

Solution Chemistry and Reactivity of Tris(*N,N*-dialkyldithiocarbamato)-oxomolybdenum(vi) Cationic Complexes

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The preparation of the orange diamagnetic compounds $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{X}$ ($\text{R} = \text{Me}$ or Et , $\text{X} = \text{BF}_4^-$, PF_6^- , or ClO_4^- ; $\text{R} = \text{Pr}^i$, $\text{X} = \text{BF}_4^-$) from the reaction of *cis*- $[\text{MoO}_2(\text{S}_2\text{CNR}_2)_2]$ complexes and HX in acetone is described. Details of the ^1H and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r., i.r., and electronic spectra of the complexes are presented. The monomeric complex cations possess a rigid pentagonal-bipyramidal geometry in solution at room temperature. The complex $[\text{MoO}(\text{S}_2\text{CNET}_2)_3]^+$ catalytically converts PPh_3 into OPPh_3 in air, gives $[\text{Mo}(\text{NPh})(\text{S}_2\text{CNET}_2)_3]^+$ with PhNCO , undergoes replacement of one $\text{S}_2\text{CNET}_2^-$ ligand with Cl^- and S_2^{2-} , and yields $[\text{MoO}(\text{S}_2\text{CNET}_2)_2]$ upon reduction.

Although the crystal structure of the mono-oxomolybdenum(vi) cation $[\text{MoO}(\text{S}_2\text{CNET}_2)_3]^+$ was described some years ago¹ and there has been brief mention of this complex subsequently,²⁻⁴ there have been no reports of its further characterisation and, in particular, its solution chemistry. In the original work the complex was isolated as $[\text{MoO}(\text{S}_2\text{CNET}_2)_3][\text{Mo}_2\text{O}_4\text{F}_6]$ and shown to have a pentagonal-bipyramidal geometry. We have been interested in the reactivity of this cation, both from the point of view of new syntheses and in relation to oxygen-atom-transfer reactions of molybdoenzymes. In this context, recent extended *X*-ray absorption fine structure (EXAFS) studies have suggested the presence of a mono-oxomolybdenum(vi) centre in a predominantly S-donor environment for functional xanthine oxidase.⁵ Previous workers^{6,7} have examined oxygen-atom-transfer reactions of various *cis*-dioxomolybdenum(vi) complexes with a view to providing models for molybdoenzymes.

Here we report the preparation of the complexes $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{X}$ [$\text{R} = \text{Me}$ (1) or Et (2), $\text{X} = \text{BF}_4^-$, PF_6^- , or ClO_4^- ; $\text{R} = \text{Pr}^i$ (4), $\text{X} = \text{BF}_4^-$], and $[\text{MoO}(\text{S}_2\text{CNET}_2)_3][\text{Mo}_6\text{O}_{19}]$ (3) together with spectroscopic data for their characterisation and some observations of their reactions in solution.

Results and Discussion

The orange title compounds are readily prepared from *cis*- $[\text{MoO}_2(\text{S}_2\text{CNR}_2)_2]$ and HX in acetone. These reactions are undoubtedly complex but probably proceed by initial oxo-ligand protonation. The yields of the $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]\text{X}$ products range from 50 to 70% and the remainder of the molybdenum is ultimately converted into $[\text{Mo}_6\text{O}_{19}]^{2-}$. In solution at room temperature the complexes maintain a rigid pentagonal-bipyramidal geometry similar to that found in the solid-state structure of $[\text{MoO}(\text{S}_2\text{CNET}_2)_3]^+$. N.m.r. studies have been interpreted on the basis of the structure shown in Figure 1. Here the Mo and O atoms and the dithiocarbamate ligand (II) lie in the quasi-mirror plane of the complex, while the dithiocarbamate ligands (I) are symmetrically disposed about this plane. The rigid double-bond character of the CN bonds leads to four inequivalent alkyl substituents a, a', b, and c. The substituent configuration is apparent in the spectrum of $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$ which displays four resonances of relative intensity 2 : 1 : 2 : 1.

The influence of the anisotropic Mo-O_i bond on the substituent chemical shifts is important in the specific assignment

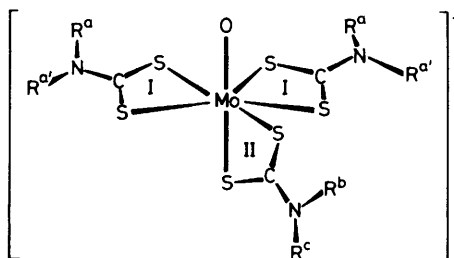


Figure 1. The solution structure of the $[\text{MoO}(\text{S}_2\text{CNR}_2)_3]^+$ complexes

of the n.m.r. resonances and significant π bonding within the Mo-O_i group in these complexes is likely to arise. To describe the field effects of the Mo-O_i bond two susceptibilities, χ_{\parallel} and χ_{\perp} (parallel and perpendicular to the bond axis respectively), are necessary. Here the anisotropic shift of a resonating ^1H nucleus, $\Delta\sigma$, is given by equation (1)⁸ where r is the length of

$$\Delta\sigma = \delta_{\text{no anisot.}} - \delta_{\text{anisot.}} = (\chi_{\parallel} - \chi_{\perp})(1 - 3\cos^2\theta)/12\pi r^3 \quad (1)$$

the vector between the centre of the Mo-O_i bond and the ^1H nucleus and θ is the angle between this vector and the principal symmetry axis of the Mo-O_i bond. In this case χ_{\parallel} will be large and negative in relation to χ_{\perp} due to the high π -electron diamagnetic susceptibility parallel to the Mo-O_i bond axis. For $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$ (1) this results in the (de)shielding zones shown in Figure 2. Here all methyl groups except CH₃-c lie within the deshielding zone of Mo-O_i and thus the high-field resonance at δ 3.15 p.p.m. may be assigned to this group. It follows from the integration that the resonance at δ 3.45 p.p.m. arises from CH₃-b. Unambiguous assignment of the CH₃-a and CH₃-a' resonances is prevented by the similarity of their chemical shifts. The n.m.r. spectra of complexes (2)–(4) may be similarly interpreted and application of the Mo-O_i anisotropy model leads to the given assignments.

The $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra are also readily interpreted in terms of a pentagonal-bipyramidal cation structure. As well as the expected CH₃, CH₂, and CH resonance, the spectra exhibit two S₂CN resonances (relative intensity 2 : 1) attributable to the inequivalent ligand sets (I) and (II) respectively.

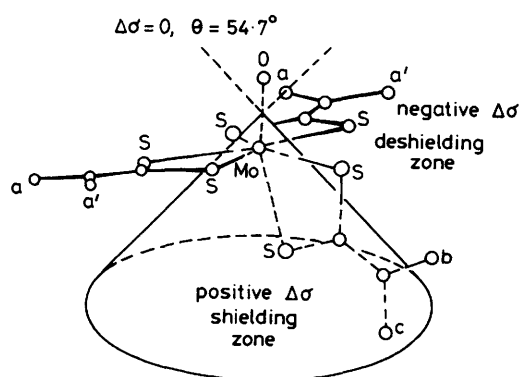


Figure 2. The conical shielding zone associated with the Mo-O bond in $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$. The solid line portions of the structure lie outside the shielding zone

The spectrum of $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$ (2) is identical to that of $[\text{Mo}(\text{S}_2\text{CNMe}_2)_3(\text{NO})]$, a complex also thought to possess a pentagonal-bipyramidal structure in solution.^{9,10} Variable-temperature $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectroscopy indicates that $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$ becomes stereochemically non-rigid at *ca.* 65 °C and fully fluxional at *ca.* 95 °C.

The electronic spectra of the compounds in CH_3NO_2 are characterised by strong absorptions at *ca.* 405 nm (ϵ *ca.* 4 200 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). This absorption band obeys Beer's law over the concentration range 10^{-3} – 10^{-4} mol dm^{-3} , supporting the presence of discrete stable monomer species in this solvent. The assignment of this band to a charge-transfer transition is based on the high molar absorption coefficient which is absent in the spectra of the free ligands. Below 400 nm, $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$ exhibits very intense absorptions [250 (56 000) and 212 nm (27 500 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)] assigned to $\pi \rightarrow \pi^*$ transitions within the dithiocarbamate-ligands.¹¹

The i.r. spectra show absorption bands characteristic of symmetrical bidentate dithiocarbamate-ligands¹¹ [$\nu(\text{CN})$ 1 570–1 520 cm^{-1} and single $\nu(\text{C}=\text{S})$ bands at 1 050 (1), 1 003 (2), and 950 cm^{-1} (4)]. Bands at 380 and 370 cm^{-1} may be assigned to $\nu(\text{Mo}-\text{S})$ vibrational modes. Recent investigations employing ^{18}O - and $^{18}\text{O}/^{17}\text{O}$ -enriched molybdenum complexes¹² have shown that $\nu(\text{Mo}-^{16}\text{O}_i)$ modes occur between 970 and 800 cm^{-1} . The bands at 935 cm^{-1} of compounds (1)–(4) were thus assigned to $\nu(\text{Mo}-\text{O}_i)$, and this was confirmed for (2) by ^{18}O -labelling experiments. The $[\text{Mo}^{18}\text{O}(\text{S}_2\text{CNMe}_2)_3]^+$ complex, prepared by the reaction² of $[\text{MoCl}(\text{S}_2\text{CNMe}_2)_3]$ and 98% $^{18}\text{O}_2$ and isolated as the BF_4^- salt, exhibited an i.r. band at 889 cm^{-1} . A simple harmonic oscillator treatment predicts the presence of $\nu(\text{Mo}-^{18}\text{O}_i)$ at 889 cm^{-1} [assuming $\nu(\text{Mo}-^{16}\text{O}_i)$ at 935 cm^{-1}], in excellent agreement with that observed.

Reactions of $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$.—The cation (2) is found to undergo redox reactions at the metal centre, with or without oxygen-atom transfer, as well as substitution reactions in which only one of the three dithiocarbamate ligands is replaced. The catalytic oxidation of dichloromethane solutions of PPh_3 to OPPh_3 by dioxygen in the presence of the mono-oxo-complex (2) closely resembles the corresponding catalytic oxidation brought about by *cis*-dioxomolybdenum(vi) complexes^{6,7} and is the first example of such an oxidation for mono-oxo-species. Up to five equivalents of PPh_3 may be converted but there is a small amount of complex decomposition. The presence of complex (2) and OPPh_3 upon completion of the cycle has been established by chemical and spectroscopic means. The reaction is likely to involve attack

of the nucleophile at the electron-deficient oxo-ligand giving OPPh_3 and, presumably, $[\text{Mo}(\text{S}_2\text{CNMe}_2)_3]^+$. Although we have no direct evidence for this species it is interesting that the same reaction in the absence of dioxygen gives the mixed-oxidation-state complex $[\text{Mo}_2\text{O}(\text{S}_2\text{CNMe}_2)_6]^+$.¹³ If $[\text{Mo}(\text{S}_2\text{CNMe}_2)_3]^+$ is a very good electrophile and is further reduced, this product can be accounted for. Reactivity of the oxo-group in complex (2) is also shown by its reaction with phenyl isocyanate to yield $[\text{Mo}(\text{NPh})(\text{S}_2\text{CNMe}_2)_3]\text{BF}_4$, a complex recently prepared by Maatta and Wentworth³ using a different synthetic route. In methanol slow conversion into $[\text{MoO}(\text{S}_2\text{CNMe}_2)_3]^+$ and *cis*- $[\text{MoO}_2(\text{S}_2\text{CNMe}_2)_2]$ is found so that some contribution due to these species cannot be eliminated.

Replacement of one dithiocarbamate ligand in complex (2) by chloride or disulphide takes place readily in aqueous solutions giving the known *cis-mer*- $[\text{MoOCl}_2(\text{S}_2\text{CNMe}_2)_2]$ and $[\text{MoO}(\text{S}_2)(\text{S}_2\text{CNMe}_2)_2]$ products respectively.^{14,15} Reduction of (2) with zinc or sodium dithionite leads to loss of ligand with formation of the molybdenum(IV) complex $[\text{MoO}(\text{S}_2\text{CNMe}_2)_2]$.¹⁶ On the other hand the molybdenum(V) complexes $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{S}_2\text{CNMe}_2)_2]$ ¹⁷ and $[\text{Mo}_2\text{O}_3(\text{S}_2\text{CNMe}_2)_4]$ ¹⁸ are obtained from reductive reactions using $[\text{MoS}_4]^{2-}$ or SO_3^{2-} respectively.

Experimental

The complexes *cis*- $[\text{MoO}_2(\text{S}_2\text{CNR}_2)_2]$ (R = Me or Et) were prepared by the method of Moore and Larson¹⁹ and a similar method was adapted to the preparation of *cis*- $[\text{MoO}_2(\text{S}_2\text{CN-Pr}^i)_2]$. The method of Bishop *et al.*²⁰ was used to prepare $[\text{MoCl}(\text{S}_2\text{CNMe}_2)_3]$. All chemicals and solvents were of Laboratory Reagent quality. Standard Schlenk techniques and deoxygenated solvents were used for all inert-atmosphere chemistry.

Infrared spectra were measured on a Perkin-Elmer 683 spectrophotometer using the CsI disc technique. Proton and $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectra were recorded on a Varian CFT-20 spectrometer [80 MHz for ^1H , 20 MHz (pulse delay 2 s) for ^{13}C] and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra on a JEOL-HX-90Q (37.9 MHz for ^{31}P) spectrometer. Electronic spectra were obtained with a Cary 219 spectrophotometer. Conductivity measurements employed a Philips P.R. 9500 direct-reading conductivity bridge and 10^{-3} mol dm^{-3} acetonitrile solutions.

Tris(N,N-dimethyldithiocarbamate)oxomolybdenum(vi) Tetrafluoroborate (1).—A suspension of *cis*- $[\text{MoO}_2(\text{S}_2\text{CNMe}_2)_2]$ (0.82 g, 2.2 mmol) in acetone (100 cm^3) was treated with 31% aqueous HBF_4 (1 cm^3) and stirred in the dark for 4 h. Following filtration of the reaction mixture, diethyl ether (160 cm^3) was added to the filtrate to yield a yellow-green solid (0.7 g). The solid was extracted with dichloromethane (170 cm^3) and after filtration, ether was added to the filtrate to yield a yellow solid. Compound (1) was recrystallised from dichloromethane–diethyl ether. Yield 0.45 g (55%) (Found: C, 19.5; H, 3.8; Mo, 17.5; N, 7.4; S, 34.4. Calc. for $\text{C}_9\text{H}_{18}\text{BF}_4\text{MoN}_3\text{O}_6$: C, 19.3; H, 3.2; Mo, 17.2; N, 7.5; S 34.4%). Conductivity, $\Lambda = 83 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Infrared: $\nu(\text{CN})$ 1 573s, 1 570s, 1 547s, and 1 537s, $\nu(\text{NC}_2)$ 1 243 m, $\nu(\text{Mo}-\text{O}_i)$ 935s, $\nu(\text{Mo}-\text{S})$ 380m and 370m, BF_4^- 1 100s(br), 530w, and 520w cm^{-1} . N.m.r.: ^1H (CD_3CN), δ 3.15 (s, 3 H, $\text{CH}_3\text{-c}$), 3.40 (s, 6 H, 2 \times $\text{CH}_3\text{-a}$ or $\text{-a}'$), 3.45 (s, 3 H, $\text{CH}_3\text{-b}$), 3.49 (s, 6 H, 2 \times $\text{CH}_3\text{-a}$ or $\text{-a}'$) (see Results and Discussion for description of assignments); $^{13}\text{C}\{-^1\text{H}\}$ ($\text{CDCl}_3\text{-CD}_3\text{NO}_2$), δ 36.95 (100%) and 38.52 (98) ($\text{CH}_3\text{-a}$, $\text{-a}'$), 40.88 (50) and 41.27 (50) ($\text{CH}_3\text{-b}$, c), 194.72 (18) and 197.47 (10) [S_2CN (I), (II)]. Electronic spectrum (CH_3NO_2): λ_{max} , 404 nm (ϵ 4 060 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$).

The hexafluorophosphate and perchlorate salts may be similarly prepared using the following reagent quantities: *cis*-[MoO₂(S₂CNMe₂)₂], 2.0 g, 5.43 mmol; acetone, 150 cm³; 65% HPF₆, 1 cm³ or 68% HClO₄, 2 cm³. Yields: PF₆⁻ salt, 45%; ClO₄⁻ salt, 42%. These salts gave the correct analyses and possessed properties which were virtually identical to (1). The PF₆⁻ salt showed a weak ν(C=S) band at 1 050 cm⁻¹.

Tris(N,N-diethyldithiocarbamato)oxomolybdenum(vi) Tetrafluoroborate (2).—A suspension of *cis*-[MoO₂(S₂CNEt₂)₂] (10.0 g, 23 mmol) in acetone (120 cm³) was treated with 31% aqueous HBF₄ (10 cm³) and stirred in the dark for 3 h. The suspension was reduced in volume to 25 cm³ and following the addition of methanol (25 cm³) was filtered to remove an insoluble green-brown solid (F1). The filtrate was treated with dichloromethane (25 cm³) then diethyl ether to precipitate the orange product (2). The solid was recrystallised from methanol-diethyl ether and dried *in vacuo*; yield 6.7 g (68%) (Found: C, 28.1; H, 5.0; Mo, 14.7; N, 6.5; S, 29.5. Calc. for C₁₅H₃₀BF₄MoN₃OS₆: C, 28.0; H, 4.7; Mo, 14.9; N, 6.5; S, 29.8%). Conductivity, Λ = 84 Ω⁻¹ cm² mol⁻¹. Infrared: ν(CN) 1 550s and 1 520s, ν(NC₂) 1 155s, ν(C=S) 1 005m, ν(Mo—O_i) 935s, ν(Mo—S) 380m and 370m, BF₄ 1 095s(br), 530w, and 520w cm⁻¹. N.m.r.: ¹H (CDCl₃), δ 1.20 (t, J 7.2 3 H, CH₃-c), 1.44 (t, J 7.0, 6 H, 2 × CH₃-a or -a'), 1.45 (t, J 7.0, 3 H, CH₃-b), 1.47 (t, J 7.0, 6 H, 2 × CH₃-a or -a'), 3.66 (q, J 7.0 Hz, 2 H, CH₂-c), and 3.8—4.2 (three overlapping q, 10 H, 5 × CH₂-a, -a', -b). ¹³C-{¹H} (CD₃NO₂) δ 12.07 (25%), 12.64 (100), and 12.99 (68) (CH₃), 45.54 (50), and 47.07 (48) (CH₂-a, -a'), 48.26 (23) and 48.86 (25) (CH₂-b, -c), 195.06 (25) and 197.63 (16) [S₂CN (I), (II)]. Electronic spectra: CH₃NO₂, λ_{max}. 405 (4 270); CH₃OH, λ_{max}. 405 (4 200), 250 (56 000), and 212 nm (ε 27 500 dm³ mol⁻¹ cm⁻¹).

The green-brown solid (F1) was recrystallised twice from dichloromethane-diethyl ether to yield 1.2 g (21% based on Mo) of orange [MoO(S₂CNEt₂)₃]₂[Mo₆O₁₉] (3) (Found: C, 18.2; H, 3.1; Mo, 38.5; N, 4.4; O, 16.8; S, 19.3. Calc. for C₃₀H₆₀Mo₈N₆O₂₁S₁₂: C, 18.1; H, 3.0; Mo, 38.5; N, 4.0; O, 16.9; S, 19.3%). Conductivity, Λ = 135 Ω⁻¹ cm² mol⁻¹. Infrared: ν(CN) 1 545s and 1 515s, ν(NC₂) 1 155m, ν(Mo—O_i) 955s and 935s, ν(Mo—S) 375w and 355w, others 1 075m and 800vs cm⁻¹. Proton n.m.r. as for (2).

The hexafluorophosphate and perchlorate salts of [MoO(S₂CNEt₂)₃]⁺ were prepared as follows. A suspension of *cis*-[MoO₂(S₂CNEt₂)₂] (2.0 g, 4.6 mmol) in acetone (50 cm³) was treated with the appropriate acid (65% HPF₆ or 68% HClO₄, 1 cm³) and the mixture was stirred in the dark for 4 h. The volume of the solution was reduced to 15 cm³ and then filtered. Methanol (15 cm³) was added to the filtrate, followed by diethyl ether to precipitate the orange complexes which were recrystallised from methanol-diethyl ether. Yields: PF₆⁻ salt, 51%; ClO₄⁻ salt, 70%.

Tris(N,N-diisopropyldithiocarbamato)oxomolybdenum(vi) Tetrafluoroborate (4).—A solution of *cis*-[MoO₂(S₂CNPrⁱ)₂] (0.35 g, 0.73 mmol) in acetone (30 cm³) was treated with 31% aqueous HBF₄ (0.7 cm³). The solution was stirred in the dark for 16 h whereupon a yellow solid precipitated. The compound was isolated by filtration and recrystallised from dichloromethane-diethyl ether. The yield was 0.18 g (50%) (Found: C, 34.4; H, 5.7; Mo, 13.5; N, 5.7; S, 26.1. Calc. for C₂₁H₄₂BF₄MoN₃OS₆: C, 34.7; H, 5.8; Mo, 13.2; N, 5.8; S, 26.4%). Conductivity, Λ = 83 Ω⁻¹ cm² mol⁻¹. Infrared: ν(CN) 1 532s, 1 520s, and 1 498s, ν(NC₂) 1 150s, ν(C=S) 950(sh), ν(Mo—O_i) 935s, ν(Mo—S) 380w and 370w, BF₄ 1 067s(br), 530w, and 520w cm⁻¹. N.m.r.: ¹H (CDCl₃-SiMe₄), δ 1.39 (d, J 6.0, 6 H, 2 × CH₃-c), 1.62 (dd, J 6.0 Hz, 30 H, 10 × CH₃-a, -a', -b), 4.5—5.0 (m, 6 H, 6 × CH-a, -a', -b, -c);

¹³C-{¹H} (CDCl₃-SiMe₄), δ 19.48 (33%), 19.66 (33), 19.83 (20), and 20.25 (100) (CH₃), 52.70 (31) and 53.76 (41) (CH), 194.59 (12) and 196.42 (8) [S₂CN (I), (II)]. Electronic spectrum (CH₃NO₂): λ_{max}. 405 nm (ε 4 120 dm³ mol⁻¹ cm⁻¹).

Reactions of Complex (2).—With PPh₃. Addition of PPh₃ to solutions of complex (2) in dichloromethane, methanol, or nitromethane results in the immediate formation of red-brown solutions which, upon standing in air, revert to their original orange colour. The final products of the cyclic reaction were shown to be (2) and OPPh₃ by the following experiments.

Isolation of (2) from reaction mixture. A solution of complex (2) (0.2 g, 0.31 mmol) in dichloromethane (10 cm³) was treated with PPh₃ (0.12 g, 0.45 mmol) and stirred until the original colour had reformed (*ca.* 6 h). Methanol (20 cm³) was added to the solution, followed by diethyl ether whereupon orange crystals precipitated. The yield was 1.69 g (85%). The product was identified by comparison of its X-ray powder-diffraction pattern with that of an authentic sample.

¹H N.m.r. of reaction mixture. A reaction mixture obtained by the above procedure was evaporated to dryness and the residue examined by n.m.r. spectroscopy in CDCl₃. Complex (2) and OPPh₃ were identified as the only products. In methanol, a similar experiment indicated that slow conversion of [MoO(S₂CNEt₂)₃]⁺ into *cis*-[MoO₂(S₂CNEt₂)₂] occurs.

³¹P-{¹H} N.m.r. spectrum of reaction mixture. A solution of complex (2) (0.1 g, 0.16 mmol) in methanol (5 cm³) was treated with PPh₃ (0.041 g, 0.16 mmol) and stirred until the original colour reformed. The ³¹P-{¹H} n.m.r. spectrum of this solution showed only one resonance at δ 30.7 p.p.m. (relative to trimethyl phosphate), characteristic of OPPh₃ (for PPh₃, δ = -7.6 p.p.m.). Triphenylphosphine is *not* converted into OPPh₃ in methanol in the absence of complex (2).

With PhNCO. A suspension of complex (2) (0.10 g, 0.16 mmol) in deoxygenated toluene (10 cm³) under dinitrogen was treated with PhNCO (0.084 cm³, 0.77 mmol) and the mixture refluxed for 4.5 h. The toluene was decanted to leave a red oil which was triturated with diethyl ether (*ca.* 15 cm³) in air to yield a yellow solid. Recrystallisation from dichloromethane-n-hexane yielded yellow [Mo(NPh)(S₂CNEt₂)₃]BF₄ (0.089 g, 80%) which was identified from the published properties.³

With HCl. A stirred solution of complex (2) (0.10 g, 0.16 mmol) in acetone (1 cm³) was treated with concentrated hydrochloric acid (1 cm³). After 1 h, water (10 cm³) was added and the solution was cooled to yield yellow crystals. These were filtered off, washed with water, and dried *in vacuo*. The product was [MoOCl₂(S₂CNEt₂)₂] (0.07 g, 90%).¹⁵

With Na₂S. A solution of complex (2) (0.22 g, 0.34 mmol) in acetone-benzene (1 : 1, 24 cm³) was treated with a solution of Na₂S·9H₂O (0.082 g, 0.34 mmol) in water (25 cm³), stirred for 6 h, and evaporated to dryness. The residue was dissolved in dichloromethane (10 cm³) and extracted with water (3 × 20 cm³). The organic phase was dried over molecular sieve 4A. The addition of cyclohexane to this solution followed by slow evaporation led to a small amount of blue [MoO(S₂CNEt₂)₂]₂.¹⁴

With Zn. A mixture of complex (2) (0.20 g, 0.31 mmol) and zinc metal (0.10 g) under dinitrogen was treated with deoxygenated dichloromethane (25 cm³) and the mixture stirred for 1 h and filtered. The filtrate was evaporated to dryness under vacuum and then triturated under dinitrogen with deoxygenated ethanol (40 cm³). The red solid was filtered off, washed with ethanol, and vacuum dried. The yield of [MoO(S₂CNEt₂)₂] was 0.12 g (92%).¹⁶

With Na₂S₂O₄. The reaction of complex (2) and Na₂S₂O₄ in dichloromethane-water (1 : 1) carried out under analogous conditions to the zinc reaction also gives [MoO(S₂CNEt₂)₂].

With $[\text{NEt}_4]_2[\text{MoS}_4]$. A solution of $[\text{NEt}_4]_2[\text{MoS}_4]$ (0.048 g, 0.1 mmol) in acetonitrile (2 cm³) was added slowly to a stirred solution of complex (2) (0.063 g, 0.1 mmol) in acetonitrile (2 cm³) to give an immediate red-brown colouration. After 1.5 h, the solution was filtered to yield yellow crystals of $[\text{Mo}_2\text{O}_2\text{S}_2(\text{S}_2\text{CNEt}_2)_2]$ which were recrystallised from dichloromethane-diethyl ether. The yield was 0.04 g (35%).¹⁷

With Na_2SO_3 or $(\text{PPh}_4)_2\text{SO}_3$. The reaction of solutions of complex (2) with one equivalent of Na_2SO_3 or $(\text{PPh}_4)_2\text{SO}_3$ in various solvents in the temperature range 25–40 °C gave $[\text{Mo}_2\text{O}_3(\text{S}_2\text{CNEt}_2)_4]$.¹⁸

With xanthine or salicylaldehyde. Addition of these reagents to a solution of complex (2) gave no reaction.

Acknowledgements

We thank the Australian Research Grants Committee for financial support and the Australian National University for the award of a scholarship (to C. G. Y.).

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Received 20th December 1982; Paper 2/2120