Five-co-ordinate Nitrosyl Thiolato-complexes of Molybdenum and Tungsten. The Preparation and *X*-Ray Crystal Structures of $[NHEt_3][Mo(SPh)_4(NO)]$, $[PPh_4][WCl(SPh)_3(NO)]$, and $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(NH_3)(NO)]$ [‡]

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Reaction of either $[MCl_3(PPh_3)_2(NO)]$ (M = Mo or W) or '$\{Mo(NH_2O)(H_2O)_x(NO)\}_n$' with ^-SR (R = Ph, C_6H_4Me-4, C_6H_4Cl-4, $C_6H_2Me_3$-2,4,6, or Bu^t) in methanol gives the anionic five-co-ordinate complexes $[M(SR)_4(NO)]^-$ (M = Mo; R = Ph, C_6H_4Me-4, C_6H_4Cl-4, or $C_6H_2Me_3$-2,4,6), $[MCl(SR)_3(NO)]^-$ (M = Mo, R = Bu^t; M = W, R = Ph). Crystal data: for $[NHEt_3][Mo(SPh)_4(NO)]$, space group $P2_1/n$ with a = 10.996(2), b = 16.127(4), c = 18.845(4) Å, α = 90.00, β = 105.94(1), γ = 90.00°, and Z = 4; 2 786 reflections used in structure solution, giving R = 0.0516; for $[PPh_4][WCl(SPh)_3(NO)]$, space group $P2_1/c$, a = 10.809(1), b = 19.677(3), c = 19.250(3) Å, α = 90.00, β = 105.85(1), γ = 90.00°, and Z = 4; 1 895 reflections giving R = 0.0375. Both anions have overall trigonal-bipyramidal geometries with apical NO groups. The reaction of the polymeric species '$\{Mo(NH_2O)(H_2O)_x(NO)\}_n$' with the sterically hindered thiol 2,4,6-tri-isopropylthiophenol in refluxing methanol affords the ammine complex $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(NH_3)(NO)]$. Crystal data: space group $P2_1/n$ with a = 10.477(3), b = 26.359(5), c = 20.124(4) Å, β = 87.21(1)°, and Z = 4; 1 040 reflections giving R = 0.078. The complex again has trigonal-bipyramidal geometry with apical NO and NH_3 groups. The co-ordinated ammonia ligand arises from reduction of the co-ordinated hydroxylamido-group.

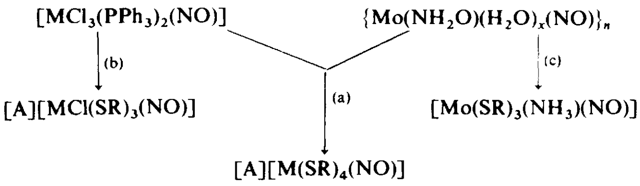
The enzyme nitrogenase is widely believed to contain an active site that involves a Mo–Fe–S cluster. This observation has led us to investigate transition-metal species predominantly ligated by sulphur, as potential binding sites for nitrogenase substrate molecules.[1]

We here describe the synthesis, structural, and spectroscopic properties of the first examples of series of molybdenum and tungsten nitrosylthiolato-complexes. The nitric oxide cation, NO^+, is formally isoelectronic with N_2, and co-ordinated NO is analogous to the diazenido-ligand NNH^-, a proposed intermediate in the biological reduction of N_2. In addition, the value of v(NO) in the i.r. spectrum provides a useful probe of the electronic state of the metal.

Previously reported mononuclear molybdenum nitrosyl complexes with sulphur ligands are $[Mo(dtc)_3(NO)]$,[2] $[Mo(dtc)_2(NO)_2]$[3] (dtc = dithiocarbamate), and $[Mo(mnt)_2(NO)_2]^{2-}$[4] (mnt = maleonitriledithiolate). Some cluster nitrosyl complexes with sulphido-ligands have also been reported.[5]

Results and Discussion

Preparation and Characterisation of Complexes.—The reaction of either $[MCl_3(PPh_3)_2(NO)]$[6] (M = Mo or W) or '$\{Mo(NH_2O)(H_2O)_x(NO)\}_n$'[7] with a range of monodentate thiols gives a series of five-co-ordinate nitrosylthiolato-complexes as summarised in the Scheme and Table 1. In all instances the thiolate anions were generated *in situ* using triethylamine. Reactions with $[MCl_3(PPh_3)_2(NO)]$ were carried out at room temperature in methanol whereas with '$\{Mo(NH_2O)(H_2O)_x(NO)\}_n$' the reaction mixtures were heated to reflux temperature. The dark red ionic complexes of general formula $[A][Mo(SR)_4(NO)]$ (**1**)—(**4**) (A = cation) can be synthesised *via* route (a). Route (b) generates ionic yellow complexes, $[A][MCl(SR)_3(NO)]$ (M = Mo or W). In general complexes (**1**)—(**6**) precipitated from the reaction solution as triethylammonium salts, but could also be isolated as tetraphenylphosphonium salts by addition of $[PPh_4]Br$. Complex (**5**) is soluble in methanol, but is obtained in reasonable yield by evaporation of the methanol and precipitation with propan-2-ol. Well defined, sharp ^1H n.m.r. solution spectra of the complexes confirmed their diamagnetism, and conductivity measurements (*ca.* 0.01 mol dm^{-3} solution in acetonitrile) demonstrated that they are 1:1 electrolytes (Table 1).



Scheme. A = $NHEt_3$ or PPh_4. (a) M = Mo, R = Ph (**1**), C_6H_4Me-4 (**2**), C_6H_4Cl-4 (**3**), or $C_6H_2Me_3$-2,4,6 (**4**); (b) M = Mo, R = Bu^t (**5**) or M = W, R = Ph (**6**); (c) R = $C_6H_2Pr^i{}_3$-2,4,6 (**7**)

The yellow neutral complex $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(NH_3)(NO)]$ (**7**) is obtained *via* route (c) using '$\{Mo(NH_2O)(H_2O)_x(NO)\}_n$' as the precursor. Interestingly the co-ordinated ammonia ligand present in (**7**) is formed by reduction of the co-ordinated hydroxylamido(1 –)-ligand. The non-sterically hindered thiophenolate anion also reduces the hydroxylamido(1 –)-ligand but in this instance the ammonia is not

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[‡] Triethylammonium nitrosyltetrakis(thiophenolato)molybdate, tetraphenylphosphonium chloronitrosyltris(thiophenolato)tungstate, and amminenitrosyltris(2,4,6-tri-isopropylthiophenolato)molybdenum.

Supplementary data available (No. SUP 56475, 17 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Properties of the molybdenum and tungsten compounds

Compound	Analysis[a] C	H	N	^{1}H N.m.r.[b]	I.r.[c] ν(NO)/cm^{-1}	U.v.[d]	Λ[e]/ Ω^{-1} cm^2 mol^{-1}
(1) $[NHEt_3][Mo(SPh)_4(NO)]$	53.9 (54.2)	5.3 (5.4)	4.1 (4.2)	1.2—1.4 (9 H, t, CH_3) 3.1—3.3 (6 H, q, CH_2) 7.1—7.9 (20 H, m, aryl)	1 675	365 (8 260) 305 (13 100)	101.0
(2) $[PPh_4][Mo(SC_6H_4Me\text{-}4)_4(NO)]$	64.6 (64.9)	5.3 (5.3)	1.4 (1.4)	2.2 (3 H, s, CH_3) 2.9 (9 H, s, CH_3) 7.4—7.8 (36 H, m, aryl)	1 665	370 (5 000)	71.0
(3) $[PPh_4][Mo(SC_6H_4Cl\text{-}4)_4(NO)]$	54.8 (55.2)	3.9 (3.5)	1.3 (1.3)	7.3—7.8 (—, m, aryl)	1 670	368 (15 700) 305 (25 500)	80.0
(4) $[PPh_4][Mo(SC_6H_2Me_3\text{-}2,4,6)_4(NO)]$	67.5 (67.3)	6.0 (5.8)	1.4 (1.3)	2.0—2.2 (36 H, m, CH_3) 6.6—6.8 (8 H, m, aryl) 7.4—7.9 (20 H, m, aryl)	1 650	360 (10 600)	100.0
(5) $[PPh_4][MoCl(SBu^t)_3(NO)]$[f]	56.0 (56.3)	6.7 (6.1)	1.5 (1.8)	1.6 (27 H, s, CH_3) 7.4—7.9 (20 H, m, aryl)	1 610	363 (13 400)	93.0
(6) $[PPh_4][WCl(SPh)_3(NO)]$	54.3 (55.1)	3.9 (3.9)	1.4 (1.5)	7.1—7.9 (—, m, aryl)	1 645	369 (57 070) 279 (19 400)	62.3
(7) $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(NO)]$	64.9 (63.5)	9.5 (8.5)	3.4 (3.3)	0.8—1.4 (60 H, m, CH_3) 2.5—3.2 (9 H, m, CH_2, CH) 3.5—3.9 (6 H, h, CH)	1 680	362 (27 800)	—

[a] Theoretical values in parentheses. [b] δ (p.p.m.), solvent CD_2Cl_2, relative to $SiMe_4$; positive values to low field. Relative integration values in parentheses; s = singlet, t = triplet, q = quartet, m = multiplet, and h = heptet. [c] Nujol mull spectra. [d] Absorption maxima, nm, in acetonitrile solution; molar absorption coefficient, dm^3 mol^{-1} cm^{-1}, in parentheses. [e] Molar conductivity in acetonitrile solution. [f] Cl 4.5 (4.6), S 12.9 (12.5%).

incorporated in the complex. The free ammonia in solution was determined by the indophenol colorimetric method.[8] Free hydroxylamine is not reduced by thiols under similar reaction conditions. Evidently the smaller arenethiols permit formation of the anionic tetrakis(thiolato)-complexes. With the bulky $SC_6H_2Pr^i_3$-2,4,6 ligand, co-ordination of four thiolates around molybdenum is sterically unfavourable and thus retention of the ammonia ligand is preferred. Electrochemical reduction of co-ordinated NO to NH_3 is reported to occur on ruthenium *via* a proposed intermediate containing a H_2NO^- ligand.[9]

The 90-MHz ^{1}H n.m.r. spectra (Table 1) of complexes (**1**)—(**7**) confirm their purity and stoicheiometry, and are consistent with the metal ions having formal oxidation states of +2. Complex (**2**) exhibits two singlets, in a ratio of 3:1, assignable to the methyl substituents on the thiolato-ligands and this is consistent with the presence of three equatorial and one axial thiolato-ligands. These signals persist at elevated temperatures (*ca.* 60 °C) showing that complex (**2**) is stereochemically rigid in solution at the elevated temperature. Complex (**5**) has a sharp singlet (1.6 p.p.m.) in its ^{1}H n.m.r. spectrum consistent with three equivalent equatorial thiolato-ligands and therefore axial nitrosyl and chloro-ligands. The spectrum of $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(NO)]$ (**7**) shows several overlapping broad multiplets, as resonances assignable to the methyl protons of the Pr^i groups are superimposed on those due to the alkyl protons of the hexane molecules of crystallisation.

I.r. data for the complexes (**1**)—(**7**) are summarised in Table 1. The values for ν(NO) are comparable to that of $[MoCl_4(NO)]^-$ (1 695 cm^{-1}). Even so, the values are relatively low and reflect the strong electron-releasing nature of the thiolato-ligand, causing a relatively electron-rich metal site and hence enhanced $d_\pi \longrightarrow NO\ \pi^*$ donation. The ν(NO) values for (**1**)—(**6**) are about 35 cm^{-1} lower than those of the neutral isoelectronic rhenium thiolatonitrosyl complexes.[10]

X-Ray crystal structure determinations were carried out for $[NHEt_3][Mo(SPh)_4(NO)]$ (**1**), $[PPh_4][WCl(SPh)_3(NO)]$ (**6**), and $[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(NO)]$ (**7**). ORTEP views for these complexes are given in Figures 1, 2, and 3, selected bond lengths and angles in Table 2, and atomic co-ordinates in Tables 3, 4, and 5.

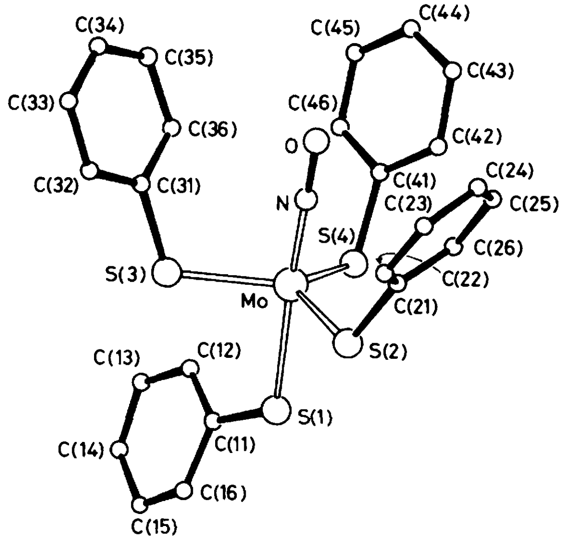

Figure 1. ORTEP view of the structure of $[Mo(SPh)_4(NO)]^-$ showing the atom labelling scheme

The dominant common feature of the structures of these metal nitrosylthiolato-complexes is that they all exhibit trigonal-bipyramidal geometries. Thiolato-ligands occupy the equatorial sites and the NO ligands are in axial sites, *trans* to thiolate (**1**), chloride (**6**), or ammine (**7**) ligands. The M–N–O angles are all close to 180° and the NO ligand is formally acting as a three-electron donor towards the metal. If the thiolato-ligands are considered to be one-electron donors then these nitrosyl complexes contain a total of 14 valence electrons. A comparison of the M–N and N–O bond lengths and the

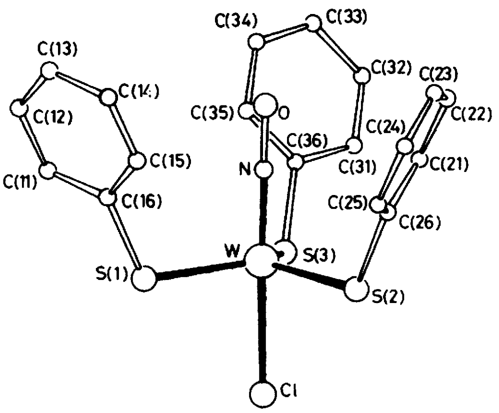

Figure 2. ORTEP view of the structure of [WCl(SPh)$_3$(NO)]$^-$ showing the atom labelling scheme

Table 2. Selected bond lengths (Å) and angles (°) for the nitrosyl complexes

[NHEt$_3$][Mo(SPh)$_4$(NO)]			
Mo–N	1.766(6)	Mo–N–O	178.7(5)
N–O	1.188(8)	Mo–S(1)–C(11)	116.2(3)
Mo–S(1)	2.524(2)	Mo–S(2)–C(21)	110.0(3)
Mo–S(2)	2.337(2)	Mo–S(3)–C(31)	110.3(3)
Mo–S(3)	2.326(3)	Mo–S(4)–C(41)	108.9(2)
[PPh$_4$][WCl(SPh)$_3$(NO)]			
W–N	1.744(13)	W–N–O	178.5(11)
N–O	1.235(17)	W–S(1)–C(16)	110.0(4)
W–S(1)	2.328(4)	W–S(2)–C(26)	110.6(6)
W–S(2)	2.315(4)	W–S(3)–C(36)	113.4(5)
W–Cl	2.320(4)		
W–Cl	2.490(4)		
[Mo(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(NH$_3$)(NO)]			
Mo–N(1)	1.775(29)	Mo–N(1)–O	176.1(30)
N(1)–O	1.141(40)	Mo–S(2)–C(11)	113.4(13)
Mo–N(2)	2.218(21)	Mo–S(1)–C(31)	109.3(11)
Mo–S(1)	2.319(10)	Mo–S(3)–C(21)	114.8(11)
Mo–S(2)	2.302(11)		
Mo–S(3)	2.316(11)		

M–N–O angles with those of other structurally characterised five-co-ordinate complexes (Table 6) reveals that the M–N–O moieties are all close to linear and there is no great variation in the M–N or N–O bond lengths. This is despite the presence of a considerable range of equatorial and axial substituents.

Trigonal-bipyramidal complexes with a formal count of 14 valence electrons appear to be particularly stable when equatorial thiolate or alkoxide ligands[11] are combined with the presence of axial π-acceptor ligands (CO,[1] MeCN,[12] NO,[10] or PR$_3$ [13]). A possible rationale of this stability is the enhanced stabilisation of the highest occupied molecular orbital (h.o.m.o.)

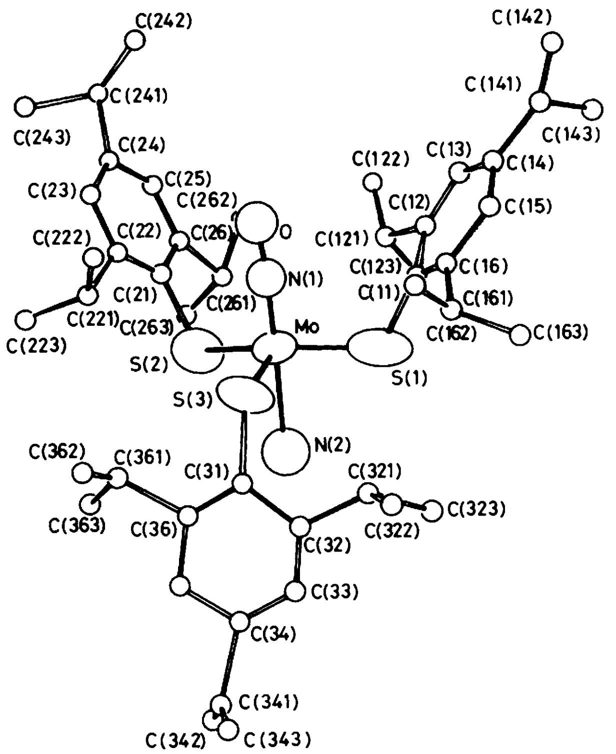

Figure 3. ORTEP view of the structure of [Mo(SC$_6$H$_2$Pr$^i{}_3$-2,4,6)$_3$(NH$_3$)(NO)] showing a partial atom labelling scheme

Table 3. Atom co-ordinates (× 10^4) for [NHEt$_3$][Mo(SPh)$_4$(NO)] (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	1 926(1)	2 467(1)	352(1)	C(31)	895(7)	3 986(5)	1 284(4)
N	3 048(5)	3 257(4)	688(3)	C(32)	899(8)	4 155(6)	1 993(5)
O	3 788(5)	3 800(4)	906(3)	C(33)	1 215(9)	4 937(6)	2 273(5)
S(1)	455(2)	1 266(1)	−119(1)	C(34)	1 522(9)	5 533(7)	1 860(6)
S(2)	3 304(2)	1 399(1)	893(1)	C(35)	1 522(9)	5 398(6)	1 167(5)
S(3)	418(2)	2 991(1)	887(1)	C(36)	1 199(8)	4 605(5)	850(5)
S(4)	1 692(2)	2 776(1)	−873(1)	C(41)	2 552(7)	3 707(5)	−929(4)
C(11)	−1 170(8)	1 515(5)	−478(4)	C(42)	3 816(9)	3 721(6)	−862(5)
C(12)	−1 653(9)	2 286(5)	−760(5)	C(43)	4 396(9)	4 497(6)	−905(5)
C(13)	−2 955(8)	2 431(5)	−1 056(5)	C(44)	3 737(10)	5 186(6)	−1 007(5)
C(14)	−3 755(10)	1 790(6)	−1 098(5)	C(45)	2 491(11)	5 187(7)	−1 102(6)
C(15)	−3 305(8)	1 006(5)	−815(5)	C(46)	1 906(9)	4 429(6)	−1 055(5)
C(16)	−2 088(8)	885(5)	−519(5)	N(1)	5 731(9)	4 575(6)	3 355(5)
C(21)	4 863(7)	1 776(5)	1 183(4)	C(1)	4 950(11)	5 294(7)	3 407(6)
C(22)	5 554(8)	1 733(5)	1 906(5)	C(2)	4 807(11)	5 919(7)	2 814(6)
C(23)	6 782(9)	2 024(6)	2 125(5)	C(3)	5 357(15)	4 047(10)	2 728(8)
C(24)	7 346(9)	2 365(5)	1 631(5)	C(4)	4 207(11)	3 536(7)	2 687(7)
C(25)	6 687(10)	2 371(5)	924(5)	C(5)	7 083(22)	4 873(14)	3 469(14)
C(26)	5 466(9)	2 078(6)	687(5)	C(6)	8 031(19)	4 550(13)	3 775(11)

Table 4. Atom co-ordinates (× 10^4) for $[PPh_4][WCl(SPh)_3(NO)]$ (**6**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	−521(1)	887(1)	2 457(1)	P	5 005(4)	2 816(2)	4 306(2)
Cl	730(3)	265(2)	1 747(2)	C(111)	4 221(14)	3 237(8)	2 895(8)
N	−1 422(10)	1 342(6)	2 926(6)	C(112)	3 513(15)	3 176(8)	2 188(9)
O	−2 039(10)	1 676(5)	3 260(6)	C(113)	2 922(15)	2 583(8)	1 945(8)
S(1)	1 253(4)	714(2)	3 445(2)	C(114)	3 015(13)	2 043(8)	2 415(8)
S(2)	−454(4)	1 757(2)	1 659(2)	C(115)	3 690(12)	2 084(7)	3 116(7)
S(3)	−1 991(4)	12(2)	2 077(2)	C(116)	4 277(13)	2 681(7)	3 380(7)
C(11)	1 009(14)	727(9)	4 804(9)	C(121)	7 196(11)	3 243(8)	3 981(8)
C(12)	785(22)	1 001(12)	5 403(13)	C(122)	8 269(16)	3 655(9)	4 086(8)
C(13)	574(14)	1 685(11)	5 426(8)	C(123)	8 549(13)	4 127(10)	4 613(8)
C(14)	592(14)	2 079(8)	4 862(8)	C(124)	7 782(14)	4 241(8)	5 050(7)
C(15)	816(11)	1 805(7)	4 263(10)	C(125)	6 680(15)	3 850(7)	4 958(8)
C(16)	1 004(12)	1 113(6)	4 222(7)	C(126)	6 410(13)	3 353(7)	4 435(7)
C(21)	−2 539(16)	2 466(9)	1 778(9)	C(131)	4 056(14)	3 254(7)	5 413(9)
C(22)	−3 187(18)	3 052(11)	1 913(8)	C(132)	3 249(16)	3 622(7)	5 710(8)
C(23)	−2 433(24)	3 615(14)	2 183(11)	C(133)	2 188(16)	3 932(7)	5 270(9)
C(24)	−1 150(29)	3 650(12)	2 245(12)	C(134)	1 961(16)	3 913(8)	4 513(8)
C(25)	−547(18)	3 053(11)	2 111(8)	C(135)	2 808(14)	3 558(8)	4 234(9)
C(26)	−1 242(16)	2 483(9)	1 858(7)	C(136)	3 840(15)	3 222(8)	4 671(9)
C(31)	−4 594(13)	66(7)	1 880(7)	C(141)	6 641(13)	1 760(8)	4 884(7)
C(32)	−5 720(14)	104(8)	2 106(12)	C(142)	6 973(15)	1 138(6)	5 210(8)
C(33)	−5 623(18)	245(9)	2 820(11)	C(143)	6 080(18)	764(8)	5 421(8)
C(34)	−4 461(16)	301(9)	3 292(10)	C(144)	4 874(19)	1 005(10)	5 284(9)
C(35)	−3 357(13)	237(8)	3 076(8)	C(145)	4 542(16)	1 627(8)	4 958(8)
C(36)	−3 431(13)	107(7)	2 378(7)	C(146)	5 446(16)	2 022(7)	4 745(7)

Table 5. Atom co-ordinates (× 10^4) for $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(NH_3)(NO)]\cdot C_6H_{14}$ (**7**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	631(3)	336(1)	2 439(2)	C(222)	3 245(42)	964(16)	944(22)
S(1)	2 738(9)	52(4)	2 507(5)	C(223)	2 130(43)	575(17)	−109(21)
S(2)	−540(10)	345(5)	3 376(5)	C(241)	146(42)	2 429(17)	−150(22)
S(3)	−358(10)	446(4)	1 389(5)	C(242)	253(40)	2 888(14)	283(20)
O	1 562(27)	1 376(10)	2 589(13)	C(243)	−987(39)	2 412(17)	−642(21)
N(1)	1 240(28)	963(11)	2 528(15)	C(261)	−2 230(48)	1 328(18)	1 461(21)
N(2)	−61(19)	−458(8)	2 338(9)	C(262)	−2 835(46)	1 751(23)	1 667(27)
C(11)	−520(37)	933(13)	3 779(17)	C(263)	−3 204(45)	1 082(22)	1 091(26)
C(12)	−1 671(36)	1 192(15)	3 747(17)	C(31)	2 751(30)	−626(12)	2 489(19)
C(13)	−1 763(38)	1 655(15)	4 088(18)	C(32)	2 786(35)	−933(16)	3 063(18)
C(14)	−663(40)	1 859(14)	4 391(17)	C(33)	2 872(32)	−1 428(16)	3 101(20)
C(15)	544(39)	1 569(15)	4 501(18)	C(34)	2 853(34)	−1 653(13)	2 498(23)
C(16)	484(38)	1 087(16)	4 179(19)	C(35)	2 852(30)	−1 402(14)	1 898(18)
C(121)	−2 882(38)	1 028(15)	3 418(18)	C(36)	2 854(33)	−862(15)	1 889(18)
C(122)	−3 517(31)	611(12)	3 847(15)	C(321)	2 761(38)	−662(15)	3 758(20)
C(123)	−3 953(35)	1 406(14)	3 276(19)	C(322)	1 857(37)	−904(14)	4 216(18)
C(141)	−535(48)	2 371(21)	4 821(26)	C(323)	4 035(35)	−601(15)	4 078(19)
C(142)	−165(59)	2 757(23)	4 531(29)	C(341)	2 933(40)	−2 261(17)	2 488(23)
C(143)	−526(57)	2 329(23)	5 457(29)	C(342)	4 213(54)	−2 396(21)	2 790(28)
C(161)	1 687(43)	753(17)	4 258(19)	C(343)	1 892(38)	−2 524(16)	2 739(20)
C(162)	1 802(47)	511(20)	4 949(21)	C(361)	2 753(44)	−655(15)	1 196(21)
C(163)	2 963(43)	1 056(21)	4 200(24)	C(362)	1 682(38)	−808(16)	717(19)
C(21)	−127(30)	1 061(13)	1 027(15)	C(363)	3 936(41)	−694(19)	865(22)
C(22)	912(33)	1 143(14)	646(17)	C(1)	1 758(50)	1 549(21)	8 137(26)
C(23)	955(37)	1 621(15)	251(17)	C(2)	2 865(67)	1 482(26)	6 573(37)
C(24)	5(60)	1 937(22)	294(27)	C(3)	3 355(51)	556(22)	7 411(25)
C(25)	−1 025(41)	1 861(16)	651(19)	C(4)	3 501(41)	150(17)	7 883(17)
C(26)	−1 087(39)	1 432(15)	1 074(19)	C(5)	2 323(40)	955(15)	7 511(17)
C(221)	1 969(41)	730(16)	561(21)	C(6)	1 895(52)	1 187(26)	6 837(32)

due to weak π donation by the equatorial thiolate or alkoxide ligands.[10] Maximisation of equatorial π bonding and relief of steric strain accounts for the *endo* and *exo* (with respect to the NO ligand) configuration of the arene rings of the $SC_6H_2Pr^i{}_3$ ligands in complex (**7**) (Figure 3). The least sterically demanding configuration would involve a propeller-like orientation of the $SC_6H_2Pr^i{}_3$ arene groups about the Mo atom.[10] The 'two up, one down' arene-group configuration is also observed in the complexes $[Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(CO)_2]^-$[1] and $[Ru(SC_6H_2Pr^i{}_3\text{-}2,4,6)_4(MeCN)]$.[14]

Unlike complex (**7**), the thiolate-phenyl rings in complexes (**1**) and (**6**) are disposed to form a cavity around the NO ligand. In addition the Mo atom (Figure 1) is displaced 0.1870 Å above the S(2)–S(3)–S(4) plane and the tungsten atom (Figure 2) 0.2351 Å above the S(1)–S(2)–S(3) equatorial plane.[15] This minimises the repulsive forces between the equatorial sulphur

Table 6. M–N and N–O distances (Å) and M–N–O angles (°) of five-co-ordinate nitrosyl complexes

Compound	M–N	N–O	M–N–O	Ref.
$[Mo(SPh)_4(NO)]^-$	1.766(6)	1.188(8)	178.7(5)	*a*
$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(NO)]$	1.775(29)	1.141(40)	176.1(30)	*a*
$[WCl(SPh)_3(NO)]^-$	1.744(13)	1.235(17)	178.5(11)	*a*
$[Re(SC_6H_3Pr^i_2\text{-}2,6)_4(NO)]$	1.7881(16)	1.167(24)	173.6(14)	11
$[W(OBu^t)_3(py)(NO)]$	1.732(8)	1.25(1)	179.2(8)	*b*
$[\{Mo(OPr^i)_3(NO)\}_2]$	1.754(7)	1.19(1)	178(1)	*c*

[a] This work. [b] py = Pyridine; M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *Inorg. Chem.*, 1979, **18**, 116. [c] M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelly, *J. Am. Chem. Soc.*, 1978, **100**, 3354.

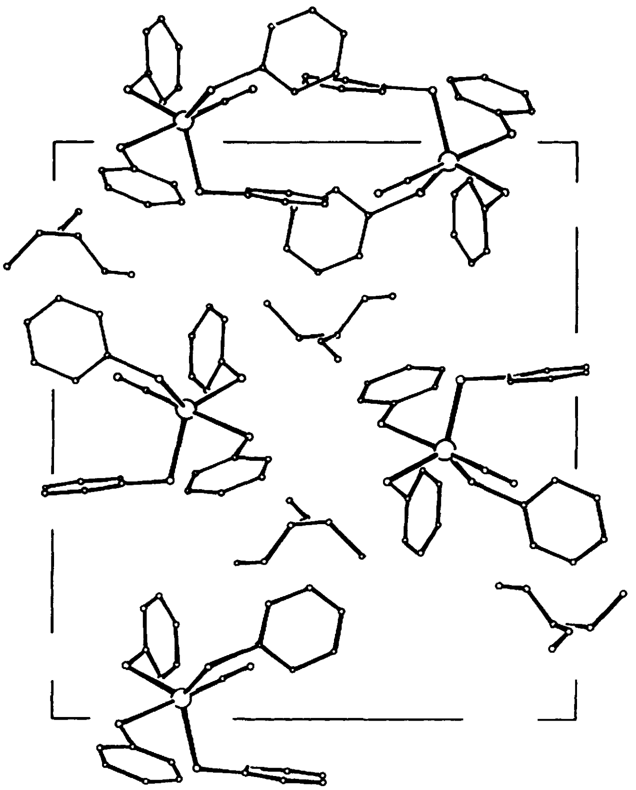

Figure 4. Unit-cell packing diagram of $[NHEt_3][Mo(SPh)_4(NO)]$ viewed down the *a* axis

lone pairs and the π electrons in the M–NO bonding system. The packing arrangement of molecules of complex (**1**) within the unit cell in Figure 4 clearly illustrates the orientation of the thiolate-phenyl groups. They are twisted about the carbon–sulphur bond vector and similar orientations are observed in other structurally characterised trigonal-bipyramidal complexes containing equatorial thiophenolato-ligands (Table 7). The rotation about the S–C bond occurs to minimise intramolecular interactions between the phenyl rings. An analysis[15] of intermolecular distances within and outside the unit cell confirms that the phenyl-ring orientations are not due to crystal-packing effects.

Experimental

All reactions were carried out under nitrogen using dry freshly distilled solvents in conventional Schlenk apparatus.

Crystal parameters and experimental details for the *X*-ray diffraction studies are given in Table 8.

Table 7. Torsion angles (°) about S–C bond vectors

Compound	Bond system	Angle
$[NHEt_3][Mo(SPh)_4(NO)]$	Mo–S(2)–C(21)–C(22)	120.8
	Mo–S(2)–C(21)–C(26)	−63.3
	Mo–S(3)–C(31)–C(36)	54.1
	Mo–S(3)–C(31)–C(32)	−129.4
	Mo–S(4)–C(41)–C(46)	−98.1
	Mo–S(4)–C(41)–C(42)	82.9
$[PPh_4][WCl(SPh)_3(NO)]$	W–S(1)–C(16)–C(11)	119.8
	W–S(1)–C(16)–C(15)	−60.8
	W–S(2)–C(26)–C(21)	−65.6
	W–S(2)–C(26)–C(25)	112.5
	W–S(3)–C(36)–C(31)	128.2
	W–S(3)–C(36)–C(35)	−49.2
$[Re(SPh)_3(MeCN)(PPh_3)]$ *	Re–S(1)–C–C	−66.2
	Re–S(1)–C–C	113.3
	Re–S(2)–C–C	−106.9
	Re–S(2)–C–C	78.0
	Re–S(3)–C–C	123.4
	Re–S(3)–C–C	−56.6

* Trigonal-bipyramidal complex containing equatorial thiolato-ligands, S(1), S(2), and S(3). The carbons are within the thiolate-phenyl groups and analogous to those quoted for the molybdenum and tungsten complexes. See ref. 12.

I.r. spectra were determined for Nujol mulls using a Pye-Unicam SP2000 spectrometer, electronic spectra for acetonitrile solutions using a Perkin-Elmer u.v.–visible spectrophotometer, and n.m.r. spectra for CD_2Cl_2 solutions using a JEOL FX-900 (90 MHz) instrument. Carbon, H, and N analyses were performed by Mrs. G. Olney, University of Sussex. Chlorine analyses were performed by Butterworth Laboratories Ltd., Teddington, Middlesex. Conductivity measurements for acetonitrile solutions were carried out using a Portland Electronics conductivity bridge.

The thiols were purchased commercially and used without further purification, with the exception of 2,4,6-tri-isopropylthiophenol and 2,4,6-trimethylthiophenol which were prepared *via* the $LiAlH_4$ reduction of their corresponding sulphonyl chlorides.[10] The syntheses of $[MCl_3(PPh_3)_2(NO)]$[6] (M = Mo or W) and '$\{Mo(NH_2O)(H_2O)_x(NO)\}_n$'[7] were carried out according to literature methods.

Triethylammonium Nitrosyltetrakis(thiophenolato)molybdate, $[NHEt_3][Mo(SPh)_4(NO)]$ (**1**). *Route* (*i*). The complex $[MoCl_3(PPh_3)_2(NO)]$ (1.5 g, 2 mmol) suspended in methanol (40 cm³) was treated with an excess of thiophenol (1.1 cm³, 9 mmol) and an equivalent amount of triethylamine (0.1 cm³, 9 mmol). A dark red solution formed almost immediately. The reaction mixture was stirred for a further 2 h by which time red microcrystals had precipitated from the solution. The product was filtered off and dried *in vacuo* (1.0 g, 75% yield). Crystals of

Table 8. Experimental details for *X*-ray diffraction[a]

	$[NHEt_3][Mo(SPh)_4(NO)]$ (**1**)	$[PPh_4][WCl(SPh)_3(NO)]$ (**6**)	$[Mo(SC_6H_2Pr^i_3\text{-}2,4,6)_3(NH_3)(NO)]\cdot C_6H_{14}$ (**7**)
(*a*) Crystal parameters at 23 °C[b]			
M	902.004	916.201	921.348
a/Å	10.996 (2)	10.809(1)	10.477(3)
b/Å	16.127(4)	19.677(3)	26.359(5)
c/Å	18.845(4)	19.250(3)	20.124(4)
α/°	90.00	90.00	90.00
β/°	105.94(1)	105.85(1)	87.21(1)
γ/°	90.00	90.00	90.00
U/Å^3	3 229.3(11)	3 938.3(9)	5 550.9(12)
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
D_c/g cm^{-3}	1.367	2.04	1.10
$F(000)$	1 856	1 824	1 984
(*b*) Measurement of intensity data[c]			
Crystal dimensions (mm)	0.25 × 0.33 × 0.45	0.07 × 0.12 × 0.03	0.15 × 0.25 × 0.21
Scan rate/° min^{-1}	7—30	7—30	5—30
Number of reflections collected	4 187 independent	4 122 total yielding 2 896 independent	2 549 independent
Number of independent reflections [$I > 3\sigma(I)$] used in solution	2 786	1 895	1 040
(*c*) Reduction of intensity data and summary of structure solution and refinement			
Absorption coefficient (cm^{-1})	6.68	33.92	3.58
Absorption correction	Not applied	Applied using the SHELXTL program XCMP with reflections (hkl,2 $I_{max.}/I_{min.}$): 027, 7.86, 1.16; 302, 11.36, 1.16. Merging R_{before} = 0.0203, R_{after} = 0.0104	Not applied
Final discrepancy factor,[d] R	0.0516	0.0375	0.078
R'	0.0560	0.0347	0.071
Goodness of fit[e]	1.961	1.025	1.61

[a] Details common to all three complexes: $Z = 4$; Nicolet R3m diffractometer; Mo-K_α radiation, $\lambda = 0.710\,73$ Å; scan mode, θ(crystal)—2θ(counter); scan length, $2\sigma(K_{\alpha 1}) - 1$ to $2\sigma(K_{\alpha 2}) + 1$°; background measurement, stationary crystal–stationary counter at the beginning and end of each scan for the time of the scan; standard reflections, 3 measured every 197, no significant deviations observed; structure solution, Patterson synthesis yielded the metal position, successive Fourier difference maps the remaining non-hydrogen atoms; neutral atomic scattering factors throughout the analysis (D. T. Cramer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321); anomalous dispersion applied to all non-hydrogen atoms ('International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3). [b] From a least-squares fitting of the setting angle of 25 reflections. [c] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using a local version of the Nicolet SHELXTL interactive crystallographic software package as described in G. M. Sheldrick, Nicolet SHELXTL Operations Manual, Nicolet XRD Corp. Cupertino, CA 1970, U.S.A. [d] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o) + g(F_o)^2$, $g = 0.001$. [e] $[\Sigma w(|F_o| - |F_c|)^2/(N_O - N_V)]^{\frac{1}{2}}$ where N_O is the number of observations and N_V is the number of variables.

(**1**) suitable for *X*-ray analyses were obtained by recrystallising from dichloromethane–methanol.

Route (*ii*). The complex '$\{Mo(NH_2O)(H_2O)_x(NO)\}_n$' (1 g) suspended in methanol (50 cm^3) was treated with an excess of thiophenol (3.0 cm^3, 26 mmol) and an equivalent amount of triethylamine (2.8 cm^3, 26 mmol). The reaction mixture was heated under reflux for *ca.* 6 h and then allowed to cool to room temperature. Red microcrystals precipitated from the cooled solution and were filtered off and dried *in vacuo* (2.6 g yield).

The *tetraphenylphosphonium salts* $[PPh_4][Mo(SC_6H_4\text{-}Me\text{-}4)_4(NO)]$ (**2**), $[PPh_4][Mo(SC_6H_4Cl\text{-}4)_4(NO)]$ (**3**), and $[PPh_4][Mo(SC_6H_2Me_3\text{-}2,4,6)_4(NO)]$ (**4**) were prepared in an analogous manner to complex (**1**), *via* either route (*i*) or (*ii*). Tetraphenylphosphonium bromide was added to their methanol solutions and the products precipitated as microcrystalline solids in over 75% yield.

Tetraphenylphosphonium Chlorotris(2-*methylpropane*-2-*thiolato*)*nitrosylmolybdate*, $[PPh_4][MoCl(SBu^t)_3(NO)]$ (**5**).—The complex $[MoCl_3(PPh_3)_2(NO)]$ (1.6 g, 2 mmol) suspended in propan-2-ol (50 cm^3) was treated with an excess of 2-methylpropane-2-thiol (1 cm^3, 10 mmol) and an equivalent amount of triethylamine (1.1 cm^3, 10 mmol). A pale yellow solution formed immediately to which was added tetraphenylphosphonium bromide (2 g, 4.5 mmol). The reaction mixture was stirred for *ca.* 5 h, by which time a fine pale yellow powder had precipitated from solution. This was then filtered off and dried *in vacuo* (0.72 g, 48% yield). Complex (**5**) was recrystallised from dichloromethane–diethyl ether.

Tetraphenylphosphonium Chloronitrosyltris(*thiophenolato*)*tungstate*, $[PPh_4][WCl(SPh)_3(NO)]$ (**6**).—The complex $[WCl_3(PPh_3)_2(NO)]$ (1.5 g, 1.8 mmol) suspended in methanol (50 cm^3) was treated with an excess of thiophenol (1.1 cm^3, 9 mmol) and an equivalent amount of triethylamine (1.2 cm^3, 9 mmol). A dark yellow solution formed almost immediately, to which was added tetraphenylphosphonium bromide (2 g, 4.5 mmol). The reaction mixture was then stirred for *ca.* 2 h, by which time a yellow microcrystalline solid had precipitated out of solution (1.1 g, yield 67%). Crystals of (**6**) suitable for *X*-ray analysis were obtained by recrystallising from acetonitrile–diethyl ether.

Amminenitrosyltris(2,4,6-*tri-isopropylthiophenolato*)*molybdenum*, $[\mathrm{Mo(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3(NH_3)(NO)}]$, (**7**).—The complex '$\{\mathrm{Mo(NH_2O)(H_2O)_{\mathit{x}}(NO)}\}_n$' (1 g) suspended in methanol (50 cm^3) was treated with a large excess of 2,4,6-tri-isopropylthiophenol (6.1 cm^3, 26 mmol) and an equivalent amount of triethylamine (2.8 cm^3, 26 mmol). The reaction mixture was heated to reflux temperature for *ca.* 4 h and then allowed to cool to room temperature. Solvent was stripped off *in vacuo* at *ca.* 30 °C to half volume. After *ca.* 1 h a crop of yellow crystals began to precipitate out of the methanol. The liquor was allowed to stand overnight at 0 °C and filtered under suction next morning to give cubic pale yellow crystals (0.93 g, yield). Crystals of (**7**) suitable for *X*-ray analysis were obtained from mixtures of diethyl ether and hexane.

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