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Oxomolybdenum(IV) Bis(dithiolato) Complexes

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Oxomolybdenum(IV) complexes, [$MoOL_2$] ($L^- = Et_2NCS_2^-$, $(EtO)_2PS_2^-$, $(PhO)_2PS_2^-$), were first prepared by us in 1966 [1] via reduction of molybdate(VI) in an aqueous solution containing the ligand. The dithiocarbamato complexes have attracted interest as possible models of molybdenum coordination in molyboenzymes [2]. The n-propyldithiocarbamato complex, [$MoO(Pr_2NCS_2)_2$], has been shown by single crystal X-ray analysis to be square pyramidal [3]. The basal plane is formed by four sulphur atoms. The molybdenum atom is 83 pm above the plane and the multiply-bound oxygen atom occupies the apex. Other diamagnetic five-coordinate oxomolybdenum(IV) complexes are assumed to have the square pyramidal structure. In the present paper we report the preparation and characterisation of analogous oxomolybdenum(IV) complexes of the dithiolato ligands ethane-1,2-dithiolate, $C_2H_4(S)_2^{2-}$, and toluene-3,4-dithiolate, $MeC_6H_3(S)_2^{2-}$. Our new complexes were isolated as potassium salts of the complex anions [$MoOL_2$]$^{2-}$ via reaction of the dithiol ligands with aqueous solutions of the compound $K_4[Mo(CN)_4(O)_2]\cdot 6H_2O$ [4]. The dithiolato complexes are electrolytes and soluble in water and so provide an opportunity of studying the aqueous solution chemistry of oxomolybdenum(IV) sulphur complexes.

Experimental

Preparations

All preparations and manipulations were carried out under nitrogen or *in vacuo*. Solvents were deoxygenated before use.

Potassium bis(ethane-1,2-dithiolato)oxomolybdate(IV)–ethanol(1/2), $K_2[MoO\{C_2H_4(S)_2\}_2]\cdot 2EtOH$ *(II)*

Ethane-1,2-dithiol (2.3 g) was added to $K_4[Mo(CN)_4(O)_2]\cdot 6H_2O$ [4] (2.5 g) in water (30 cm^3). The solution was stirred and its colour changed from deep blue to red in *ca.* 0.25 h. During a further 24 h a white solid precipitated and was filtered off and recrystallised from acetone (colourless needles). Found: C, 33.5; H, 4.7; N, 11.2; S, 48.8. Calc. for $C_7H_{12}N_2S_4$: C, 33.3; H, 4.8; N, 11.1; S, 50.8%. The filtrate was shaken several times with diethylether to remove any unreacted dithiol and pumped to dryness. The resulting solid was extracted with hot ethanol and gave an orange solution from which orange crystals separated on cooling. They were purified by recrystallisation from ethanol. Found: C, 20.6; H, 4.3; K, 16.7; Mo, 20.6; S, 27.5. Calc. for $C_8H_{20}K_2MoO_3S_4$: C, 20.4; H, 4.2; K, 16.4; Mo, 20.6; S, 27.3%.

Potassium oxo-bis(toluene-3,4-dithiolato)molybdate(IV)–ethanol(1/3), $K_2[MoO\{MeC_6H_3(S)_2\}_2]\cdot 3EtOH$*, (III)*

A solution of 3,4-dimercaptotoluene (3.1 g) in ethanol (20 cm^3) was added to a stirred solution of $K_4[Mo(CN)_4(O)_2]\cdot 6H_2O$ (2.5 g) in water (50 cm^3) during 0.5 h. The colour of the solution changed from blue through purple to red. The solution was pumped to dryness and the resulting solid was extracted with ethanol to yield a pale orange product. Found: C, 37.6; H, 4.6; K, 12.4; Mo, 15.2; S, 20.3. Calc. for $C_{20}H_{30}K_2MoO_4S_4$: C, 37.7; H, 4.8; K, 12.3; Mo, 15.1; S, 20.1%.

Bis(N,N-diethyldithiocarbamato)oxomolybdenum(IV), [$MoO(Et_2NCS_2)_2$]*, (IV)*

To an aqueous solution of $K_4[Mo(CN)_4(O)_2]\cdot 6H_2O$ (1.0 g) was added solid $Na(Et_2NCS_2)\cdot 3H_2O$ (0.5 g) followed by dilute hydrochloric acid. A pink solid precipitated, and was filtered off, washed with water, and dried *in vacuo*. Found: C, 29.4; H, 4.8; N, 6.9. Calc. for $C_{10}H_{20}MoN_2OS_4$: C, 29.4; H, 4.9; N, 6.9%.

Physical Measurements

Spectra (u.v. and visible, i.r., e.p.r., ^1H n.m.r.) were recorded as before [1, 2a]. Magnetic susceptibilities were determined by the Gouy method at room temperature.

Results and Discussion

Reactions Studied and Compounds Prepared

Reaction of the compound $K_4[Mo(CN)_4(O)_2]\cdot 6H_2O$ (I) with ethane-1,2-dithiol and 3,4-dimercaptotoluene in aqueous solution, followed by extraction of the products with ethanol, gave the new compounds $K_2[MoO\{C_2H_4(S)_2\}_2]\cdot 2EtOH$ (II) and $K_2[MoO\{MeC_6H_3(S)_2\}_2]\cdot 3EtOH$ (III). With sodium diethyldithiocarbamate the well known complex [$MoO(Et_2NCS_2)_2$] (IV) precipitated when the solution was acidified. In aqueous solution the [$Mo(CN)_4(O)_2$]$^{4-}$ ion is in equilibrium with protonated species

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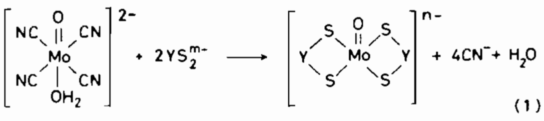
TABLE I. Spectroscopic Data.

$K_2[MoO\{C_2H_4(S)_2\}_2]\cdot 2EtOH$ (II)			$K_2[MoO\{MeC_6H_3(S)_2\}_2]\cdot 3EtOH$ (III)		
Infrared spectra: MoO and MoS vibrations[a]					
918s	355m		903s	350m	
ν(MoO)	ν(MoS)		ν(MoO)	ν(MoS)	
Electronic spectra[b]					
14.8(5)	19.9(172)	25.3(209)	14.5(3.8)	21.9(340)	
	d–d			d–d	
28.6(1000)[c]	33.8(5070)		28.6(1100)[c]	35.3(2400)	
charge-transfer			charge-transfer		
^1H n.m.r. spectra[d]					
6.42(2)	7.43(4)	9.90(3)	2.2–3.3(3)	6.42(3)	7.72(3)
CH_2(EtOH)	CH_2	CH_3	C_6H_3	CH_2	CH_3
			9.90(4.5)		
			CH_3(EtOH)		

[a] ν/cm^{-1} and relative intensities (s, strong; m, medium). Compounds in nujol mulls and KBr discs. [b] Peak positions (10^{-3} ν/cm^{-1}) and extinction coefficients (ε/mol cm^{-2}) for the compounds in water. [c] Shoulder. [d] Chemical shifts (τ relative to tetramethylsilane τ = 10) for compounds in D_2O. Relative intensities in parentheses.

$[Mo(CN)_4(O)(OH)]^{3-}$ and $[Mo(CN)_4(O)(H_2O)]^{2-}$ [4] and the overall reaction can therefore be described according to equation (1):

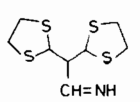


(1)

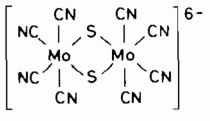
(I)

(m = 2) (II, Y = C_2H_4, n = 2)
(m = 2) (III, Y = MeC_6H_3, n = 2)
(m = 1) (IV, Y = Et_2NC, n = 0)

In the above reactions the dithiolates displace the cyanides and one oxo ligand. From the reaction with ethanedithiol we isolated a compound $C_7H_{12}N_2S_4$ (V) which apparently results from reaction of hydrolysed cyanide with excess of ethanedithiol and has the structure shown [5]. It is interesting that the reaction of the $[Mo(CN)_4(O)_2]^{4-}$ ion with hydrogen sulphide is quite different, the product being the di-μ-thio cyano complex of molybdenum(III), $[Mo_2(CN)_8(S)_2]^{6-}$ (VI) [6].



(V)



(VI)

Structures and Bonding

I.r., u.v.–visible, and ^1H n.m.r. spectra of the ethanedithiolato complex (II) and the toluenedithiolato complex (III) are given in Table I. We formulate the compounds as salts of mononuclear, five-co-ordinate oxomolybdenum(IV) complex anions $[MoOB_2]^{2-}$ (B = ethane-1,2-dithiolate, toluene-3,4-dithiolate) on the basis of the following evidence: (a) The compounds are diamagnetic as solids (Gouy method) and in solution (no e.s.r. signals) as expected for Mo(IV) (low-spin d^2) in a square-pyramidal environment with a multiply bonded oxide ligand [1]. (b) Formation of the compounds did not involve reduction of Mo(IV) (*e.g.*, no formation of disulphides). Also aerial oxidation gave e.s.r.-active species (see below) consistent with an oxidation Mo(IV) → Mo(V). (c) The presence of the MoO group is shown by strong i.r. bands at 918 and 903 cm^{-1}. (d) Binding of the dithiols as dianions is shown by the absence from the i.r. spectra of ν(SH) bands. From the ^1H n.m.r. spectra the two dithiolates in each anion are in identical environments in agreement with the square-pyramidal structure. (e) The u.v.–visible solution spectra at 12,000–25,000 cm^{-1} are characteristic of square pyramidal oxo complexes with d^2 electronic configurations (Mo(IV) [1], Re(V) [7]): a weak absorption peak assigned to a spin-forbidden d–d transition and at higher wavenumbers two stronger peaks assigned to spin-allowed d–d transitions (of which the second may sometimes be hidden under a much stronger peak arising from a

TABLE II. Aerial Oxidation of Ethanol Solutions of Oxomolybdenum(IV) Dithiolate Complexes: E.s.r. Signal Parameters.

Frozen solutions (77 K)							Room temperature (293 K)	
	g_1	g_2	g_3	A_1	A_2	A_3	g_{av}	A_{av}
$K_2[MoO\{C_2H_4(S)_2\}_2]\cdot 2EtOH$ (II)	2.047	1.981	1.981	53.6	22.8	22.8	2.000	31.1
$K_2[MoO\{MeC_6H_3(S)_2\}_2]\cdot 3EtOH$ (III)	2.022	1.985	1.977	51.3	nr[a]	nr[a]	1.993	30.7
Mo(VI) + $C_2H_4(SH)_2$[b]	2.050	1.978	1.978	55	21	21	2.002	30

[a]Not resolved. [b]Ref. 9.

charge-transfer transition). (f) The presence of solvate ethanol is shown by ν(OH) bands in the i.r. (3300–3400 cm^{-1}) and by the integrated intensities of the ^1H n.m.r. spectra.

The wavenumber of the MoO vibration is significantly lower (<920 cm^{-1}) in the dithiolato complexes than in the dithiocarbamato and phosphato complexes (>940 cm^{-1}). This suggests that binding of the dithiolates creates a greater electron density on the molybdenum and a consequent reduction of π-donation from the oxo-group and a lower MoO bond order.

Aerial Oxidation of the Mo(IV) Complexes: E.s.r. Spectra

On exposure to air or oxygen water or ethanol solutions of our dithiolato compounds (II) and (III) develop strong e.s.r. signals (Table II) which we assign to monomeric molybdenum(V) species $[MoOB_2]^-$ (B = dithiolate). We consider that the e.s.r.-active species are monomeric since the relative intensities of signals from the I = 0 and I = 5/2 molybdenum isotopes are 3:1 (*cf.* 1.5:1 expected for a paramagnetic dimer) and the weak eleven-line hyperfine spectrum expected from paramagnetic dimers which have both molybdenum nuclei with I = 5/2 [8] is not observed. The signals observed during oxidation of our ethanedithiol complex were similar to one of the two signals observed when ethanedithiol is added to aqueous Mo(VI) solutions [9] and it is possible that the same oxomolybdenum(V) species is formed by reduction of Mo(VI) in the latter system. The ultimate oxidation products of the dithiol complexes were molybdate(VI) and organic disulphides.

Conclusions

Reaction of dithiols with aqueous solutions of the compound $K_4[Mo(CN)_4(O)_2]\cdot 6H_2O$ is a convenient method of preparing salts of mononuclear, five-coordinate oxomolybdenum(IV) complex ions, $[MoOB_2]^{2-}$ (B = ethane-1,2-dithiolate, toluene-3,4-dithiolate). An analogous reaction with sodium diethyldithiocarbamate yields the compound $[MoO(Et_2NCS_2)_2]$. Aqueous solutions of the dithiolate complexes oxidise in air to paramagnetic Mo(V) species.

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References

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

2 a) P. C. H. Mitchell and R. D. Scarle, *J. Chem. Soc. Dalton*, 2552 (1975).
b) G. D. Watt, J. W. McDonald and W. E. Newton, in P. C. H. Mitchell (ed.), *Proc. Climax 2nd. Int. Conf. Chem. Uses Molybdenum*, Climax Molybdenum Co. Ltd., London (1977), p. 216.

3 L. Ricard, J. Estienne, P. Karagiannidis, P. Toledano, J. Fischer, A. Mitschler and R. Weiss, *J. Coord. Chem., 3*, 277 (1974).

4 a) Z. Jakob, *Rocz. Chem., 31*, 681 (1957).
b) J. van de Poel and H. M. Neumann, *Inorg. Chem., 7*, 2086 (1968).
c) P. R. Robinson, E. O. Schlemper and R. K. Murmann, *Inorg. Chem., 14*, 2035 (1975).

5 C. F. Pygall, *Ph.D. Thesis*, University of Reading (1976).

6 M. G. B. Drew, P. C. H. Mitchell, and C. F. Pygall, *Angew. Chem. Int. Ed. Engl., 15*, 784 (1976).

7 F. A. Cotton and S. J. Lippard, *Inorg. Chem., 5*, 9 (1966).

8 T. J. Huang and G. P. Haight, *Chem. Comm.*, 985 (1969).

9 L. S. Meriwether, W. F. Marzluff and W. G. Hodgson, *Nature, 212*, 465 (1966).