Studies in the complex chemistry of molybdenum

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"STUDIES IN THE COMPLEX CHEMISTRY OF MOLYBDENUM"

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A Study of various complexes of molybdenum (III) and (IV) has been made and various physical properties have been investigated.

Complex Halides: The magnetic moments of the complex halides show that molybdenum is trivalent with three unpaired electrons. From these moments the use of $4d^2\ 5s\ 5p^3$ orbitals is indicated for octahedral structure. The magnetic moment, 3.86 B.M. for $(NH_4)_2 Mo\ Cl_5\cdot H_2O$ is reported for the first time and its structure has been shown to be octahedral. The following compounds have been prepared for the first time: $Li_3\ Mo\ Cl_6\cdot 9H_2O$, anhydrous $(NH_4)_3 Mo\ Cl_6$ and the double salts, $Li_4\ Mo\ Cl_7\cdot 5H_2O$, $K_7\ Mo\ Cl_{10}\cdot 6H_2O$. The compounds $Li_4\ Mo\ Cl_7\cdot 5H_2O$, $(NH_4)_4\ Mo\ Cl_7\cdot 2H_2O$ and $K_7\ Mo\ Cl_{10}\cdot 6H_2O$ have been shown to be double salts involving the octahedral structure $R_3\left[Mo\ Cl_6\right]\cdot x\ R\ Cl$

Complex Cyanides: The cyano complexes are diamagnetic when the molybdenum is trivalent as in $K_4\ Mo\ (CN)_7\cdot 2H_2O$ and tetravalent as in $K Mo\ (CN)_5$, $K_4\ Mo\ O_2\ (CN)_4$ and $K_4\ Mo(CN)_8\cdot 2H_2O$. The white cyanide $K Mo\ (CN)_5$ has been reported for
the first time and its proposed structure is a tetragonal pyramid involving 4d^4 5S orbitals. The black cyanide K_4 Mo^{III} (CN)_7 * 2H_2O being diamagnetic must involve a Mo - Mo bond. It has been shown that this compound decomposes by oxidation to the yellow K_4 Mo (CN)_8, the white K Mo (CN)_5 and KOH. The anhydrous K_4 Mo O_2 (CN)_4 has been reported for the first time and its proposed structure is dodecahedral.

**Oxalato and Carbonato Complexes:** In the oxalato and carbonato complexes the molybdenum has a valency of 4 and the effective magnetic moments are diamagnetic. The oxalato complex (NH_4)_4 Mo (Ox)_8 * 8H_2O has been reported for the first time; with chelation and a co-ordination number of 8 a dodecahedral structure has been suggested involving 4d^4 5s 5p^3 orbitals. The carbonato complex K_6 Mo(CO_3)_5 * 2H_2O has been reported for the first time.

**Thiocyanato Complexes:** Magnetic susceptibility measurements have shown the molybdenum in these complexes to be trivalent with three unpaired electrons.
The following compounds have been prepared for the first time:

\[(\text{NH}_4)_3 \text{Mo(SCN)}_6 \cdot 3\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \] and \[(\text{NH}_4)_2 \text{Mo(SCN)}_5 \cdot 4\text{H}_2\text{O}\]

and it has been shown that both these compounds are octahedral.

**Compounds of Molybdenum III with Bidentate Ligands:**

Chelation complexes with o. phenanthroline and 2:2'dipyridyl have been prepared for the first time:

\[\text{Mo(phen.)}_3 \text{Cl}_3; \text{Mo(phen.)}_3 \text{Br}_3; \text{Mo(phen.)}_3 \text{I}_3;\]
\[\text{Mo(dipy.)}_3 \text{Cl}_3; \text{Mo(dipy.)}_3 \text{Br}_3; \text{Mo(dipy.)}_3 \text{I}_3;\]

The magnetic susceptibilities indicate three unpaired electrons in all of these compounds and it has been shown that \[4d^2 5s 5p^3\] orbitals are used for octahedral structures.
SECTION 1.

A. General Review

Molybdenum is an element of sub-group VIA of the Periodic System. Its atomic number is 42; atomic weight, 95.95(1). Sidgwick (2) records (p.1028) that molybdenum was discovered by Scheele in 1778, in molybdenite MoS₂. However, Killeffer and Linz (3) p.195, report that in 1764 Cromwell Mortimer, Secretary to the Royal Society, published a second edition of a work by John Andrew Cramer in Latin and estimated to be written in the early 1600's dealing with "molybdena".

Physical characteristics of molybdenum, such as density, melting point, boiling point and electrical resistivity lie between those of chromium and tungsten. Molybdenum has, like the other elements of sub-group VIA a maximum positive oxidation state of 6 besides lower oxidation states. Molybdenum forms compounds having positive oxidation states of 2, 3, 4, 5 and 6. Chromium however, forms compounds of a more limited number of oxidation states 2, 3 and 6. Chromium shows marked differences between these oxidation states, +2 being basic, +3 is amphoteric and +6 is acidic. The chromous salts are strong reducing agents and the chromates in
acid solutions are powerful oxidising agents. This diversity does not exist with molybdenum. The quinquevalent molybdenum has been used as a reducing agent for the determination of ferric ion (4) and in the potentiometric titration of iodate, bromate, dichromate and vanadate (5).

Chromium forms simple ions corresponding to Cr\(^{++}\) and Cr\(^{+++}\) whereas the lower valencies of molybdenum are largely non-ionised, for example, water insoluble Mo\(_6\) Cl\(_{12}\) and Mo Cl\(_3\). The molybdenum (IV) ions do not exist in any stable form but the uncomplexed tri-positive ion appears to be capable of existence in aqueous solutions as in Mo Cl\(_3\) when a solution of molybdic acid in hydrochloric acid is electrically reduced.

Chromium (III) is the most stable state of chromium but molybdenum (VI) is the most stable of the oxidation states for molybdenum. The chemistry of this (VI) state is complicated by the formation of isopoly and heteropoly anions. Chromium does not give these poly and hetero compound formations.

Ions such as [H\(_3\) Mo\(_6\) O\(_{21}\) \(\text{aq.}\)]\(^3-\), [Mo\(_8\) O\(_{26}\)]\(^4-\), [Mo\(_{12}\) O\(_{40}\)]\(^8-\) have been established by X-ray methods (6) (7) (8).
These indicate the possible complexity of molybdates of molybdenum (VI).

Carpeni (20) says that the constitution of molybdate solutions depends on the concentration of Mo O₃, the pH, the ionic strength, age of solution and the temperature; and that at concentrations of Mo O₃ below about 0.0003M there is only one species Mo O₄³⁻ over the whole range of pH.

Molybdenum Blue has been found from analytical values to have various compositions and these have depended on the manner in which the molybdenum blue has been produced. In all preparations of molybdenum blue the ratio of molybdenum to oxygen is greater than 1:25 but less than 1:3. (3)(9)
The blue material is colloidal (13). Tungsten forms mixed oxides of tungsten blue which are probably similar.

Molybdenum forms halides in all states but not with all halides in all states. The highest valency state of molybdenum for the fluoride is six to give Mo F₆ for the chloride it is five, the pentachloride Mo Cl₅, and for the bromide it is four to give Mo Br₄.
Mo I₂ has been produced but the tri- and tetra-iodides are not certain by direct halogenation. The halide
can be interchanged under suitable conditions of temperature (10).

In contrast to molybdenum both tungsten and uranium form hexachlorides. Chromium forms $\text{CrF}_6$, $\text{CrF}_5$. The other halides form $\text{CrCl}_3$, $\text{CrI}_3$ with chromium (III). The halides of chromium (II) are also known. Wartenberg has claimed the isolation of $\text{CrCl}_4$; it is very unstable, decomposing at $-80^\circ \text{C}$, (Sidgwick p.1009) (2).

Molybdenum forms complex halides, complex cyanides and complex thiocyanates. Salicylates, oxalates and complexes of oxo and dioxo types have been isolated.

Chromium, molybdenum and tungsten form white stable crystalline metal carbonyls of the type $\text{Mo(CO)}_6$.

Tungsten, molybdenum and chromium form oxysalts and the presence of oxygen in many of the complexes formed from these elements is common.

The electrolysis of molybdenum and tungsten trioxide acid solutions is markedly different from that of the corresponding chromium trioxide. Chromium trioxide furnishes oxygen at the anode and hydrogen and chromic chromate at the cathode. Forbes and Leighton (15), in their studies of cathodic reduction of chromic acid to a chromic salt, found that light had an effect on the electrochemical yields.

Electrolysis of the molybdenum trioxide
in acid solution does not exhibit sensitivity to light. Molybdenum (VI) can be reduced with a variety of substances; Zinc reduces molybdenum (VI) to molybdenum (III) in hydrochloric acid or sulphuric acid. Finely divided aluminium, zinc, iron, copper, lead but not mercury, will reduce molybdenum to molybdenum blue. Stannous chloride will reduce molybdenum (VI) to (V) and no further. It is in the (V) state that molybdenum gives the characteristic blood-red colour with thiocyanate

\[
\text{Mo(\text{SCN})}_5
\]  

The reduction with stannous chloride has been verified by experiments, (16). Mercaptans such as thioglycollic acid will reduce molybdenum to the molybdenum (III) state, (16).

Acid solutions of molybdenum trioxide or a molybdate are reduced by most soluble reducing agents to a blue compound although some will reduce beyond this stage. Hydriodic acid solutions will produce a blue compound but hydrobromic acid will not. Other reducing agents include sulphur dioxide, hydrogen sulphide, hydrazine, dextrose, tertiary arsine and zinc amalgam. The optimum pH for the formation of molybdenum blue is around 4.

The effect of arsine on molybdenum trioxide to give molybdenum blue has been reported by Ehrenfeld 1895.
and earlier still by Ehrlaub in 1857. In early experimental work (not included in this thesis) acid solutions of molybdenum trioxide were reduced to a blue precipitate with diphenyl methyl arsine. Analysis of the blue precipitate showed that some arsine had been complexed but very little, the larger amount of product being molybdenum blue.

When molybdous chloride Mo Cl₂ is treated with concentrated hydrochloric acid a compound of the formula H Mo₃ Cl₇ . 4H₂O is obtained, (22). In alcohol medium three of the seven chloride (23) ions can be precipitated at once by silver ions. It is probable that this compound contains a polynuclear unit. Brosset (24) has shown by analysis of X-ray diffraction data for the solid Mo Cl₄ (OH)₂ (H₂O)₈ that the polynuclear Mo₆ Cl₈⁺ is present. An analogous unit presumably functions in the chemistry of the corresponding complex bromine compounds, (25).

The affinity of molybdenum (V) for chloride ion is apparently not very great. Measurements of conductances and freezing points (26) of compounds of the type R₂ Mo O Cl₅, R¹ Mo O Cl₄ . H₂O and R¹ Mo O₂ X₂ . 2H₂O show that the Mo (V) - Cl⁻ complex ions are well dissociated. The colour of molybdenum(V) in hydrochloric acid depends on the acid concentration; green for 8M to brown for 4M (27) (28). The analagous
bromine compounds behave in a similar manner, (29).

Thiocyanate complexes of the type $R_2^1 Mo(\text{SCN})_5$ and $R_2^1 Mo_2^2 (\text{SCN})_3$ completely dissociate in dilute solutions (30). The red colour of $\text{Mo (SCN)}_5^-$ fades on dilution. (27).

Like molybdenum (IV), molybdenum (V) forms complexes with cyanide ion of co-ordination number 8. The cyanide is firmly attached in the $\text{Mo (CN)}_8^{3-}$ ion but yields when heated with mercuric chloride, (31).
B. Review of Molybdenum (III) and (IV)

(i) Simple Compounds

The chemistry of the lower oxidation states namely 2, 3, and 4 is very imperfectly known for molybdenum in comparison with chromium. While simple salts of chromium (II) and (III) are well known there is a strong tendency for complex formation, especially in solution, with tervalent chromium; the classic example being isomeric chromic chlorides. With molybdenum (III) and (IV) this tendency to form complex compounds is even more marked and the simple compounds are few in number and in some cases of doubtful existence. Molybdenum (III) does however form simple halides, for example, Mo F₃ (10), Mo Cl₃ and Mo Br₃.

Molybdenum sesquioxide probably does not exist as Mo₂ O₃ and it is more likely a mixture of Mo O₂ and Mo. Magnetic susceptibility measurements should give evidence as to the probability of the molybdenum being in the (III) state or not. Hagg and Magneli (14)(3) in their X-ray investigations failed to demonstrate the presence of Mo₂ O₃ under the conditions of their experiments. Comparable in composition with molybdenum sesquioxide is the sesquisulphide Mo₂ S₃. There does not seem to be any doubt as to this formula. Hydrochloric acid and sulphuric acid do not react with it but warm concentrated nitric acid gives molybdic anhydride.
Oxy halides are formed with molybdenum (III) with fluorine, chlorine and bromine of the type Mo OX (X = halogen). Molybdenum (III) trichloride can be produced by passing dry chlorine gas over reduced molybdenum at 280°C. The product is insoluble in cold water and is virtually impossible to purify. The hydrated molybdenum (III) trichloride can be isolated by precipitating the Mo Cl₃·2H₂O from an electrolysed solution with large amounts of ether, when the product is a copper-red colour and is no longer soluble in water. The magnetic susceptibility of this product, from preliminary experimental work for this thesis was not compatible with purity. The Mo Cl₃ (red) from electrolytic reduction is very stable in solution.

Bromine and chlorine form tetra-compounds with molybdenum (IV). These are both brown to yellowish brown in colour and are very unstable; they react with moisture in the atmosphere and form a brownish solution which turns greenish blue with the formation of oxy halides in which the molybdenum is hexavalent. In the extraordinary cycle of disproportionation which is exhibited by the halides bromine and chlorine, the trichloride of molybdenum, for example, if heated to red-heat in a stream of carbon dioxide or nitrogen will disproportionate into volatile Mo Cl₄ and leave as residue yellow Mo Cl₂ or preferably the hexamer Mo₆ Cl₁₂. A similar process applies to the tribromide (green) which disproportionates into brown or red Mo Br₄.
and leaves a residue of orange Mo Br$_2$. It was found from experimental work that hydrogen does not reduce Mo Br$_4$ to Mo Br$_3$ at temperatures up to 400°C. Because Mo F$_3$ is unstable below 800°C (10) it is most improbable that the tetrafluoride exists as reported by Berzelius (Mellor VolXI p.610). Brewer et al (32)(3) from their thermodynamic calculations, in general agree with experimental observations as to the instability of most molybdenum halides.

(ii) Complex Compounds of Molybdenum (III) and (IV)

The hetero and isopolymolybdates which are so characteristic of molybdenum (VI) have no counterpart in compounds of lower oxidation states. Complexes of molybdenum in the lower valence states generally involve radicals having a pronounced tendency to form anions. These include the halogen, cyanide and thiocyanate complexes of molybdenum. Most of the other groups which form complex anions with molybdenum are "ato" groups and oxo-, dioxo-, or peroxo salts, oxalato-peroxy salts (18)(32) such as K\[\text{MoO}_2\text{C}_2\text{O}_4\]2.5H$_2$O have been reported. This latter compound forms an insoluble additive compound with dipyridyl, K\[\text{MoO}_2\text{C}_2\text{O}_4\text{C}_10\text{H}_8\text{N}_2\]2H$_2$O (21).

No information seems to be available in literature as to the complexing of molybdenum with acetyl acetone, arsines or other similar groupings but one complex with ammonia has been reported by Bucknall, Carter and Wardlaw (33) who formed
formed an unstable \((\text{NH}_4)_2\left[\text{MoCl}_5\text{NH}_3\right]\cdot\text{H}_2\text{O}\) from diammonium molybdenum pentachloride. Two complex molybdenum cations have been reported by Rosenheim, Abel and Lewy \((34)\), \(\text{Mo(NH}_3)_6\text{Cl}_3\) and \(\text{Mo(NH}_3)_4(\text{H}_2\text{O})_2\text{Cl}_3\), but these have not been reinvestigated in recent years.

Some consideration is now given to the lability of the complex ions of molybdenum (III) and (IV).

**Molybdenum (III)**

The affinity of the chloride ion for the molybdenum(III) ion in solution is comparatively small, thus each of the compounds \(\text{K}_2\text{MoCl}_6\left(\text{NH}_4\right)_2\text{MoCl}_5\cdot\text{H}_2\text{O}\), \(\text{KMoOCl}_2\cdot3\text{H}_2\text{O}\) \((33)\) and \(\text{MoOCl}_4\cdot4\text{H}_2\text{O}\) \((35)\) undergoes slow replacement of chloride ion by water or hydroxide ion when dissolved in water. These reactions proceed at measurable speeds. Measurements of osmotic coefficients and conductivities of the solutions \((35\) and this thesis) show that these types of complexes dissolve initially without marked dissociation into chloride ions. As conductivities slowly increase with time slow hydrolysis is indicated.

When salicylate or oxalate ions are added to a solution of \(\text{K}_3\text{MoCl}_6\) colour changes are produced. These changes proceed gradually even when the solutions are heated to 70°C \((33)\). The inertia to substitution of the Mo (III) - Cl\(^-\) is demonstrated also by the fact that the red and green forms of \(\text{K}_2\text{MoCl}_5\) complexes can be formed by the electrolytic
reduction of molybdate in hydrochloric acid (36). The red form is obtained when the acidity is high, 8N, while the green form results at 2 to 4N acid and is the less stable of the two, changing gradually to the red form on standing (37). Wardlaw and Wormell (35) succeeded in isolating a brown solid of composition MoOCl₄H₂O from the red solution and a green solid of the same composition from the green. These solids dissolve, initially with little dissociation but undergo hydrolysis fairly rapidly, the green being the more rapid.

Complex bromides corresponding in composition to the chloro complexes have been prepared. MoOBr₄H₂O dissolves initially with incomplete dissociation, but bromide is released more rapidly then for the analogous chloro complex under similar conditions (38).

The conductance of a solution of $K_3Mo(SCN)_6•4H₂O$ indicates that it contains $K^+$ and $Mo(SCN)_6^{3-}$ ions and that the complex ion does not undergo appreciable dissociation over the time interval of the measurements (39). This behaviour should be attributed to its inertia (slowness of reaction) rather than to its intrinsic stability since $[Mo(SCN)_6]^{3-}$ is converted to ions of the type $[Mo(SCN)_5O\cdot H]^{3-}$ if the solution is warmed to 50 - 60°C for several days (40).

The reaction of cyanide ion with molybdenum (III) usually yields a cyanide complex which contains molybdenum (IV) with
a co-ordination number 8. Young (41) however, succeeded in preparing a compound of the formula $K_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O}$ which presumably contains cyanide ion co-ordinated to molybdenum (III). This substance is soluble in water to form a brown solution which becomes pink on great dilution. On the addition of hydroxide $\text{Mo}_2 \text{O}_3 \cdot n\text{H}_2\text{O}$ is precipitated. Young did not report on the rate of change but the change is fairly rapid (noted during work for this thesis).

There are few complexes containing Mo (III) - $\text{NH}_3$ bonds compared to those of chromium (III). Whether this is due to a lower affinity of Mo (III) for $\text{NH}_3$ or to a faster rate of hydrolysis is uncertain. The difference in the speed of hydrolysis may be an important aspect since even the chromammines dissociate in solution under ordinary conditions.

As with chromium (III) the Mo (III) - N bonds are more sensitive to alkali than to acid. Thus $[\text{Mo(NH}_3)_4 (\text{H}_2\text{O})_2]^{3+}$ and $[\text{Mo(CH}_3 \text{NH}_2)_4 \text{Cl}_2]^+$ have been shown to persist in acid solution, but hydrolyse rapidly in water. $\text{Mo(NH}_3)_6 \text{Cl}_3$ which is formed by the treatment of molybdenum trichloride with liquid ammonia, decomposes in moist air with the evolution of ammonia; concentrated hydrochloric acid produces $\text{Mo(NH}_3)_4 (\text{H}_2\text{O})_2 \text{Cl}_3$ (34).

With pyridine in place of ammonia the complexes show greater resistance to hydrolysis; compounds containing the ion $[\text{Mo(SCN)}_4 \text{py}_2]^-$ can be crystallised from warm water (34).
This fact suggested the use of bidentate ligands such as phenanthroline and dipyridyl to produce stable compounds.

**Molybdenum IV.**

No simple complex ions of co-ordination number 6 are known for this oxidation state. Solids of the type $R_2^1Mo_3O_4(C_2O_4)_3\cdot5H_2O$ which contain molybdenum in the oxidation state $+4$ have been prepared. These dissolve to give polynuclear species, trimers, which yield oxalate ions only at very low concentrations ($4\mu$). The data available from Spittle and Wardlaw (44) do not lead to any definite conclusions about the lability of Mo (IV) -- $C_2O_4^{3-}$ bond. In the complex cyanide of oxidation state $+4$, molybdenum has a co-ordination number 8. The displacement of cyanide ions is slow. Thus a solution of $H_4Mo(CN)_6$ at room temperature persists for a long period of time without change but does decompose on prolonged boiling (45). Similarly, the ion $[Mo(OH)_4(CN)_4]^{4-}$ persists in dilute acid at room temperature but loses hydrogen cyanide in strong acid at $50^\circ C$.

Adamson, Welker and Volpe (46) have studied exchange reactions, as a measure of lability, of radio active cyanide ions with the cyanide bound in various complex ions. For solutions about 0.05M in the cyanide complex ion at $25^\circ C$ and pH = 10, they observed that in Ni (CN)$_4^{3-}$, Pd (CN)$_4^{2-}$, and
Hg (CN)$_4$ the exchange is complete in less than 5 minutes; in Mn (CN)$_6$ it is about 40 per cent in 4 minutes whilst in Co (CN)$_6$, Fe (CN)$_6$, Fe (CN)$_6$, Cr (CN)$_6$ and Mo (CN)$_8$ the exchange is less than 2 per cent in 100 hours.

It appears that there is a discontinuity in rates of displacement reactions dividing the inert and labile classes. Taube (22) has pointed out that the distinction between labile and inert complexes, on the basis of electron structure is sharper for "inner orbital" complexes than for "outer orbital" complexes. Lability of the inner orbital complex appears to occur when there is a vacant orbital in the d sub-group.

The complex ions of molybdenum can be classified as "inner orbital" complex ions. That is the 4d orbitals are enclosed by 5s orbitals and probably 5p orbitals as in 4d$^2$ 5s$^2$ 5p$^3$ whereas an "outer orbital" arrangement would be as S P$^3$ D$^2$.

The occupancy of the 4d orbitals for molybdenum (III) and (V) for octahedral complexes:

- Mo (III) $d^1 d^1 d^1$ D$^2$ S P$^3$
- Mo (V) $d^1 d^0 d^0$ D$^2$ S P$^3$

The complexes of molybdenum (III) are in general more inert than those of molybdenum (V) where there are two unoccupied 4d orbitals. Molybdenum (VI) with none of the 4d orbitals occupied is labile.
The behaviour of the occupancy by an unshared electron in the last available inner d orbital is also exemplified in vanadium (III) and chromium (III) where the simple substitution reactions of V(III) are all rapid and those of Cr (III) are slow. Again, the complex ions of rhenium (IV) with three of the 5d orbitals occupied \( d^1d^1d^1 \) reach equilibrium very slowly with respect to substitution whilst those of rhenium (V) with two 5d orbitals occupied \( (d^1d^1d^0 ..) \) are much more rapid (22).

With \([\text{Mo (CN)}_8]^{4-}\), diamagnetic, and \([\text{Mo (CN)}_8]^{3-}\) with a magnetic moment theoretically corresponding to one unpaired electron (44) the electronic structures are \( d^2 D^4 S P^3 \) for \([\text{Mo (CN)}_8]^{4-}\) and \( d^1 D^4 S P^3 \) for \([\text{Mo (CN)}_8]^{3-}\). Since the inner stable orbitals \((4d)\) are completely occupied slow rates of substitution are expected for these ions and experimental observations show this to be so.

(iii) The Complex Halides of Molybdenum (III)

Early reported methods for the preparation of these complexes have been reported by Chilesotti (47), Foerster and Fricke (48), Wardlaw and Harding (38), Bucknall, Carter and Wardlaw (33), Rosenheim and Li (15) by the electrolysis of molybdenum trioxide in strong hydrochloric acid and then adding potassium chloride to the reduced solution. Foerster and Fricke in their paper on "Electrolytic Reduction of
Molybdenum Solutions" (48) described their preparation of the type \( R_2 \text{Mo} \text{Cl}_5 \) by boiling a reduced molybdenum chloride for a long time over an open flame. Bucknall, Carter and Wardlaw in their preparation of \((\text{NH}_4)_2 \text{MoCl}_5 \cdot \text{H}_2\text{O}\) used Chilesotti's method of adding a smaller amount of ammonium chloride than that required in the preparation of the hexachloro compound and Wardlaw and Harding (38) used a similar method for their preparation of \( R_2 \text{MoBr}_5 \cdot \text{H}_2\text{O} \).

One other type besides the penta and hexa chloro complexes has been reported by Carobbi (49) and that is the heptachloride. He treated a solution of 22.5 g. of ammonium chloride with a solution of molybdenum trichloride and saturated it with hydrogen chloride gas.

The complex halides of molybdenum (III) are of a brick-red colour. They hydrolyse slowly in aqueous solutions but not in acid solutions. This is similar behaviour to that found by Rius and Rodríguez (18) in regard to the peroxy salts of molybdenum and the oxalato peroxy compounds.

Due to hydrolysis of these compounds the molecular weight determinations and conductivity measurements as given by Bucknall, Carter and Wardlaw (33) are not particularly satisfactory methods for the estimation of the number of ions in solution.

The complexes \( K_3 \text{MoCl}_6 \cdot 12\text{H}_2\text{O} \) and \((\text{NH}_4)_3 \text{Mo(SCN)}_6 \cdot 4\text{H}_2\text{O}\) have been measured for magnetic susceptibility by
Bose and Bhar (50) and they found that the effective Bohr magneton number was near to the spin-only value. Ramaseshen and Suryan (51) reported the g values for these compounds as 1.86 and 1.92 respectively (discussed in Section IIA).

Bose (52), Tjabbes (53) (54), Klemm and Steinberg (55) have reported effective moments of 3.7 Bohr magnetons for \( \text{K}_3 \text{MoCl}_6 \cdot 2\text{H}_2\text{O} \) and the thiocyanate \((\text{NH}_4)_3 \text{Mo(SCN)}_6 \cdot 4\text{H}_2\text{O}\). It has been pointed out by Ramaseshen and Suryan (51) that molybdenum (III) shows a sharp resonance spectrum similar to chromium (III) and vanadium (II). These three ions are in the same electronic state \( \text{^4} \text{F}_{3/2} \). Whilst the halide complexes of potassium and ammonia are extremely soluble to give intense red solutions, the caesium one is insoluble and the rubidium one is nearly insoluble (33).

(iv) The Complex Cyanides of Molybdenum

The cyanides of molybdenum are of interest because few cyanides form complexes with tetravalent elements. Besides those formed with molybdenum (IV) there are the cyanides of tungsten of the type \( \text{R}_4 \left[ \text{W(CN)}_8 \right] \) and one of platinum \( \text{Ag}_2 \left[ \text{Pt (CN)}_4 \text{Cl}_2 \right] \) (Sidgwick (2)). Some cyanides of the tervalent elements are also known \( \text{K}_3 \left[ \text{M(CN)}_6 \right] \) \( \text{M = Mn, Fe, Co, Ir, Rh and Cr} \) and one of platinum \( \text{H} \left[ \text{Pt (CN)}_4 \right] \cdot 2\text{H}_2\text{O} \) (Sidgwick (2)), one tervalent cyanide of molybdenum is reported \( \text{K}_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O} \) by
Young (41). The tetravalent complexes are stable. Conductivity measurements plotted against time give an almost straight line curve. Octa-cyanides of the type $R_4^+ Mo (CN)_8$ have been prepared by Rosenheim and co-workers (56), Bucknall and Wardlaw (57), Jakób and Turkiewiez (58) from $K_3^+ Mo Cl_6$ and $Mo O(OH)_3$. That is the molybdenum (IV) in the cyanide complexes has been derived previously from molybdenum (III) and molybdenum (V) and the co-ordination number of molybdenum has been raised to 8 by the CN group. Rawlinson (59) prepared $K_4^+ Mo (CN)_8 \cdot 2H_2O$ by a modified method of Willard and Thickle (60) by the reduction of molybdenum trioxide with hydrazine hydrochloride:

$$2 Mo O_3 + H Cl + N_2 H_4 \rightarrow 2 Mo Cl_4 + N_2 + 6 H_2O$$

The resulting solution was made alkaline with potassium hydroxide and potassium cyanide and boiled. By processes of evaporation under suction, crystallization from alcohol and by drying at 105°C, the hydrous and anhydrous compounds were produced. In contrast to Rawlinson's method are the preparations of Chilesotti (1904), Bucknall and Wardlaw (1927) and Young (1932). The reactions in these processes can be represented:

(a) $4 K_3^+ Mo Cl_6 + 32 KCN + 2H_2O + O_2 \rightarrow 4 K_4^+ Mo (CN)_8 + 24 K Cl + 4 KOH$

(b) $K_3^+ Mo Cl_6 + 7 KCN \rightarrow K_4^+ Mo (CN)_8 + 6K Cl$ (Young).
The cyanide complexes of molybdenum (IV) cannot be titrated directly to molybdenum (VI) with potassium permanganate. A molybdenum (IV) complex can be produced from molybdenum (VI) (work in this thesis) and this lends support to other experimental findings on the oxidation of (IV) to (V). When the aqueous solutions of these complexes are made acid with sulphuric acid and then titrated with permanganate the molybdenum (IV) is oxidised to molybdenum (V). Bucknall and Wardlaw (57) have described this phenomena as an "abnormal" oxidation and Rawlinson (59) used this means of oxidation to produce potassium octacyano molybdate (V).

The co-ordination polyhedron (dodeca-hedron) for $K_4 Mo (CN)_8 \cdot 2H_2O$ has been determined by Hoad and Nordsieck (61) in their X-ray studies of this complex. They claim that the nitrogens are actually at the apices of the dodecahedron (also Wells p.542) (62). The carbon-nitrogen bonds are collinear with molybdenum-carbon bonds. Their mean lengths are $Mo - C$ 2.15A, and $C - N$ 1.15A. (62)(63) (Fig.1, Diagram d.)

By adding cyanide to quinquevalent molybdenum hydroxide Bucknall and Wardlaw (57) prepared potassium tetracyano dioxo molybdate (IV). This is the type referred to by Bucknall and Wardlaw as the red and blue cyanides. The red cyanide becomes blue on dehydration and probably depends on the equilibrium:
The alkali cation in the octocyanoide is replaceable by equivalent proportions of cadmium, thallium (univalent) manganese, pyridinium, and the ammines of silver, copper and nickel (57).
A. A DISCUSSION OF THE SIGNIFICANCE OF MAGNETIC SUSCEPTIBILITIES AND BOND ORBITALS

Early attempts to interpret magnetic susceptibilities in terms of electronic arrangement have been made by Jackson (614), Bose (65), Welo and Baudisch (66) and Sidgwick (67)(68). Sidgwick suggested that the central atom of a co-ordination complex tends to assume the external configuration of the next higher inert gas and that the co-ordinated atoms, groups or molecules are attached by co-valency to the central atom. Welo and Baudisch, and Bose found generally that compounds in which the central atom gave an effective atomic number $Z'$ equal to the inert gas exhibit diamagnetism. They also postulated that compounds with an effective atomic number different from the inert gas configurations exhibit paramagnetism. There are many exceptions to this rule and Selwood (69) quotes as examples $\left[ \text{Ni} (\text{CN})_4 \right]^{--}$ diamagnetic and that the rule would make $\left[ \text{Ni} (\text{NH}_3)_4 \right]^{++}$ paramagnetic.

The effective atomic numbers (E.A.N.) have been derived from Bose's rule:

$$Z' = N + 2p - E.$$  

$Z'$ = E.A.N.; $N$ = atomic number of co-ordinating atom; 
P = co-ordination number; $E$ = primary valency. The E.A.N. for molybdenum in a hexachloro molybdate (III) would be
According to Bose, magnetic moments of the complexes exhibiting paramagnetism is proportional to the difference between the E.A.N.'s and the A.N. of the next higher inert gas. The hexachloro molybdate (III) will then have a magnetic moment of \((54 - 51) = 3\) which places it in the three unpaired electron class.

These empirical rules of Bose will hold for some complexes when the co-ordination is an even number but they fail with others especially when there is an odd co-ordination number. For instance, the heptacyano molybdate (III) with a \(Z'\) value of 53, which would give a proportional magnetic moment of 1 and the pentacyano molybdate (IV) with a \(Z'\) value of 48 and a difference between 48 and Xenon A.N. being 6.

Magnetic measurements applied to the study of complexes is largely due to Pauling (70). Whilst \(s-s\) bonds or \(p-p\) bonds exist, many bonds are a combination of the different types of bonds which Pauling (63) calls hybridization. In the metal with which this thesis is dealing (molybdenum) the bond orbitals are 4d 5s 5p hybrids.
**ELECTRONIC ARRANGEMENTS OF MOLYBDENUM**

*(THE OUTER ORBITALS)*

<table>
<thead>
<tr>
<th>Ground State Mo</th>
<th>4d</th>
<th>5s</th>
<th>5p</th>
<th>5d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(VI)</td>
<td>↑↑↑↑</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(V)</td>
<td>↑</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(IV)</td>
<td>↑↑</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(III)</td>
<td>↑↑↑↑</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(II)</td>
<td>↑↑↑↑</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental work has shown that molybdenum (VI), (IV) and (II) are diamagnetic and molybdenum (V) and (III) are generally paramagnetic. The experimentally determined values for Mo(III) and (V) are in agreement with the calculated "spin" values. The diamagnetism of Mo(II), (IV) and (VI) means that electron pairing occurs and Hund's Rule does not apply. This appears to be characteristic of the second and third transition series as ruthenium (IV) compounds are generally diamagnetic (theoretical value of $\mu = 2.84$, if no pairing) while ruthenium (III) is paramagnetic ($\mu = 1.73$). (71).
Kimball has made a survey of possible stable bond arrangements for d s p bonds which are involved for molybdenum. The bond strengths also increase with increase of the orbital contribution to the hybrid (Wells (62), Pauling (63), Moeller (72)). The spatial arrangement will depend upon the co-ordination number and the number of unpaired electrons. The maximum co-ordination number reported for molybdenum is 8, therefore the available orbitals in the 4d, 5s, 5p and 5d are more than sufficient.

**TABLE I**

Directional Characteristics of Co-valent Bonds

<table>
<thead>
<tr>
<th>Co-valence</th>
<th>Bond Type</th>
<th>Spatial Arrangement</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>d s p^3 or d^3 s p</td>
<td>bi-pyramid</td>
</tr>
<tr>
<td></td>
<td>d^2 s p^2</td>
<td>tetragonal pyramid</td>
</tr>
<tr>
<td>6</td>
<td>d^2 s p^3</td>
<td>octahedron</td>
</tr>
<tr>
<td>7</td>
<td>d^3 s p^3, d^5 s p</td>
<td>face-centred octahedron</td>
</tr>
<tr>
<td></td>
<td>d^4 s p^2</td>
<td>face-centred trigonal prism</td>
</tr>
<tr>
<td>8</td>
<td>d^4 s p^3</td>
<td>dodocahedron</td>
</tr>
<tr>
<td></td>
<td>d^5 s p^2</td>
<td>face-centred prism</td>
</tr>
</tbody>
</table>

Distortion of bond angles occurs in hybrid orbitals. In some instances the deviation from the theoretical is small as in the octocyanide molybdenum complex, [Mo (CN)_8]^4^- (63),
whereas the bond angles for a cube show larger deviations of bond angles (73). It is therefore to be expected that spatial arrangements of co-ordinating groups around the central atom will not be necessarily symmetrical and deviations of bond angles will occur (73).

Magnetic Susceptibility

When a substance is placed in a magnetic field of $H$ oersteds the total magnetic induction $B$ is given by the relation:

$$B = H + 4 \pi I$$

where $I$ is the intensity of magnetism. On dividing throughout by $H$ the equation becomes

$$B/H = 1 + 4 \pi I/H$$

The ratio $I/H$ is known as the "volume susceptibility" and is represented by the symbol $k$. It is this volume susceptibility which is usually measured experimentally but it is more common to express magnetic susceptibility per gram of substance by $\chi$. This is related to volume susceptibility by the expression $\chi = k/\rho$, where $\rho$ is the density of the substance. (74).

For chemical compounds the molar susceptibility is more important and this is obtained by multiplying $\chi$ by the molecular weight to give $\chi M$. 
In the Gouy Method, a cylindrical sample of the material of cross-section A and length 1 (in a glass tube) is suspended from a micro balance so that one end is placed between the poles of an electro-magnet with a magnetic field strength of about 5000 to 10,000 oersteds. The length of the specimen must be such that the field strength $H_2$ at the end of the specimen away from the magnet is negligible compared to the end of the tube in the strong magnetic field $H_1$ between the poles.

The difference in pull $\Delta w$ on the balance, with the magnet off and with the magnet on is measured. The force $F$ acting on the specimen due to the magnetic field is

$$F = \Delta w \times g = \frac{1}{2}(k_1 - k_2)(H_1^2 - H_2^2) A \quad (74)$$

where $k_1$ is the volume susceptibility of the sample

$k_2$ is the volume susceptibility of the surrounding medium (air)

$A$ is the cross-sectional area

$g$ is the gravitational constant.

When $H_2$ is very small compared with $H_1$ the equation can be reduced to

$$k_1 = k_2 + \frac{2\Delta w \times g}{H_1^2 A}$$

To give the mass susceptibility, $k_1$ is replaced by

$\chi \propto$ density, then $\chi = (k_2 V + 2g \frac{V \Delta w}{H_1^2 A})/W \quad (74)$

where $V$ is the volume of the material, and $W$ is the mass of the material.
To avoid using the unknowns \( v, H, \) and \( A \) the Gouy tube may be calibrated with a tube of material of known susceptibility. With calibration of the Gouy tube with a material of known susceptibility the expression reduces to:

\[
\chi = \frac{\lambda + \beta \Delta \omega}{W}
\]

where \( \lambda \) and \( \beta \) are constants for any particular tube and field strength.

\( \lambda \) and \( \beta \) are determined from measurements of a compound such as \( \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \) whose susceptibility is accurately known.

The permanent magnetic moment of a material is of importance in describing the properties of a paramagnetic substance. If a substance with a permanent magnetic moment \( \mu \) is placed in a magnetic field the molecular magnets tend to align themselves parallel to an applied magnetic field and this alignment is resisted by the thermal agitation of the molecules. Identification of the (hypothetical) molecular magnets, with magnetic moments induced by orbital electronic motion, has been deduced by Langevin for molar paramagnetism.

\[
\chi_m = \frac{N\mu^2}{3kT}
\]

(69)

where \( N \) is Avagadro's number

\( \mu \) is the permanent magnetic moment

\( k \) the Boltzmann constant

\( T \) the absolute temperature.
As \( k = \frac{R}{N} \) the above equation can be written
\[
\chi_M = \frac{N^2 \alpha}{3RT}
\]
From this
\[
\alpha = \sqrt{\frac{3RT \chi_M}{N}}
\]

Because the magnetic moment of a particular atom in a compound is of particular interest rather than that of the molecule correction for diamagnetic susceptibilities of all atoms present is made.

that is \( \chi'_M \) for \( \chi_M \) + diamagnetic correction

Substituting \( \chi'_M \) for \( \chi_M \) in the above expression the effective magnetic moment \( \mu_{\text{eff.}} \) of the paramagnetic atom is given as:
\[
\mu_{\text{eff.}} = 2.84 \sqrt{\chi'_M x T} \quad (75) (74)
\]
The magnetic moment is expressed in Bohr magnetons. A Bohr magneton is the unit of magnetism and equals the magnetic moment of an electron assumed to be spinning on its own axis (74).
\[
\mu = -\frac{e \hbar}{4 \pi mc}
\]
when \( l = 1, \mu = 9.272 \times 10^{-21} \text{erg gauss}^{-1} \) (76) (p.273).

The value of \( \mu \) in paramagnetic substances is dependent on temperature. The \( \mu \) value obtained from
\[
\mu = 2.84 \sqrt{\chi'_M x T}
\]
is constant only when \( \chi_M \) is proportional to \( 1/T \). This relationship is expressed by Curie's Law.
\[ \chi = \frac{C}{T} \] (C is a constant) which proceeded Langevin's work by some years (69). Paramagnetic substances generally obey Curie's Law (69) (74), but more often the Curie-Wiess Law \[ \chi_M \propto \frac{1}{(T+\Theta)} \] where \( \Theta \) is a constant (75)(74).

The use of magnetic susceptibility measurements in the study of complexes arises from the fact that electrons used in covalent bond formation are of necessity paired and do not contribute to the permanent magnetic moment of the molecule. The number of unpaired electrons in any complex can be computed because the effective moment is given approximately by

\[ \mu_{\text{eff.}} = \sqrt{n(n+2)} \]

where \( n \) = the number of unpaired electrons.

Unpaired electrons have both spin momentum \( \mathbf{s} \) and orbital momentum \( \mathbf{g} \). Orbital momentum may be effectively quenched, in which case the calculated spin value is almost the same as the experimental value.

When coupling of the spin and orbital momentum occurs it is usually described according to the Russell-Saunders Scheme.

In this the spin moments (\( \mathbf{s} \)) are coupled to give a resultant spin moment \( \mathbf{s} \). The various values of the different electrons are then separately coupled to give a resultant orbital momentum \( \mathbf{l} \). The inner quantum number \( J \) is the
vectorial sum of the two resultants. Therefore $J$ measures the resultant total angular momentum. The largest number of electrons which can occupy any shell is $2(2l + 1)$ when the number of electrons $j$ in any incomplete shell is less than $2l + 1$, the value of $J$ corresponding to the spectrographic ground term is equal to $L - S$.

When $j$ is greater than $2l + 1$ the corresponding value of $J$ is $L + S$ (77).

The magnetic moment $\mu$ of an ion with $j$ electrons is given by

$$\mu_{\text{eff.}} = g \sqrt{J(J+1)}$$

where $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

$g$ is the so-called "splitting" factor for which Lande deduced the above empirical relation (76,p.275).

If it is found experimentally that $g$ lies between 0 and 2 both spin and orbital momenta are involved in the magnetic moment, but when $g = 2$ the magnetic moment arises from spin alone (74,p.382).

For example, Ramaseshan and Suryan (51) found that the $g$ values calculated from susceptibility data for Mo(III) in $K_3\text{MoCl}_6 \cdot 12\text{H}_2\text{O}$ was 1.92 and the $g$ value for $(\text{NH}_4)_3\text{Mo(SCN)}_6 \cdot 4\text{H}_2\text{O}$ was 1.86. Both these $g$ values are very close to 2 and the interpretation that the magnetic moment is near the spin value alone agrees with the experimental magnetic moments determined in this thesis for the Mo(III) in the complexed chloride and the thiocyanate as 3.84 Bohr magnetons.
Most 1st Transition elements obey spin-only formula showing that orbital contribution can be ignored.

The 2nd and 3rd Transition elements have not been studied as much but they also seem to obey spin-only.

For example, $K_3^3 Mo Cl_6, 3.7, (NH_4)_3 Mo(SCN)_6 \cdot 4H_2O, 3.7$. The $\mu$ values agreeing with three unpaired electrons and $K_4 Mo (CN)_8$ diamagnetic with no unpaired electrons (55).

The orbital contribution appears to be more effective in the rare earth and trans-uranic elements. This is probably due to the filling of the $f$ sub-orbital. With orbital contribution wholly or partly quenched, Russell-Saunders coupling is not fully applicable.

If $z$ is the number of unpaired electrons in an atom then $S = z/2$ and the multiplicity is $2S + 1$.

For Mo(III) with three unpaired electrons $S = \frac{3}{2}$ and the multiplicity is $2 \times \frac{3}{2} + 1 = 4$.

With $S = \frac{3}{2}, \ell = 3$ and because the $4d$ sub-shell is less than half full $j = \ell - S = \frac{3}{2}$. The term symbol then for Mo(III) is $^{4}F_{3/2}$; the prefix giving the spin multiplicity and the suffix the value of $J$.

Hund's rules state: (i) $S$ has the highest value allowed by the Pauli principle; (ii) the value of $L$ is the highest then allowed; (iii) $J_o = L - S$ if the shell is less than half full and $J_o = L + S$ if the shell is more than half full.
The $g$ value for Mo(III) calculated from the equation
\[ g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} = \frac{2}{5} \]
whence \[ \mu = g \sqrt{J(J + 1)} = 0.77 \text{ B.M.} \]

This calculated magnetic moment of 0.77 B.M. does not agree with experimental figures and indicates that the coupling between the L and S moment for Mo(III) is weak and that the effective magnetic moment arises from spin-only.

From experimental work in this thesis Mo(IV) with two electrons in 4d orbits are paired and the moment is diamagnetic. Hund's rules are not applicable; the first rule which requires that in the filling up of a sub-shell (for Mo, the 4d), the maximum number of orbitals will be singly filled before pairing occurs.
B. The Complex Halides of Molybdenum (III)

The complex molybdenum (III) halides are of three types, \( \text{R}_2 \text{Mo} \text{Cl}_5 \cdot \text{H}_2\text{O}, \text{R}_3 \text{Mo} \text{Cl}_6 \) and \( \text{R}_4 \text{Mo} \text{Cl}_7 \). The first two of these involve hexa-co-ordinated molybdenum. It is reasonable to assume that the six Mo – X bonds arise from \( d^2 s^p^3 \) hybridization. On this basis and assuming that Hund's Rule applies there will be three unpaired \( d \) electrons and a resulting magnetic moment of about 3.8 Bohr magnetons.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Effective Moments B.M.(determined)</th>
<th>Effective Moments B.M.(spin-only,calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{(NH}_4 \text{)}_3 \text{Mo} \text{Cl}_6 )</td>
<td>3.84</td>
<td>3.88</td>
</tr>
<tr>
<td>( \text{K}_3 \text{Mo} \text{Cl}_6 )</td>
<td>3.7</td>
<td>3.88</td>
</tr>
<tr>
<td>( \text{(NH}_4 \text{)}_2 \text{Mo} \text{Cl}_5 \cdot \text{H}_2\text{O} )</td>
<td>3.86</td>
<td>3.88</td>
</tr>
<tr>
<td>( \text{(NH}_4 \text{)}_4 \text{Mo} \text{Cl}_7 \cdot 2\text{H}_2\text{O} )</td>
<td>3.7</td>
<td>3.88</td>
</tr>
<tr>
<td>( \text{K}_3 \text{Mo} \text{Br}_6 )</td>
<td>3.84</td>
<td>3.88</td>
</tr>
<tr>
<td>( \text{Li}_3 \text{Mo} \text{Cl}_6 \cdot 9\text{H}_2\text{O} )</td>
<td>3.84</td>
<td>3.88</td>
</tr>
</tbody>
</table>

Table 2 supports the assignation of \( d^2 s^p^3 \) hybridization to these compounds and it can be seen that the orbital contribution is negligible.

It is worthy of mention here that Mo(IV) compounds are diamagnetic indicating the breakdown of Hund's Rule. The other second and third transition group elements which could be expected to give three unpaired electrons are Re(IV).
and W(III). Re(IV) in fact gives only one unpaired electron, also showing a breakdown of Hund's Rule.

Many attempts were made to repeat the preparation K$_3$MoBr$_6$ described by Wardlaw and Harding (38). The compound finally obtained differed in some respects from Wardlaw's compound in that it is soluble in alcohol but analysis, magnetic susceptibility and conductivity show it to be K$_3$MoBr$_6$.

With three unpaired electrons and a bond type to suit an octahedral spatial arrangement there is no question of an unpaired electron being promoted to an orbital above the 4d$^2$ 5s 5p$^3$ orbitals used for bond formation. If and when such a promotion occurs it is to be expected that this electron should be in an excited state and capable of being removed fairly easily by oxidation.

If complexes of the type R$_4$[Mo Cl$_7$] existed they would probably be face-centred octahedrons and one of the electrons from the 4d would have to be promoted to the 5d level on the basis of Pauling's theory of promoted electrons and on Huggin's theory (78), the [Mo Cl$_7$] should be unstable. The R$_4$Mo Cl$_7$ is discussed later in relation to ultra-violet spectra.

A preparation of K$_3$MoCl$_6$ using Wardlaw's method was made by reducing a solution of Mo O$_3$ in concentrated hydrochloric acid to the molybdenum (III) state, evaporating under suction at 70°C and then adding air-free alcohol. Wardlaw removes excess K Cl at this stage. However in this case a pink precipitate formed which was removed and then on further addition
of alcohol excess K Cl precipitated.

The magnetic susceptibility of this pink $K_3 Mo Cl_6$ gave a $\mu$ value of 3.06. From this figure it was assumed that the product was not pure. Now this pink $K_3 Mo Cl_6$ with probably some K Cl associated with it, was taken into solution, evaporated under suction and re-precipitated with alcohol. The precipitate suspended in the solution was kept in the refrigerator for two weeks. The precipitate was then brown. This precipitate is not nearly so soluble as the hexachloro complex and gave a brown solution instead of a red one as with the hexachloro complex. The analysis agreed with $K_7 Mo Cl_{10} \cdot 6H_2O$.

This product is mentioned and its ultra-violet spectrum is later compared to other double salts.

Two products which gave an analysis corresponding to $(NH_4)_4 Mo Cl_7 \cdot 2H_2O$ and $Li_4 Mo Cl_7 \cdot 5H_2O$ were produced in a similar manner to the corresponding $(NH_4)_3 Mo Cl_6$ and $Li_3 Mo Cl_6$ with this difference, that after the hexachloro complexes had been formed during electrolytic reduction lithium carbonate or ammonium carbonate was added to the appropriate complex. Two preparations of the ammonium compound and one of the lithium compound were made, and these preparations seemed to be in agreement with Carrobi (49).

When $R Cl$ is added to $Mo Cl_3$ a complex is produced. It was considered probable then that if the $R$ content ($R = NH_4$ or Li in this case) is increased in a hydrochloric acid solution of the hexachloro complex a heptachloro complex of
molybdenum (III) could be formed. This assumption was proved incorrect.

From experimental work two probable ions $\left[\text{Mo Cl}_6\right]^{3-}$ and $\left[\text{Mo Cl}_7\right]^{4-}$ are indicated and a possible $\left[\text{Mo Cl}_{10}\right]^{7-}$. It is probable that the compound represented from analysis as $(\text{NH}_4)_4\text{Mo Cl}_7$ is actually $(\text{NH}_4)_3\text{Mo Cl}_6 \cdot \text{NH}_4\text{Cl}$, and that $\text{Li}_4\text{Mo Cl}_7$ is $\text{Li}_3\text{Mo Cl}_6 \cdot \text{Li Cl}$.

Ultra-violet spectrum analysis of these preparations and the reported $K_7\text{Mo Cl}_{10}$ shows that there is an ion common to these complexes which by comparison to $(\text{NH}_4)_3\text{Mo Cl}_6$ and $K_3\text{Mo Cl}_6$ is $\left[\text{Mo Cl}_6\right]^{3-}$. The wavelengths at deflections of the curves are almost identical and at these wave-lengths the densities are comparable. Another marked characteristic of the behaviour of the $\left[\text{Mo Cl}_6\right]^{3-}$ ion is the final rise of the curve from a wavelength of 354 Angstrom units.

Experiments in the visible range gave a comparatively straight line and it was concluded that the visible range was not suitable for comparison of these compounds. For the experiments in the ultra-violet range 0.02% solutions were used and a few drops of hydrochloric acid were added to prevent hydrolysis.

The different density levels of the curves, for example, between those of $(\text{NH}_4)_3\text{Mo Cl}_6$ and $(\text{NH}_4)_4\text{Mo Cl}_7$ are due to different molecular concentrations, the $(\text{NH}_4)_4\text{Mo Cl}_7$ being in effect $(\text{NH}_4)_3\text{Mo Cl}_6 \cdot \text{NH}_4\text{Cl}$.
The maximum wave absorptions occur at wavelengths of 293 and 214 Angstrom units. Constant absorption occurs between 192 and 209 for the ammonium complexes and between 195 and 209 for the potassium complexes. The ammonium complexes show another maximum wave absorption at a wavelength of 187. The pinnacle for the K₇ Mo Cl₁₀ at a wavelength of 189 is attributed to some impurity present in the compound.

In the ion [Mo Cl₇]⁴⁻ the molybdenum would have a coordination number of 7 and Kimball's stable bond arrangements (79) give bond types d³ s p³, d⁵ s p, d⁴ s p², d⁴ p³ and d⁵ p². for this coordination number. The most probable arrangement of these bond types would be d³ s p³ as a face-centred octahedron. However this arrangement would require the molybdenum to have two electrons in the first 4d orbital and one unpaired electron in the second 4d orbital. The effective magnetic moment of one unpaired electron is not compatible with experimental figures.

Because the effective magnetic moment indicates three unpaired electrons (which would occupy the first three 4d orbitals) none of the above bond types would harmonise with the electronic arrangement of molybdenum (III).

If the molybdenum in the complex ion had a coordination number of 8 then the ion would be represented as [Mo Cl₇ .H₂O]⁴⁻. The stable bond arrangements for a coordination number of 8 are d⁴ s p³, d⁵ p³, and d⁵ s p² (79). Here again the stable
bond arrangements are not applicable to Mo(III) with three unpaired electrons.

The molecular conductance figures of Li₄ Mo Cl₇ •5H₂O show that this compound hydrolyses and markedly so after about six minutes. They also indicate that the compound may be a double salt because the sum of the conductivities of Li₃ Mo Cl₆ •9H₂O and Li Cl are approximately that of the compound Li₄ Mo Cl₇ •5H₂O. The salt (NH₄)₄ Mo Cl₇ •2H₂O does not hydrolyse in the same manner as the lithium salt and is more stable. The conductivity of (NH₄)₃ Mo Cl₆ •2H₂O is 730 compared to that of (NH₄)₃ Mo Cl₆ of 375.

The magnetic susceptibility of (NH₄)₄ Mo Cl₇ •2H₂O is 3.7 B.M. The experimental figure of 3.4 B.M. determined for Li₄ Mo Cl₇ •9H₂O is lower than that expected because the salt was very hygroscopic.

From conductivity measurements, ultra-violet spectra and the possibility of stable bond arrangements it is concluded that the [Mo Cl₇]⁴⁻ ion does not exist and that the compounds (NH₄)₄ Mo Cl₇ •2H₂O and Li₄ Mo Cl₇ •9H₂O are double salts (NH₄)₃ Mo Cl₆ •NH₄ Cl •2H₂O and Li₃ Mo Cl₆ •Li Cl •9H₂O respectively.

Therefore the preparation reported as (NH₄)₄ Mo Cl₇ by Carrobi is also concluded to be a double salt.

This information of double salts is not confined to these two compounds as the compound K₇ Mo Cl₁₀ •6H₂O has also been isolated. Ultra violet spectra show that this is
K₃MoCl₆·4KCl·6H₂O. Numerous preparations of the hexachloro complexes of molybdenum (III) were made, mostly by methods of earlier workers. The expected magnetic susceptibilities were in all cases just over 3 B.M. The excellent products finally obtained warrant some comment on their manner of preparation; this is done in section III.

Complex halides of the type $R_3M X_6$ comprise the alkali salts of ions of the type $[M X_6]^{3-}$ (62)(80) which include the complexes $R_3MoCl_6$. No sodium salt of the ion $[MoCl_6]^{3-}$ has yet been produced and the only lithium salt known has been prepared in the work described in this thesis.

The molybdenum (III) complexes are strong reducing agents as exemplified in the titration of these complexes with potassium permanganate to the Mo(IV) state. As it is possible to have a molybdenum (III) cyano complex besides the molybdenum (IV) type it was thought that a molybdenum (IV) chloro complex might exist. A solution of $(NH_4)_3MoCl_6$ was titrated with stannic chloride solution and with permanganate solution; there were no colour changes. The red/ox potentials were taken but no evidence of a stable tetravalent molybdenum could be established.
C. The Complex Cyanides of Molybdenum

The octa-cyanide $K_4 Mo(CN)_8$ is quite a stable compound and has been investigated thoroughly. The only other previously known cyanides of Molybdenum (III) and (IV) are the compounds which have been formulated as $K_4 Mo(CN)_7 \cdot 2H_2O$, $K_4 Mo(OH)_4 (CN)_4 \cdot 4H_2O$ and $K_3 Mo(OH)_3 (CN)_4 H_2O \cdot 2H_2O$.

The magnetic susceptibilities of these previously described compounds (with the exception of $K_4 Mo(OH)_4 (CN)_4 \cdot 4H_2O$ and $K_3 Mo(OH)_3 (CN)_4 3H_2O$) and the two new cyanides $K_4 MoO_2 (CN)_4$ and $K Mo(CN)_5$ are reported in Table 3. Several attempts to prepare $K_3 Mo(OH)_3 (CN)_4 \cdot 3H_2O$ according to Bucknall and Wardlaw's method have failed.

Attempts to prepare $K_4 Mo(OH)_4 (CN)_4 \cdot 4H_2O$ according to Bucknall and Wardlaw's method also failed; the results of analysis showed the preparation to be $K_4 MoO_2 (CN)_4$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Effective Moments B.M.</th>
<th>Experimental</th>
<th>Number of Unpaired Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K Mo(CN)_5$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$K_4 Mo(CN)_8 \cdot 2H_2O$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$K_4 MoO_2 (CN)_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$K_4 Mo(CN)_7 \cdot 2H_2O$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
The molybdenum (III) and (IV) cyanides are diamagnetic. The molybdenum in the octoj-cyanide complex is in the (IV) state and the two electrons in the outer orbitals are paired and fill the first orbital of the 4d electronic arrangement. If the next consecutive orbitals are to be filled by the eight cyanide groups then the hybridization of bond orbitals would be \(4d^4 \ 5s^3\) and this arrangement harmonises with the spatial arrangement given by Kimball (79) as a dodecahedron. Other alternative bond types for a co-ordination number of 8 would be \(d^5 \ p^3\) and \(d^5 \ s \ p^2\).

If the shape were an antiprism \((d^5 \ p^3)\) the 5s orbital would be vacant with the cyanide groups occupying four 4d, three 5p and one 5d orbitals.

If the shape were a face-centred prism \((d^5 \ s \ p^2)\) then the cyanide groups would occupy four 4d, one 5s, two 5p and one 5d orbits.

X-ray measurements (61) have established the dodecahedral spatial arrangement of the eight cyanide groups around the molybdenum (IV) in the \([\text{Mo(CN)}_8]^{4^-}\) ion. The spatial arrangement is shown in Fig.1(d) and the formulation of the complex is expressed as in Fig.1(c). Infra-red spectroscopy showed no evidence of cyanide bridging in \([\text{Mo (CN)}_8]^{4^-}\) (81).

The molybdenum in the pentacyano complex \(K \text{Mo(CN)}_5\) (not previously reported) is also in the (IV) state.

The molecular weight determinations clearly show the
formation of two ions from $\text{K Mo(CN)}_5$. The results of conductance measurements tend to agree with the existence of $\text{[Mo(CN)}_5]$ ion.

The co-ordination number of the molybdenum atom is thus 5 and the compound was found to be diamagnetic.

If single bonding between the molybdenum and cyanide occurs the possible electronic arrangements for bonding orbitals are:

\[
\begin{array}{c|c|c|c}
\text{d}^4 \text{s} & 4d & 5s & 5p \\
\hline
\downarrow \uparrow & & & \\
\text{d}^3 \text{s} \text{p} & & & \\
\downarrow \uparrow & & & \\
\text{d}^2 \text{s} \text{p}^2 & & & \\
\downarrow \uparrow & & & \\
\text{d} \text{s} \text{p}^3 & & & \\
\end{array}
\]

Because the complex is diamagnetic the two electrons in the 4d sub-shell for Mo(IV) must be paired.

Either bipyramid or tetragonal pyramid are possible spatial arrangements. However the complex $\text{K Mo(CN)}_5$ is a very stable substance and its behaviour is in keeping with the "inner orbital" type of complex. It may therefore be expected that the bond orbitals would be $\text{d}^4\text{s}$ and not $\text{d}^3\text{s} \text{p}$, $\text{d}^2\text{s} \text{p}^2$ or $\text{d} \text{s} \text{p}^3$. With the filling of the first 4d orbitals by the paired electrons of the molybdenum (IV) the next available orbitals are four 4d and one 5s, and these would be
used for bonding with the five cyanide groups.

The spatial arrangement for d^4 bonds could be with the molybdenum as the central atom in the same plane as the four cyanide groups with the fifth cyanide group vertical; or that the molybdenum atom could be out of the basal plane as indicated in Fig. 1(b).

Infra-red spectroscopy (81) shows no evidence of bridging of cyanide groups.

Partial double-bond character of metal-carbon bond appears in anionic cyanide complexes of other transitional elements such as [Fe(CN)_6]^{3-}, [Co(CN)_6]^{3-}, [Mn(CN)_6]^{4-}, [Ni(CN)_4]^{2-}, [Cr(CN)_6]^{4-} (63) and resonance can be assumed between M=C=N, M-C=N and M^+(CN)^-.

Double bonding may occur in cyanide complexes where there is evidence for the existence of d^π - p^π bonding with a penultimate d^σ orbital. The notable stability of the planar tetracyanide anion [Ni(CN)_4]^{2-} and other ions lend support to the possibility of reinforcement by such double-bonding (82).

The stability and inertness of the [Mo(CN)_5]^- ion suggest some double bonding character besides an "inner orbital" type of formation and the filled 4d orbital could in fact give rise to some π bonding.

It is obvious that the structure of K Mo(CN)_5 cannot be solved without recourse to an X-ray study.
The potassium and ammonium octacyano complexes are yellow. They crystallise in the orthorhombic system as pyramids/pinacoids (3); the crystal habit of the octacyanides prepared in work for this thesis was pyramids. Coloured precipitates were formed by substituting the potassium with metallic ions. Thallous thallium forms orange-yellow $\text{Tl}_4\text{Mo(CN)}_8$ (57); cadmium forms yellow, cobalt forms reddish-yellow, copper forms violet-brown, and manganese a bright yellow precipitate. The potassium in $\text{K Mo(CN)}_5$ is not replaced by copper, cobalt, cadmium or manganese as occurred with the octacyanide, indicating again a monovalent anion.

The Mo(IV) in the white cyanide, $\text{K Mo(CN)}_5$ was produced from Mo(VI) in Mo $\text{O}_3$. A red cyanide containing Mo(IV) was also produced from Mo $\text{O}_3$ (this thesis). Bucknall and Wardlaw (42) prepared their red cyanide by the addition of potassium cyanide (saturated solution) to the brown hydroxide of quinquevalent molybdenum. In the preparation of the $\text{K Mo(CN)}_5$ it was found that if care was not taken some brown product was likely to form. Molybdenum trioxide and solid potassium cyanide were ground together, water was then added and the mixture refluxed. Red crystals formed which on removal of potassium hydroxide became brownish. This was comparable to Bucknall & Wardlaw's red cyanide $\text{K}_4\text{Mo(OH)}_4\text{(CN)}_4\cdot4\text{H}_2\text{O}$. The product described in this thesis is of the composition,
The red cyanide is stable towards dilute mineral acids but appears to be decomposed by organic acids such as salicylic acid or oxalic acids although no definite compounds have been obtained (57).

Conductance measurements and molecular weight determinations (42) have indicated that more than five ions are present in dilute solutions. This is supported by the fact that a dilute solution is alkaline.

Apart from the red cyanide $K_4 Mo O_2 (CN)_4$ it is possible to produce a cyanide from molybdenum (V) as $K_3 Mo(CN)_8$ (57). However this is unstable and reverts to $K_4 Mo(CN)_8$.

As a test for the valency of molybdenum in the heptacyanide, a solution of this complex was added to ferric alum - phosphoric acid solution and the ferrous salt formed was titrated with standard permanganate solution. The titration figures showed that three electron equivalents were involved in the oxidation that is $Mo^{3+}$ was oxidised to $Mo^{6+}$. Young (41) has also shown the molybdenum in this complex to be in the trivalent state. He oxidised the heptacyanide with hot ferric alum solution in the presence of mercuric sulphate and titrated the ferrous salt formed with standard permanganate solution.

The magnetic susceptibility determinations (on all three modes of preparation) showed the black cyanide complex to be diamagnetic. This diamagnetism is unique for a trivalent
molybdenum compound and indicates that the compound must involve a Mo - Mo bond.

Young (41) states that the black cyanide \( K_4 Mo(CN)_7 \cdot 2H_2O \) is unstable and reverts to the yellow octacyanide \( K_4 Mo(CN)_8 \) in the presence of moist air. It was decided to further investigate this change.

A fresh preparation of the dry black cyanide was left exposed to air for about 2 hours. The potassium hydroxide and the yellow \( K_4 Mo(CN)_8 \) were leached with cold water leaving a white residue. The weight of this white residue approximated the theoretical yield expected according to the equation:

\[
3K_4 Mo(CN)_7 \cdot 2H_2O + \frac{1}{4}O_2 \rightarrow 2K_4 Mo(CN)_8 + KMo(CN)_5 + 3KOH + \frac{9}{2}H_2O
\]

The crystal habit and appearance of this white product appeared to be the same as the previously reported potassium penta-cyano molybdate (IV). The analysis confirmed that this white residue was indeed \( K Mo(CN)_5 \). (Found: Mo 36.5; CN 49.0; calculated Mo 36.3; CN 49.3).

Conductance and pH measurements also indicate the reaction to proceed according to the above equation.

This is further evidence of the existence of the white cyano complex \( K Mo(CN)_5 \).
D. The Complex Thiocyanates of Molybdenum (III)

The thiocyanate complexes of molybdenum (III) have greater relationship to the hexachlorides than to the cyanides. The bond orbitals, the octahedral structure and the magnetic susceptibility are similar. Two preparations of the ammonium hexa-thiocyanato molybdate (III) were made and some comments on the preparation of one of them is warranted.

In the preparation of \((\text{NH}_4)_3\text{Mo(SCN)}_6\), electrolysis of the molybdenum solution containing ammonium thiocyanate must be at a temperature of over 60°C (60 - 70°C) so as to volatilise any \(\text{Mo(SCN)}_5\) which is formed during reduction. In experimental work it was found that if this temperature was not maintained the final product was coloured red.

It was thought that this colour might be due to \(\text{Mo(SCN)}_5\). To confirm this some \(\text{Mo(SCN)}_5\) solution was prepared; when warmed it lost its colour but regained it on cooling. The same behaviour occurred in the first preparation of \((\text{NH}_4)_3\text{Mo(SCN)}_6\) but continued heating under reduced pressure at 70°C prevented the formation of the red colour on cooling.

When the hexa-thiocyanate is crystallised from water, water molecules are attached. On crystallisation from hydrochlorine acid \((\text{NH}_4)_3\text{Mo(SCN)}_6\cdot\text{HCl} \cdot \text{H}_2\text{O}\) can be formed and the alcoololate \((\text{NH}_4)_3\text{Mo(SCN)}_6\cdot\text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}\) has been produced (16). When the compound was allowed to crystallise from acetone
(NH₄)₃ Mo(SCN)₆ • 3CH₃ • CO • CH₃ was formed. This compound has not been reported previously. The acetone can be removed by heat, especially from water solution at 70°C. This characteristic of the thiocyanate complex to have varying additives is absent in the corresponding halides.

The ammonium hexa-thiocyanate complex was also prepared from (NH₄)₃ Mo Cl₆ when thiocyanate replaced the chlorine according to the reaction:

(NH₄)₃ Mo Cl₆ + 6NH₄ CNS → (NH₄)₃ Mo(SCN)₆ + 6NH₄ Cl

This reaction occurs without oxidation whereas the molybdenum (III) with cyanide is oxidised to molybdenum (IV). (This has been dealt with under Section IIc).

The molecular conductance of the thiocyanate complex is 375 mhos and is comparable with the complex chlorides in that four ions are indicated. The effective magnetic moments obtained (3.86 B.M. for (NH₄)₃ Mo(SCN)₆ • 4H₂O and 3.72 B.M. three for (NH₄)₃ Mo(SCN)₆ • 3CH₃ • CO • CH₃) showed the expected/ unpaired electrons which would occupy the first three 4d orbitals.

Therefore the orbitals used for bond formation by molybdenum (III) in the hexa-thiocyanate are the same as those in the hexa-chloride i.e. 4d² 5s 5p³. The spatial arrangement would be octahedral, (Fig. 2(e)).

If the penta-thiocyanato molybdate (III), (NH₄)₂ Mo(SCN)₅ • 4H₂O with a magnetic moment of 3.84 B.M. is octahedral then the formula would be (NH₄)₂[Mo (SCN)₅ • H₂O] which can be
compared to the penta-chloro complex \((\text{NH}_4)_2\left[\text{Mo Cl}_5 \cdot \text{H}_2\text{O}\right]\). Thio-cyanate replaced chlorine in the penta-chloro complex to form the penta-thiocyanate complex. The molecular conductance of the penta-thiocyanate complex is 276 mhos and is comparable with the penta-chloride complex in that three ions are indicated.
E. **Compounds of Molybdenum (III) with some Bidentate Ligands**

The co-ordination of bidentate ligands such as o-phenanthroline and 2:2' dipyridyl with molybdenum (III) have not been reported previously.

Octahedral chelate complexes of the type Mo(phen)$_3$X$_3$ and Mo(dipy)$_3$X$_3$ (X = Cl, Br, I) have been formed and the magnetic susceptibilities showing 3 unpaired electrons agree with 4d$^2$ 5s 5p$^3$ binding.

These might be compared to the tervalent chromium complex

$$\left[\text{Cr(dipy)}_3\right]\left[\text{ClO}_4\right]_3$$

with an effective magnetic moment of 3.76 Bohr magnetons (84).

From Table 4 it can be seen that the effective magnetic moments approximate the spin-only value for three unpaired electrons and Hund's Rule is obeyed.

Analysis, conductivity and magnetic susceptibility determinations have shown the complexes to be $\left[\text{Mo(dipy)}_3\right]X_3$ or $\left[\text{Mo(phen)}_3\right]X_3$. 
### TABLE 4.

Magnetic Susceptibilities Chelate Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Effective Moment B.M. (experimental)</th>
<th>Effective Moment B.M. Spin value (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(dipy)$_3$ Cl$_3$</td>
<td>3.66</td>
<td>3.88</td>
</tr>
<tr>
<td>Mo(dipy)$_3$ Br$_3$</td>
<td>3.84</td>
<td>3.88</td>
</tr>
<tr>
<td>Mo(dipy)$_3$ I$_3$</td>
<td>3.84</td>
<td>3.88</td>
</tr>
<tr>
<td>Mo(phen)$_3$ Cl$_3$</td>
<td>3.83</td>
<td>3.88</td>
</tr>
<tr>
<td>Mo(phen)$_3$ Br$_3$</td>
<td>3.83</td>
<td>3.88</td>
</tr>
<tr>
<td>Mo(phen)$_3$ I$_3$</td>
<td>3.84</td>
<td>3.88</td>
</tr>
</tbody>
</table>

The lower figure for Mo(dipy)$_3$ Cl$_3$ is attributed to impurity.

The halogen compounds were prepared in alcoholic solution of (NH$_4$)$_3$ Mo Cl$_6$ and the appropriate chelating group. Attempts were made to prepare the perchlorates by replacement of the bromine in the bromide complexes by perchloric acid without avail.

The chlorides are dark red, the bromides orange, the iodides chocolate.

Chelation with the bidentates o-phenanthroline and 2:2'-dipyridyl is through nitrogen whereas with the oxalates and salicylates linkage is through oxygen.
The tris-phenanthroline and the tris-dipyridyl complexes of Mo(III) appear to be very stable and this is further indication that the lower d orbitals are used in the binding.

It has been suggested that the major factor responsible for electron pairing and strong binding is the formation of double bonds (π bonds) using 4d electron pairs (in the case of molybdenum) as proposed by Pauling ((63)p.250). No electron pairing, however, occurs (3 unpaired electrons) and it is most probable that only single-bond structures exist such as the following example using dipyridyl:
(i) The Oxalato Complex

The oxalato trichelate salt $K_3\text{Cr(C}_2\text{O}_4)_3$ is known but any attempts to form a similar molybdenum compound have failed. Poerster and Fricke tried to produce an oxalate by dissolving $\text{Mo(OH)}_3$ in oxalic acid. Spittle and Wardlaw also tried to produce an oxalate with reduced molybdenum following the earlier work of Chilesotti ($\text{Z. Electrochem 12, 146, 1906}$).

It seemed probable, however, that if the molybdenum was reduced electrolytically in the presence of the cation there would be a greater probability of producing a complex of the type $\text{R}_4\text{MoOX}_4$. This procedure has been found to be effective and with good results in the preparation of other complexes for work in this thesis. Therefore an ammonium molybdate solution containing oxalic acid was electrolytically reduced. The product was $(\text{NH}_4)_4\text{Mo(OX)}_4\cdot8\text{H}_2\text{O}$ by analysis and the detailed method is reported in Section III (a).

This complex is diamagnetic and like the octa-cyanides it is possible that the bond orbitals are $4d^{10}5s^25p^3$. It is however probable that the $(\text{NH}_4)_4\text{Mo(OX)}_4\cdot8\text{H}_2\text{O}$ is a double salt $(\text{NH}_4)_2\text{Mo(OX)}_3\cdot(\text{NH}_4)_2\text{OX}\cdot8\text{H}_2\text{O}$.

The conductance $\text{M}/1000$ is 730 and comparable with the double salt $(\text{NH}_4)_3\text{MoCl}_6\cdot\text{NH}_4\text{Cl}\cdot2\text{H}_2\text{O}, 730$. 
(ii) **The Carbonato Complex**

Mellor is his "Treatise on Inorganic Chemistry" (15) (page 659) states that no molybdenum carbonate has been reported. No observed literature reports any carbonates or carbonato complex for molybdenum.

The carbonato complex reported here was formed when an attempt was made to produce an iodo complex with molybdenum (III).

Potassium molybdate was made acid with hydriodic acid and about 2g of potassium iodide added. This solution was electrolysed using a mercury cathode and a carbon anode. Iodine liberated markedly corroded the carbon anode and a carbon deposit formed which was filtered off. The carbon was replaced with a platinum anode and electrolysis was continued. The final reduced solution was a very light-brown-red colour which was quite different from the more intense red-coloured reduced solutions of chloride and bromide molybdenum (III).

The reduced solution was evaporated under suction at 70°C. to about 50 ml.; alcohol was added; two layers formed, the electrolysed solution and the alcohol layer. Carbon dioxide was bubbled through the reduced electrolyte and a white precipitate formed from the aqueous layer. The precipitate was filtered, washed with alcohol and dried at 100°C.

The analysis was: Mo 14.7; CO$_3$ 45.0; K 35.4.

This is in agreement with $K_6$Mo(CO$_3$)$_5$.2H$_2$O or $K_4$Mo(CO$_3$)$_4$.5H$_2$O.
\[ K_2CO_3 \cdot 2H_2O. \]

The molecular conductivity of M/1016 at 25°C. = 680 and it hydrolyses slightly.

Magnetic susceptibility measurements show this compound to be diamagnetic (\( \chi \times 10^6 = -0.052 \)) involving Mo(IV).

Heide and Hofmann (Z. anorg. Chem. 12, 277, 1896) reduced an acid solution of molybdenum trioxide with potassium iodide. The excess iodine was removed during electrolysis. To this solution they added potassium cyanide to obtain red crystals of the red cyanide to which they assigned the formula 4KCN·MoO_2·10H_2O.

This process is to be compared to that just described for the preparation of the carbonate complex. In both cases an exhaustively reduced solution of molybdenum (III) with potassium iodide is produced— in one case potassium cyanide is added and in the other carbon dioxide; both additions producing complexes.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Electronic Arrangement</th>
<th>Bond Orbitals</th>
<th>Shape</th>
<th>Magnetic Moment</th>
<th>Bohr Magnetons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium hexachloro molybdate (III)</td>
<td>Bright red</td>
<td></td>
<td>$4d^2 5s 5p^3$</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Ammonium pentachloro molybdate (III)</td>
<td>Bright brick red</td>
<td></td>
<td>$4d^2 5s 5p^3$</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.86</td>
</tr>
<tr>
<td>Potassium hexachloro molybdate (III)</td>
<td>Brick red</td>
<td></td>
<td>$4d^2 5s 5p^3$</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.7</td>
</tr>
<tr>
<td>Lithium hexachloro molybdate (III)</td>
<td>Wine red</td>
<td></td>
<td>$4d^2 5s 5p^3$</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Potassium hexabromo molybdate (III)</td>
<td>Brick red</td>
<td></td>
<td>$4d^2 5s 5p^3$</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Ammonium hexathiocyanato molybdate (III)</td>
<td>Yellow</td>
<td></td>
<td>$4d^2 5s 5p^3$</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.86</td>
</tr>
<tr>
<td>Ammonium pentathiocyanato molybdate (III)</td>
<td>Bright yellow</td>
<td></td>
<td>$4d^2 5s 5p^3$</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Potassium pentacyano molybdate (IV)</td>
<td>White</td>
<td></td>
<td>$4d^4 5s$</td>
<td>Tetragonal</td>
<td>0</td>
<td>$-0.127$</td>
</tr>
<tr>
<td>Potassium octacyano molybdate (IV)</td>
<td>Yellow</td>
<td></td>
<td>$4d^4 5s 5p^3$</td>
<td>Dodecahedron</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Potassium tetracyanodioxo molybdate (IV)</td>
<td>Reddish brown</td>
<td></td>
<td>$4d^4 5s 5p^3$</td>
<td>Dodecahedron?</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Potassium heptacyano molybdate (III)</td>
<td>Black</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complex</td>
<td>Colour</td>
<td>Electronic Arrangement</td>
<td>Bond Orbitals</td>
<td>Shape</td>
<td>Magnetic Moment Bohr Magnetons</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Ammonium oxalato molybdate(IV)Complex</td>
<td>Light Brown</td>
<td>↓↑</td>
<td>4d↑5s↑5p↓</td>
<td>Trigonal prism?</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Potassium Carbonate molybdate(IV)Complex</td>
<td>White</td>
<td></td>
<td>4d↑5s↑5p↓</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.83</td>
</tr>
<tr>
<td>Tris-o-phenanthroline molybdenum(III)Chloride</td>
<td>Dark Red</td>
<td>↓↓↓</td>
<td>4d2 5s 5p3</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.83</td>
</tr>
<tr>
<td>Tris-o-phenanthroline molybdenum (III)Bromide</td>
<td>Orange</td>
<td>↓↓↓</td>
<td>4d2 5s 5p3</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Tris-o-phenanthroline molybdenum(III)Iodide</td>
<td>Chocolate</td>
<td>↓↓↓</td>
<td>4d2 5s 5p3</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Tris-2:2' dipirydyl molybdenum(III)Chloride</td>
<td>Dark Red</td>
<td>↓↓↓</td>
<td>4d2 5s 5p3</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Tris-2:2' dipirydyl molybdenum(III)Bromide</td>
<td>Orange</td>
<td>↓↓↓</td>
<td>4d2 5s 5p3</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
</tr>
<tr>
<td>Tris-2:2' dipirydyl Molybdenum (III) Iodide</td>
<td>Chocolate</td>
<td>↓↓↓</td>
<td>4d2 5s 5p3</td>
<td>Octahedral</td>
<td>3.88</td>
<td>3.84</td>
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</table>
Fig. 1.
Fig 2
SECTION III

A. PREPARATION OF COMPOUNDS

In the preparation of the hexa-halide complexes of molybdenum (III) electrolytic reduction was made (using a mercury cathode) from a solution of molybdenum trioxide in hydrochloric acid (or hydrobromic acid) to which was added the appropriate cation or from acidified molybdate solution.

The second important point in the preparation of these compounds is the saturation of the reduced solution with hydrogen chloride (or hydrogen bromide) gas carried by carbon dioxide to maintain an inert atmosphere.
10g ammonium molybdate, (NH₄)₂MoO₄ and 10g of ammonium carbonate were dissolved in hydrochloric acid and diluted to 200 ml with 8N hydrochloric acid. This solution was a pale yellow colour. The solution was electrolysed 8 to 10 hours at 2-3 amperes and 14 volts, using a mercury cathode and platinum anode. The partition between the anolyte and the catholyte was sintered glass.

During electrolysis the colour changed from pale yellow to brown to red. The red colour and the free evolution of hydrogen indicated complete reduction to the Mo(III) state.

The reduced solution was then saturated with hydrogen chloride gas carried by carbon dioxide. Bright red acicular crystals separated. The solution and crystals were cooled in the refrigerator and the crystals filtered off by suction using a buchner funnel. The crystals were washed with alcohol and dried at 60°C.

Analysis of (NH₄)₃MoCl₆:

Calculated: Mo 26.5; Cl 58.6; NH₄ 14.8:

Found: Mo 26.5; Cl 58.6; NH₄ 14.8:

In subsequent preparations of (NH₄)₃MoCl₆ electrolytic reduction was made from ammonium molybdate in hydrochloric acid. Very pure products were obtained and the products were brick-red.
(ii) **Potassium hexachloro molybdate (III)**  
\[ \text{K}_3 \text{MoCl}_6 \]

20g molybdenum trioxide \( \text{MoO}_3 \) were dissolved in the minimum amount of saturated potassium hydroxide solution until crystals of potassium molybdate formed with excess potassium hydroxide. 300 ml of 8N hydrochloric acid were added. The solution was then electrolysed using a mercury cathode and a carbon anode at 12 to 14 volts with a current of 3 to 4 amperes. The partition of anolyte from catholyte was effected with sintered glass. The time of reduction to the molybdenum (III) state was 5 to 6 hours. During this electrolysis the anolyte was renewed once with 8N hydrochloric acid. A carbon dioxide atmosphere was maintained during reduction. The electrolyte colour was initially colourless and the solution changed through green, molybdenum (V) to red, molybdenum (III). When hydrogen gas was being freely evolved, that is when the molybdenum had been reduced to the tervalent state the carbon dioxide atmosphere was discontinued.

The reduced solution was collected from the electrolysis cell, saturated with hydrogen chloride gas mixed with carbon dioxide and allowed to cool in the refrigerator.

Deposition of brick-red crystals occurred immediately on cooling. These were filtered off, washed with absolute alcohol and dried at 50°C.

**Analysis of K₃MoCl₆**:  

*Calculated:*  
Mo 22.5; Cl 50.0; K 27.5;  

*Found:*  
Mo 22.3; Cl 50.0; K 27.6.
(iii) Potassium hexabromo molybdate (III)

\[ K_3 \text{ Mo Br}_6 \]

10g potassium molybdate were dissolved in 30 ml water and diluted to 400 ml with hydrobromic acid (48%). This solution was electrolysed for 72 hours at 1 ampere using a platinum anode and a mercury cathode. The solution colour changed from a pale red to a final cherry-red. The reduced solution was saturated with hydrogen bromide gas carried by carbon dioxide. The solution was then evaporated at 70°C under reduced pressure and a red solid separated in crystalline form. The precipitate was washed firstly with hydrobromic acid and then with a minimum of absolute alcohol as the complex is alcohol soluble.

Analysis of \( K_3 \text{ Mo Br}_6 \):-

Calculated: Mo 13.8; Br 69.3:

Found: Mo 13.8; Br 69.2:
(iv) **Lithium hexachloro molybdate (III)**

\[ \text{Li}_3 \text{MoCl}_6 \cdot 9\text{H}_2\text{O} \]

20g molybdenum trioxide and 10g of lithium carbonate were dissolved in 200 ml of 4N hydrochloric acid. The cell conditions were similar to those used in the preparations of \(\text{K}_3 \text{MoCl}_6\); mercury cathode, carbon anode, 12-14 volts. The amperage was lower, 2 amps, and the time of electrolysis, that is until the molybdenum was tervalent, was 12 hours. An atmosphere of carbon dioxide was maintained.

The colour of the reduced solution was amber. The reduced solution was removed from the electrolysis cell and hydrogen chloride gas and carbon dioxide were passed through the solution until saturated. No precipitate formed. The solution was concentrated by evaporation under suction to about 40-50 ml. This was placed in a vacuum desiccator to produce a super saturated solution. This solution was seeded with some crystals of the lithium complex from a previous product and wine-red crystals separated.

**Analysis of Li\(_3\)MoCl\(_6\) \cdot 9\text{H}_2\text{O} :**

**Calculated:** Mo 19.5; Cl 43.2

**Found:** Mo 19.2; Cl 42.6
(v) **Ammonium pentachloro molybdate (III)**

\[(\text{NH}_4)_2\text{MoCl}_5\cdot\text{H}_2\text{O}\]

100 ml of 33% Mo Cl\(_3\) (electrolysed solution) was added to 90 ml of 10% aqueous ammonium chloride. The resulting solution was concentrated by evaporation at 70\(^\circ\)C under reduced pressure until crystallisation commenced. The mixture was then rapidly cooled and filtered. The precipitate was washed with 95% alcohol and finally with absolute alcohol. The crystalline product was dried in vacuo. The colour of the preparation was bright brick-red.

**Analysis of \((\text{NH}_4)_2\text{MoCl}_5\cdot\text{H}_2\text{O}\):**

- **Calculated:** Mo 29.4; Cl 54.3;
- **Found:** Mo 29.4; Cl 54.3;
Ammonium hexa thiocyanato molybdate (III)  
\((\text{NH}_4)_3 \text{Mo(SCN)}_6 \cdot 3(\text{CH}_3)_2 \text{CO}\)

10g of ammonium molybdate were dissolved in 50 ml of warm water. 33g of ammonium thiocyanate were then added. A white precipitate formed. 50 ml of dilute sulphuric acid (15 ml concentrated sulphuric acid (1.84) diluted to 50 ml) were then added. The white precipitate dissolved and a blood red solution resulted due to some \(\text{Mo(SCN)}_5\) being formed.

This solution was exhaustively reduced in the electrolysis cell with the following conditions: sintered glass diaphragm; lead anode; mercury cathode; 4 amps; 38 (thirty eight) volts; time 6 hours. No protective atmosphere was used.

As electrolysis commenced the solution became viscous. The colour changed to reddish-brown and finally yellow after \(5\frac{1}{2}\) hours. Hydrogen was by this time being freely evolved. The temperature of the catholyte was 70°C. A small amount of black insoluble material was removed. The filtrate - yellow - was allowed to cool and some brownish-yellow crystals formed. These were dried and were found to be paramagnetic and of the ratio 2.7 Mo to 37.7 SCN and obviously impure.

This product was treated with acetone.

The acetone from the acetone extractable portion was evaporated under vacuum to give a yellow product.

Analysis of \((\text{NH}_4)_3 \text{Mo(SCN)}_6 \cdot 3(\text{CH}_3)_2 \text{CO}\):

Calculated: Mo 14.2; SCN 51.8; NH\(_3\) 8.1; \((\text{CH}_3)_2\) CO 25.8;

Found: Mo 14.2; SCN 52.0; NH\(_3\) 8.4; \((\text{CH}_3)_2\) CO 25.7;
(vii) **2nd PREPARATION**

**Ammonium hexa thiocyanato molybdate (III)**

$\text{(NH}_4\text{)}_3 \text{Mo(SCN)}_6 \cdot 4\text{H}_2\text{O}$

4g of $(\text{NH}_4)_3 \text{MoCl}_6$ and 8g of ammonium thiocyanate were dissolved together in 75 ml water. This solution was concentrated under suction at 50-60°C to approximately 30 ml (when crystallisation commenced). The solution was allowed to crystallise. The crystals were filtered off and dried in a vacuum desiccator. This product was redissolved in a minimum of water and recrystallised three times under suction and the temperature was below 60°C.

The mother liquor from the final crystallisation was dried off on filter paper. The product was yellow.
(viii) **Ammonium penta thiocyanato molybdate (III)**

\[(\text{NH}_4)_2 \text{Mo(SCN)}_5 \cdot 4\text{H}_2\text{O}\]

2g of \((\text{NH}_4)_2 \text{MoCl}_5 \cdot \text{H}_2\text{O}\) and 4g of \(\text{NH}_4\text{CNS}\) were dissolved together in 100 ml water. This solution was concentrated by evaporation at 60°C under reduced pressure until crystals appeared. The mixture was cooled and the precipitate filtered. The precipitated crystals were dissolved in water and recrystallised again under reduced pressure.

The product was bright yellow.

**Analysis of \((\text{NH}_4)_2 \text{Mo(SCN)}_5 \cdot 4\text{H}_2\text{O}\)**

- **Calculated:** Mo 19.4; CNS 58.7;
- **Found:** Mo 19.4; CNS 58.8:
(ix) **Potassium pentacyano molybdate (IV)**

\[ \text{K Mo(CN)}_5 \]

Equal parts (gravimetric) of molybdenum trioxide and potassium cyanide were weighed. The molybdenum trioxide was dissolved in excess aqueous solution of potassium cyanide. The solution was filtered and concentrated by boiling. The solution was allowed to crystallise over a period of three weeks and white crystals separated. These crystals were redissolved and reprecipitated.

Analysis of K Mo(CN)\(_5\) :-

**Calculated:** Mo 36.3; CN 49.3; K 14.7;

**Found:** Mo 36.4; CN 49.1; K 14.8;
(x) **Potassium octacyano molybdate (IV)**

\[ K_4 \text{Mo(CN)}_8 \cdot 2\text{H}_2\text{O} \]

10g molybdenyl hydroxide \( \text{MoO(OH)}_3 \) and 20g of solid potassium cyanide were ground together in an agate mortar. Over a period of two hours, 60g of water were added with frequent mixing.

This mixture (brown) was poured into a flask and refluxed for three hours. The colour changes were from brown to green to yellowish-green. The water was then evaporated and a mixed product resulted, yellow crystals and green crystals. These were dehydrated in a beaker over an open flame about 200-300\(^\circ\)C when only yellow crystals remained.

The cyano complex, yellow crystals, was then dissolved in a small amount of water and the solution remained yellow. This solution, 20 ml, was poured slowly into 200 ml alcohol with brisk stirring. Very small crystals precipitated. By analysis these were found to be impure - contaminated with potassium cyanide.

Purification was achieved by brisk stirring in 70:30 alcohol and water, decanting the liquid and repeating the operation 8 to 10 times. The yellow crystals were given a final wash with absolute alcohol and dried at 40\(^\circ\)C.

**Analysis of \( K_4 \text{Mo(CN)}_8 \cdot 2\text{H}_2\text{O} \):**

- **Calculated:** Mo 19.3; CN 41.9; K 31.4
- **Found:** Mo 19.4; CN 42.2; K 31.3
The molybdenum hydroxide MoO(OH$_3^-$) for the above preparation of K$_4$ Mo(CN)$_8$ .2H$_2$O was prepared by Palmer’s Method "Experimental Inorganic Chemistry" - Palmer page 406 (48). Ammonium molybdate solution with hydrochloric acid and mercury is shaken to give a dark red solution. Ammonium carbonate is added to the filtrate and heated to boil whilst passing a current of carbon dioxide. The preparation is cooled with continued passage of carbon dioxide. The precipitate is filtered, washed with air-free water and finally with acetone.

(xi) 2nd Preparation
Potassium octacyano molybdate (IV)

K$_4$ Mo(CN)$_8$ .2H$_2$O

4g K$_3$ Mo Cl$_6$ were dissolved in 40 ml water. The solution was refluxed for about 10 hours. A small amount of dark green precipitate formed and this was filtered. The filtrate was evaporated by boiling until crystals just began to form. Alcohol was added and the precipitate of small yellow-green crystals were separated. Excess potassium cyanide was extracted from this product by several leachings with 70:30 alcohol/water mixture. The final product was a canary yellow.

Analysis:- K 31.4; Mo 19.3; CN 42.0;
Preparation of potassium tetracyanodioxo molybdate(IV)

$K_4 MoO_2 (CN)_4$

10g of molybdenum trioxide $MoO_3$ and 20g of solid potassium cyanide were mixed by grinding together in an agate mortar. To this mixture were added 60g water over a period of 2 hours. The solution was refluxed 3 hours and gave a yellowish-brown coloured solution. The solution was then evaporated until saturated and on crystallisation red crystals formed.

The crystals were redissolved in 20 ml water, giving again a yellowish-brown solution. The cyanide complex was purified by stirring them briskly in a mixture of alcohol and water, 70:30, decanting the supernatant liquor and repeating the process 8-10 times. The final product was washed with absolute alcohol and dried at 40°C and the colour was brownish-red.

Analysis of $K_4 MoO_2 (CN)_4$: -

Calculated: $K 40.1$; $Mo 24.7$; $CN 26.9$;

Found: $K 39.9$; $Mo 24.5$; $CN 27.0$;
Following Bucknall and Wardlaw's method for

\[ \text{K}_4 \text{Mo(OH)}_4(\text{CN})_4 \cdot 4\text{H}_2\text{O} \]

150 ml of 10% \( \text{MoO}_3 \) in 3N hydrochloric acid were electrolysed (using a mercury cathode and platinum anode). to the molybdenum (V) state. The electrolysed solution was concentrated under reduced pressure at 60-70\(^\circ\)C to about 15 ml. On the careful addition of very concentrated potassium hydroxide the brown hydroxide of quinquevalent molybdenum was obtained. On the addition of the theoretical amount of potassium cyanide (27g) as a saturated solution the hydroxide slowly dissolved. This solution was concentrated under reduced pressure at 70\(^\circ\)C and alcohol was added when a red precipitate formed. The product was washed with absolute alcohol and dried.

**Analysis:**

Calculated: Mo 24.7; CN 26.8;

Found: Mo 24.7; CN 26.9;
The Preparations of Potassium heptacyano molybdate (III)  

\[ K_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O} \]

The tervalent molybdenum cyanide complex \( K_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O} \) was prepared in three ways. One following Young's method of allowing \( K_3 \text{MoCl}_6 \) to react with KCN and water in a nitrogen atmosphere and subsequently precipitating the black cyanide from solution with alcohol. The second method was similar; \((\text{NH}_4)_3 \text{MoCl}_6 \) and KCN (7g to 12g) were mixed together and were allowed to react with a small amount of water in a carbon dioxide atmosphere over a period of 15 to 18 hours. In the third method potassium cyanide was added to a solution of \( \text{MoCl}_3 \) in hydrochloric acid and the resultant solution was placed in an electrolysis cell and electrolysed for 15 hours. The black cyanide was precipitated by introducing air-free alcohol saturated with hydrogen.
(xiv) **Potassium heptacyano molybdate (III)**

\[ K_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O} \]

2g \( K_3 \text{MoCl}_6 \) and 3.5g KCN and 20 ml of air-free water were introduced into a reaction vessel and an inert nitrogen atmosphere was maintained for 18 hours. The red solution changed to brown and a precipitate formed, probably an hydroxide, the solution became black and ultimately all the precipitate dissolved to give a dark red-brown solution. Air-free absolute alcohol was introduced and a black precipitate formed. This was washed by decantation several times with absolute alcohol and finally filtered and again washed with absolute alcohol. A nitrogen atmosphere was maintained throughout.

(xv) **2nd Preparation**

2g \((\text{NH}_4)_3 \text{MoCl}_6\) and 3.5g KCN were mixed together and about 10 ml of air-free water added in a small flask in which a carbon dioxide atmosphere was maintained over a period of 15 hours. Air-free, \(\text{CO}_2\) saturated, absolute alcohol was added and washing done by decantation. The black product was filtered under a \(\text{CO}_2\) atmosphere and washed with absolute alcohol.
250 ml of Mo Cl₃ solution (250g H₂MoO₄/1) in hydrochloric acid were added to 36g KCN. This solution was placed in an electrolysis cell and electrolysed for 18 hours using a mercury cathode and a platinum anode.

Absolute alcohol air-free and saturated with hydrogen was introduced under pressure into the cell and a black precipitate formed from a dark reddish-brown solution.

The black precipitate was tapped off from the bottom of the electrolysis cell into air-free absolute alcohol, washed by decantation with absolute alcohol and filtered and again washed. Hydrogen atmosphere was maintained except for the final filtration. Provided that as much water as possible is removed by decantation processes and that filtration is done quickly, the product does not alter appreciably.

Analysis of K₄Mo(CN)₇·2H₂O:

Calculated:  K 33.2;  Mo 20.4;  CN 38.7;

Found:  K 33.3;  Mo 20.4;  CN 38.5;
Ammonium tetraoxalato molybdenum (IV)  
\((\text{NH}_4)_4\text{Mo(OX)}_4\cdot 8\text{H}_2\text{O}\)

Or the double salt \((\text{NH}_4)_2\text{Mo(OX)}_3\cdot (\text{NH}_4)_2\text{OX}\cdot 8\text{H}_2\text{O}\)

This preparation was made by electrolytic reduction. The electrolyte was made by dissolving 10g ammonium molybdate, \((\text{NH}_4)_2\text{MoO}_4\), 10g of ammonium oxalate, 20g oxalic acid in 250 ml of water. The electrodes were platinum anode, mercury cathode (1\(\frac{1}{2}\)" diam.), sintered glass partition was used to separate the anolyte from the catholyte. The electrolysis proceeded at 24 volts, 2 to 3 amps, for 12-14 hours.

The initial colour of the electrolyte was a clear, slightly brown, colour. At the commencement of electrolysis the colour became a golden yellow and changed to yellowish-brown to a reddish-brown when hydrogen commenced to be evolved at the cathode (the Mo(III) stage). The temperature rose to 75°C during electrolysis and the final colour of the reduced electrolyte was red.

The reduced electrolyte was removed from the cell without any protective atmosphere and was placed in the refrigerator for crystallisation after being filtered.

A small amount (1-2g) of brownish material separated. This was filtered off and washed with alcohol. Before washing with alcohol this precipitate began to change to a bluish colour on the surface as soon as the mother liquor had drained off. After the alcohol wash this product was dried to a light
fawn colour. This material was set aside for later investigation.

Alcohol was added to the filtrate and a yellowish-brown precipitate formed giving a good yield. This precipitate was very light and after filtering and washing with alcohol it was dried at 40°C to give a light brown product. This ammonium oxalato molybdates (IV) charred at 60°C.

Analysis of (NH₄)₄ Mo(OX)₄ ⋅ 8H₂O

Calculated: Mo 14.5; OX 53.6; NH₄ 10.8;

Found: Mo 14.5; OX 53.3; NH₄ 10.8;
(xviii) Tris-o-phenanthroline molybdenum (III) chloride

\[
\text{Mo(phen)}_3 \text{Cl}_3
\]

0.5g \(\text{Mo Cl}_6\) were dissolved in water and alcohol and a few ml of HCl added. To this solution was added 0.5g of o-phenanthroline alcohol solution. The red solution was concentrated under reduced pressure at 60°C.

The dark red product was washed with water and then with a little alcohol.

Calculated: Mo 12.35; Cl 13.6:
Found: Mo 12.2; Cl 13.5:

(xix) Tris-o-phenanthroline molybdenum (III) iodide

\[
\text{Mo(phen)}_3 \text{I}_3
\]

0.5g \(\text{NH}_4\) \(\text{Mo Cl}_6\) were dissolved in water with a few grams of KI, alcohol was added and a few ml of HI. To this solution was added 0.6g o-phenanthroline dissolved in alcohol. The mixture was red. On concentrating under reduced pressure at 60°C a dark chocolate precipitate formed. This was water washed and alcohol washed.

Calculated: Mo 9.1; I 36.1:
Found: Mo 9.0; I 36.5:
Tris-2,2'-dipyridyl molybdenum (III) chloride
Mo(dipy)_3 Cl_3

0.6g (NH_4)_3 Mo Cl_6 were dissolved in water and alcohol; a few ml of H Cl were added. This was mixed with an alcohol solution of 0.78g of 2:2'-dipyridyl. The solution was red and was concentrated under reduced pressure 60°C. The dark red product was water washed, then washed with alcohol.

Calculated: Mo 14.3; Cl 15.85;
Found: Mo 14.4; Cl 15.8;
(xxii) **Tris-2:2-dipyridyl molybdenum (III) iodide**

\[
\text{Mo(dipy)}_3 \text{I}_3
\]

0.6g \( \text{NH}_4 \text{Cl}_3 \) Mo Cl\(_6\) were dissolved in water and alcohol and HI (drops) and added to 0.78g of 2:2 dipyridyl in alcohol. The solution was red. This red solution was reduced concentrated under pressure at 60°C. The chocolate coloured product was water washed and alcohol washed.

Calculated: Mo 10.15; I 40.2:

Found: Mo 10.0; I 40.1:

(xxiii) **Tris-2:2-dipyridyl molybdenum (III) bromide**

\[
\text{Mo(dipy)}_3 \text{Br}_3
\]

0.35g K\(_3\) Mo Br\(_6\) dissolved in water and alcohol with a few ml of H Br added. This was mixed with 0.25g of 2:2 dipyridyl solution in alcohol. An orange-yellow precipitate formed immediately.

The mixture was concentrated under reduced pressure at 60°C and the product was washed with water and with alcohol.

Calculated: Mo 11.8; Br 29.2:

Found: Mo 11.8; Br 29.3:
B. METHODS OF ANALYSIS

(i) Tervalent Molybdenum Halo Complexes

Molybdenum ion: A known weight of the tervalent molybdenum Halo complexes was dissolved in water and titrated directly with standard potassium permanganate solution. With valency 3, 1 ml of 0.1 N. permanganate equals Mol. Wt. of Mo\(^{3+}\) = 0.0032.

\[
\% \text{ Mo} = \frac{\text{ml titrant} \times 0.1 \text{N. KMnO}_4 \times 0.0032}{\text{wt. of sample}} \times 100.
\]

The molybdenum was also determined by dissolving the complex in water, adding sulphuric acid and reducing the molybdenum, or any molybdenum which may have oxidised, with zinc to the tervalent state. The reduced solution was transferred to a solution of ferric alum and phosphoric acid and titrated with potassium permanganate standard solution.

Ammonium ion: The ammonium ion was determined by the chloroplatinate method. The platinum in the ammonium chloroplatinate was reduced with aluminium and weighed as platinum after washing with alcohol and drying. The ammonium ion content being calculated from the weight of platinum.

Potassium ion: The potassium ion was determined by the chloroplatinate method. The platinum in the potassium salt being reduced with aluminium and weighed as platinum from which the potassium was calculated.
Halogen ion:- The halogen ion was determined by (a) titration with standard silver nitrate solution and (b) gravimetric determination as silver halide.

(ii) Tervalent Molybdenum Hexathiocyanato Complex.

Molybdenum ion:- The tervalent molybdenum in this complex could not be titrated directly with potassium permanganate because of the oxidation of the thiocyanate ion. The complex was fumed with sulphuric acid to destroy the thiocyanate ion, diluted with water; the molybdenum was reduced with zinc to the Mo(III) state, the reduced solution was transferred to a solution of ferric alum and phosphoric acid and titrated with standard potassium permanganate.

Ammonium ion:- The ammonium ion was determined by distillation.

Thiocyanate ion:- The thiocyanate ion was determined by adding an excess of standard silver nitrate and back titrating the excess silver nitrate with a standard solution of thiocyanate.

Acetone:- The acetone was determined by slowly adding standard iodine solution in excess. The excess iodine was back titrated with standard thiosulphate solution. A blank was run with a known amount of thiocyanate.

Scott and Furman "Standard Methods of Chemical Analysis" Vol.2. 2134 (85).
(iii) The Cyano Complexes of Molybdenum

**Molybdenum ion:** The molybdenum ion was determined by destroying the cyanide by sulphuric acid digestion. The molybdenum being reduced with zinc, the reduced solution being transferred to a ferric alum-phosphoric acid solution and titrated with standard potassium permanganate.

**Potassium ion:** The potassium ion was determined by the chloro platinic method and reduction to platinum.

**Cyanide ion:** The cyanide was determined by precipitating the cyanide as silver cyanide gravimetric method.

In $K_4 \text{Mo(CN)}_8 \cdot 2\text{H}_2\text{O}$ the cyanide was determined by distillation with ammonium sulphate in a micro kjeldahl flask. The cyanide was collected in an acidified silver nitrate solution as $\text{AgCN}$.

In $K\text{Mo(CN)}_5$ the cyanide was also determined by the distillation of nitrogen as ammonia.
Molybdenum ion: The molybdenum was determined after digestion with sulphuric acid to destroy the oxalate and carbonate groups by the reduction with zinc method.

Ammonium ion: The ammonium was determined by the chloro platinate method and reduction to platinum.

Potassium ion: The potassium was determined by the chloroplatinate method and reduction to platinum.

Oxalate ion: The oxalate was determined by precipitating the oxalate as calcium oxalate. The oxalic acid liberated from the calcium oxalate with sulphuric acid was titrated at 80°C with standard potassium permanganate.

Carbonate ion: The carbonate was determined gravimetrically as barium carbonate.
**GENERAL PROPERTIES**

\( \text{K}_5 \text{Mo(CN)}_5 \)

White crystals, are not very soluble in water - colourless solution, insoluble in general organic solvents. Soluble in KCN solution. On heating the crystals colour-change to brown then give a yellow melt and on cooling a white crystalline product.

\( \text{K}_4 \text{Mo(CN)}_8 \cdot 2\text{H}_2\text{O} \)

Yellow crystals; very soluble in water to give a yellow solution; not soluble in the common organic solvents; melts at about 300°C to give a black solid.

\( \text{K}_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O} \)

Black solid; soluble in water to give a brown solution; insoluble in alcohol; changes to yellow cyanide in the presence of moisture.

\( \text{K}_4 \text{MoO}_2\text{(CN)}_4 \)

Brown compound, red when moistened with potassium hydroxide; very soluble in water to give a yellowish-brown solution; it does not melt but decomposes to give off cyanide and leave a white water insoluble residue.

\( \text{(NH}_4\text{)}_3 \text{MoCl}_6 \)

Rose red crystals; very soluble in water to give a red solution; insoluble in general organic solvents; on heating it decomposes to give off ammonium chloride and a yellow residue.

\( \text{K}_3 \text{MoCl}_6 \)

Brick red compound; very soluble in water to give a red solution; insoluble in general organic solvents; on heating it melts and decomposes and leaves a black residue.
Li$_3$MoCl$_6$·9H$_2$O  Wine-red crystals extremely soluble in water to give a red solution; the crystals are very hygroscopic; soluble in acetone, alcohol, and ether.

(NH$_4$)$_3$Mo(SCN)$_6$·4H$_2$O  Yellow crystals very soluble in water; soluble in acetone and alcohol. Decomposes at about 60°C.

NH$_4$Mo(OX)$_4$·8H$_2$O  Brown compound; very soluble in water to give a reddish-brown solution; insoluble in general organic solvents; it chars at 60°C.

(NH$_4$)$_2$MoCl$_5$·H$_2$O  Bright brick-red crystals; very soluble in water to give a light red solution. Permanaganate oxidises the complex in solution to a deep blue colour which disappears on complete oxidation.

K$_3$Mo Br$_6$  Brick-red crystals, soluble in water and alcohol to give a yellow solution.

(NH$_4$)$_2$Mo(SCN)$_5$·4H$_2$O  Bright yellow crystals; similar properties to the hexathiocyanate. Addition products HCl or acetic acid do not seem to occur with the penta complex as happens with the hexathiocyanate.

The above compounds are not soluble in nitrobenzene.
Mo(phen)$_3$ Cl$_3$  
Dark-red powder; slightly soluble in alcohol and acetone; insoluble in water and nitrobenzene.

Mo(phen)$_3$ I$_3$  
Chocolate powder; slightly soluble in alcohol and acetone; insoluble in water and nitrobenzene.

Mo(dipy)$_3$ Cl$_3$  
Dark-red powder; slightly soluble in alcohol and acetone; insoluble in water and nitrobenzene.

Mo(dipy)$_3$ I$_3$  
Chocolate powder; slightly soluble in alcohol and acetone; insoluble in water and nitrobenzene.

Mo(phen)$_3$ Br$_3$  
Orange powder, insoluble in water and alcohol; soluble in nitrobenzene.

Mo(dipy)$_3$ Br$_3$  
Orange-yellow powder; insoluble in water and alcohol; soluble in nitrobenzene.

The colours of the dipyridyl complexes are brighter than those of the corresponding phenanthroline complexes.
C. Magnetic Susceptibility Determinations

The Gouy method was used for the determination of magnetic susceptibilities in this thesis.

The Magnet: The electro-magnet was constructed by winding two coils of 1460 turns of 14 gauge enamelled copper wire around one inch mild steel cores. The pole pieces were set 0.4 inches apart and by using an amperage of 16 the field across the pole pieces was 10,000 gauss. No residual field remained beyond one second after the current had been switched off.

The Gouy tube was of glass and was suspended by a glass ferrule and a thin glass rod from a semi-micro balance. To determine the height of the material to be used the relationship between $H_2$ and $H_1$ was established from the following figures:
Pull on CuSO\(_4\) \(\cdot\) 5H\(_2\)O (powdered) V

Height in Gouy Tube

Amps. 16.0  Temp. 20.8°C.

<table>
<thead>
<tr>
<th>Height (Cms.)</th>
<th>Mag. off</th>
<th>Mag. On</th>
<th>(\Delta W)</th>
<th>Pull on CuSO(_4) (\cdot) 5H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.17080</td>
<td>3.17052</td>
<td>-0.28</td>
<td>1.35</td>
</tr>
<tr>
<td>2</td>
<td>3.29440</td>
<td>3.30327</td>
<td>+8.87</td>
<td>10.50</td>
</tr>
<tr>
<td>3</td>
<td>3.42679</td>
<td>3.43804</td>
<td>+11.25</td>
<td>12.88</td>
</tr>
<tr>
<td>4</td>
<td>3.55794</td>
<td>3.56978</td>
<td>+11.84</td>
<td>13.47</td>
</tr>
<tr>
<td>5</td>
<td>3.68190</td>
<td>3.69374</td>
<td>+11.84</td>
<td>13.47</td>
</tr>
<tr>
<td>6</td>
<td>3.82760</td>
<td>3.83944</td>
<td>+11.84</td>
<td>13.47</td>
</tr>
</tbody>
</table>

4 Cms. Height

Amps. V. Pull.

<table>
<thead>
<tr>
<th>Amps.</th>
<th>Pull on CuSO(_4) (\cdot) 5H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>3.54998 + 2.37 4.00</td>
</tr>
<tr>
<td>3</td>
<td>3.55150 + 3.89 5.52</td>
</tr>
<tr>
<td>6</td>
<td>3.55418 + 6.57 8.20</td>
</tr>
<tr>
<td>8</td>
<td>3.55562 + 8.01 9.64</td>
</tr>
<tr>
<td>10</td>
<td>3.55620 + 8.59 10.22</td>
</tr>
<tr>
<td>12</td>
<td>3.55750 + 9.89 11.52</td>
</tr>
<tr>
<td>14</td>
<td>3.55800 +10.39 12.02</td>
</tr>
<tr>
<td>16</td>
<td>3.55860 +10.99 12.62</td>
</tr>
<tr>
<td>18</td>
<td>3.55920 +11.39 13.02</td>
</tr>
<tr>
<td>20</td>
<td>3.55952 +11.71 13.34</td>
</tr>
</tbody>
</table>
From the graph the required height of the material to be taken is 4 cm.

Using 4 cm of powdered CuSO₄·5H₂O the pull on the material was recorded against increasing amperage. This only showed that increasing amperage gave increasing pull on the balance but it was noted that at 16 amps and higher the temperature of the coils increased. At 16 amps the temperature was constant particularly with intermittent work and it was decided to use 16 amps.

Having established the height of the material to be taken and having selected the amperage to be used in the circuit, the Gouy tube was calibrated using powdered CuSO₄·5H₂O \((\chi \times 10^6 = 5.90 \text{ at } 20^\circ \text{C})\)

Having calibrated the tube the reduced expression

\[
\chi = \frac{\lambda + \beta \Delta w}{W}
\]

was used to determine the \(\chi\) value.

The value of \(\lambda\) was determined by multiplying the volume susceptibility of air taken as 0.029 by the volume of 4 cm of the tube \(\lambda = 0.029 V = 0.010\).

The constant \(\beta\) was calculated from the expression

\[
10^6 \chi = \frac{\lambda + \beta F'}{W}
\]

where \(F'\) = the pull on the tube, \(F\) plus the pull \(\varepsilon\) on the tube. That is \(F' = F + \varepsilon\)

From these calculations \(\beta = 0.223\)
<table>
<thead>
<tr>
<th>Wt. of 4cm water (g)</th>
<th>Tube Weight</th>
<th>Volume (ml)</th>
<th>Temp. °C</th>
<th>λ (0.029 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.38629</td>
<td>3.03860</td>
<td>0.34769</td>
<td>17</td>
<td>0.01008</td>
</tr>
<tr>
<td>3.38550</td>
<td>&quot;</td>
<td>0.34690</td>
<td>&quot;</td>
<td>0.01006</td>
</tr>
<tr>
<td>3.38776</td>
<td>&quot;</td>
<td>0.34916</td>
<td>&quot;</td>
<td>0.01012</td>
</tr>
<tr>
<td>3.38750</td>
<td>&quot;</td>
<td>0.34860</td>
<td>&quot;</td>
<td>0.01011</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Magnet</th>
<th>Δ w m.g.</th>
<th>Amps.</th>
<th>Temp. °C</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off</td>
<td>On</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.43942</td>
<td>3.44781</td>
<td>+8.39</td>
<td>16</td>
<td>17.9</td>
</tr>
<tr>
<td>3.42451</td>
<td>3.43304</td>
<td>+8.53</td>
<td>16</td>
<td>17.5</td>
</tr>
<tr>
<td>3.49336</td>
<td>3.50364</td>
<td>10.28</td>
<td>16</td>
<td>18.1</td>
</tr>
<tr>
<td>3.49032</td>
<td>3.50070</td>
<td>10.38</td>
<td>16</td>
<td>17.3</td>
</tr>
<tr>
<td>3.49172</td>
<td>3.50212</td>
<td>10.40</td>
<td>16</td>
<td>17.5</td>
</tr>
<tr>
<td>3.49182</td>
<td>3.50223</td>
<td>10.41</td>
<td>16</td>
<td>17.7</td>
</tr>
<tr>
<td>3.51162</td>
<td>3.52252</td>
<td>10.90</td>
<td>16</td>
<td>17.7</td>
</tr>
<tr>
<td>3.49232</td>
<td>3.50292</td>
<td>10.60</td>
<td>16</td>
<td>17.8</td>
</tr>
<tr>
<td>3.45239</td>
<td>3.46169</td>
<td>9.30</td>
<td>16</td>
<td>18.1</td>
</tr>
<tr>
<td>3.43311</td>
<td>3.44210</td>
<td>8.99</td>
<td>16</td>
<td>18.3</td>
</tr>
</tbody>
</table>

(Using powdered CuSO₄·5H₂O)
\[ \chi_m' \text{ is equal to } \chi_m + \text{diamagnetic corrections} \]
and the effective magnetic moments of the molybdenum in
the paramagnetic complexes were calculated from the
expression,
\[
\mu(\text{eff}) = 2.84 \sqrt{\chi_m' \times T}
\]

The diamagnetic corrections used in the experimental
work were from Selwood "Magneto Chemistry" pp. 36, 46, (55)
and Van Vleck "Electric and Magnetic Susceptibilities"
pp. 223, 225 (61).

<table>
<thead>
<tr>
<th>ATOM</th>
<th>$-\chi \times 10^{-6}$</th>
<th>ATOM</th>
<th>$-\chi \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>23.4</td>
<td>CN$^-$</td>
<td>13.0</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>1.0</td>
<td>NCS$^-$</td>
<td>31.0</td>
</tr>
<tr>
<td>K$^+$</td>
<td>14.9</td>
<td>NH$_4^+$</td>
<td>13.3</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>34.6</td>
<td>O (covalent)</td>
<td>4.6</td>
</tr>
<tr>
<td>I$^-$</td>
<td>50.6</td>
<td>C (covalent)</td>
<td>6.0</td>
</tr>
<tr>
<td>H (covalent)</td>
<td>2.93</td>
<td>N (ring)</td>
<td>4.6</td>
</tr>
<tr>
<td>Water</td>
<td>$\chi \times 10^6$</td>
<td>at $20^\circ$</td>
<td>$= -0.7218$</td>
</tr>
</tbody>
</table>

The magnetic susceptibilities of the complexes are
given in tabular form on the following two pages.
### Magnetic Susceptibility Measurements

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\chi \times 10^6$</th>
<th>$\chi_m \times 10^6$</th>
<th>$(\chi_m) + \text{Diamagnetic Corrections}$</th>
<th>Temp. °C</th>
<th>Magnetic Moments $\mu$ (Bohr Magnetons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{NH}_4)_3\text{[MoCl}_6\text{]}$</td>
<td>16.49</td>
<td>5986</td>
<td>6166</td>
<td>24</td>
<td>3.84</td>
</tr>
<tr>
<td>$K_3\text{[MoCl}_6\text{]}$</td>
<td>13.15</td>
<td>5604</td>
<td>5789</td>
<td>18</td>
<td>3.7</td>
</tr>
<tr>
<td>$K_3\text{[MoBr}_6\text{]}$</td>
<td>8.68</td>
<td>5918</td>
<td>6239</td>
<td>19.5</td>
<td>3.84</td>
</tr>
<tr>
<td>$\text{Li}_3\text{[MoCl}_6\text{]} \cdot 9\text{H}_2\text{O}$</td>
<td>11.58</td>
<td>5796</td>
<td>6145</td>
<td>24</td>
<td>3.84</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2\text{[MoCl}_5 \cdot \text{H}_2\text{O]}$</td>
<td>17.9</td>
<td>5853</td>
<td>6007</td>
<td>21</td>
<td>3.86</td>
</tr>
<tr>
<td>$(\text{NH}_4)_3\text{[Mo(SCN)]}_6 \cdot 4\text{H}_2\text{O}$</td>
<td>10.80</td>
<td>6156</td>
<td>6434</td>
<td>22.4</td>
<td>3.86</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2\text{[Mo(SCN)]}_5 \cdot 4\text{H}_2\text{O}$</td>
<td>12.37</td>
<td>6110</td>
<td>6344</td>
<td>16</td>
<td>3.84</td>
</tr>
<tr>
<td>$(\text{NH}_4)_3\text{[Mo(SCN)]}_6 \cdot 3\text{CH}_3\text{CO} \cdot \text{CH}_3$</td>
<td>8.01</td>
<td>5443</td>
<td>5792</td>
<td>20</td>
<td>3.72</td>
</tr>
</tbody>
</table>

<p>| $K\text{[Mo(CN)]}_5$                  | -0.127              |                       | Diamagnetic                                 |          | 0                                      |
| $K_4\text{[Mo(CN)]}_8 \cdot 2\text{H}_2\text{O}$ |                      |                       | &quot;                                           |          | 0                                      |
| $K_4\text{[MoO}_2\text{(CN)}_4\text{]}$ |                      |                       | &quot;                                           |          | 0                                      |
| $K_4\text{[Mo(CN)]}_7 \cdot 2\text{H}_2\text{O}$ |                      |                       | &quot;                                           |          | 0                                      |</p>
<table>
<thead>
<tr>
<th>Complex</th>
<th>$\chi \times 10^6$</th>
<th>$\chi_m \times 10^6$</th>
<th>$\chi_m' \times 10^6$</th>
<th>Temp. °C</th>
<th>Magnetic Moments (Bohr Magnetons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mo(phen)$_3$] Br$_3$</td>
<td>6.38</td>
<td>5819</td>
<td>6238</td>
<td>19.5</td>
<td>3.83</td>
</tr>
<tr>
<td>[Mo(dipy)$_3$] Br$_3$</td>
<td>7.26</td>
<td>5837</td>
<td>6256</td>
<td>20.1</td>
<td>3.84</td>
</tr>
<tr>
<td>[Mo(dipy)$_3$] Cl$_3$</td>
<td>7.84</td>
<td>5263</td>
<td>5648</td>
<td>20.5</td>
<td>3.66</td>
</tr>
<tr>
<td>[Mo(phen)$_3$] Cl$_3$</td>
<td>7.43</td>
<td>5780</td>
<td>6300</td>
<td>20.</td>
<td>3.83</td>
</tr>
<tr>
<td>[Mo(dipy)$_3$] I$_3$</td>
<td>6.13</td>
<td>5790</td>
<td>6290</td>
<td>17.7</td>
<td>3.84</td>
</tr>
<tr>
<td>[Mo(phen)$_3$] I$_3$</td>
<td>5.80</td>
<td>6130</td>
<td>6630</td>
<td>19.</td>
<td>3.84</td>
</tr>
</tbody>
</table>
D. CONDUCTIVITY MEASUREMENTS

Conductivity measurements show that the chloride complexes hydrolysed slightly and that the cyanides were comparatively stable with very slight hydrolysis.

In the first instance measurements were taken on \((\text{NH}_4)_3\text{MoCl}_6\) with dilution.

The conductivity cell had fixed electrodes (1 cm apart); the cell constant was 0.3853 cm

One gram of \((\text{NH}_4)_3\text{MoCl}_6\) was dissolved in 25 ml of conductivity water and the resistance measured at 25°C and 1°C.

<table>
<thead>
<tr>
<th>Dilution (ml)</th>
<th>Conc.</th>
<th>√Conc.</th>
<th>Molecular Conductance at 25°C</th>
<th>Molecular Conductance at 1°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.1103</td>
<td>0.332</td>
<td>115</td>
<td>233</td>
</tr>
<tr>
<td>50</td>
<td>0.0552</td>
<td>0.234</td>
<td>115</td>
<td>249</td>
</tr>
<tr>
<td>100</td>
<td>0.0272</td>
<td>0.165</td>
<td>125</td>
<td>268</td>
</tr>
<tr>
<td>200</td>
<td>0.0138</td>
<td>0.1175</td>
<td>134</td>
<td>304</td>
</tr>
<tr>
<td>400</td>
<td>0.0069</td>
<td>0.083</td>
<td>147</td>
<td>331</td>
</tr>
<tr>
<td>800</td>
<td>0.0035</td>
<td>0.059</td>
<td>159</td>
<td>380</td>
</tr>
<tr>
<td>1600</td>
<td>0.00175</td>
<td>0.0417</td>
<td>192</td>
<td>425</td>
</tr>
<tr>
<td>3200</td>
<td>0.000875</td>
<td>0.0296</td>
<td>269</td>
<td>529</td>
</tr>
</tbody>
</table>

Molecular conductivity of \((\text{NH}_4)_3\text{MoCl}_6\) at infinite dilution was then plotted against time as hydrolysis was indicated from the molecular conductivities on progressive dilution.

A solution one gram mol. per 1024 litres was made and the following figures show how the molecular conductivity increased with time at 25°C.
Time (mins.) 2.5, 3.5, 4.5, 5.0, 6.0, 7.0, 8.0. 
Mol. Cond.(M/1024) 375, 364, 360, 381, 384, 394, 394, 398, 400. 
Time (mins.) 9.0, 9.5, 10.0, 11.0, 12.0, 13.0, 14.0, 15.0, 16.0. 
Time (mins.) 17.0, 18.0, 19.0, 20.0, 21.0, 22.0, 23.0, 24.0. 
Time (mins.) 25.0, 26.0, 27.0, 28.0, 29.0, 30.0, 31.0, 32.0. 
Time (mins.) 33.0, 34.0, 35.0, 36.0, 37.0, 38.0, 39.0, 40.0. 
Mol. Cond. 466, 467, 469, 471, 475, 490, 510, 795. 
Time (mins.) 41.0, 42.0, 43.0, 44.0, 45.0, 50.0, 60.0, 195. 

These conductivity measurements show that hydrolysis occurs with time. Molecular conductivity at infinite dilution at zero time, a conductivity of 375 mho is obtained. With three ammonium ions and one triple charged anion the molecular conductance indicates four ions present.

K₃MoCl₆ 0.0416g in 100 ml water 25°C

Mol. Cond.(M/1024) 375, 391, 393, 398, 407, 412, 418, 422, 442, 470, 480, 483 
Time (mins.) 3, 4.5, 5, 6, 7, 8, 9, 10, 15, 20, 22, 25. 
Mol. Cond. 486, 494, 503, 517, 553, 563. 
Time (mins.) 30, 35, 40, 45, 56, 60.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass (g) in 100 ml water, Temp.</th>
<th>Mol. Cond. (M/1000)</th>
<th>Time (mins.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_3\text{MoBr}_6$</td>
<td>0.0693g in 100 ml water, 25°C</td>
<td>360, 365, 367, 372, 389, 391, 392.</td>
<td>1, 2, 3, 5, 15, 20, 25.</td>
</tr>
<tr>
<td>$(NH_4)_2\text{MoCl}_5 \cdot H_2O$</td>
<td>0.0327g/100 ml water, 25°C</td>
<td>265, 266, 273, 284, 287, 289, 302.</td>
<td>0.5, 2, 3, 6, 8, 10, 15.</td>
</tr>
<tr>
<td>$Li_3\text{MoCl}_6 \cdot 9H_2O$</td>
<td>0.0572g/100 ml water, 25°C M/980.</td>
<td>275, 275, 277</td>
<td>5, 10, 30.</td>
</tr>
<tr>
<td>$(NH_4)_3\text{Mo(SCN)}_6 \cdot 3(CH_3)_2 CO$</td>
<td>0.0671g/100 ml water, 25°C</td>
<td>546, 547, 548, 549.</td>
<td>3, 6, 13, 18.</td>
</tr>
<tr>
<td>$(NH_4)_3\text{Mo(SCN)}_6 \cdot 4H_2O$</td>
<td>0.0584g/100 ml water, M/960.</td>
<td>372, 375.</td>
<td>5, 75.</td>
</tr>
<tr>
<td>$(NH_4)_2\text{Mo(SCN)}_5 \cdot 4H_2O$</td>
<td>0.0494g/100 ml water, 25°C</td>
<td>276, 279, 281, 282, 282.</td>
<td>1, 2, 5, 12, 15.</td>
</tr>
<tr>
<td>$K_4\text{MoO}_2 (CN)_4$ (reddish-brown) M.W. 338</td>
<td>0.0338g/100 water, 25°C</td>
<td>354, 354, 354, 354.</td>
<td>3, 4, 5, 10.</td>
</tr>
<tr>
<td>$K_4\text{Mo(CN)}_8 \cdot 2H_2O$ (light yellow from $K_3\text{MoCl}_6$)</td>
<td></td>
<td>487, 487, 487, 487, 487, 487.</td>
<td>3, 4, 5, 6, 10.</td>
</tr>
</tbody>
</table>
\[ K_4 \text{Mo(CN)}_6 \cdot 2\text{H}_2\text{O} \quad \text{(yellow)} \quad 0.0248g/50 \text{ ml water, } 25^\circ\text{C.} \]

Mol. Cond. (M/1000) 506

\[ \text{K Mo(CN)}_5 \quad \text{(white)} \quad 0.0265g/50 \text{ ml water, } 25^\circ\text{C.} \]

Mol. Cond. (M/500) 160, 158, 157, 157, 157, 157, 157,
Time (mins.) 5, 6, 7, 8, 12, 24, 30.

\[ K_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O} \quad \text{(Black). } 0.0565g/100 \text{ ml water, } 25^\circ\text{C} \]

Mol. Cond. (M/1000) 474, 474, 474, 510, 512.
Time (mins.) 3.5, 8, 20, 45, 90.

\[ K_4 \text{Mo(CN)}_7 \cdot 2\text{H}_2\text{O}. \quad 0.0565g/100 \text{ ml water, } 25^\circ\text{C and air blown through solution.} \]

Mol. Cond. (M/1000) 520, 520, 520, 520, 520, 520.
Time (mins.) 1, 2, 3, 4, 5, 6.

pH
\[ \begin{array}{cccc}
9.26 & 9.32 & 9.34 & 9.35 \\
\hline
9.46 & - & - & -
\end{array} \]

cont'd.
10, 15, 20, 25, 80.
10.23, 10.84, 10.92, 10.93, 11.0.

\[ K_6\text{Mo(OC}_3)_5 \cdot 2\text{H}_2\text{O} \quad \text{M.W. 666. } 0.0328g/50 \text{ ml water, } 25^\circ\text{C M/1016} \]

Time (mins.) 2.5, 3, 4, 5, 6, 10, 13, 15, 25.

\[ (\text{NH}_4)_4 \text{Mo(OX)}_4 \cdot 8\text{H}_2\text{O} \]

Mol. Cond. (M/1000) 727, 730, 731, 731, 735, 735.
Time (mins.) 3.5, 5, 6, 7, 10, 160.

after this time 160 mins, the solution was diluted with the following results:

<table>
<thead>
<tr>
<th>Dilution (M/2000)</th>
<th>M/4000</th>
<th>M/8000</th>
<th>M/16000</th>
<th>M/32000</th>
<th>M/64000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. Cond.</td>
<td>790</td>
<td>845</td>
<td>936</td>
<td>1038</td>
<td>1226</td>
</tr>
<tr>
<td>Compound</td>
<td>Mol. Cond. (M/994)</td>
<td>Time (mins.)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------</td>
<td>--------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH₄)₃MoCl₆·NH₄Cl·2H₂O</td>
<td>730, 730, 730</td>
<td>3, 6, 9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li₃MoCl₆·LiCl·5H₂O</td>
<td>0.0452g/100 ml water, 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Cond. (M/1017)</td>
<td>315, 354, 422, 681</td>
<td>4, 6, 10, 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(dipy)₃Br₃</td>
<td>0.0201g/25 ml nitrobenzene, 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Cond. (M/1000)</td>
<td>45.3, 45.3, 45.3</td>
<td>2, 5, 8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(phen)₃Br₃</td>
<td>0.0228g/25 ml nitrobenzene, 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Cond. (M/1000)</td>
<td>43.6, 43.6</td>
<td>2, 16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(phen)₃Cl₂</td>
<td>0.0024g/25 ml absolute alcohol, 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Cond. (M/8000)</td>
<td>42.6, 42.6, 42.6</td>
<td>4, 12, 16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(dipy)₃Cl₃</td>
<td>0.0021g/25 ml alcohol absolute, 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Cond. (M/8000)</td>
<td>43.4, 43.4</td>
<td>9, 15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo(phen)₃I₃</td>
<td>0.0033g/25 ml absolute alcohol, 25°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mol. Cond. (M/8000)</td>
<td>43.2, 43.2, 43.2</td>
<td>2, 13, 15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**MOLECULAR CONDUCTIVITY**

of complex ions (Calculated).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Formula Weight in x litres</th>
<th>Molecular Complex Ionic Cond. (calc'd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_3[\text{MoCl}_6]$</td>
<td>1024</td>
<td>375 $[\text{MoCl}_6]^{3-}$</td>
</tr>
<tr>
<td>$\text{K}_3[\text{MoBr}_6]$</td>
<td>1000</td>
<td>370 $[\text{MoBr}_6]^{3-}$</td>
</tr>
<tr>
<td>$(\text{NH}_4)_3[\text{MoCl}_6]$</td>
<td>1024</td>
<td>375 $[\text{MoCl}_6]^{3-}$</td>
</tr>
<tr>
<td>$\text{K}_4[\text{Mo(CN)}_8] \cdot 2\text{H}_2\text{O}$</td>
<td>1000</td>
<td>504 $[\text{Mo(CN)}_8]^{4-}$</td>
</tr>
<tr>
<td>$\text{K}[\text{Mo(CN)}_5]$</td>
<td>1000</td>
<td>156 $[\text{Mo(CN)}_5]^{4-}$</td>
</tr>
<tr>
<td>$\text{K}_4[\text{MoCN}_7] \cdot 2\text{H}_2\text{O}$</td>
<td>1000</td>
<td>454 $[\text{MoCN}_7]^{4-}$</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2[\text{Mo(SCN)}_6] \cdot 4\text{H}_2\text{O}$</td>
<td>960</td>
<td>375 $[\text{Mo(SCN)}_6]^{3-}$</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2[\text{MoCl}_5] \cdot \text{H}_2\text{O}$</td>
<td>1000</td>
<td>267 $[\text{MoCl}_5]^{2-}$</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2[\text{Mo(SCN)}_5] \cdot 4\text{H}_2\text{O}$</td>
<td>1000</td>
<td>276 $[\text{Mo(SCN)}_5]^{3-}$</td>
</tr>
<tr>
<td>$[\text{Mo(dipy)}_3] \cdot \text{Br}_3$</td>
<td>1000</td>
<td>45.3 $[\text{Mo(dipy)}_3]^{3+}$</td>
</tr>
<tr>
<td>$[\text{Mo(phen)}_3] \cdot \text{Br}_3$</td>
<td>1000</td>
<td>43.6 $[\text{Mo(phen)}_3]^{3+}$</td>
</tr>
</tbody>
</table>

Values of $\lambda_0$ from Kortum and Bockris "Electrochemistry" Vol. II, (86), $\text{Li} = 38.7$; $\text{K} = 73.5$; $\text{NH}_4 = 73.5$; $\text{Cl} = 76.3$

International Critical Tables: $\text{CH}_3 = 39.9$. $\text{H}_2\text{S} = 77$; $\text{Br} = 79$. 

$0.0029g/25\text{ ml absolute alcohol. 25°C.}$
E. **MOLECULAR WEIGHT DETERMINATIONS**

\[ \text{K}_4 \text{Mo(CN)}_8 : \text{Depression of freezing point method;}
\]
with water as solvent the apparent M.W. equalled 100.4 which indicates 5 particles.

\[ \text{K}_4 \text{Mo(CN)}_7 : \text{Depression of freezing point method;}
\]
with water as solvent the apparent M.W. equalled 21.9 which indicates 20 particles. (These 20 particles arise from alteration products which are discussed in the Section on Cyanides).

\[ \text{K} \text{Mo(CN)}_5 : \text{Elevation of boiling point method; with}
\]
water as solvent the apparent M.W. equalled 132 which indicates 2 particles.
APPENDIX

A study of the colour changes during the electrolysis of Molybdenum trioxide in Hydrochloric Acid.

As a preliminary work to the preparation of Molybdenum (III) complexes by electrolysis it was considered desirable to ascertain the colour changes and the valency state of the molybdenum at certain colours. From the electrolysis of solutions of molybdenum trioxide in strong hydrochloric acid the following states occur.

Molybdenum (VI) pale yellow,
Molybdenum (V) dark green,
Molybdenum (III) cherry red.
Electrolysis of Molybdenum Trioxide MoO₃ dissolved in various Hydrochloric Acid Concentrations.

The Electrodes used for reduction were a bright platinum anode and a platinum black cathode. The electrolyte was made by dissolving 50g per litre of molybdenum trioxide in 10N, 7N and 5N hydrochloric acid.

If the electrolyte normality is greater than 8N in respect to hydrochloric acid irrespective of the concentration of molybdenum (50 to 200 g/l) the colour changes in the catholyte are from the original pale yellow to green to brown to red. The anolyte changes slightly from the original pale yellow to a slightly darker yellow colour and is probably a change from the hydroxy oxy chloride (MoO(OH)₂Cl₂) to an oxy chloride.

Electrolysis in 10N Hydrochloric Acid.

The current density was maintained at 0.014 amps per square cm. The catholyte colour change was from yellow to light green to dark green to brown to red.
<table>
<thead>
<tr>
<th>Colour</th>
<th>Redox</th>
<th>Cathode</th>
<th>Potential (Volts)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Yellow</td>
<td>+ 0.76</td>
<td>+ 0.78</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Apple Green</td>
<td>+ 0.63</td>
<td>+ 0.45</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Dark Green</td>
<td>+ 0.59</td>
<td>+ 0.47</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Between Dark Green and</td>
<td>Big drop in potential</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brown</td>
<td>+ 0.56</td>
<td>+ 0.48</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Brownish Red</td>
<td>+ 0.59</td>
<td>+ 0.49</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

A calomel reference electrode was used for figures obtained in Table 1 and Table 2.

Ether extractions were made on the various colours produced and it was found that neither the light yellow nor the apple green were extractable. The dark green gave a green ether layer and a yellow aqueous layer. The ether extractable green colour changed to yellow on further dilution with ether. The ether extractable green is tervalent; the molybdenum has three unpaired electrons calculated from magnetic susceptibility determinations.

There was a big drop in cathode potential after the green colour and before the reddish brown. This was from a positive to a large negative value but returned again to a positive potential - the change being too rapid to measure.
Electrolysis in 7N and 5N Hydrochloric Acid.

The current density was 0.014 amps per sq. cm. The anolyte behaved in a similar manner to that with 10N hydrochloric acid.

In the catholyte, however, no green colour formed, the first colour change being to brown. Further reduction gave a brownish solution as with 10N hydrochloric acid.

TABLE 2.

Potential Changes with Mo O\textsubscript{3} in 7N and 5N, HCl, Reduction

<table>
<thead>
<tr>
<th>Colour</th>
<th>Redox Potential (volts)</th>
<th>Cathode Potential (volts)</th>
<th>pH (7N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td>+0.68</td>
<td>+0.66</td>
<td>+0.03</td>
</tr>
<tr>
<td>Brown</td>
<td>+0.47</td>
<td>+0.57</td>
<td>+0.04</td>
</tr>
<tr>
<td>Brownish Red</td>
<td>+0.49</td>
<td>+0.58</td>
<td>+0.06</td>
</tr>
</tbody>
</table>

The brown solution gave a green ether extraction and a red aqueous layer the same as with 10N HCl.

The large potential change was not recorded in Table 2. It was not detected but probably occurred.

As a matter of interest the normality of electrolysed solutions of 50g/l MoO\textsubscript{3} in 10N, 7N and 5N hydrochloric acid were examined after electrolysis and these solutions were neutralized with sodium hydroxide solution.
TABLE 3.

Neutralization of Electrolysed Solutions with Sodium Hydroxide

<table>
<thead>
<tr>
<th>Original Normality</th>
<th>Normality after Electrolysis</th>
<th>Reaction with $\text{NaOH}$ at pH 7</th>
<th>$\text{NaOH}$ Redox Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>10N</td>
<td>9N</td>
<td>Blue &amp; Brown ppt.</td>
<td>-</td>
</tr>
<tr>
<td>7N</td>
<td>6.7N</td>
<td>Red ppt.</td>
<td>-</td>
</tr>
<tr>
<td>5N</td>
<td>4.9N</td>
<td>Blue ppt.</td>
<td>0.26 V.</td>
</tr>
</tbody>
</table>

(Molybdenum Blue)

Magnetic susceptibility determinations were made during the progressive electrolysis of a 50g per litre Mo $\text{O}_3$ in 10N hydrochloric acid using platinum anode and a platinized platinum cathode; voltage 4.2; amperage 0.24. The resistance of the circuit was calculated at 17.5 ohms. The anolyte and catholyte were separated in this experiment by a filter paper plug. The cathode current density was 0.178 amps. per sq. cm.

56 determinations on the Magnetic balance were made and the magnetic susceptibility was progressive until the cherry red colour was reached to give a $\mu$ value of 3.72 B.M.

From 19 hours to 35 hours the electrolysis proceeded overnight.
### TABLE 4

**Magnetic Susceptibilities vs Electrolysis**

<table>
<thead>
<tr>
<th>Colour</th>
<th>Electrolysis time (hours)</th>
<th>Magnetic Susceptibility (B.M)</th>
<th>Valency State of Molybdenum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow</td>
<td></td>
<td>diastigmatic</td>
<td>Mo (VI)</td>
</tr>
<tr>
<td>Pale Green</td>
<td>1/12 - 3/12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>1/3 - 5/12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark Green</td>
<td>1/2 - 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intense Green 3.5 - 4</td>
<td>1.64</td>
<td>Mo(V) Mo(VI)</td>
<td></td>
</tr>
<tr>
<td>Intense Green 4.5</td>
<td>1.72</td>
<td>Mo(V)</td>
<td></td>
</tr>
<tr>
<td>Brown with some Green 7.5</td>
<td>2.72</td>
<td>Mo(V) Mo(III)</td>
<td></td>
</tr>
<tr>
<td>Brown</td>
<td>9 - 10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark Brown</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brown with some Red 11.5</td>
<td>90% Mo(III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brownish Red 12 - 14</td>
<td></td>
<td>90% Mo(III)</td>
<td></td>
</tr>
<tr>
<td>Red-Brown</td>
<td>15 - 17</td>
<td>90% Mo(III)</td>
<td></td>
</tr>
<tr>
<td>Deep-Red-Brown 17 - 19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cherry Red 35</td>
<td>3.72</td>
<td>Mo(III)</td>
<td></td>
</tr>
<tr>
<td>&quot; 37</td>
<td>3.72</td>
<td>Mo(III)</td>
<td></td>
</tr>
<tr>
<td>&quot; 67</td>
<td>3.72</td>
<td>Mo(III)</td>
<td></td>
</tr>
</tbody>
</table>
DISCUSSION

The big drop in potential observed in the cathode potential in the 10N between the dark green and brown colour indicates a change from Mo(V) to Mo(IV). Mo(IV) is diamagnetic having paired electrons and it is reasonable to say that at this stage Mo(IV) is formed and it is so unstable that it does not persist for any appreciable length of time.

Poerster, Fricke and Hauswald (88)(89) in their studies on the electrolytic reduction of acid molybdenum solutions found that the Mo(IV) step is "a sudden jump" and that reduction beyond the Mo(III) step is impossible. This is in keeping with experimental work for this thesis and even 400% of current in excess of that required theoretically failed to reduce to the Mo(II) state. It was found that to produce a green state of all Mo(V) an excess of coulombs, about 12.5% above the theoretical was required; and to produce a red solution, all Mo(III), 125% extra coulombs were necessary under the conditions of the experimental electrolysis.

These excesses of the electrical equivalents over that theoretically required are due to polarization effects and probably due to the formation of a diaphragm and probably a mixture of Mo(VI) and Mo(V), \((\text{MoO}_3\text{Mo}_2\text{O}_5\cdot x\text{H}_2\text{O})\) (88)(89). The reduction Mo(V) to Mo(III) is due to concentration polarization.
The dark green solution Mo(V) was complexed with thio
cyanate and gave the characteristic blood red colour of Mo(SCN)\textsubscript{5}.

It was found that aluminium and zinc reduced Mo(VI) in 8N and 10N to green through to red whereas stannous chloride reduced the Mo(VI) to Mo(V) only; which is at a maximum of 1:1 Mo(VI)/Sn(II) (91).

The dark green Mo(V) and the cherry red Mo(III) states were confirmed by titration with standard potassium permanganate solution.

The only reported reduction of molybdenum (VI) to molybdenum (IV) is by Lois Meites. This occurred during polarographic determinations by apparently forming a stable citrate complex (92).

Molybdenum (IV), olive green, has been reported by Glemser and Sutz (93) by reduction of MoO\textsubscript{3}, suspended in hydrochloric acid, using zinc powder. The olive green compound produced is air-sensitive and unstable and they give it the formula H\textsubscript{2}Mo\textsubscript{5}O\textsubscript{7}(OH)\textsubscript{3}.

Experimental work on electrolysis for this paper has been confined to the higher concentrations of hydrochloric acid as work on electrolysis in producing various molybdenum complexes was done in strong hydrochloric acid.

Therefore no consideration was given to acid concentrations of the order 2N and conditions such as the green
Mo(III)(94) from dilute acid would not be used.

The progressive electrolysis in 8N or 10N hydrochloric acid in regard to colour-changes-valency state may be summarized as:-

Pale Yellow, Mo(VI); Dark Green, Mo(V); Cherry Red, Mo(III).

No attempt was made in determining potentials to duplicate the work of Foerster, Fricke and Hauswald.

Concentrations of MoO₃ of 200 g/l, 100g/l, and 10g/l besides the 50 g/l were investigated for colour changes and it was found that the determining factor was acid concentration and not molybdenum concentrations within this range.

The colour changes were the same when mercury was used as a cathode and platinum as the anode.
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