A Convenient Route to Complexes of the Type $[MoO(SR)_4]^-$ (R = aryl) and $[MoO\{S(CH_2)_nS\}_2]^-$ (*n* = 2 or 3): Preparation and Crystal Structure of $[PPh_4][Mo(NNMe_2)O(SC_6H_5)_3]\cdot(C_2H_5)_2O$ †

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The complexes $[MoO(SR)_4]^-$ (R = aryl) and $[MoO\{S(CH_2)_nS\}_2]^-$ (*n* = 2 or 3) can be prepared by reaction of an Mo^{VI} butanediolato-complex with thiolate anion in methanol. The complexes $[MoO(SPh)_4]^-$ react with R'_2NNH_2 [R'_2 = Me_2 or $(CH_2)_5$] in refluxing CH_3CN to give $[Mo(NNR'_2)O(SPh)_3]^-$. Crystal Data for $[PPh_4][Mo(NNMe_2)O(SC_6H_5)_3]\cdot(C_2H_5)_2O$: space group *Pbca*, a = 12.789(4), b = 19.375(3), c = 36.941(3) Å, Z = 8. 3 225 Independent reflections with $I > 3\sigma(I)$ gave R = 0.076. The geometry is essentially square-pyramidal with an apical oxo-group and the $NNMe_2$ group in the basal plane. Although the Mo–N and N–N distances of 1.821(9) and 1.292(14) Å respectively are analogous to other hydrazido(2−) complexes, the Mo–N–NMe_2 system is anomalously bent with Mo–N–N = 152.5(10)°.

Although there have been extensive recent studies of molybdenum complexes with sulphur ligands, very few simple monomeric molybdenum thiolato-complexes have been reported. One such is $[MoO(SR)_4]^-$, originally prepared by reaction of arenethiolate ions with $MoOCl_3$ or $[MoOCl_5]^{2-}$.[1] Here we report a more convenient preparation from a Mo^{VI} precursor of both $[MoO(SR)_4]^-$ and $[MoO\{S(CH_2)_nS\}_2]^-$ (*n* = 2 or 3). The latter complexes were not obtainable by the previously reported route.[1] We also report the reaction of $[MoO(SPh)_4]^-$ with substituted hydrazines to give five-co-ordinate oxo hydrazido(2−) complexes.

The complex $[MoO_2\{CH_3CH(O)CH(OH)CH_3\}_2]\cdot2[CH_3CH(OH)CH(OH)CH_3]$ derived from 2,3-butanediol can be used to prepare a variety of Mo^{VI} oxo-complexes by virtue of the lability of the co-ordinated diols.[2,3] It also reacts with thiophenol and thiophenolate in methanol at room temperature to generate $[MoO(SPh)_4]^-$, isolable in 50—60% yield as a tetraethylammonium or tetraphenylphosphonium salt. Both thiophenol and thiophenolate must be present for the blue Mo^V complex to be formed; 1,2- and 1,3-dithiols react analogously to give $[MoO\{S(CH_2)_nS\}_2]^-$ (*n* = 2 or 3) in similar yields.

Addition of tetra-n-butylammonium bromide to an aqueous solution of ammonium paramolybdate gives a white precipitate which may be a salt of $[Mo_8O_{26}]^{4-}$.[4] Recrystallisation from CH_2Cl_2–MeOH produces a yellow crystalline material identified as the known $[NBu^n_4]_2[Mo_6O_{19}]$ [5] by an *X*-ray structure determination. Although the identity of the initial white precipitate is not certain it is a useful precursor for the synthesis of some molybdenum oxo-complexes. It also reacts with thiophenol plus thiophenolate to give $[MoO(SPh)_4]^-$ but yields are lower and it is difficult to free the product from a white contaminant. Curiously, the white polymolybdate is the starting material of choice for the synthesis of other molybdenum oxo-complexes such as $[MoO(SCH_2CH_2PPh_2)_2]$, giving products in better yield and of higher purity than the butanediolato-complex.

There are now several examples of the preparation of molybdenum hydrazido(2−) complexes by reaction of hydrazines with oxo-complexes,[6,7] but none of these involves complexes with simple thiolato-ligands. We studied the reactions of $[MoO(SPh)_4]^-$ with substituted hydrazines in an attempt to replace the oxo-group by a hydrazido(2−) ligand. However, the $[MoO(SPh)_4]^-$ anion reacted with 1,1-disubstituted hydrazines with retention of the oxo-group and replacement of a thiophenolate group by the hydrazido(2−) ligand giving $[Mo(NNR'_2)O(SPh)_3]^-$. The reactions are not simple metatheses as concomitant oxidation of the metal from Mo^V to Mo^{VI} occurs. The hydrazido(1−) species $[Mo(NHNR'_2)O(SPh)_3]^-$ may well be intermediates and the formation of a strong molybdenum–nitrogen multiple bond would then provide the driving force for oxidative elimination of the hydrogen on the α-nitrogen. A similar facile hydrogen loss has been observed in the preparation of molybdenum and tungsten hydrazido(2−) complexes from silylated hydrazines.[8] The $[MoO(SPh)_4]^-$ anion also reacts with monosubstituted hydrazines to yield what appear to be the related hydrazido-(2−) complexes $[Mo(NNHR')O(SPh)_3]^-$, but these could not be obtained as analytically pure.

The complexes $[PPh_4][Mo(NNR'_2)O(SPh)_3]$ and $[NEt_4][Mo(NNR'_2)O(SPh_3)]$ [R'_2 = Me_2 or $(CH_2)_5$] are isolated as bright yellow air-stable complexes. These are diamagnetic, consistent with their being formally Mo^{VI} species. The i.r. spectrum of $[NEt_4][Mo(NNMe_2)O(SPh)_3]$ has a band at 910 cm^{-1} assigned to ν(Mo=O) compared with 940 cm^{-1} in the parent $[MoO(SPh)_4]^-$ species. There is no band clearly assignable to ν(Mo=N) but a medium intensity band at 1 510 cm^{-1} is characteristic of molybdenum dialkylhydrazido(2−) complexes and may be associated with the N–N bond. The ^1H n.m.r. spectrum of $[NEt_4][Mo(NNMe_2)O(SPh)_3]$ shows a well resolved doublet at 2.55 and 2.71 p.p.m. due to the hydrazido-methyls. This inequivalence shows that the complex is not fluxional in solution, in contrast to the complex [Mo-

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† Tetraphenylphosphonium *NN*-dimethylhydrazido(2−)oxotris-(thiophenolato)molybdate(VI)—diethyl ether (1/1).

Supplementary data available (No SUP 23387, 19 pp.): observed and calculated structure factors, thermal parameters, hydrogen atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 mmHg ≈ 13.6 × 9.8 Pa.

Table 1. Experimental details of the *X*-ray diffraction study of $[PPh_4][Mo(NNMe_2)O(SPh)_3]\cdot(C_2H_5)_2O$

(*a*) Crystal parameters[a] at 23 °C

a = 12.789(4) Å	Space group: *Pbca*
b = 19.375(3) Å	$Z = 8$
c = 36.941(3) Å	D_c = 1.27 g cm^{-3}
U = 9 153.31 Å^3	D_m (by flotation) = 1.25 g cm^{-3}

(*b*) Measurement of intensity data

Instrument: Nonius CAD4 automated diffractometer

Radiation: Mo-K_α (λ = 0.710 69 Å)

Attenuator: used for counts >10 000 s^{-1}

Scan mode: coupled θ (crystal)—2θ (counter)

Scan rate: variable, within limits of 0.10 to 2.0° min^{-1}

Scan range: $2.0 < 2\theta < 45.0°$

ω Scan angle: 1.2°

Background measurements: total ω scan angle 1.8°; 0.3° at each end used for background measurement

Standards: three reflections measured every 100 data

No. of independent reflections collected: 4 277

(*c*) Reduction of intensity data[b]

Data corrected for background, attenuators, and Lorentz polarization factors using SHELX

$F(000) = 3\ 551.65$

Absorption coefficient: 4.41 cm^{-1}

Observed data: 3 225 with $I > 3.0\sigma(I)$

(*d*) Structure solution and refinement

Mo position located from a three-dimensional Patterson map; all other non-hydrogen atoms were located in a subsequent difference-Fourier synthesis. The phenyls were refined as rigid groups. Hydrogen atoms were introduced in idealised positions in the final cycles of full-matrix least-squares refinement. Final discrepancy factor R = 0.076

[a] From a least-squares fit to the setting angles of 12 reflections.

[b] Programs used in this work are compiled in SHELX.

$(NNMe_2)O(S_2CNMe_2)_2]$ where the hydrazido-methyls are equivalent except at low temperatures.[6] The spectroscopic data were not sufficient to indicate that the complexes were monomeric, and conductivity measurements coupled with the use of Debye-Onsager plots gave ambiguous results. Accordingly an *X*-ray structure determination of $[PPh_4][Mo(NNMe_2)O(SPh)_3]$ was undertaken.

Experimental

Preparation of Complexes.—Reactions were carried out in dried solvents under an atmosphere of dinitrogen using conventional Schlenk tube techniques. Recrystallisations were performed under similar conditions. The complex $[MoO_2\{CH_3CH(O)CH(OH)CH_3\}_2]\cdot2[CH_3CH(OH)CH(OH)CH_3]$ was prepared by the literature method from MoO_3.[2,3] The hydrazines Me_2NNH_2 and $(CH_2)_5NNH_2$ were obtained commercially and used without further purification.

Carbon, hydrogen, and nitrogen analyses were carried out by Mr. and Mrs. A. G. Olney at the University of Sussex. Infrared spectra were recorded in the range 400—4 000 cm^{-1} as Nujol mulls on KBr plates using a Pye Unicam SP2000 spectrophotometer. ^1H N.m.r. spectra were recorded at 100 MHz using JEOL P.S. 100 or JEOL FX 90Q instruments with $SiMe_4$ as internal standard.

Tetraphenylphosphonium Oxotetrakis(thiophenolato)-molybdate(V).—The complex $[MoO_2\{CH_3C(HO)CH(OH)CH_3\}_2]\cdot2[CH_3CH(OH)CH(OH)CH_3]$ (10 g) was dissolved in dry methanol (60 cm^3) and triethylamine (15 cm^3) added followed by thiophenol (20 g). The solution became very dark blue after stirring for 1—2 h at room temperature, and tetraphenylphosphonium bromide (5.0 g) was added. After stirring for a further 15 min, the very dark blue product was filtered off (10.6 g, 57% yield).

Derivatives with other substituted aromatic thiols or dithiols or counter ions can be prepared using the appropriate thiols and counter ions.

Tetraphenylphosphonium NN-*Dimethylhydrazido*(2−)*oxo-tris*(*thiophenolato*)*molybdate*(VI).—The complex $[PPh_4][MoO(SPh)_4]$ (1.0 g) and *NN*-dimethylhydrazine (0.5 cm^3) were heated under reflux in acetonitrile (40 cm^3) for 1 h to give a brownish yellow solution. Evaporation of the solvent at 10^{-2} mmHg gave a sticky brown solid, solidified by stirring with diethyl ether. The complex was recrystallised as yellow plates from dichloromethane–diethyl ether (1:1) (Found: C, 63.0; H, 5.3; N, 3.3. $C_{44}H_{41}MoN_2OPS_3$ requires C, 63.2; H, 4.9; N, 3.4%).

The following complexes were prepared similarly using the appropriate counter ions and hydrazine. $[PPh_4][Mo\{NN(CH_2)_5\}O(SPh)_3]$. Found: C, 64.7; H, 5.7; N, 3.2. $C_{47}H_{45}MoN_2OPS_3$ requires C, 64.4; H, 5.1; N, 3.2%. $[NEt_4][Mo\{NNMe_2\}O(SPh)_3]$. Found: C, 52.8; H, 6.1; N, 6.8. $C_{28}H_{41}MoN_3OS_3$ requires C, 53.6; H, 6.5; N, 6.7%. $[NEt_4][Mo\{NN(CH_2)_5\}O(SPh)_3]$. Found: C, 55.7; H, 6.7; N, 6.4. $C_{31}H_{45}MoN_3OS_3$ requires C, 55.7; H, 6.8; N, 6.3%.

X-*Ray Crystal Structure of* $[PPh_4][Mo(NNMe_2)O(SPh)_3]\cdot(C_2H_5)_2O$.—Well defined plate-like yellow crystals of $[PPh_4][Mo(NNMe_2)O(SPh)_3]\cdot(C_2H_5)_2O$ were obtained by slow recrystallisation from dichloromethane–diethyl ether. Samples used for elemental analyses were dried by heating *in vacuo*, whereas the crystalline material for the structural study was used as recrystallised. The experimental details of the data collection and reduction are summarised in Table 1.

Discussion

The atomic co-ordinates and important bond lengths and angles are listed in Tables 2 and 3 respectively. The Figure is an ORTEP view of the structure indicating the atom numbering scheme used.

The geometry about the molybdenum is best described as distorted square-pyramidal with the oxo-ligand in the apical position. The basal plane is defined by three thiolato-sulphur atoms and N(1) of the hydrazido(2−) group. The Mo atom lies *ca.* 0.7 Å above the mean NS_3 basal plane.

The Mo–O distance of 1.705(8) Å is similar to that observed for the parent anion $[MoO(SPh)_4]^-$ (1.699 Å).[9] The larger value in this case reflects the competition between the oxo- and hydrazido(2−) ligands for metal orbitals and electrons. The average of the Mo–S distances, 2.437(6) Å, is significantly longer than in $[MoO(SPh)_4]^-$ [2.402(4) Å]. This is partly attributable to the *trans* influence of the hydrazido(2−) ligand which results in a large value for Mo–S(2) in the pseudo-*trans* position.

The overall square-pyramidal geometry adopted by $[Mo(NNMe_2)O(SPh)_3]^-$ is similar to that adopted by other five-co-ordinate molybdenum oxo-species such as $[MoO(S_2CNPr^n{}_2)_2]$,[10] $[Mo_2O_4(S_2CNEt_2)_2]$,[11] and $[MoO(SPh)_4]^-$.[9] The presence of the oxo-group in the apical position is consistent with the tendency of cylindrically symmetrical π-donors to occupy this position in order to maximise interactions with the metal d_{xz} and d_{yz} orbitals.[12]

The final map revealed a poorly defined solvent molecule, presumably Et_2O, as this was identified by ^1H n.m.r. as present in a solution of crystals used for the structure deter-

Table 2. Atomic co-ordinates for $[PPh_4][Mo(NNMe_2)O(SPh)_3]$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	0.291 70(9)	0.004 49(6)	0.852 39(3)	C(21)	0.532 0(7)	0.396 6(5)	0.041 1(2)
S(1)	0.209 6(3)	0.112 3(2)	0.870 4(1)	C(22)	0.503 5(7)	0.413 8(5)	0.005 8(2)
S(2)	0.277 5(3)	−0.005 6(2)	0.918 7(1)	C(23)	0.409 6(7)	0.389 4(5)	−0.008 5(2)
S(3)	0.457 7(3)	−0.052 1(2)	0.861 6(1)	C(24)	0.344 2(7)	0.348 0(5)	0.012 4(2)
P	0.292 9(3)	0.270 4(2)	0.072 2(1)	C(25)	0.336 8(7)	0.265 6(5)	0.117 4(2)
O	0.201 1(7)	−0.051 0(5)	0.835 2(2)	C(26)	0.432 7(7)	0.234 6(5)	0.125 2(2)
N(1)	0.348 6(10)	0.047 1(6)	0.813 1(3)	C(27)	0.466 1(7)	0.228 8(5)	0.161 1(2)
N(2)	0.410 5(10)	0.091 0(7)	0.798 2(3)	C(28)	0.403 8(7)	0.254 1(5)	0.189 1(2)
C(1)	0.210 6(8)	0.171 2(5)	0.833 2(2)	C(29)	0.307 9(7)	0.285 1(5)	0.181 3(2)
C(2)	0.256 6(8)	0.235 9(5)	0.837 6(2)	C(30)	0.274 5(7)	0.290 8(5)	0.145 5(2)
C(3)	0.255 5(8)	0.283 3(5)	0.809 2(2)	C(31)	0.297 3(8)	0.185 2(4)	0.053 4(2)
C(4)	0.208 3(8)	0.266 0(5)	0.776 4(2)	C(32)	0.293 7(8)	0.174 9(4)	0.016 1(2)
C(5)	0.162 2(8)	0.201 3(5)	0.772 0(2)	C(33)	0.287 8(8)	0.108 2(4)	0.002 1(2)
C(6)	0.163 4(8)	0.153 9(5)	0.800 4(2)	C(34)	0.285 5(8)	0.051 7(4)	0.025 5(2)
C(7)	0.330 3(7)	−0.084 5(4)	0.934 3(2)	C(35)	0.289 1(8)	0.061 9(4)	0.062 9(2)
C(8)	0.399 3(7)	−0.083 5(4)	0.963 5(2)	C(36)	0.295 0(8)	0.128 7(4)	0.076 8(2)
C(9)	0.434 4(7)	−0.145 4(4)	0.978 6(2)	C(37)	0.578 1(7)	0.254 2(3)	0.431 4(2)
C(10)	0.400 5(7)	−0.208 2(4)	0.964 3(2)	C(38)	0.475 4(7)	0.277 9(3)	0.428 7(2)
C(11)	0.331 5(7)	−0.209 2(4)	0.935 1(2)	C(39)	0.455 8(7)	0.348 1(3)	0.423 8(2)
C(12)	0.296 4(7)	−0.147 3(4)	0.920 1(2)	C(40)	0.538 9(7)	0.394 6(3)	0.421 6(2)
C(13)	0.528 9(7)	−0.051 8(5)	0.820 8(3)	C(41)	0.641 5(7)	0.370 9(3)	0.424 4(2)
C(14)	0.484 2(7)	−0.073 4(5)	0.788 3(3)	C(42)	0.661 2(7)	0.300 7(3)	0.429 2(2)
C(15)	0.543 6(7)	−0.073 5(5)	0.756 6(3)	C(43)	0.412 0(15)	0.095 7(9)	0.759 2(5)
C(16)	0.647 6(7)	−0.052 1(5)	0.757 4(3)	C(44)	0.485 4(14)	0.128 9(9)	0.820 9(5)
C(17)	0.692 4(7)	−0.030 5(5)	0.790 0(3)	O(1)	0.444 3(28)	0.544 5(22)	0.126 3(9)
C(18)	0.633 0(7)	−0.030 4(5)	0.821 6(3)	C(45)	0.437 9(28)	0.483 2(20)	0.150 0(10)
C(19)	0.372 7(7)	0.330 8(5)	0.047 8(2)	C(46)	0.438 2(37)	0.592 5(27)	0.141 1(13)
C(20)	0.466 6(7)	0.355 2(5)	0.062 1(2)	C(47)	0.433 7(36)	0.657 3(25)	0.162 9(12)

Table 3. Selected bond lengths (Å) and angles (°) for $[PPh_4][Mo(NNMe_2)O(SPh)_3]$

Mo-S(1)	2.432(4)	P-C(19)	1.795(9)
Mo-S(2)	2.465(3)	P-C(25)	1.767(9)
Mo-S(3)	2.415(4)	P-C(31)	1.789(9)
Mo-O	1.705(8)	P-C(42)	1.787(9)
Mo-N(1)	1.821(9)		
N(1)-N(2)	1.292(14)		
N(2)-C(43)	1.450(17)		
N(2)-C(44)	1.470(18)		
S(1)-C(1)	1.787(9)		
S(2)-C(7)	1.769(9)		
S(3)-C(13)	1.760(11)		
S(1)-Mo-S(2)	76.3(1)	Mo-N(1)-N(2)	152.5(10)
S(1)-Mo-S(3)	173.0(1)	N(1)-N(2)-C(43)	117.5(13)
S(1)-Mo-N(1)	90.0(3)	N(1)-N(2)-C(44)	119.4(12)
S(1)-Mo-O	110.5(3)	Mo-S(1)-C(1)	109.5(3)
S(2)-Mo-S(3)	83.6(1)	Mo-S(2)-C(7)	111.2(3)
S(2)-Mo-N(1)	149.0(4)	Mo-S(3)-C(13)	109.4(3)
S(2)-Mo-O	105.7(3)	C(43)-N(2)-C(44)	122.7(14)
S(3)-Mo-N(1)	88.2(3)		
S(3)-Mo-O	111.4(3)		
N(1)-Mo-O	105.2(5)		

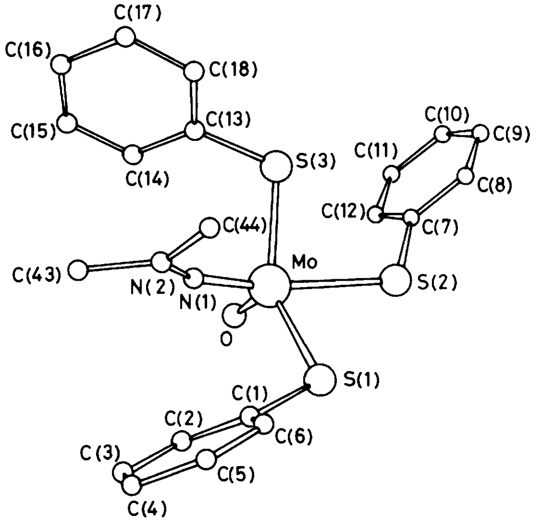

Figure. Structure of $[PPh_4][Mo(NNMe_2)O(SPh)_3]$ showing the atom labelling scheme. The tetraphenylphosphonium cation is omitted for clarity

mination. Further refinement did not improve the resolution and as the molecule was well removed from the co-ordination sphere it was not pursued further.

The Mo-N and N-N distances for the hydrazido(2−) ligand of 1.821(9) and 1.292(14) Å respectively lie well within the range found for other hydrazido(2−) complexes. However, the Mo-N-N system is definitely non-linear with an Mo-N(1)-N(2) angle of 152.5(10)°. Simple electron-counting arguments do not account for this geometry, and *ab initio* calculations are in progress to shed further light on this problem. Although the $NNMe_2$ ligand lies in the basal plane, the Mo-N distance of 1.821(9) Å indicates that it π-bonds strongly to the molybdenum. The hydrazido-group has two orbitals available for π bonding, the *p* orbital located on N(1) in the plane of the hydrazido-alkyl groups and the N-N π-antibonding orbital perpendicular to this plane. The dialkylhydrazido-plane eclipses the Mo-O bond which ensures that the N(1) *p* orbital overlaps with the metal d_{z^2} orbitals. The π-antibonding orbital has the correct symmetry to interact with the metal d_{xy} orbital.

Acknowledgements

We wish to thank the National Institute of Health for the award of a grant (to J. A. Z.) and NATO for a research grant (to J. A. Z. and J. R. D.) and C. A. Raggio and P. T. Bishop for experimental assistance.

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Received 11*th February* 1982; *Paper* 2/257