882. *Some Complexes of Molybdenum.*

By P. C. H. Mitchell and R. J. P. Williams.

The chemical, spectroscopic, and magnetic properties of complexes of molybdenum in the oxidation states +3, +4, and +5 have been investigated. We have confirmed in some cases, and found in others, that (*a*) the visible spectra of the chloride and the cyanide complexes arise from *d*–*d* transitions, (*b*) the spectra of the thiocyanate complexes and of the complexes of molybdenum(v) with organic ligands arise from charge-transfer transitions, (*c*) the spectroscopic properties of the organic complexes of molybdenum(v) are similar to those of iron(III), the direction of charge-transfer in both cases being from the ligands to the cation, and (*d*) the magnetic moments of the complexes are close to the spin-only values except for many of the molybdenum(v) complexes. The low moments of the latter are attributed to dimerisation of the complexes. The organic complexes of molybdenum(v) do not react with nitrate or nitro-groups.

The results are discussed on the basis of structural information available for molybdenum complexes.

This paper describes an investigation of the chemical, spectroscopic, and magnetic properties of some complexes of molybdenum in the oxidation states +3, +4, and +5. A number of these complexes have been known for many years and where their properties have been previously investigated we shall make comparison with our own results.

The objects of the work have been to obtain (*a*) information essential for a systematic discussion of molybdenum chemistry, and (*b*) information which may throw light on the role of molybdenum compounds in enzyme systems. It has been suggested [1] that molybdenum is associated with the flavin part of such enzymes as nitrate reductase and xanthine oxidase, and that in reactions catalysed by these enzymes the oxidation state of the metal changes from +6 to +5. It was therefore decided to study the organic complexes of molybdenum(v) in some detail. The reactions of molybdenum compounds with riboflavin have also been studied but this work will be reported elsewhere. A further paper will describe some measurements of the oxidation–reduction potentials of molybdenum complexes.

RESULTS

The preparations and analyses of the complexes to be described below are given in the Experimental section.

(*a*) *Complexes with Inorganic Ligands.*—The magnetic and spectroscopic properties of the complexes are given in Table 1. It was confirmed that the spectra of solutions of $(NH_4)_2MoOCl_5$ in hydrochloric acid depended on the acid concentration except at very high acidities.

The conductivities in nitrobenzene of $(pyH)_2Mo(NCS)_6$ and $(pyH)_2MoO_2(NCS)_3$ (py = pyridine) were measured with the object of deducing the molecular formula of the latter. The molar conductivities of 10^{-3}M-solutions of the complexes were $(pyH)_2Mo(NCS)_6$ 44·3 mhos, $(pyH)_2MoO_2(NCS)_3$ 33·2 mhos, and $(pyH)_4Mo_2O_4(NCS)_6$ 66·4 mhos. The molar conductivity of the molybdenum(IV) complex is of the order of value expected for a 2 : 1 electrolyte. The molybdenum(v) complex formulated as a dimer gives five ions, and the ratio of its conductivity to that of the molybdenum(IV) complex should be ~5 : 3; the observed ratio is 4·5 : 3, which suggests that the molybdenum(v) complex is a dimer.

(*b*) *Complexes with Organic Ligands.*—The empirical formulæ of the complexes prepared and their magnetic and spectroscopic properties are given in Tables 2 and 3. For some of the complexes susceptibilities were measured over a range of temperatures. With the exceptions of the " acidic " oxinate of molybdenum(v) (*i.e.*, the complex precipitated from acid solution) and the acetylacetonate the susceptibilities are much less than expected for d^1 ($\sim 1300 \times 10^{-6}$

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[1] Bray, " The Enzymes," Academic Press, New York, Vol. VII, in the press.

TABLE 1.

Compound	μ_{eff} [a]	Temp. (K)	$\lambda_{max.}$ (mμ) [b]	ε	Transition
$K_4Mo(CN)_7,2H_2O$	1·77	293°	505	66	*d–d*
	1·78	109	380	110	*d–d*
			220	$>$19,000	Charge
$K_4Mo(CN)_8$	Diamag.		410 *	90	*d–d*
			370	158	*d–d*
			238	12,000	Charge
$Ag_3Mo(CN)_8$	1·77	293			
$K_3Mo(CN)_8$			377 *	1200	*d–d*
			386	1280	*d–d*
			400 *	1100	*d–d*
			265	2550	Charge
			247	2960	Charge
$(pyH)_3Mo(NCS)_6$	3·86	297	$<$360	$>$10,000	Charge
$(pyH)_2Mo(NCS)_6$	2·45 [c]	297	565	25,600	Charge
			420 *	53,000	Charge
			410	62,500	Charge
$(pyH)_4Mo_2O_4(NCS)_6$	0·59	293	463	13,500	Charge
	0·39	120			
K_3MoCl_6	3·73	293	649 *	$<$20	*d–d*
			495	49	*d–d*
			395	83	*d–d*
$MoBr_3py_3$	3·85	293	365	3200	Charge
			285	8700	Charge
			255	14,800	Charge
$(NH_4)_2MoOCl_5$	1·74	293	710	17 [d]	*d–d*
			443	17	*d–d*

* Shoulder. $\lambda_{max.}$ is accurate to *ca.* ±5 mμ.

[a] All in Bohr magnetons and corrected for diamagnetism. [b] Measured in the following solvents; cyanide complexes in water; thiocyanates in acetone; K_3MoCl_6 in 2N-hydrochloric acid; $MoBr_3py_3$ in chloroform. [c] For samples which had been kept for some months in sealed tubes values of μ_{eff} = 3·0—3·5 were obtained and we suspect that the molybdenum(IV) compound disproportionates even in the solid state. [d] In 10N-HCl; the effect of diluting the acid is referred to in the text (see also Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73; Simon and Souchay, *Bull. Soc. chim. France*, 1956, 1402.

Earlier measurements on these complexes are referred to in the text and by Figgis and Lewis and by Dunn in " Modern Coordination Chemistry " (ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960), Figgis, Lewis, and Mobbs (*J.*, 1961, 3142), and Lewis, Nyholm, and Smith (*J.*, 1961, 4590).

TABLE 2.

Compound	$\lambda_{max.}$ (mμ)	$\nu_{max.}$ (cm.$^{-1}$)	ε	Solvent
$Na_2Mo_2O_4(EDTA),4H_2O$	298	33,600	9600	H_2O
	385	26,000	380	
$MoO(OH)(oxine)_2$:				
(i) pptd. from alkali	385	26,000	*ca.* 10,000 [d]	EtOH
	540	18,500		
(ii) pptd. from acid	389	25,700	50,000	,,
	537	18,600	22,800	
$MoOCl(oxine)_2$	383	26,100	3640	Pyridine
	593	16,900	1870	
$Mo(OH)_3(acac)_2,3H_2O$ [a]	490	20,400	5000	C_6H_6
$MoO(OH)Cl_2phen$ [b]	435	23,000	1600	$PhNO_2$
	528	18,900	1860	
$MoCl_2(OPh)_3$	465	21,500	11,000	C_6H_6
	470	21,300	15,600	$PhNO_2$
	490	20,400	20,800	Pyridine
$MoCl_2(O{\cdot}C_6H_4Me)_3$	490	20,400	4100	C_6H_6
$MoCl_2(O{\cdot}C_6H_4{\cdot}CO_2H)_3$	441	22,700	~10,000 [e]	$CHCl_3$
1 : 1 Complexes: [c]				
with oxine	388	25,800	4000	EtOH
with 5-methyloxine	405	24,700	4400	,,

[a] acac = Acetylacetone. [b] phen = 1,10-Phenanthroline. [c] From spectrophotometric investigation of reaction between molybdenum(V) and ligands. [d] Incompletely soluble. [e] Impure.

TABLE 3.[a]

Compound	$10^6\chi_M$ [b]	Temp. (K)	$\mu_{eff}(\beta)$ [c]	Compound	$10^6\chi_M$ [b]	Temp. (K)	$\mu_{eff}(\beta)$ [c]
$Na_2Mo_2O_4(EDTA),4H_2O$	38 ± 5	293°	0·30	$MoO(OH)(oxine)_2$			
$MoOCl(oxine)_2$	778 ± 7	294	1·36	(i) basic	189 ± 5	290°	0·66
$MoO(OH)Cl_2phen$ [d]	168 ± 2	292	0·63		199	220	0·60
$MoCl_2(O{\cdot}C_6H_4Me)_3$	27 ± 9	292	0·25		184	190	0·53
	108	202	0·42		184	170	0·50
	94	154	0·34		199	137	0·46
	166	134	0·42				
				(ii) acidic	1371	291	1·79
$MoCl_2(OPh)_3$	76 ± 4	289	0·42		1371	247	1·65
	72	221	0·36		1467	220	1·61
	72	193	0·33		1486	176	1·45
	66	172	0·30		1467	156	1·36
	61	132	0·25		1561	138	1·31
$Mo(OH)_3(acac)_2,3H_2O$ [d]	1363 ± 3	291	1·79				
	1386	222	1·57				
	1407	186	1·45				
	1434	160	1·36				
	1464	135	1·26				

[a] Preliminary measurements of the magnetic susceptibilities of some of the complexes were reported at the 6th Internat. Conference on Co-ordination Chemistry (Detroit, 1961). The values given here are averages for two series of measurements; the results published earlier represent only one series of measurements. [b] Corrected for diamagnetism. [c] Apparent values of the magnetic moments calculated from $\mu_{eff} = 2{\cdot}84(\chi_M T)^{0{\cdot}5}$. [d] See footnotes to Table 2.

c.g.s. at 293°K and 2800×10^{-6} c.g.s. at 135°K). The temperature-dependence of the susceptibilities does not follow Curie's law.

Only the compounds $MoCl_2(OPh)_3$ and $MoCl_2(O{\cdot}C_6H_4Me)_3$ were sufficiently soluble in nitrobenzene for conductivity measurements to be made. The molar conductivities of 10^{-3}M-solutions were 1·1 mhos for the phenoxide and 1·0 mho for the *p*-tolyl oxide. Thus the compounds are non-electrolytes.

Some attempted chemical reactions of the complexes are described below.

DISCUSSION

(*a*) *Structures of the Complexes.*—Direct structural information is available only for $K_4Mo(CN)_8,2H_2O$ and $MoCl_2(OPh)_3$. In the former the eight cyanide groups are arranged dodecahedrally around the molybdenum(IV) cation.[2] The phenoxide[3] is dimerised through two chlorine bridges and the molybdenum–molybdenum distance of 2·8 Å compares with molybdenum–molybdenum distances of 2·73 Å in the metal,[4] 3·222 Å in Mo_2(cyclopentadiene)$_2(CO)_6$,[5] and 3·84 Å in solid molybdenum pentachloride[6] (which is also dimerised through chloride bridges). The relatively short distance in the phenoxide and the low magnetic moment imply direct interaction between adjacent molybdenum(V) cations.

Infrared spectra of the thiocyanate complexes have been previously reported.[7] The position of the C–N stretching frequency indicates that the thiocyanate group is bonded to the molybdenum through nitrogen. Thus molybdenum(V) appears to behave as a class (*a*) metal.[8] The conductivity measurements in nitrobenzene show that $(pyH)_2MoO_2(NCS)_3$ is dimeric. We know also that all the pyridine in this compound is present as the pyridinium cation[9] and that there is an Mo–O stretching frequency at

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[2] Hoard and Nordsieck. *J. Amer. Chem. Soc.*, 1939, **61**, 2853.

[3] Mitchell and Prout, unpublished work.

[4] Pauling, " Nature of the Chemical Bond," Oxford University Press, 2nd edn., 1948, p. 409.

[5] Wilson and Schoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

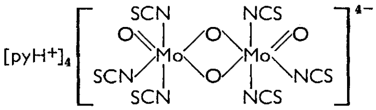
[6] Sands and Zalkin, *Acta Cryst.*, 1959, **12**, 723.

[7] Mitchell and Williams, *J.*, 1960, 1912.

[8] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

[9] Mitchell, *J. Inorg. Nuclear Chem.*, 1961, **21**, 383; Barraclough, Lewis, and Nyholm, *J.*, 1959, 3552.

952 cm.$^{-1}$. We found no evidence for hydroxide groups. We suggest that the compound should be formulated as annexed. The low magnetic moment then arises either by interaction through the oxide bridges or by direct spin–spin interaction.



(*b*) *Crystal-field Splittings and Electron Configurations.*—In agreement with the results of earlier work [10] we have observed moments close to the spin-only values for K_3MoCl_6, $(pyH)_3Mo(NCS)_6$, and $MoBr_3py_3$. For $(pyH)_2Mo(NCS)_6$ the magnetic moment is somewhat less than the spin-only value for molybdenum(IV), presumably because of spin–orbit coupling. The only other molybdenum(IV) compound (apart from the cyanide) of which the magnetic moment has been reported is $MoDiarsBr_4$ [11] (where Diars is *o*-phenylenebisdimethylarsine) for which μ_{eff} at room temperature is 1·96β.

The magnetic properties of the cyanide complexes of molybdenum(III) and molybdenum(IV) show that in these compounds two of the electrons are paired. The results imply that in both compounds two electrons are in a low-lying singlet orbital. This is in accordance with the splitting of the *d*-orbitals in the field of the ligands. The order of increasing repulsion of the *d*-orbitals in $K_4Mo(CN)_8$ is [12] $d_{xy} << d_{x^2-y^2} < d_{z^2} < d_{xz} = d_{yz}$. For $K_4Mo(CN)_7,2H_2O$ it is uncertain whether a water molecule is in the co-ordination sphere of the molybdenum(III) cation, *i.e.*, whether the ion is 7- or 8-co-ordinate. Magnetic measurements will not distinguish between the two possibilities. (A 7-co-ordinate pentagonal bipyramid structure would give a low-lying doubly degenerate orbital in which two of the three electrons would be paired.[13])

The compound $K_3Mo(CN)_8$ has the expected spin-only moment and its structure presumably approximates to the dodecahedral structure observed for the molybdenum(IV) compound.

The magnetic moments of the thiocyanate and organic complexes of molybdenum(V) are discussed below, for these compounds show considerable spin–spin interaction and polymerisation. Before examining them we shall discuss the spectra of the simpler salts.

(*c*) *Spectra of the Complexes.*—(i) *Origin of the spectra.* The absorption peaks in the visible or near-ultraviolet region may arise from either *d–d* transitions, with an expected molar extinction coefficient of about 100, or from charge-transfer transitions, with an expected molar extinction coefficient of the order of 10^4. The suggested origins of the peaks are given in the last column of Table 1.

(ii) d–d *Transitions.* In accordance with crystal-field theory we assign the transitions in $MoCl_6^{3-}$ as follows: ${}^4A_{2g} \longrightarrow {}^4T_2$ at 20,200 cm.$^{-1}$, ${}^4A_{2g} \longrightarrow {}^4T_1$ at 25,300 cm.$^{-1}$, ${}^4A_{2g} \longrightarrow {}^2E_g$ at about 15,000 cm.$^{-1}$. The assignments are in reasonable agreement with previous work.[14] Our measurements of the spectrum of $(NH_4)_2MoOCl_5$ are in general agreement with those reported.[15] The spectrum of molybdenum(V) in 9—12N-hydrochloric acid is probably due to the species $MoOCl_5^{2-}$. Dilution of the acid causes polymerisation and hydrolysis of this species. The broad peak at ~710 mμ disappears while that at 443 mμ increases in

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[10] Figgis and Lewis in " Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., 1960, p. 444; Figgis, Lewis, and Mabbs, *J.*, 1961, 3142; Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

[11] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1803.

[12] Orgel, *J. Inorg. Nuclear Chem.*, 1960, **14**, 136, and references therein.

[13] Basolo and Pearson, " Mechanisms of Inorganic Reactions," Wiley, Inc.. New York, 1958, p. 55.

[14] Dunn in " Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., 1960, p. 292; Chilessotti, *Z. Elektrochem.*, 1906, **12**, 173; Hartman and Schmidt, *Z. phys. Chem.* (*Frankfurt*), 1957, **11**, 234.

[15] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 73; Simon and Souchay, *Bull. Soc. chim. France*, 1956, 1402.

intensity and at still lower acidities (<4N) merges with the charge-transfer peak in the near-ultraviolet region.

There appears to have been no previous discussion of the spectra of the molybdenum cyanide complexes, although $K_3Mo(CN)_8$ has been studied by electron-spin resonance.[16] For this compound three transitions from $(d_{xy})^1$ should be possible. We observed a peak at 25,900 cm.$^{-1}$ and shoulders at ~25,000 and 26,500 cm.$^{-1}$ and suggest that these arise from the transitions: $(d_{xy})^1$ to $(d_{x^2-y^2})^1$ at ~25,000 cm.$^{-1}$; $(d_{xy})^1$ to $(d_{z^2})^1$ at 25,900 cm.$^{-1}$; and $(d_{xy})^1$ to $(d_{xz})^1$ or $(d_{yz})^1$ at 26,500 cm.$^{-1}$.

The energy levels in $K_4Mo(CN)_8$ and $K_4Mo(CN)_7,2H_2O$ will depend on the crystal-field splittings and electron-repulsion terms. In general, the crystal-field splitting decreases as the oxidation number of the cation decreases. This is well illustrated by the molybdenum cyanide complexes, the frequencies of the lowest-energy transitions decreasing in the order Mo(V) > Mo(IV) > Mo(III). Assignment of the transitions in these complexes would require a detailed theoretical discussion which would take into account electron-repulsion terms and we shall not attempt this at this stage.

(iii) *Charge-transfer transitions.* The spectra of $MoBr_3py_3$ and the molybdenum thiocyanate complexes originate in charge-transfer transitions. The transitions in the molybdenum(III) compounds are of higher energy than in the thiocyanate complexes of molybdenum(IV) and molybdenum(V). This is explicable if the charge-transfer is from the ligands to the metal for all three cations since compounds of molybdenum(III) are much less easily reduced than those of molybdenum(IV) or molybdenum(V).

With the cyanide complexes charge-transfer transitions give peaks in the ultraviolet region. The order of increasing energy of the transitions is the same as the order of increasing difficulty of reduction of the complexes [Mo(V) < Mo(IV) < Mo(III)].

Properties of Molybdenum(V) *Complexes.*—(a) *Spectra of the complexes.* The spectra of the organic complexes of molybdenum(V) arise from charge-transfer transitions (Table 2). That the charge-transfer process involves primarily the organic ligands, and not the oxide or chloride ligands also present in the complexes, is suggested by the fact that a charge-transfer band in the visible region is not observed in the oxide chloride complexes of molybdenum(V) whether they are polymerised or not.

The question arises whether the charge-transfer in the organic complexes is from the molybdenum cations to the ligands or from the ligands to the cations. This problem has been studied in some detail for iron(II) and iron(III).[17] The general observation for ferric complexes has been that, for a series of similar high-spin ferric complexes, as the electron-donor character of the ligands increases, the peak positions move to longer wavelengths, *i.e.*, the transitions become of lower energy. This indicates that the charge-transfer is from the ligands to the cation. With change of ligand the absorption peaks of molybdenum(V) complexes move in a similar manner to those of iron(III) complexes. So the charge transfer here too is probably from ligand to cation in the molybdenum(V) complexes. The ligands giving these spectra are reducing rather than oxidising agents.

The analogy between molybdenum(V) and iron(III) is reinforced when the ligands are arranged in order of increasing $\lambda_{max.}$ for complexes of molybdenum(V) and high-spin iron(III). For molybdenum(V) the sequence is: EDTA < *p*-hydroxybenzoic acid < NCS^- ≳ phenol <acetylacetone ≳ *p*-cresol < oxine < 5-methyloxine (1 : 1 complex). For high-spin iron(III) the sequence is: EDTA, *p*-hydroxybenzoic acid < acetylacetone < NCS^- < phenol < *p*-cresol < oxine < 5-methyloxine. Except for the position of acetylacetone the ligand sequence is the same for the two metals.

To these measurements may be added the qualitative observations that mixed solutions (in ethanol) of molybdenum(V) and 5-cyano- and 5-formyl-oxine are brown, whereas solutions containing oxine and 5-methyloxine are red. The colour changes imply that the

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[16] Griffiths, Owen, and Ward, *Proc. Roy. Soc.*, 1953, *A*, **219**, 526.

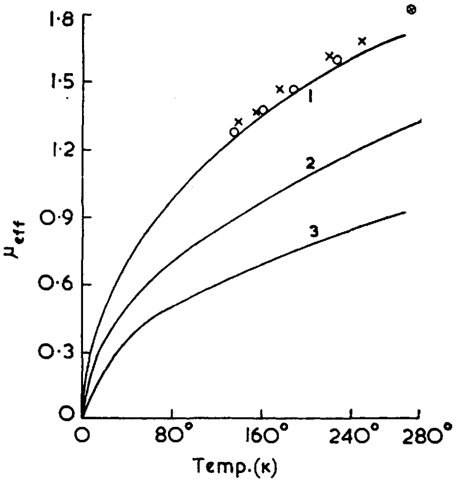
[17] Williams, *J.*, 1955, 137; *Chem. Rev.*, 1956, **56**, 299; Tomkinson and Williams, *J.*, 1958, **1153**.

absorption peaks of the complexes formed shift to shorter wavelengths when the electron-attracting cyano- and formyl groups are introduced into oxine. A similar observation has been made for the iron(III) complexes.

There are other analogies between the spectra of molybdenum(V) and iron(III) complexes. The peak positions in complexes of both cations are solvent-sensitive [cf. MoCl$_2$(OPh)$_3$]. Steric hindrance of ligands is observed in molybdenum(V) as in iron(III). Thus, while oxine, 1,10-phenanthroline, and 2,2′-bipyridyl produce intense colour changes and precipitates with alcoholic solutions of (NH$_4$)$_2$MoOCl$_5$, yet 2-methyloxine, 2,9-dimethyl-1,10-phenanthroline, and 2,2′-biquinolyl do not.

Work on these ligands is still in progress and the spectra will be reported in a future paper.

(b) *Magnetic properties of molybdenum*(V) *complexes.* The magnetic properties of the complexes are given in Table 3. The empirical formulæ are based on the analyses and it is assumed that the complexes are magnetically dilute since the ligands are large organic molecules and there are no maxima in the plots of magnetic moment against temperature.



Variation with temperature of the magnetic moments of the acetylacetone (○) and the acidic oxine (×) complex of Mo(V). Lines are calculated with the following values of the spin-orbit coupling constants (△): 1, 250; 2, 500; 3, 1000.

According to the values of the moments the molybdenum(V) complexes may be divided into two groups: those with moments close to the spin-only value for d^1, and those with moments much less than this. This applies also to other molybdenum(V) complexes not studied in the present work.[10] We are not prepared to interpret these results in detail since the structures of the complexes are not known (except the phenoxide, see below); but we believe that our results and those of other workers [6,18] indicate that many of the complexes in the first group are monomeric and those in the second group are polymerised.

The magnetic moments of the "high-spin" acetylacetone and oxine complexes are plotted against temperature in the Figure, which also shows Kotani plots[20] for d^1_ε systems. Although the experimental points lie close to the curve for $A = 250$ cm.$^{-1}$ it is difficult to attach much significance to a value of A obtained in this way since the complexes are not symmetrical.[21]

We suggest that the low magnetic moment observed for the phenol complex MoCl$_2$(OPh)$_3$ is due, at least in part, to intramolecular antiferromagnetism (metal–metal interaction) of the type observed in cupric acetate.[22] Evidence in favour of this is the

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[18] Sacconi and Cini, *J. Amer. Chem. Soc.*, 1954, **76**, 4239.

[20] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

[21] Figgis and Lewis, in "Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, p. 428; Hargreaves and Peacock, *J.*, 1958, 3776.

[22] Martina and Waterman, *J.*, 1957, 2545; 1959, 1361, 2960; Figgis and Martin, *J.*, 1956, 3837.

short Mo–Mo distance of 2·8 Å in the phenoxide and the contrast between its properties and those of molybdenum pentachloride. For the latter, Mo–Mo = 3·84 Å and the susceptibility [23] is nearly twenty times that for the phenoxide. Since both compounds contain bridging chlorine it appears that an exchange interaction *via* the bridging atoms is not of dominant importance in reducing the susceptibility of the phenoxide.

The structure of the *p*-cresol complex is probably similar to that of the phenol complex; but the structures of the oxy-complexes are very uncertain and we believe that complete structural determinations are desirable for compounds of this type. In that oxide bridges are known to lead to large reductions of susceptibility [24] it is possible that the oxy-complexes of molybdenum(V) dimerise through oxide bridges.

(c) *Reactions.* In order to test the possibility that the molybdenum(V) complexes might function in nitrate or nitro-group reduction systems we examined spectrophotometrically mixed solutions of the complexes and nitrate or *p*-nitrophenol. In no case was there evidence of reaction. According to Nicholas and Stevens [25] uncomplexed molybdenum(V) is not effective in the non-enzymic reduction of nitrate and it appears from our results that molybdenum(V) complexes are also ineffective. Thus it seems unlikely that molybdenum(V) is the reactive species in nitrate reductions, a conclusion which is in agreement with recent suggestions [26] that molybdenum(IV) is the reactive state.

Some exchange reactions were attempted with the complexes. Solutions of the complexes were mixed with solutions of organic ligands (phenols, oxines, phenanthrolines, bipyridyls, acetylacetone), and the spectra were recorded during 48 hours. No changes were observed in the spectra, so the complexes appear to be inert. The oxine complexes dissolved when heated with dilute hydrochloric acid, and the solutions reacted with thiocyanate giving the thiocyanate complex of molybdenum(V).

The reactions of ethanolic solutions of $(NH_4)_2MoOCl_5$ with some organic ligands were also investigated. The molybdenum(V) solutions were brown and so probably contained a polymeric species; they were stored, and the reactions were carried out, under nitrogen. Precipitates were obtained with oxine and 1,10-phenanthroline and were separated and analysed. The reactions with oxine and 5-methyloxine were also studied spectrophotometrically by Job's method. The ethanol was buffered with acetic acid and potassium acetate. Spectra were recorded immediately after mixing of the solutions and showed the formation of 1 : 1 complexes, with both ligands absorbing at 388 (oxine) and 405 mμ (5-methyloxine). The spectra were recorded again after 48 hours. There was no change in the spectra of the solutions containing 5-methyloxine; but with oxine a further peak had appeared at 540 mμ in those solutions for which the oxine : Mo ratio exceeded 2 : 1. This peak is probably due to a 2 : 1 or 3 : 1 oxine–Mo(V) complex. Further work on the reactions of $(NH_4)_2MoOCl_5$ with organic compounds will be reported in future papers.

EXPERIMENTAL

Preparations and Analyses.—The following compounds were prepared according to procedures described in the literature. All were dried *in vacuo* over P_2O_5.

K_3MoCl_6 [27] (Found: Mo, 22·3; Cl, 49·7. Calc.: Mo, 22·5; Cl, 50·0%). The oxidation number of the molybdenum, determined by titration with ceric sulphate, was 3·0.

$(NH_4)_2MoOCl_5$ [28] (Found: Mo, 29·3; Cl, 54·7. Calc.: Mo, 29·5; Cl, 54·6%). The oxidation number of the molybdenum, determined by titration with ceric sulphate, was 5·0.

$MoBr_3py_3$ [29] (Found: Mo, 16·4; Br, 41·9; C, 31·6; H, 2·8; N, 7·4. Calc.: Mo, 16·8; Br, 41·9; C, 31·4; H, 2·6; N, 7·3%).

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[23] Knox and Coffey, *J. Amer. Chem. Soc.*, 1959, **81**, 5.

[24] Earnshaw and Lewis, *J.*, 1961, 396.

[25] Nicholas and Stevens, *Nature*, 1955, **176**, 1066.

[26] Haight, *Acta Chem. Scand.*, 1961, **15**, 2012 and references there cited.

[27] *Inorg. Synth.*, 1953, **4**, 97.

[28] Palmer, " Experimental Inorganic Chemistry," Cambridge, 1954, p. 408.

[29] Brauer, " Handbuch der präparativen anorganischen Chemie," Ferdinandenkeverlag, Stuttgart, 1952, p. 1052.

$(NH_4)_3Mo(NCS)_6,H_2O$ [30] (Found: Mo, 18·1; NCS, 66·4; NH_4, 10·0; H_2O, 5·5. Calc.: Mo, 18·6; NCS, 67·4; NH_4, 10·5; H_2O, 3·5%).

$(pyH)_2Mo(NCS)_6$ [31] (Found: Mo, 16·0; C, 31·4; H, 2·2; N, 18·2. Calc.: Mo, 15·9; C, 31·8; H, 2·0; N, 18·5%).

$(pyH)_2MoO_2(NCS)_3$ [32] (Found: Mo, 20·4; NCS, 36·2; pyridine, 32·8. Calc.: Mo, 20·8; NCS, 37·7; pyridine, 34·4%). The oxidation number of the molybdenum, determined by titration with ferric alum, was 5·06.

$(pyH)_3Mo(NCS)_6$ [31] (Found: Mo, 14·3; NCS, 51·1; pyridine, 34·2. Calc.: Mo, 14·0; NCS, 50·9; pyridine, 35·1%).

$K_4Mo(CN)_7,2H_2O$ [33] [Found: Mo, 21·0. Calc.: 21·3 (monohydrate), 20·4% (dihydrate)].

$K_4Mo(CN)_8$ [32] (Found: Mo, 20·9. Calc.: Mo, 20·9%).

$Na_2Mo_2O_4(C_{10}H_{12}O_8N_2),4H_2O$ [34] (EDTA complex) (Found: Mo, 29·0; C, 18·6; H, 2·9; N, 4·1. Calc.: Mo, 29·0; C, 18·1; H, 3·0; N, 4·2%).

$MoCl_2(OC_6H_5)_3$ [35] (Found: Mo, 21·8; Cl, 16·5; C, 48·0; H, 3·1. Calc.: Mo, 21·6; Cl, 15·9; C, 48·5; H, 3·4%).

$MoCl_2(OC_6H_4CH_3)_3$ [35] (Found: Mo, 19·7; Cl, 14·5. Calc.: Mo, 19·7; Cl, 14·6%).

$Mo(OH)_3(C_{10}H_{16}O_2),3H_2O$ [35] (Found: Mo, 24·5; C, 30·9. Calc.: Mo, 24·6; C, 30·9%).

The remaining compounds were prepared as described below.

Salts $K_3Mo(CN)_8$ *and* $Ag_3Mo(CN)_8$. The compound $K_4Mo(CN)_8$ was oxidised quantitatively in dilute sulphuric acid with ceric sulphate. At the end-point silver nitrate solution was added dropwise until precipitation of the silver salt was complete. The precipitate was filtered by suction and dried *in vacuo* over P_2O_5. The potassium salt is highly photosensitive and was prepared as required by triturating the silver salt with potassium chloride solution. Solutions of the compound were estimated by potentiometric titration with ferrocyanide.

Compound $MoCl_2(O{\cdot}C_6H_4{\cdot}CO_2H)_3$. Molybdenum pentachloride and *p*-hydroxybenzoic acid were refluxed in suspension in benzene under nitrogen for 24 hr. There was very little reaction. The pentachloride (5·5 g.) and the acid (10·0 g.) gave only 0·05 g. of the required tris-*p*-carboxyphenoxydichloromolybdenum on repeated extraction with chloroform (Found: Mo, 15·0; C, 47·6; H, 3·6. Calc. for $C_{21}H_{15}Cl_2MoO_9$: Mo, 16·6; C, 43·6; H, 2·6%), contaminated with, probably, *p*-hydroxybenzoic acid, and further purification was not practicable.

Compound $MoO(OH)Cl_2phen$. A solution of the compound $(NH_4)_2MoOCl_5$ (1 g.) in absolute ethanol (40 ml.) was treated with 1,10-phenanthroline monohydrate (1·2 g.) in absolute ethanol (10 ml.). There was an immediate dark precipitate. The suspension was set aside for 1 hr. and then filtered by suction under carbon dioxide. The residual *oxo-oxidodichloro-*(1,10-*phenanthroline*)*molybdenum* (1 g.) was washed with ether and dried *in vacuo* over P_2O_5 (Found: Mo, 25·9; Cl, 18·7; phen, 46·4. $C_{12}H_9Cl_2MoN_2O_2$ requires Mo, 25·2; Cl, 17·6; phen, 47·3%). The oxidation number of the molybdenum, determined by titration with ceric sulphate, was 5·04. 1,10-Phenanthroline was determined by rendering alkaline the solution from the ceric titration and extracting the filtrate with chloroform; the ligand in the combined chloroform extracts was determined spectrophotometrically.

"*Basic oxinate*" *of molybdenum*(v). A molybdenum(v) solution, prepared by reducing with mercury a 0·1M-molybdenum(vi) solution (100 ml.) in dilute sulphuric acid, was added to a 0·2M-solution (100 ml.) of oxine in dilute acetic acid. The resulting deep orange solution was evaporated to 50 ml. and filtered. Sodium hydroxide solution was added to the filtrate, a dark brown precipitate being formed. The suspension was heated, cooled, and filtered. The dark purple residue was washed with cold water and dried *in vacuo* over P_2O_5. (Found: Mo, 22·4; C, 52·05; H, 3·0; N, 5·8%).

"*Acidic oxinate*" *of molybdenum*(v). Molybdenum oxide trihydroxide, $MoO(OH)_3$ (0·4 g.), was dissolved in concentrated hydrochloric acid (5 ml.) with slight warming. The deep green solution was added to a solution of oxine (5 g.) in ethanol (50 ml.), and was followed by water (20 ml.). The resulting reddish-brown suspension was set aside for 10 min. and then filtered off by suction. The filtrate was poured into water (400 ml.); the liquid became cloudy. It

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[30] Palmer, "Experimental Inorganic Chemistry," Cambridge, 1949, p. 408.

[31] Barbieri, *Atti Accad. R. Lincei.*, 1930, VI, **12**, 55.

[32] *Inorg. Synth.*, 1953, **3**, 160.

[33] Young, *J. Amer. Chem. Soc.*, 1934, **54**, 1402.

[34] Pecsock and Sawyer, *J. Amer. Chem. Soc.*, 1956, **78**, 5496.

[35] Rosenheim and Nernst, *Z. anorg. Chem.*, 1933, **214**, 209.

was heated to 60°; dark purple particles separated and settled. The suspension was filtered and the dark purple residue was washed with water and ether and dried *in vacuo* over P_2O_5 (Found: Mo, 23·7; C, 50·5; H, 3·35; N, 5·5%). The formula which most closely fits the analyses is MoO(OH)(oxine)$_2$ (Calc. for $C_{18}H_{13}MoN_2O_4$: Mo, 23·0; C, 51·8; H, 3·1; N, 6·7%). By a procedure similar to that used for the acid precipitation Stevens [36] obtained a compound with an analysis Mo, 19·2; C, 50·3; H, 3·1; N, 6·25%. The magnetic susceptibility of the basic compound is much less than that of the acidic compound and the former is probably polymerised.

Compound MoOCl(oxine)$_2$. A solution of the compound $(NH_4)_2MoOCl_5$ (1 g.) in alcohol (10 ml.) was filtered and added to a solution of oxine (0·9 g.) in ethanol (25 ml.). There was no immediate precipitate but during two weeks crystals were formed. These were filtered off, washed with ethanol and ether, and dried *in vacuo*. The impure product was a green powder (Found: Mo, 20·6; Cl, 7·7; C, 46·2; H, 3·4; N, 5·6. Calc. for $C_{18}H_{12}ClMoN_2O_3$: Mo, 22·0; Cl, 8·2; C, 49·6; H, 2·8; N, 6·4%). The analyses for the oxinate complexes were not very satisfactory, but attempts to obtain better characterised compounds were not successful.

Analytical Procedures.—Molybdenum was determined gravimetrically as lead molybdate or as oxo-oxine complex [37] or spectrophotometrically.[38] Molybdenum and chloride or bromide together were determined as silver molybdate and silver halide.[39] Pyridine was determined by the method described by Palmer,[40] and thiocyanate by permanganate titration [41] (with correction for permanganate consumed in oxidation of lower-valent molybdenum). Microanalyses for carbon, hydrogen and nitrogen were carried out when no suitable procedure could be found for direct determination of ligands.

For the molybdenum determination the organic complexes were decomposed by heating them to fuming for 0·5 hr. with 1 : 1 concentrated nitric and sulphuric acid. This procedure failed for the phenol complexes which were decomposed by heating them for 1 hr. with concentrated sulphuric acid and then treating them at the b. p. with ammonium nitrate.

Magnetic Susceptibilities.—These were measured by the Gouy method in an apparatus designed by Dr. C. K. Prout (Thesis, Oxford, 1959). The weight of the samples was 0·5—1·0 g. and the weighings were reproducible to ±0·00001 g. Three determinations were made with separate samples of each compound; the moments were reproducible to ±0·5%. For the complexes of molybdenum(V) with low susceptibility the relative deviations in the susceptibilities were between ±10% and ±50%. Temperature-measurement and -control was accurate to ±1°. Molar susceptibilities given have been corrected for the diamagnetism of the constituent molecules and ions.[42] The corrections were checked by measuring the molar susceptibility of oxine. The experimental value of $-76·7 \times 10^{-6}$ c.g.s. is to be compared with a calculated value of -74×10^{-6} c.g.s.

Ultraviolet and Visible Spectra.—These were measured with a Beckman recording spectrophotometer model DK2 against a control of the appropriate solvent.

Conductivities in Nitrobenzene.—These were measured with a Mullard type E 7566 conductivity bridge and bright platinum electrodes.

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INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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[39] Palmer, " Experimental Inorganic Chemistry," Cambridge, 1954, p. 424.
[40] Ref. 39, p. 147.
[41] Reinitzer and Pollet, *Z. anal. Chem.*, 1930, **81**, 286.
[42] Figgis and Lewis, in " Modern Coordination Chemistry," ed. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960 p. 403.