3. Analytical Data for Caesium Bromomolybdate(2.5)

A/Mo	% Mo	% Br	% Cs	Br:Mo	Oxid. No.	Yield
3:2	14.8	52.4	-	4.25	2.76	-
3:2	15.3	52.4	-	4.10	2.75	70
3:2	14.9	49.5	30.5	3.99	2.59	65
3:2	15.2	52.4	32.3	4.13	2.49	63
3:2	15.2	50.3	31.5	3.97	2.57	63
Theory	15.6	52.0	32.4	4.00	2.50	-

Table 6.4. Analytical Data of Rubidium Bromomolybdate

A/Mo Atomic Ratio	% Mo	% Br	Br:Mo	Oxid. No.	Yield
3:2	16.7	59.3	4.26	3.1	20-30%
"	16.1	57.9	4.31	3.1	"
"	16.5	58.6	4.26	3.1	"
"	16.5	58.8	4.28	3.1	"
"	16.2	58.1	4.30	3.0	"
"	16.2	59.5	4.40	3.1	"
"	16.2	58.6	4.33	3.0	"
5:1	16.4	54.6	4.00	2.8	53
10:1	15.3	53.4	4.19	2.4	53
10:1	16.6	54.5	3.99	2.4	62
$Rb_3Mo_2Br_8$	17.6	58.8	4.00	2.5	-
$Rb_3Mo_2Br_9$	16.4	61.7	4.50	3.0	-

recrystallisation yields the monomeric $Rb_2[Mo^{III}Br_5.H_2O]$ in all cases.

Found: Mo = 15.0%, Br = 59.5%; Br/Mo = 4.8; Oxid. No. = 3.1

Calcd. for: Mo = 14.0%, Br = 58.5%; Br/Mo = 5.0; Oxid. No. = 3.0

$Rb_2[Mo^{III}Br_5.H_2O]$

Other species may possibly exist e.g. $Rb_4Mo_2Br_9$ and $Rb_2Mo_2^{III}Cl_8$, but in larger excesses of rubidium the species $Rb_3Mo_2Cl_8$ predominates.

The further possibility exists that the preparation yields a non-stoichiometric phase.

(2) Formulation

The discovery of compounds of oxidation number 2.5 has attracted our close attention to ensure that this oxidation number is genuine. It is possible that these compounds contain molybdenum in two different oxidation numbers e.g. +2 and +3 and may be crystalline double complexes. The apparent molybdenum oxidation number of $K_6Mo_3Cl_{12}$ in hydrochloric acid has been measured with respect to time and acid strength(11). The rate of molybdenum oxidation increases with acid concentration and at a high concentration a terminal oxidation number of 2.5 is quickly reached. This observation is only explicable by the presence in solution of individual molybdenum species of oxidation number 2.5, not a mixture of oxidation states.

It is of interest to note that a number of niobium(32) and technetium(39) halogeno compounds have been reported in which the oxidation number is 2.5.

The compounds were confirmed to be genuine by the eventual successful recrystallisation of the rubidium, caesium and triphenylphosphonium chloromolybdates(2.5) with analytical figures as good or better than the starting materials. The caesium compound gives small irregular flakes, and the rubidium compound hexagonal plates. The bromomolybdates(2.5) quickly decompose in hot hydrobromic acid to produce $A_2[MoBr_5.H_2O]$ (A = Rb, Cs).

Halogenomolybdates(2.5) display a quite general insolubility in non-aqueous solvents, and whilst dissolving in water and hydrohalic acids are obviously decomposed by these, even in the absence of oxygen, at a rate dependent on the acid strength. Thus nothing can be learned directly of the solution phase degree of polymerisation.

The initial report(40) of the preparation of these compounds proposed a tetrameric formulation. This proposal, based on magnetic evidence, was made before a clear theory of "metal cluster" formation had been developed. It is now recognised that molybdates(2.5) are most unlikely to have such a tetrameric formulation, and would, in preference adopt for a Cl:Mo coordination number of 6, a dimeric structure displaying just one Mo-Mo contact of normal distance i.e. ≈ 2.7 Å, although a somewhat less likely but not impossible alternative would be a dimer of the $[Re_2Cl_8]^{2-}$ type with a very short Mo-Mo distance.

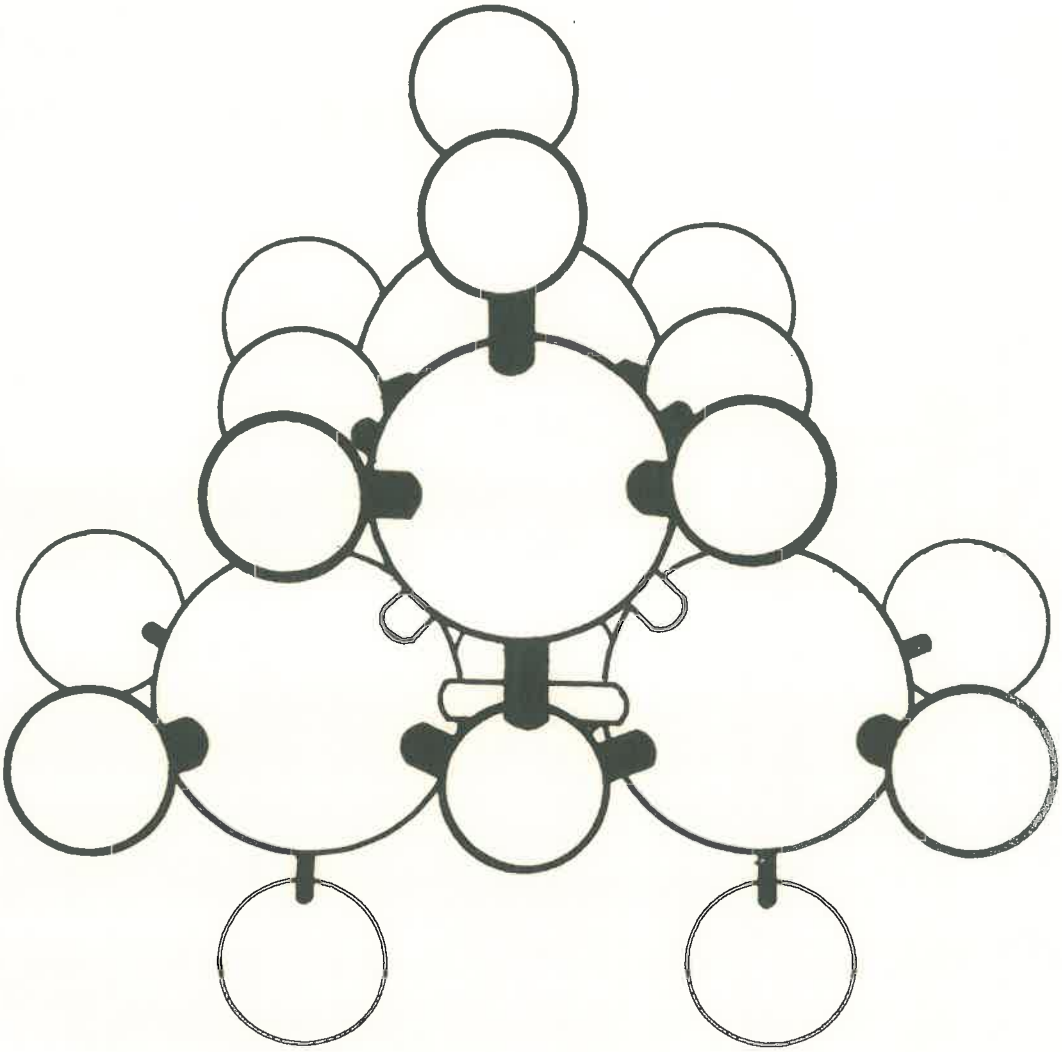
(3) Evidence for Structure

(a) Magnetic: If it is assumed that these compounds would display the minimum number of unpaired electrons (i.e. 1, 0 and 1 for dimers, tetramers and hexamers respectively) and that a spin only behaviour is given by such electrons, then the μ_{eff} would be ~ 1.2, 0 and ~ 0.7 B.M. for Mo_2, Mo_4 and Mo_6 compounds. The measured values are 0.41, 0.53 and 0.41 B.M. for the caesium and rubidium chloromolybdates and the caesium bromomolybdate respectively.

Since a feasible structure for an Mo_6X_{24} complex seems unlikely, the magnetic evidence suggests a tetrameric formulation. Fig. 7 shows a plausible structure of the Mo_4X_{16} group and indicates its derivation from the Mo_3X_{13} unit.

(b) Conductivity and Molecular Weights: These measurements(12) on the triphenylphosphonium compound were hampered by the decomposition of compound in solution. The conductance data is inconclusive while the molecular weights obtained are best interpreted on a tetrameric formulation.

The proposed structure of the Mo_4Cl_{16} group.



Large circles – Mo
Small circles – Halogen

FIG. 7.

(c) X-Ray Crystal Structure: A preliminary X-ray crystal structure determination(4) of the triphenylphosphonium compound indicates that tetramers are unlikely.

(d) Spectra: The solid state and solution spectra of rubidium chloromolybdate(2.5) were recorded. The results are given in Table 6.5 and Fig. 8, as well as a comparison with the spectra obtained for caesium chloromolybdate(2.5)(11). It is now observed that the absorption spectra in 8 M hydrochloric acid for chloromolybdates(2.5) are very similar to that reported for $K_3W_2Cl_9$(41). This may arise through the presence in solution of the equilibrium

$$Mo_2Cl_8^{3-} + Cl' \rightleftharpoons Mo_2Cl_9^{4-} .$$

The behaviour of chloromolybdates(2.5) in solution is rather complex. The species present in high acid concentration is most likely $Mo_2Cl_9^{4-}$, but it is suspected that in dilute acid solution a different, oxidimetrically unstable, form may exist.

(e) Powder Photographs: The X-ray powder diffraction patterns bear a close resemblance to the patterns of $K_3W_2Cl_9$ and $Rb_3W_2Cl_9$. Table 6.6 lists the d spacings of some halogenomolybdates(2.5) together with those of $K_3W_2Cl_9$(42) and $Rb_3W_2Cl_9$. The photograph of

Table 6.5. Electronic Absorption Spectra of Caesium and Rubidium Chloromolybdates(2.5)

Medium	$Rb_6Mo_4Cl_{16}$			$Cs_6Mo_4Cl_{16}$ (11)		
	Feature	λ (KK)	ϵ_m	Feature	λ (KK)	ϵ_m
1 M HCl	P	46.4	21400	P	46.0	21500
	S	~34.0	-	S	~35.3	~2100
	P	27.0	1270	P	26.3	1260
	S	~19.4	-	P	19.4	360
	P	15.0	175	P	15.1	300
8 M HCl	P	42.2	20500	P	47.4	40000
	S	~34.0	-	P	42.0	60000
	P	23.6	2770	P	23.6	3300
	S	~19.0	-	S	19.4	270
	P	13.2	238	P	13.2	190
KCl Disc	P	22.4	-	P	22.2	5200
	S	~19.0	-	S	18.8	4600
	P	14.5	-	P	14.3	3400
Nujol Mull	P	23.0	-	P	22.2	-
	S	19.2	-	S	18.8	-
	P	14.4	-	P	14.5	-

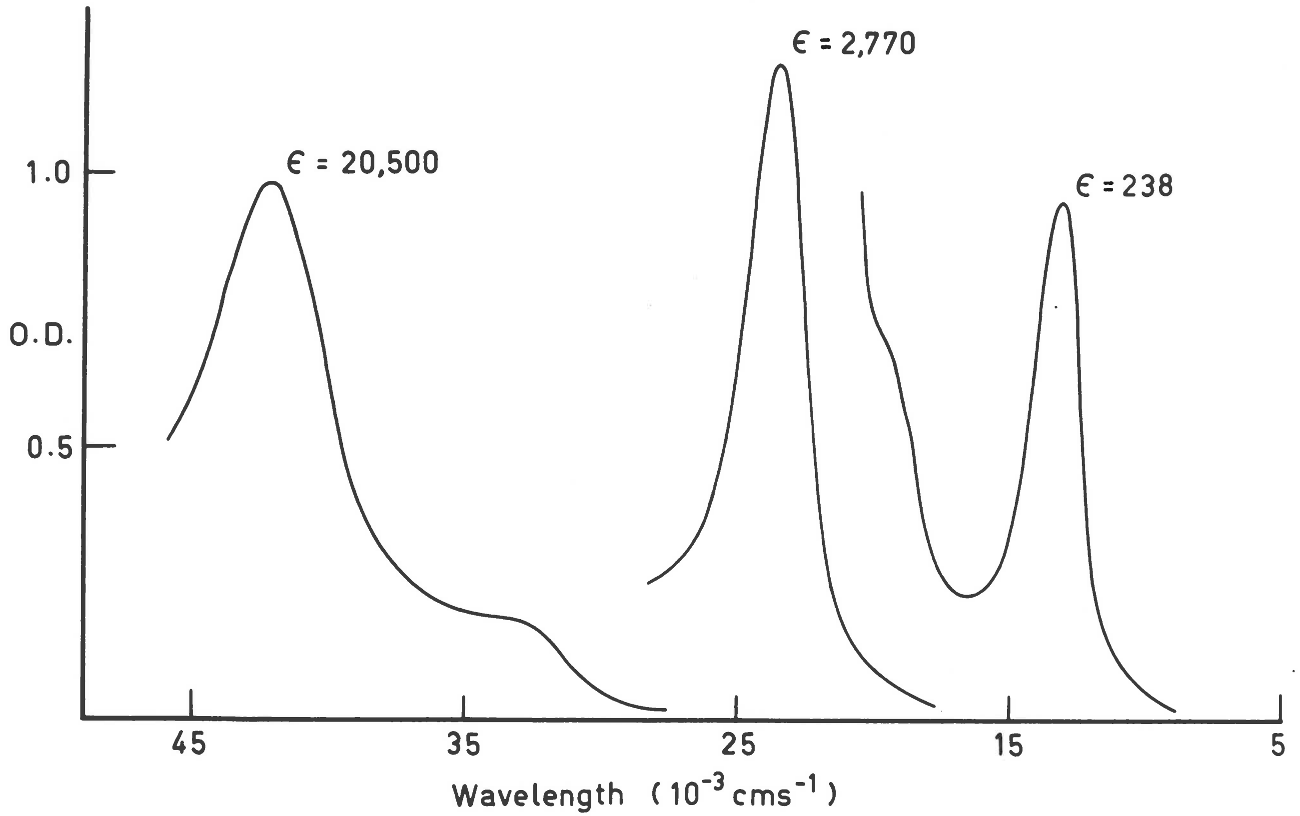

Electronic absorption spectrum of $Rb_3Mo_2Cl_8$ in 8M HCl

FIG. 8.

Table 6.6. X-Ray Powder Diffraction Data for Molybdenum(2.5) and Tungsten(3.0) Halides

h k l(42)	$K_3W_2Cl_9$(42)		$K_3W_2Cl_9$		$Rb_3W_2Cl_9$		$Rb_3Mo_2Cl_8$		$Cs_3Mo_2Cl_8$		$Cs_3Mo_2Br_8$	
	d	Int	d	Int	d	Int	d	Int	d	Int	d	Int
			8.29	4	8.34	8	8.26	7	8.58	m		
			7.89	8								
			6.17	2	6.28	2	6.10	2	6.40	s	6.55	w
			5.79	10	5.89	9	5.75	8	6.02	s	6.15	w
			4.91	1					5.12	s		
103 004	4.06	w	4.01	2	4.14	3	4.08	6	4.24	s	4.37	w
110	3.59	s	3.57	6	3.63	8	3.55	9	3.70	v.s.	3.80	s
104	3.39	v.w.	3.36	1	3.46	3	3.42	1	3.56	w		
112	3.28	m	3.26	4	3.32	4	3.27	2	3.41	v.w.		
200	3.11	v.w.	3.09	1			3.09	1				
201	3.05	w	3.02	2								
113	2.99	w	2.96	2								
202	2.90	w	-	-								
105	2.87	v.s.	2.85	8	2.93	10	2.91	10	3.01	v.s.	3.10	v.s.
203 114	2.69	s	2.68	7	2.74	7	2.75 2.69	3 10	2.86 2.79	w v.s.	2.92 2.88	w v.s.
106	2.48	m	2.46	7	2.51	7	2.48	8	2.57	v.s.	2.65	v.s.
204	2.46	m	-	-								
120 210	2.35	v.w.	-	-								

(continued)

Table 6.6 (contd.)

h k l(42)	$K_3W_2Cl_9$(42)		$K_3W_2Cl_9$		$Rb_3W_2Cl_9$		$Rb_3Mo_2Cl_8$		$Cs_3Mo_2Cl_8$		$Cs_3Mo_2Br_8$	
	d	Int	d	Int	d	Int	d	Int	d	Int	d	Int
121 211	2.32	s	2.30	6	2.35	4	2.31	4				
122 212	2.25	v.w.	-	-								
205	2.24	m	2.23	6	2.28	5	2.26	6	2.34	m	2.43	m
107	2.17	m	2.16	8	2.21	6	2.21	4				
116 123 213	2.15	s	2.15	8	2.19	2	2.16	4	2.23	m	2.30	m
300	2.07	w	2.07	2	2.09	1	2.12	1	2.17	m	2.21	m
206	2.04	w	2.03	2	2.07	2	2.06	5	2.10	v.v.w.		
008	2.02	v.w.	2.01	2	2.03	1						
302	2.01	v.w.	2.00	2			2.00	1	2.03	v.v.w.		
303	1.94	-	-	-								
108	1.92	w	1.92	5	1.97	6	1.96	6	2.03	m	2.09	m
125 215	1.90	m	1.89	5	1.92	5	1.91	6	1.98	m	2.04	m
207	1.86	m	1.85	7	1.89	5	1.88	6	1.94	m	2.01	m
220	1.79	w	-	-	1.80	8	1.82	10	1.85	s	1.92	s

$K_3W_2Cl_9$ has been re-measured to ascertain any lines not reported by Brosset.

The spectra and the diffraction data are the most reliable evidence and it must be concluded that these halogenomolybdates(2.5) are dimeric with the W_2Cl_9-type structure. The theory suggests the most likely structure has m:n values of 1:6. The W_2Cl_9-type structure satisfies this combination. However, the preparation of ligand deficient derivatives of this structure is quite anomalous and unexpected. There seems to be no apparent reason why Mo_2X_8 species should form in preference to Mo_2X_9 species.

The possibility that a water molecule may occupy the "ligand deficient" position, thus effectively raising the number of ligands to nine, has been examined. There is no evidence for the water molecule in the infra red spectrum. Additionally, the unit cell dimensions have been determined for samples of the caesium chloromolybdate. The experimentally determined(11) value for the density of this compound was used to calculate the number of formula units in the unit cell. The result of 1.93 indicates that there are two dimeric units per unit cell. Moreover, any increase in the molecular weight e.g. by the addition of a water molecule, decreases this value to one outside the limits of experimental error. Table 6.7 lists the unit cell parameters of some halogenomolybdates compared with the tungsten(III) compounds.

Table 6.7. Unit cell Parameters of Halogenomolybdates(2.5)

Compound	a (Å)	c (Å)
$Rb_3Mo_2Cl_8$	7.15	16.32
$Cs_3Mo_2Cl_8$	7.36	16.98
$Cs_3Mo_2Br_8$	7.66	17.48
$Rb_3W_2Cl_9$ (42)	7.24	16.95
$Cs_3W_2Cl_9$ (42)	7.35	17.06

(4) Properties

The properties of halogenomolybdates(2.5) are very similar to those of halogenotrimolybdates(II). The room temperature magnetic moment of rubidium bromomolybdate prepared from small excesses of rubidium chloride was 1.3 B.M. per Mo atom, (cf. $Rb_2[MoBr_5.H_2O]$: Found = 3.72 B.M. per Mo atom) which is consistent with considerable m-m bonding occurring.

A spectroscopic investigation of these bromomolybdate samples yielded the results listed in Table 6.8. These results are not inconsistent with the samples containing both $Rb_3Mo_2Br_8$ and $Rb_3Mo_2Br_9$, which is found to have peaks at 18.0 KK (ϵ = 680) and 22.0 KK (ϵ = 380) in 8 M HBr(12).

Concluding Remarks

Compounds of the type $A_3Mo_2X_8$ (A = Rb, Cs; X = Cl, Br) have been prepared and characterised. The evidence regarding their structure is conflicting. The most reliable evidence indicates they are dimeric with a ligand deficient W_2Cl_9-type structure.

The alkali metal halogenomolybdates(2.5) give small crystals unsuitable for a crystal structure determination. A study of the structure of the triphenylphosphonium compound is under way(4), and the results are awaited with interest.

Table 6.8. The Electronic Absorption Spectrum of Rubidium Bromomolybdate(2.5)

8 M HBr			1 M HBr			Nujol Mull		KBr Disc	
Feature	λ (KK)	ε	Feature	λ (KK)	ε	Feature	λ (KK)	Feature	λ (KK)
P	41.05	41000	P	42.95	30000		-		-
S	~38.0	~34000	-	-	-		-		-
S	~34.0	~18000	P	34.05	12000		-		-
S	~31.0	~13000	P	30.60	8000		-		-
P	22.6	2520	S	~23.0	~1500	P	21.7	P	21.7
P	17.95	440	P	17.9	1170	P	17.9	S	~18.0
P	12.7	230	P	15.4	575	P	13.8	S	~14.0

Experimental

Preparation of Halogenomolybdates(2.5)

These compounds can be prepared by two methods. The first involves the oxidation of halogenomolybdates(II) in hydrohalic acid solution, and the second, the precipitation from oxidised diacetate/hydrohalic acid solutions. The latter method, using homogeneous reaction mixtures is preferred.

Method (a): Crushed molybdenum(II) acetate was added to a solution of concentrated hydrohalic acid, containing stoichiometric amounts of the appropriate alkali metal halide. The resulting bright violet solution slowly turned amber green and the insoluble halogenomolybdate(2.5) precipitated. When A/Mo ratios > 2 were used in the preparative mixtures, the halogenomolybdate(II) was formed and the solution was shaken for 2-4 hours by which time the molybdenum(II) compound decomposed to produce the required halogenomolybdate(2.5). The precipitate was collected by filtration, washed with several aliquots of cold acid, acetone, diethyl ether and dried in vacuum at room temperature.

The chloromolybdates(2.5) were recrystallised by gentle warming in concentrated A.R. HCl. Prolonged vigorous heating produced the monomeric $A_2[MoCl_5.H_2O]$.

Method (b): Solutions of molybdenum(II) acetate in concentrated hydrohalic acid were allowed to age until the amber green solution appeared. Acid solutions of the appropriate cation were used to precipitate the halogenomolybdates(2.5) which were worked up as described above.

The analytical methods and physical techniques used were similar to those described in Chapter 2.

Chapter 7. The Reaction of Hydrated Rhenium Dioxide with Carbon Tetrachloride at High Temperature

Introduction

The preparation of β-$ReCl_4$ has not been successfully repeated since its unexpected delivery from a commercial source. The compound has already displayed some interesting chemistry and it is worthwhile to investigate other methods of preparation so that further study is not frustrated by lack of starting materials.

β-$ReCl_4$ was prepared by the thermal decomposition of rhenium(V) chloride under nitrogen at 350-375°C. Subsequent attempts(8) to repeat this preparation produced only Re_3Cl_9 under these conditions, and apparently the exact conditions of its preparation remain unknown. The preparation of α-$ReCl_4$ has been re-examined in Chapter 3.

It is possible that the appearance of these different forms depends on the formation temperature, and it was considered worthwhile to investigate the chlorination of rhenium dioxide at high temperature as a means of synthesis of β-$ReCl_4$.

The production of anhydrous transition metal chlorides by chlorination of oxides with CCl_4 in a bomb is well established(43), although the method is likely to give oxychlorides in addition. In general terms the following reaction occurs:

$$M_2O_n + nCCl_4 \rightarrow 2MCl_n + nCOCl_2$$

The chlorination of rhenium(VII) oxide produced rhenium pentachloride(44). The reaction of hydrated rhenium(IV) oxide with CCl_4 at high temperature and pressure in a steel bomb has been studied.

Results and Discussion

(1) Preparation

The reaction has been carried out under a variety of conditions over forty times, but it must be concluded that this method of preparation is unsatisfactory. Table 7.1 lists the preparative and analytical data for the 19 samples for which both chlorine and rhenium figures were determined. In the remaining samples the chlorine content varied considerably but in most cases was between 30-40%.

The products generally display low total rhenium and chlorine content, usually > 90%, and contain several percent of carbon. The Cl:Re ratio varies from 3.0 to 4.3 with a reasonable proportion of samples giving ratios close to 4.0.

As expected from the wide variation in composition, the materials give a number of different X-ray powder diffraction patterns but none of them resemble α-$ReCl_4$. It has not been possible to verify if these high temperature reaction products contain β-$ReCl_4$ directly since it appears(45) that a powder photograph of the

Table 7.1. Preparative and Analytical Data for β-$ReCl_4$

Sample	Time of heating (hours)	Temp. °C	% Cl	% Re	Cl:Re	C	H
1	4	340	43.9	55.2	4.2	-	-
2	6	340	41.6	56.6	3.9	-	-
3	6	340	45.0	55.3	4.3	-	-
4	6	340	37.9	47.6	4.2	4.1	0.6
5	6	340	37.5	47.0	4.2	3.8	0.8
6	6	340	35.0	48.7	3.9	4.3	0.4
7	6	340	35.0	49.6	3.7	3.2	0.6
8	6	300	40.0	61.2	3.4	-	-
9	5	300	37.1	63.8	3.1	-	-
10	6	280	37.1	49.2	4.0	7.6	0.3
11	6	280	36.6	48.7	3.9	7.3	0.5
12	6	280	39.6	60.6	3.4	0.9	0.5
13	6	280	38.3	64.0	3.1	0.8	1.1
14	6	280	37.4	58.8	3.3	1.9	1.0
[a] 15	7	250	367	63.4	3.0	-	-
16	7	250	36.7	60.8	3.2	-	-
17	6	250	41.7	54.2	4.0	-	-
18	6	250	39.6	54.1	3.8	-	-
19	6	250	39.4	55.6	3.7	-	-

[a] Samples 15-19: Dioxide from Zn/HCl reduction of $KReO_4$.

original β-$ReCl_4$ is not available and no intensity data has been published to facilitate the comparison of our powder photographs with the published$^{(22)}$ unit cell data.

Nonetheless, the CCl_4-$ReO_2.2H_2O$ reaction gives an appreciable quantity of some rhenium chloride which undergoes every reaction published$^{(8)}$ as characteristic of β-$ReCl_4$. Table 7.2 lists the derivative compounds prepared from the high temperature chlorination products.

The products from the bomb are usually contaminated by a black insoluble carbonaceous impurity. This black material causes no difficulty in the solution studies since it may be removed by filtration.

It is possible that the samples contain some oxychlorides of rhenium, but there are grounds to believe this is not the case. The infra red spectrum from 4000-650 cm^{-1} does not contain any absorption bands attributable to either bridging or terminal oxygen groups.

The physical and chemical properties of these materials do not resemble those of the two known$^{(46)}$ oxychlorides of rhenium viz. ReO_3Cl (m.pt. = 4.5°C) and $ReCl_4O$ (m.pt. ≈ 30°C), although some of the analytical figures are not inconsistent with the formulation $ReCl_4O$.

Table 7.2. Derivatives Characteristic of β-$ReCl_4$ and Obtained with the Product of CCl_4-$ReO_2.nH_2O$ at High Temperature

Derivative	Yield (%)		% Composition				
	Found	Reported(8)	C	H	N	S	Cl
$[(nC_4H_9)_4N]_2Re_2Cl_8$	36	39	33.7	6.6	2.7	-	24.4
Required			33.6	6.4	2.5	-	24.9
$[(nC_4H_9)_4N]_2Re_2Cl_9$	46	-	32.7	6.0	2.7	-	26.5
Required			32.7	6.1	2.4	-	27.2
$[(C_6H_5)_4As]_2Re_2Cl_8$	50	46	-	-	-	-	-
$[(C_6H_5)_4As]_2Re_2Cl_9$	44	52	-	-	-	-	-
$ReCl_3(tu)_3.{}^1/_3(CH_3.CO.CH_3)$ [a]	-	-	8.2	3.4	15.3	17.8	18.8
Required			8.9	2.6	15.3	17.8	19.7
$ReCl_3(C_6H_5)_3P$	32	50	38.9	3.4	-	-	18.3
Required			39.0	2.7	-	-	19.2
$ReOCl_3.bipy$ [b]	-	-	26.2	2.0	6.1	-	22.5
Required			25.8	1.7	6.0	-	22.9
$ReOCl_3[(C_6H_5)_3P]_2$	32	-	51.0	4.2	-	-	-
Required			52.0	3.6	-	-	-
$(bipy.H)ReOCl_4$	-	-	23.3	2.1	4.9	-	-
Required			23.9	1.8	5.6	-	-
$Re_2O_3(C_5H_5N)_4Cl_4$	-	-	27.5	2.3	5.4	-	-
Required			27.3	2.3	6.3	-	-
Green ppt. from $ReCl_4$-C_5H_5N-C_2H_6O	-	-	16.2	1.9	3.3	-	-
Reported(8)	-	-	18.2	1.9	2.9	-	-

a tu = thiourea

b bipy = 2,2'-bipyridyl

It is possible that the product is an oxychloride not previously reported. However, it is reasonable to expect that such an oxychloride would involve rhenium in a high oxidation state, and would likely be soluble in carbon tetrachloride, whereas the samples used are the CCl_4 insoluble fractions of the reaction. Moreover, for such an oxychloride to display the reactions characteristic of β-$ReCl_4$, it would probably involve a series of complex disproportionation reactions.

In the absence of any evidence to the contrary, it is proposed that this form of $ReCl_4$ present in our materials is the β-form. The method of preparation is unsatisfactory in producing pure $ReCl_4$, but it does provide a useful starting point for examining new derivatives of $ReCl_4$.

(2) Properties and Derivatives

The product from the bomb preparation is a black, microcrystalline solid, which is very easily hydrolysed in air and must be handled in a dry nitrogen atmosphere. The product of this hydrolysis is a black, sticky mass, soluble in acetone, from which may be precipitated rhenium(III) complexes, e.g. $[ReCl_3.P(C_6H_5)_3]_n$.

Purification by sublimation is not possible since the product appears to disproportionate into Re(III) and Re(V) chlorides when heated in a nitrogen atmosphere at ~300°C. It is insoluble in many non-polar solvents, but is soluble, with reaction in acetone, ethanol, methanol, dimethylsulphoxide and hydrochloric acid. The products of the dissolution of these materials are generally dimeric Re(III) species and other oxidised rhenium products, usually Re(V) species (see Table 7.2).

The properties reported(8) for the $Re_2Cl_9^{2-}$ species have been confirmed. Thus, on shaking with acetone or prolonged heating with 12 M HCl, the $Re_2Cl_8^{2-}$ species are produced. The reaction with acetic acid under nitrogen gives dichlorotetraacetatodirhenium(III) i.e. $Re_2(O_2C.CH_3)_4Cl_2$.

Calcd. for $Re_2(O_2C.CH_3)_4Cl_2$: Cl = 10.5%

Found: Cl = 10.5%

(3) Electronic Absorption Spectra

Table 7.3 lists the ultra violet and visible spectra of some rhenium compounds prepared in this study, compared with other data previously reported. Since the $ReCl_4$ is not pure the optical densities and extinction coefficients are slightly low, but they serve to indicate the relative magnitude of the absorption bands.

The spectra obtained are in very good agreement with those published.(8) The spectrum of β-$ReCl_4$ in MeOH/HCl is shown in Fig. 9.

Table 7.3. Electronic Absorption Spectra of Rhenium Compounds

Compound	Solvent	Absorption Maxima (KK) and extinction coefficients or optical densities (in parenthesis)				Ref.
$ReCl_4$	$MeOH/HCl^a$	14.1 (350)	18.4 (184)	~29.0 (sh)	31.1 (3720)	
		36.3 (4270)				
$ReCl_4{}^b$	$MeOH/HCl^a$	14.2 (1.61)	18.7 (0.84)			
β-$ReCl_4$	$MeOH/HCl^a$	13.99 (400)	18.73 (200)	29.85 (sh)	31.55 (sh)	(8)
		36.50 (5000)				
$ReCl_4$	6 M HCl	14.4 (0.06)	19.4 (0.06)	~29 (sh)	32.7 (.75)	
		35.6 (.85)	39.2 (.87)			
$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_9$	$MeOH/HCl^a$	14.0 (1080)	18.5 (790)	~28 (sh)	31.8 (7900)	
		36.70 (14300)				
$[(C_6H_5)_4As]_2Re_2Cl_9$	CH_3CN	14.62 (0.09)	18.35 (0.03)	28.25	31.95 (0.62)	(8)
		36.90 (0.92)^c	37.80 (1.0)^c	38.76 (0.94)^c		
$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$	$MeOH/HCl^a$	14.3 (0.20)	~28 (sh)	32.7 (0.75)	39.2 (1.20)	
$[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$	$MeOH/HCl^a$	14.5 (1530)	32.8 (5650)	39.2 (8840)		(8)(18)

a. MeOH contains a few drops of HCl to prevent hydrolysis

b. Dioxide from Zn/HCl reduction of $KReO_4$

c. Components of a closely spaced triplet

d. Spectrum in CH_3CN shows bands at 27.03 (sh) and 46.3 (13000)$^{(8)}$

The visible spectrum of the product of the $ReO_2.2H_2O/CCl_4$ reaction in MeOH/HCl

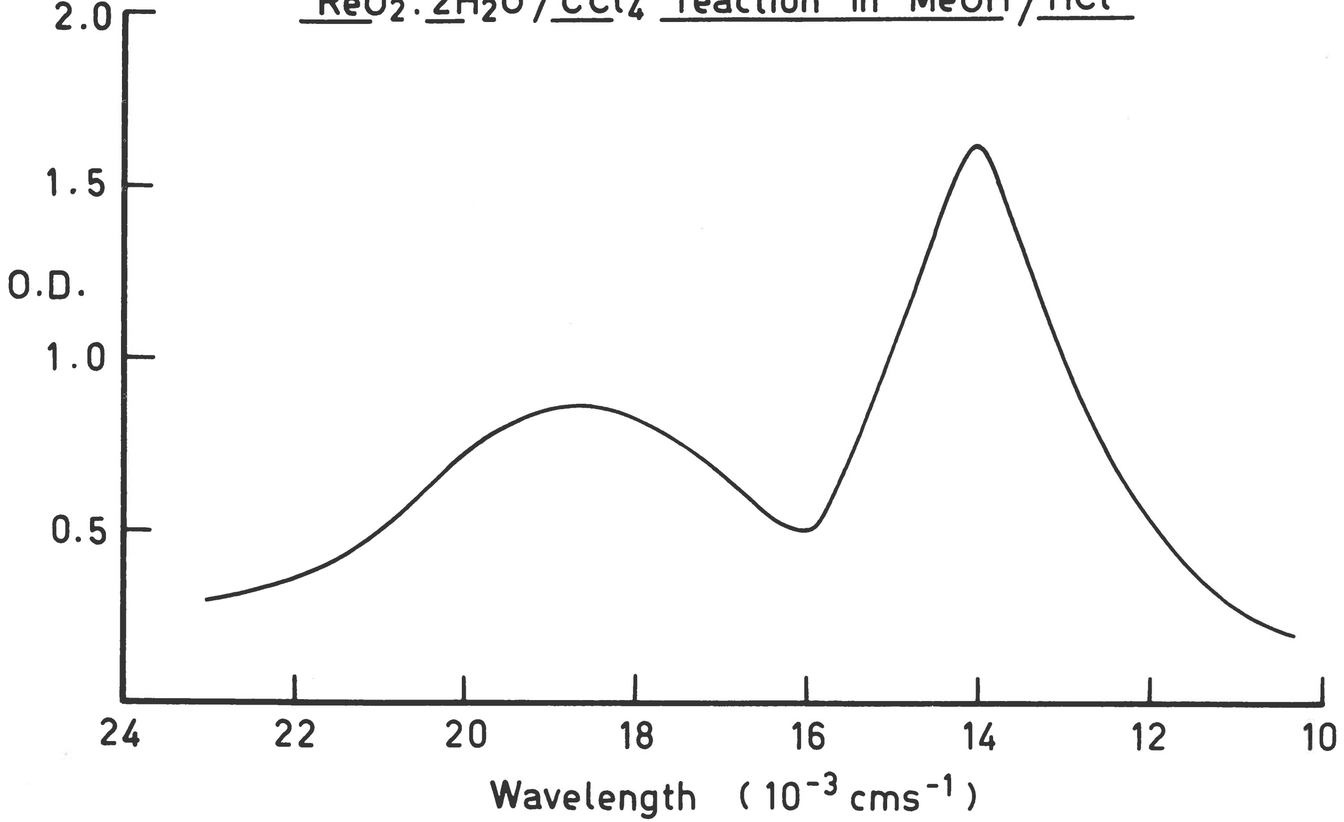


FIG. 9.

Concluding Remarks

The chemical and physical properties of the product from this high temperature chlorination appear to be the same as those reported for β-$ReCl_4$. The method is unsatisfactory in that it does not give a pure product, but it provides a useful means of synthesising new derivatives of β-$ReCl_4$.

Experimental

Preparation of Hydrated Rhenium Dioxide

The dioxide was prepared by the Zn/HCl reduction of potassium perrhenate or by the aqueous hydrolysis of $ReCl_5$. The precipitated dioxide was washed with water, and acetone, and dried in vacuum at room temperature.

The Reaction of Hydrated Rhenium Dioxide with Carbon Tetrachloride at High Temperature

This reaction was carried out using the method of Eperson et al.(43). The heating times were varied from 2-10 hours and the temperature from 250-340°C. The optimum conditions appear to be 5-6 hours heating at 300-340°C. Yields were approximately 90%. The reaction vessel was a modified 300 ccs. stirred autoclave obtained from Autoclave Engineers, Inc., Pennsylvania, U.S.A.

Preparation of Derivatives of β-$ReCl_4$

These preparations were carried out in the same manner as that reported by Cotton et al.(8). The analytical and preparative results are listed in Table 7.2.

Analysis

The elemental analyses were determined by the methods previously described in Chapter 3.

Spectra

The ultra violet and visible spectra were obtained using a Unicam SP800 Spectrophotometer and a pair of 1 cm. matched silica cells.

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PUBLICATIONS

It is intended that the material described in this thesis will be published in due course. Two papers have already been published:

1) Three New Staphylonuclear Chloromolybdates:
   I.R. Anderson and J.C. Sheldon, Aust. J. Chem., 18, 271 (1965);

2) The Preparation of Halogenotrimolybdate(II) Compounds:
   G.B. Allison, I.R. Anderson and J.C. Sheldon,
   Aust. J. Chem., 20, 869 (1967).

A paper consisting of the work described in Chapters 3 and 7 has been submitted for publication. It is anticipated that the work on the halogenomolybdates(2.5) will be a contribution to a combined paper from these laboratories and the preparation of β-$MoCl_2$ will constitute a note when more details of its structure become available.