Reactions of the Di-μ-oxo-bis[(L-cysteinato)oxomolybdate(V)] Ion

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Reactions of the complex $Na_2[Mo_2(O)_4(cyst)_2],5H_2O$ (cyst = L-cysteinato) (I) have been studied. In aqueous solution (pH < 6) the co-ordinated carboxylate groups of the complex are protonated and replaced by water. Complex (I) reacts with phosphate and tartrate, but not with borate, carbonate, acetate, and phthalate ions. With diazomethane the co-ordinated thiolate group of (I) is methylated and the complex decomposes. Co-ordination of amino-acids to molybdenum(V) is facilitated by thiol groups. The following complexes have been isolated: $[Mo_2(O)_3(Etcyst)_4]$ (Etcyst = ethyl L-cysteinato) (II); $[Mo_2(O)_3(quinolin\text{-}8\text{-}olate)_4].H_2O$ (III); $[Mo_2(O)_4(SO_4)(phen)_2].3H_2O$ (IV); $[Mo_2(O)_4Cl_2(phen)_2]$ (V); $[Mo_2(O)_4(MoO_4)(phen)_2].2H_2O$ (VI); and $[Mo_3(O)_4(Etcyst)_4(phen)_2]$ (phen = 1,10-phenanthroline) (VII). I.r., u.v., and visible spectra, and magnetic moments of the complexes are reported and structures proposed.

COMPLEXES of molybdenum with L-cysteine and related ligands [1a–c] are of interest as models for molybdenum co-ordination in enzymes.[1b,2] The structure of the molybdenum(V) complex, $Na_2[Mo_2(O)_4(cyst)_2],5H_2O$ (cyst = L-cysteinato) (I) has been determined by single-crystal *X*-ray crystallography [3] and is shown in the Scheme. L-Cysteine is bonded to molybdenum through sulphur, nitrogen, and oxygen atoms and the co-ordination of molybdenum is six; the Mo–O (carboxy) bond is weak.[3] The structures of the complexes di-μ-oxo-bis-[(ethyl L-cysteinato-*SN*)oxomolybdenum(V)], $[Mo_2(O)_4(Etcyst)_2]$,[4] and di-μ-sulphido-bis[(methyl L-cysteinato-*SN*)oxomolybdenum(V)], $[Mo_2(O)_2S_2(Mecyst)_2]$,[5] have also been determined. The cysteine esters are bonded through nitrogen and sulphur atoms only and the co-ordination number of molybdenum is five. For the enzyme xanthine oxidase, which catalyses the oxidation of xanthine to uric acid,[2,6] it has been shown by e.s.r. spectroscopy that xanthine co-ordinates to molybdenum during the catalysed reaction and that a proton is transferred to a site close to molybdenum. We have suggested [1a] that, for substrate co-ordination to occur, the molybdenum in the enzyme must have a vacant co-ordination site or a site with a weakly bound group. The molybdenum(V) complexes with L-cysteine and L-cysteine esters have these features. In this paper we report reactions of the L-cysteine complex (I) (see the Scheme).

EXPERIMENTAL

Sodium di-μ-oxo-bis[(L-cysteinato)oxomolybdate(V)] pentahydrate (I) was prepared as before.[1b] Solutions were prepared in deionised water and were stored and handled under an atmosphere of deoxygenated nitrogen, unless otherwise stated, and, for quantitative measurements, were thermostatted at 25 °C.

*μ-Oxo-bis[bis(ethyl L-cysteinato-*SN*)oxomolybdenum*(V)], $[Mo_2(O)_3(Etcyst)_4]$ (II).—A solution of ethyl L-cysteinate hydrochloride (4 g) in water (30 cm^3) was added to a solution of complex (I) (3·2 g) in water (50 cm^3). The solution was stirred and 2M-sodium hydroxide was added dropwise. The initial yellow precipitate which formed slowly changed colour to magenta. The solid was then filtered off, washed with water, and dried *in vacuo* over P_2O_5 (Found: C, 27·8; H, 4·8; Mo, 23·0; N, 6·6. Calc. for $C_{20}H_{40}Mo_2N_4O_{11}S_4$: C, 28·9; H, 4·8; Mo, 23·1; N, 6·7%).

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[1] (*a*) A. Kay and P. C. H. Mitchell, *Nature*, 1968, **219**, 267; (*b*) A. Kay and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 2421; (*c*) L. R. Melby, *Inorg. Chem.*, 1969, **8**, 349.

[2] J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475 and references therein.

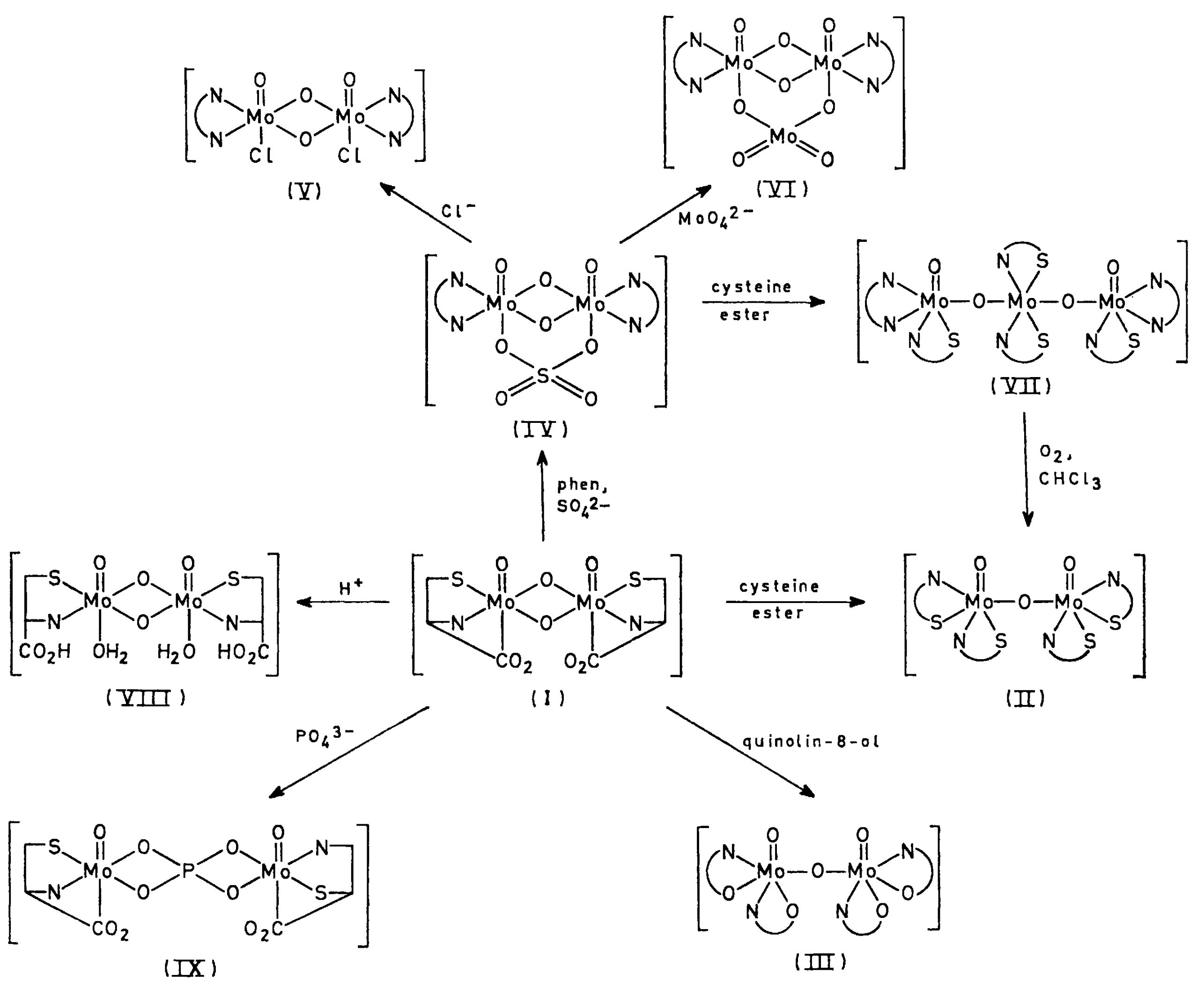
[3] J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1857.

[4] M. G. B. Drew and A. Kay, *J. Chem. Soc.* (*A*), 1971, 1846.

[5] M. G. B. Drew and A. Kay, *J. Chem. Soc.* (*A*), 1971, 1851.

[6] R. C. Bray and J. C. Swann, *Structure and Bonding*, 1972, **11**, 108.

μ-Oxo-bis[oxobis(quinolin-8-olato)molybdenum(V)] *Hydrate*, $[Mo_2(O)_3(C_9H_6NO)_4],H_2O$ (III).—A solution of quinolin-8-ol (2·4 g) in acetic acid (60 cm^3) was added to a solution of complex (I) (2 g) in water (100 cm^3). The resulting solution was boiled and an initial yellow precipitate darkened to red. After 15 min a purple solid was filtered off, washed with water, and dried *in vacuo* over P_2O_5 (Found: C, 52·0; H, 2·9; Mo, 23·4; N, 6·7. Calc. for $C_{36}H_{26}Mo_2N_4O_8$: C, 51·8; H, 3·1; Mo, 23·0; N, 6·7%). Analysis of the initial yellow precipitate showed the absence of cysteine (no sulphur), but did not correspond to a definite composition.



SCHEME Reaction scheme and proposed structures (charges on ions are omitted). Complexes (I)—(VII) have been isolated, (VIII) and (IX) are species postulated in aqueous solutions. The oxidation state of molybdenum is V except in complex (VII) where it is IV. Reactions are in aqueous solution except for the oxidation (VII) ⟶ (II) which is in chloroform

Di-μ-oxo-μ-sulphato-bis[oxo(1,10-phenanthroline)molybdenum(V)] *Trihydrate*, $[Mo_2(O)_4(SO_4)(phen)_2],3H_2O$ (IV).—A solution containing 1,10-phenanthroline (1·4 g), phthalate buffer (50 cm^3), and 1M-sulphuric acid (20 cm^3) was added to a solution of complex (I) (2 g) in phthalate buffer (50 cm^3). A buff coloured precipitate formed over a period of 10 min. The *complex* was filtered off, washed with water, and dried *in vacuo* over P_2O_5 (Found: C, 37·6; H, 2·7; Mo, 24·8; N, 7·0; S, 3·95. Calc. for $C_{24}H_{24}Mo_2N_4O_{11}S$: C, 37·5; H, 3·1; Mo, 25·0; N, 7·3; S, 4·15%). The complex was insoluble in water and organic solvents.

Di-μ-oxo-bis[chloro-oxo(1,10-phenanthroline)molybdenum (V)], $[Mo_2(O)_4Cl_2(phen)_2]$ (V).—Complex (IV) (2 g) was warmed with 2M-hydrochloric acid (5 min). A yellow *solid* which formed was filtered off, washed with water, and dried *in vacuo* over P_2O_5 (Found: C, 42·1; H, 2·5; Cl, 10·35; Mo, 27·9; N, 8·25. Calc. for $C_{12}H_8ClMoN_2O_2$: C, 42·0; H, 2·3; Cl, 10·2; Mo, 28·0; N, 8·2%). The complex was insoluble in water and organic solvents.

Di-μ-oxo-μ-tetraoxomolybdate(VI)-*bis[oxo*(1,10-*phenanthroline)molybdenum*(V)] *Dihydrate*, $[Mo_3(O)_8(phen)_2],2H_2O$ (VI).—Complex (IV) (2 g) was added to a boiling solution of sodium tetraoxomolybdate(VI) (2 g) in water (100 cm^3). A brick-red *solid* was formed which was filtered off, washed with water, and dried *in vacuo* over P_2O_5 (Found: C, 34·8; H, 2·4; Mo, 35·4; N, 6·5. Calc. for $C_{12}H_{12}Mo_3N_2O_{10}$: C, 35·4; H, 2·5; Mo, 35·5; N, 6·9%). The complex was insoluble in water and organic solvents.

μ-[Bis(ethyl L-*cysteinato-*SN*)dioxomolybdate*(IV)*-*OO*]-bis-[(ethyl* L-*cysteinato-*SN*)oxo(*1,10*-phenanthroline)molybdenum-*(IV)], $[Mo_3(O)_4(Etcyst)_4(phen)_2]$ (VII). To a mixture of complex (IV) (6 g) and ethyl L-cysteinate hydrochloride (6 g) was added concentrated ammonia solution (10 cm³) and the resulting solution was shaken vigorously. Chloroform (60 cm³), presaturated with nitrogen, was then added. A dark blue chloroform layer was obtained, which was separated and dried over molecular sieves (10 min). The latter were filtered off and light petroleum was added to the filtrate. A blue solid was obtained which was filtered off under an atmosphere of nitrogen gas. A solution of the solid in chloroform was purified by chromatography, under an atmosphere of nitrogen gas, on alumina using chloroform–ethanol (10 : 1) as eluant. The *complex* was precipitated by light petroleum and dried *in vacuo* (Found: C, 40·0; H, 4·5; Mo, 21·5; N, 8·5; S, 9·9. Calc. for $C_{44}H_{56}Mo_3N_8O_{12}S_4$: C, 40·5; H, 4·3; Mo, 22·1; N, 8·6; S, 9·8%). The complex was readily soluble in organic solvents. It decomposed in the presence of air and moisture to complex (II).

Reactions of Complex (I).—Complex (I) was recovered unchanged from attempted reactions with pyridine and xanthine.

With tartaric acid. Tartaric acid (1·5 g) was added to a solution of complex (I) (3·16 g) in water (50 cm³). There was no immediate reaction. On boiling the solution for a few minutes a gradual darkening of colour was observed. A solution of barium chloride (2 g) in water (20 cm³) was added and the solution was allowed to cool. A brown solid separated and was filtered off and dried *in vacuo* over P_2O_5 (Found: C, 16·2; H, 2·7; Mo, 28·7; N, 2·5%). The reaction was repeated several times but the products had variable analyses depending on the tartrate : complex (I) ratio.

With diazomethane. Diazomethane, generated from Diazald and potassium hydroxide,[7] was passed as an ether vapour into a solution of complex (I) (3 g) in water for several hours. A darkening of the aqueous solution occurred. A portion of the solution was evaporated to dryness *in vacuo*. The i.r. spectrum of the solid showed the presence of unreacted (I), molybdenum(V) hydroxide, $MoO(OH)_3$, and a free amino-acid. The latter was separated from the reaction mixture by chromatography on a cellulose column, using water–acetone (3 : 7) as eluant, and was characterised as *S*-methyl-L-cysteine from analysis and i.r. and n.m.r. spectra.

Reactions in solution were carried out in a closed system under an atmosphere of nitrogen gas. Reactions were followed spectrophotometrically and potentiometrically (see Results and Discussion section). U.v. and visible spectra of solutions were recorded on a Unicam SP 800 spectrophotometer using matched silica cells and appropriate reference solutions. Diffuse-reflectance spectra of solids were recorded on a Unicam SP 700C spectrophotometer against a blank of magnesium oxide. I.r. spectra of solids in potassium bromide discs or Nujol mulls were recorded on a Unicam SP 200 spectrophotometer. N.m.r. spectra were recorded on a Varian HA100 instrument by the Physico Chemical Measurements Unit, Harwell. Magnetic susceptibilities of powdered solids at room temperature were measured on a Newport Instruments Ltd. Gouy balance calibrated with cobalt tetrathiocyanatomercurate(II). Potentiometric titrations were carried out with a Radiometer type TTT1 automatic titrimeter. Carbon, hydrogen, nitrogen, and sulphur were determined by standard microanalytical procedures. Molybdenum was determined gravimetrically as the quinolin-8-olate complex $[Mo(O)_2(C_9H_6NO_2)]$ after complexes had been decomposed by heating with conc. nitric acid–conc. sulphuric acid (1 : 1).

RESULTS AND DISCUSSION

Reactions in Solution.—Protonation. The site of protonation of the complex ion $[Mo_2(O)_4(cyst)_2]^{2-}$ (cyst = L-cysteinato) (I) was determined by a spectrophotometric, potentiometric, and n.m.r. study of its aqueous solutions; concentrations were in the range 10^{-4}—10^{-2}M.

U.v. spectra of complex (I) in various buffer solutions (carbonate, borate, and acetate) covering the pH range 9—1 were recorded. At pH >6 and <3 the spectrum was unaffected by changes of pH. Between pH 6 and 3 the extinction coefficient of the absorption peak at 32 700 cm^{-1} decreased from 13 500 to 300 l mol^{-1} cm^{-1} and the peak was ultimately replaced by a new peak at 33 900 cm^{-1}. To determine the number of protons combining a solution of complex (I) (10^{-4}M) was titrated against 1M-sulphuric acid. The decrease in intensity of the 32 700 cm^{-1} peak was plotted against added acid. The end-point corresponded to two protons per molecule of complex (I).

Approximate pK values were determined by potentiometric titrations of complex (I) (10^{-2}M) with 0·5M-sulphuric acid and calculated according to the procedure of Clement and Hartz:[8] pK_1 2·03; pK_2 4·07 (10^{-2}M, 25 °C). Our value of pK_1 for complex (I) is close to the value (2·12)[8] for cysteine which refers to ionisation of the carboxy group of the fully protonated acid $HSCH_2CH(NH_3^+)CO_2H$. We consider, therefore, that the complex (I) behaves as a dicarboxylic acid and that both pK_1 and pK_2 refer to protonation of the carboxyl group. The difference between pK_1 and pK_2 arises,

TABLE 1

^{1}H N.m.r. spectra *

L-Cysteine hydrochloride D_2O	Complex (I)	
	H_2O and D_2O	Aqueous HCl
6·85(d) α-CH	6·70(q) α-CH^1	6·70(q) α-CH^1
5·60(t) β-CH	6·02(q) α-CH^2	6·02(q) α-CH^2
J(α-CH, β-CH) 5	5·06, β-CH †	
	3·56 NH_2	3·56 NH_2
	J(α-CH^1, α-CH^2) 12	1·7b OH
	J(α-CH^1, β-CH) 4	

* τ Values relative to tetramethyl silane (=10); splittings (b = broad, d = doublet, t = triplet, q = quartet); and assignments. For structural notation see text, p. 1391. Coupling constants J/Hz. Temperature 0 °C. † In D_2O only.

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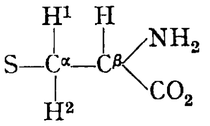
[7] R. J. Ellis and M. M. Chey, *J. Chem. Soc.* (*A*), 1966, 553; W. von Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 729.

[8] G. E. Clement and T. P. Hartz, *J. Chem. Educ.*, 1971, **48**, 395.

of course, because the first protonation step is favoured over that of the second.[9]

To confirm that the site of protonation was the carboxy groups, we recorded ^{1}H n.m.r. spectra of complex (I) and L-cysteine hydrochloride in water, deuterium oxide, and dilute hydrochloric acid at 0 °C (Table 1). The spectra are interpreted with reference to the structure of L-cysteinate below. In the spectrum



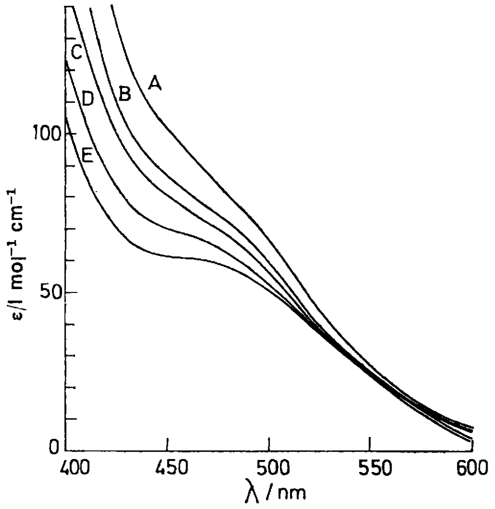
$$\mathrm{S{-}\overset{H^1}{\underset{H^2}{C^{\alpha}}}{-}\overset{H}{C^{\beta}}\!\left<\begin{matrix}NH_2\\CO_2\end{matrix}\right.}$$

of L-cysteine hydrochloride protons on the nitrogen and sulphur atoms were not resolved. The α-carbon protons gave a doublet signal and those of the β-carbon gave a triplet. In complex (I) the α-carbon protons are non-equivalent and coupled and produced two sets of doublets which were further split into two quartets by coupling with β-carbon protons. The β-carbon proton signal was observed for solutions of complex (I) in deuterium oxide (τ 5·06), but was near to the water proton peak and not resolved into the expected doublet. Signals of both the α- and β-carbon protons were observed at lower fields in complex (I) than in L-cysteine hydrochloride, indicating deshielding on co-ordination. The NH_2 proton signal of complex (I) was observed in water at 0 °C. The spectrum of complex (I) in hydrochloric acid (at concentrations such that $[H^+]/[\text{complex}] = 2/1$) was similar to that in water down to τ 3.

There were no signals due to free cysteine showing that there was no dissociation of the ligand. However, in the solution in hydrochloric acid a new signal was observed at τ 1·7. The positions and shapes of the signals were consistent with a hydroxyl group, the proton of which is rapidly exchanging with protons in the immediate environment. Thus protonation occurred at oxygen rather than at the nitrogen or sulphur atoms. The most probable site of protonation is the weakly co-ordinated oxygen atom of the carboxyl group of L-cysteine, since it is unlikely that terminal or bridging oxo-groups bonded to the molybdenum are protonated.[10] We conclude that protonation of complex (I) occurs at the carboxyl group of the cysteine ligand and that, in aqueous solution, there is an equilibrium between two forms of the complex, one in which a carboxyl group is bound to the molybdenum, and one in which a water molecule replaces the carboxyl group.

Changes in the u.v. spectrum of complex (I) are of interest in the context of a recent discussion of the electronic states of this and structurally similar complexes.[11] The absorption peak at 32 700 cm^{-1} is assigned to a transition between ground- and excited-state molecular orbitals, which are based almost entirely on molybdenum atomic orbitals and can be regarded as Mo–Mo bonding and anti-bonding molecular orbitals. According to our results, the decrease in intensity of this peak and its shift to a higher wavenumber when complex (I) is protonated are due to replacement of bound carboxyl groups by water. Since water is higher in the spectrochemical series than the carboxyl group,[12] such a shift is expected for a transition involving orbitals localised on molybdenum.

With phosphate, tartrate, and other anions. E.s.r. spectra have been obtained for aqueous molybdenum(V) solutions containing tartrate[13] and phosphate[14] ions and assigned respectively to a paramagnetic monomeric and polymeric species with phosphato-bridges. Huang and Haight[15] observed e.s.r. spectra of solutions of complex (I) in phosphate buffers at pH values between 6 and 10. The paramagnetic species are of interest as models for e.s.r.-active species observed during reactions catalysed by, for example, xanthine oxidase.[6]



Visible spectra for the reaction of complex (I) (1·39 × 10^{-2}M) with $H_2PO_4^-$ (0·2M, pH 4·6) at various times: (A), 0; (B), 50 min; (C), 2; (D), 5; (E), 24 h

Spectra of solutions of complex (I) (10^{-3}M) in 0·2M-solutions of trisodium phosphate (pH 12·3), sodium hydrogen phosphate (pH 3·6), and sodium dihydrogen phosphate (pH 4·6) were recorded over a period of 24 h. Absorbance at wavenumbers $<$25 000 cm^{-1} decreased with time and a peak at 21 000—22 000 cm^{-1} appeared. Typical spectra are shown in the Figure. Similar results were obtained in solutions of potassium tartrate. Because of the slowness of the reactions we could not make equilibrium studies. The spectrum of the complex in acetate, phthalate, borate, and carbonate buffer solutions did not change with time. Thus complex (I) reacts with

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[9] J. E. Prue, 'Ionic Equilibria,' Pergamon Press, London, 1966, p. 85.

[10] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.

[11] D. H. Brown, P. G. Perkins, and J. J. Stewart, *J.C.S. Dalton*, 1972, 1105.

[12] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, London, p. 109.

[13] J. T. Spence and M. Heydanek, *Inorg. Chem.*, 1967, **6**, 1489.

[14] I. N. Marov, Yu. N. Dubrov, V. K. Belyaeva, and A. N. Ermakov, *Doklady Akad. Nauk S.S.S.R.*, 1967, **177**, 1166.

[15] T. J. Huang and G. P. Haight, *Chem. Comm.*, 1969, 985.

phosphate and tartrate ions possibly, in view of previous work,[14,15] with replacement of bridging oxo-groups by those of phosphate or tartrate to give a paramagnetic species.

Oxidation. On exposure of aqueous solutions of complex (I) to air, the u.v. absorption peak at 32 700 cm^{-1} decreased in intensity and a new peak appeared at 31 600 cm^{-1}. The spectroscopic changes were accelerated by oxygen, increase of pH, L-cysteine, iron(II), and iron(III). This is consistent with oxidation of molybdenum(V) to molybdenum(VI) [equation (1)]. That iron(II)

$$[Mo_2(O)_4(cyst)_2]^{2-} + 2\,cyst^{2-} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow 2[Mo(O)_2(cyst)_2]^{2-} + H_2O \quad (1)$$

and iron(III) ions promoted the oxidation is perhaps significant in view of the occurrence of iron and molybdenum together in molybdenum-containing enzymes, and the reaction is being studied in more detail.[16] It appears that iron(II) ion facilitates electron transfer from molybdenum(V) in complex (I).

There were no spectroscopic changes when xanthine and pyridine were added to aqueous solutions of complex (I). The spectra remained unchanged when carbon monoxide, nitrous oxide, and hydrogen were passed through the solution. There was no absorption of these gases, nor of dinitrogen, by aqueous solutions containing complex (I) and sodium tetrahydroborate.

Complexes Isolated.—The preparation of the following complexes by reaction of complex (I) with the appropriate ligand is described in the Experimental section: $[Mo_2(O)_3(Etcyst)_4]$ (Etcyst = ethyl L-cysteinato) (II); $[Mo_2(O)_3(quinolin\text{-}8\text{-}olate)_4]$ (III); and $[Mo_2(O)_4(phen)_2(SO_4)]$, $3H_2O$ (phen = 1,10-phenanthroline) (VI). The following complexes were prepared from complex (IV): $[(Mo_2(O)_4Cl_2(phen)_2]$ (V); $[Mo_3(O)_8(phen)_2],2H_2O$ (VI); and $[Mo_3(O)_4(Etcyst)_4(phen)_2]$ (VII). Reactions and proposed structures of the complexes are shown in the Scheme. The formulae of the complexes are based on analyses and physical measurements. The oxidation state of molybdenum was established as V, except for complex (VII), by titration with cerium(IV) ions or, for complexes with oxidisable ligands, by showing that the visible spectra of the complexes and that of the complex $(NH_4)_2[Mo(O)Cl_5]$ in concentrated hydrochloric acid were identical. The complexes of ethyl L-cysteinate, (II),[1b,c] and quinolin-8-ol, (III),[17] have been prepared previously although not from complex (I).

Magnetic properties. The complexes had apparent magnetic moments of 0·4—0·6 B.M. at *ca.* 20 °C. These are below the spin-only value for molybdenum(V) (1·73 B.M.) and indicate the presence of bi- or polynuclear groups in which there is coupling of electron spins on adjacent molybdenum(V) atoms through metal–metal bonding and/or oxo-bridges.[10] The magnetic moment of the molybdenum(IV) complex (VII) was 0·4 B.M. at *ca.* 20 °C. This low moment could arise from coupling of the electron spins on adjacent molybdenum(IV) atoms or from a low-spin d^2 configuration.[18]

I.r. spectra. The positions and assignments of the main bands are given in Table 2.

TABLE 2

I.r. spectra *

$Na_2[Mo_2(O)_4(cyst)_2],5H_2O$ (I)				
3430vs H_2O	3100s,b $\nu(NH)$	1630vs $\nu_{asym}(CO)_2$	1590vs $\delta(NH)$	1390s $\nu_{sym}(CO)_2$
955vs $\nu(MoO)$	735s $\nu(MoO_2Mo)$			
$[Mo_2(O)_3(Etcyst)_4]$ (II)				
3120m $\nu(NH)$	1725s $\nu_{asym}(CO)_2$	1569s $\delta(NH)$	943mb $\nu(MoO)$	
$[Mo_2(O)_3(quinolin\text{-}8\text{-}olate)_4],H_2O$ (III)				
3500m H_2O	1575s	1565vs	1470vs quinolin-8-olate	1385vs
1320vs	1265s	1105vs	940vs,b $\nu(MoO)$	
830s quinolin-8-olate	745vs			
$[Mo_2(O)_4(SO_4)(phen)_2],3H_2O$ (IV)				
3475vs H_2O	1709s	1527s phen	1439vs phen	1211s $\nu(SO_4)$
1127s $\nu(SO_4)$	1119vs $\nu(SO_4)$	959vs $\nu(SO_4)$	943vs $\nu(MoO)$	864s phen
747s $\nu(MoO_2Mo)$	726s phen			
$[Mo_2(O)_4Cl_2(phen)_2]$ (V)				
3050s H_2O	1524m phen	1430s phen	959vs $\nu(MoO)$	860vs phen
729vs	734vs $\nu(MoO_2Mo)$	722vs phen		
$[Mo_3(O)_8(phen)_2],2H_2O$ (VI)				
3500s,b H_2O	1528m phen	1434m phen	959vs $\nu(MoO)$	898s $\nu(MoO)$
880s $\nu(MoO)$	858vs phen	782s $\nu(MoO)$	728vs phen	716s $\nu(MoO)$
$[Mo_3(O)_4(Etcyst)_4(phen)_2]$ (VII)				
v. broad	1727vs $\nu_{asym}(CO)_2$	1565m $\delta(NH)$	1525m phen	1435s phen
931vs $\nu(MoO)$	907s $\nu(MoO)$	860s phen	725s	

* Main bands ($\bar{\nu}$/cm^{-1}) and relative intensities (vs, very strong; s, strong; m, medium; b, broad). Assignments (ν, stretching; asym, asymmetric; sym, symmetric; δ, bending) are based on comparisons with the free ligands and other complexes (see ref. 24). cyst = L-Cysteinato; Etcyst = ethyl L-cysteinato; phen = 1,10-phenanthroline.

(*a*) *Molybdenum–oxygen stretching vibrations.* We distinguish between terminal oxo- (O_t) and bridging oxo-groups (O_b).[10] All the complexes had a strong band at 930—960 cm^{-1} assigned to a Mo–O_t stretching vibration. For complexes (II), (III), and (VII) there was a second band, or a broadening of the main band, at >900 cm^{-1}, as expected for structures with one terminal and one bridging oxo-group per molybdenum

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[16] P. C. H. Mitchell and D. A. Parker, unpublished work.

[17] (*a*) H. M. Stevens, *Analyt. Chim. Acta*, 1956, **14**, 128; (*b*) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1962, 4570; (*c*) C. Bertoglio and F. Guerrieri, *Ann. Chim.* (*Italy*), 1967, **37**, 873.

[18] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1969, 2632.

atom (*cf.* the Scheme).[19] The lower wavenumbers of the molybdenum–oxygen stretching vibrations for complex (VII) are expected for molybdenum(IV).[18] The remaining complexes had a strong band at 730—750 cm^{-1} which is assigned as the ν_3 vibration of the Mo–$(O)_2$–Mo group.[10,19,20] For complex (VI) at least five bands are assigned to molybdenum–oxygen vibrations. The number of bands indicates co-ordinated rather than ionic tetraoxomolybdate(VI). For the latter, only one additional band at *ca.* 830 cm^{-1} would be expected.[21]

(*b*) *Water.* A strong band at *ca.* 3500 cm^{-1} in the spectra of complexes (I), (III), (IV), and (VI) is assigned to the O–H stretching vibration of lattice water.[22]

(*c*) *Sulphate.* In the spectrum of complex (IV) there were four bands which can be assigned to S–O vibrations of the sulphato-group (see Table 2). These bands were absent from the other phenanthroline complexes (V) and (VI) for which similar structures are proposed and which do not contain the sulphato-group. The occurrence of four sulphate bands shows the presence of a bidentate sulphato-group (C_{2v}) bridging two metal atoms as in the complex $[(NH_3)_4Co\cdot\mu(NH_2,SO_4)\cdot Co(NH_3)_4](NO_3)_3$.[23]

(*d*) *Organic ligands.* Assignments were made by comparison with the spectra of the free ligands and other complexes.[1b,24]

TABLE 3

Electronic spectra *

$Na_2[Mo_2(O)_4(cyst)_2],5H_2O$ (I)		
	Solid (reflectance)	45·2, 35·3,[a] 29·3[a]
	Solution (H_2O)	48·8(9500), 32·7(6400)
$[Mo_2(O)_3(Etcyst)_4]$ (II)		
	Solid (reflectance)	37·7, 29·9, 21·0,[b] 14·0sh[c]
	Solution ($CHCl_3$)	30·5(3650), 19·6(7550)
$[Mo_2(O)_3(quinolin\text{-}8\text{-}olate)_4],H_2O$ (III)		
	Solution (EtOH)	41·2(31 200),[d] 39·2(36 100),[d] 32·8(6 600),[d] 25·0(8 400),[d] 18·4(5 200)[c]
$[Mo_2(O)_4(SO_4)(phen)_2],3H_2O$ (IV)		
	Solid (reflectance)	37·5,[d] 30·7,[a] 29·4sh,[a] 28·3sh,[a] 22·2sh[a]
$[Mo_2(O)_4Cl_2(phen)_2]$ (V)		
	Solid (reflectance)	36·8,[d] 32·0,[a] 25·3[a]
$[Mo_3(O)_8(phen)_2],2H_2O$ (VI)		
	Solid (reflectance)	37·1,[d] 33·0,[a] 31·3,[a] 24·0[a]
$[Mo_3(O)_4(Etcyst)_4(phen)_2]$ (VII)		
	Solid (reflectance)	37·6,[d] 33·6, 26·5, 16·0,[b] 15·0[c]

* Peak positions (10^{-3} $\bar{\nu}$/cm^{-1}), extinction coefficients (ε/l mol^{-1} cm^{-1}) in parentheses. Probable assignments: [a] Mo–Mo transitions (ref. 11); [b] Mo $\longrightarrow$ cysteine ester (?); [c] Organic ligand $\longrightarrow$ Mo, charge-transfer transitions; and [d] internal transitions ($\pi \longrightarrow \pi^*$) of organic ligands. cyst = L-Cysteinato; Etcyst = ethyl L-cysteinato; phen = 1,10-phenanthroline.

Electronic spectra. Peak positions are given in Table 3. Transitions in the u.v. region are assigned to internal transitions ($\pi \longrightarrow \pi^*$) of organic ligands and, for complexes with the Mo–$(O)_2$–Mo group, to transitions involving orbitals mainly located on the molybdenum atoms.[11] Absorption peaks below *ca.* 20 000 cm^{-1} were observed for complexes (II), (III), and (VI) and are assigned to charge-transfer transitions between the organic ligand and molybdenum.[17b,24] The phenanthroline–cysteine ester complex of molybdenum(IV), (VII), had a strong peak (ε 3000 l mol^{-1} cm^{-1}) at 16 900 cm^{-1}; the spectrum resembles that of xanthine oxidase in this region.

Reaction with Diazomethane.—In the hope of obtaining a dinitrogen complex, we passed diazomethane into an aqueous solution of complex (I). The reaction product was a mixture of *S*-methyl-L-cysteine, hydrated molybdenum(V) oxide, and unreacted (I). There was no evidence (*e.g.* i.r. spectrum) for a dinitrogen complex. The reaction with diazomethane did, however, demonstrate the importance of thiol groups in the bonding of amino-acids to molybdenum(V); methylation of the thiol group caused decomposition of complex (I). This is consistent with our failure to obtain molybdenum(V) complexes of *S*-methyl-L-cysteine and with qualitative [1b] and quantitative [25] observations that the formation of amino-acid complexes of molybdenum(V) is enhanced by the presence of thiol groups.

CONCLUSIONS

Protonation of complex (I) occurred at the co-ordinated carboxyl group. Dissociation of this group did not lead to decomposition of the complex. However, methylation of the co-ordinated thiolate group in the reaction with diazomethane caused decomposition of the complex, so co-ordination of L-cysteine to molybdenum(V) is dependent on the thiol group. A feature of complex (I) is the lability of the weakly bound carboxyl group. In complexes of the $Mo_2(O)_4$ group with cysteine esters the $-CO_2R$ group is not co-ordinated and unique five-co-ordinate structures are formed.[1b,4,5]

With phosphate and tartrate ions in aqueous solution complex (I) forms paramagnetic species. L-Cysteine remains co-ordinated and the anions probably replace oxo-bridges giving either monomeric species or dimers with anion bridges. Complex (I) reacts only with tetrahedral or chelating anions; there was no evidence of reaction with borate, carbonate, acetate, or phthalate ions. In reactions of complex (I) with ethyl L-cysteinate and quinolin-8-ol one bridging oxo-group of the $Mo_2(O)_4$ group was replaced giving complexes of the $Mo_2(O)_3$ group. In reactions with 1,10-phenanthroline the $Mo_2(O)_3$ group was preserved. It appears that displacement of the bridging oxo-group requires chelating ligands with $-OH$ or $-SH$ groups. Possibly, there is initial proton attack on the bridging oxo-group as

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suggested for reactions with hydrogen sulphide (which give μ-sulphido-complexes)[1b] and in solution equilibria in hydrochloric acid.[10] In the reactions with ethyl L-cysteine and quinolin-8-ol cysteine is completely displaced from the complex (I). We were unable to prepare mixed-ligand complexes analogous to those obtained from reactions of the complex ion $[Mo_2(O)_4(C_2O_4)_2(H_2O)_2]^{2-}$ under similar conditions.[24] Thus ligand replacement is more facile with complex (I) than with the oxalato-complex.

Complex (IV) was reduced by ethyl L-cysteinate to a molybdenum(IV) complex, (VII), containing both co-ordinated 1,10-phenantholine and cysteine ester. That reduction occurs, is in agreement with previous observations that *N*-heterocyclics and thiolate anions stabilise molybdenum(IV).[26] When complex (VII) was oxidised in air, phenanthroline was released from co-ordination to molybdenum and the molybdenum(V)–ethyl L-cysteinate complex (II) was formed.

Aerial oxidation of complex (I) gave a molybdenum(VI) cysteinate complex. The oxidation rate was increased by increase of pH, L-cysteine, iron(II), and iron(III). The cysteine complex (I) did not react with or catalyse the oxidation of xanthine or the reduction of dinitrogen. The complex apparently has no catalytic properties in aqueous solution. In terms of co-ordination around molybdenum, complex (I) may be regarded as a model for molybdenum co-ordination in xanthine oxidase (*e.g.*, e.s.r. signals with similar *g* and *A* values) but, in terms of its reactions, it is not a good model. The spectrum of the mixed 1,10-phenanthroline–cysteine ester complex (VII) at $<20\,000$ cm^{-1} was very similar to that of xanthine oxidase. It is probable that the cysteine ester complexes are better models for molybdenum in enzymes and we are currently studying their reactions.

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[26] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1969, 1476.