Mono- and Bis-thiolato, Mixed Thiolato–Monoalkylamido, and Thiolato–Alkoxy Complexes of Nitrosyl[tris(3,5-dimethylpyrazolyl)-borato]molybdenum, and the Crystal and Molecular Structure of $[Mo\{HB(3,5\text{-}Me_2C_3N_2H)_3\}(NO)I(SC_6H_{11})]$ †

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$[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (Me_2pz = 3,5-dimethylpyrazolyl) reacted with NaSEt or RSH giving $[Mo\{HB(Me_2pz)_3\}(NO)I(SR)]$ (R = Et, Bu^n, C_6H_{11}, $C_{16}H_{33}$, CH_2Ph, Ph, and C_6H_4Me-*p*) and with AgO_2CMe and RSH giving $[Mo\{HB(Me_2pz)_3\}(NO)(SR)_2]$ (R = Bu^n or Ph). Treatment of $[Mo\{HB(Me_2pz)_3\}(NO)I(SR)]$ with NHR′ gave $[Mo\{HB(Me_2pz)_3\}(NO)(SR)(NHR')]$ (R = Bu^n or Ph, R′ = Me, Et, Pr^n, or Bu^n) and treatment with AgO_2CMe followed by R′OH gave $[Mo\{HB(Me_2pz)_3\}(NO)(SR)(OR')]$ (R = Bu^n or Ph, R′ = Me or Et). A brief comparison is made of the NO stretching frequencies of the series $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ (X = I, Y = OR, NHR, and SR; X = OR, Y = NHR and SR; X = SR, Y = NHR; X = Y = OR and SR), and the crystal and molecular structure of $[Mo\{HB(Me_2pz)_3\}(NO)I(SC_6H_{11})]$ has been determined by *X*-ray analysis.

In preceding papers we have described the chemistry of the formally co-ordinatively unsaturated Mo^{II} species $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ (1) (X = Y = I; Me_2pz = 3,5-dimethylpyrazolyl; NO ligand treated as neutral for the purposes of oxidation state calculations), in particular the formation of alkoxy (X = I, Y = OR; X = Y = OR; X = OR, Y = OR′),[1,2] monoalkyl- and monoaryl-amido (X = I, Y = NHR),[3,4] and hydrazido(1−) (X = I, Y = NHNRR′)[5] complexes. These complexes contain the bulky tris(3,5-dimethylpyrazolyl)borato-ligand which effectively prevents expansion of the co-ordination sphere of the metal above six, and is, in part, responsible for the remarkable air- and moisture-stability of the alkoxides and amides.

In a continuation of this work, we have prepared a series of mono- and bis-thiolato-complexes (1; X = I, Y = SR) and (1; X = Y = SR). These complexes are similar to the η-cyclopentadienyl complexes $[\{Mo(\eta^5\text{-}C_5H_5)(NO)I(SR)\}_2]$ and $[Mo(\eta^5\text{-}C_5H_5)(NO)(SR)_2]$ which we described some years ago.[6] Unlike the former cyclopentadienyl complexes, however, we expected that (1; X = I, Y = SR) would be monomeric, and this has been confirmed, both by molecular weight studies in solution and by a full *X*-ray structural characterisation of (1; X = I, Y = SC_6H_{11}). We also report the synthesis of the mixed-ligand complexes (1; X = OR, Y = SR′) and (1; X = NHR, Y = SR′), which are similar to the mixed amido–alkoxy complexes (1; X = NHR, Y = OR′) described earlier.[2,4]

Experimental

All reagents were used as purchased without further purification, except $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ which was prepared as described in the literature.[7] Solvents were specially purified, dried, and degassed (N_2) by standard methods.

Molecular weights were determined osmometrically in $CHCl_3$, i.r. spectra were obtained using PE 297 and 180 spectrophotometers, and n.m.r. spectra were measured using PE R12, R34 and JEOL PFT 90 instruments. Microanalyses were performed by the Microanalytical Laboratory of this Department. All yields are quoted relative to the Mo-containing precursor, and all reactions were carried out under N_2. Data are in Tables 1 and 2.

$[Mo\{HB(Me_2pz)_3\}(NO)I(SEt)]$.—Sodium ethanethiolate was prepared by stirring NaH (0.05 g, 50% dispersion) in tetrahydrofuran (thf) (20 cm^3) with an excess of ethanethiol under N_2 for 2 h. To the resulting solution was added $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (0.5 g) and the mixture was refluxed overnight. After this time a brown solution had formed, and this was cooled and reduced *in vacuo* to *ca.* 10 cm^3. On standing at −5 °C, the *complex* crystallised as black microcrystals which were filtered off and washed with a small amount of cold methanol. Yield 0.28 g, 63%.

$[Mo\{HB(Me_2pz)_3\}(NO)I(SBu^n)]$.—A mixture of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (0.5 g) and n-butanethiol (0.2 cm^3) was refluxed overnight in n-heptane. The red-brown solution which formed was cooled, filtered and evaporated *in vacuo* to low volume. On cooling to −5 °C, the *complex* formed as black crystals. Yield 0.35 g, 75%.

$[Mo\{HB(Me_2pz)_3\}(NO)I(SPh)]$.—A mixture of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (0.5 g) and thiophenol (0.2 cm^3) was refluxed overnight, giving a deep vermillion solution. This was cooled in ice and filtered to give a black powder. The solid was washed with a small amount of diethyl ether and recrystallised from ethanol or light petroleum (b.p. >120 °C) affording the *complex* as black crystals. Yield 0.4 g, 82%.

The related complexes $[Mo\{HB(Me_2pz)_3\}(NO)I(SR)]$, R = C_6H_4Me-*p* (79%), CH_2Ph (61%), and C_6H_{11} (59%) were obtained similarly, that derived from cyclohexanethiol being recrystallised from chloroform–n-hexane mixtures.

$[Mo\{HB(Me_2pz)_3\}(NO)I(SC_{16}H_{33})]$.—A mixture of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ (0.5 g) and hexadecanethiol (0.4 cm^3) was refluxed overnight in methylcyclohexane. The red-brown mixture was evaporated to dryness, extracted with diethyl ether, and the extract filtered. The filtrate was evaporated to dryness giving a yellow-brown oil which was crystallised from

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† Cyclohexanethiolato(iodo)nitrosyl[tris(3,5-dimethylpyrazolyl)-borato]molybdenum.

Supplementary data available (No. SUP 23424, 24 pp.): observed structure amplitudes, calculated structure factors, anisotropic and isotropic thermal parameters, predicted hydrogen atom positional parameters, full bond length and angle data, full i.r. and ^1H n.m.r. data, details of planar fragments. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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Table 1. Analytical and molecular weight data obtained from the complexes [Mo{HB($Me_2pz)_3$}(NO)XY]

		Analysis * (%)					
X	Y	C	H	N	S	I	*M* *
I	SEt	33.2 (33.4)	4.3 (4.5)	16.4 (16.0)	5.0 (5.3)	20.5 (20.8)	629 (611)
I	SBu^n	35.7 (35.7)	5.2 (4.9)	15.4 (15.3)	5.4 (5.0)	20.2 (19.9)	829 (808)
I	SPh	38.3 (38.3)	4.3 (4.1)	14.6 (14.9)	4.8 (4.9)	19.1 (19.3)	663 (659)
I	$S(C_6H_4Me$-*p*)	39.4 (39.3)	4.3 (4.3)	14.8 (14.6)	4.6 (4.8)	19.0 (18.9)	685 (673)
I	SCH_2Ph	39.0 (39.3)	4.2 (4.3)	14.6 (14.6)	4.4 (4.8)	18.5 (18.9)	647 (673)
I	SC_6H_{11}	38.1 (37.9)	4.7 (5.0)	14.6 (14.7)	5.0 (4.8)	19.3 (19.1)	640 (665)
I	$SC_{16}H_{33}$	46.2 (46.1)	7.0 (6.9)	12.4 (12.1)	4.3 (4.0)	15.9 (15.7)	829 (808)
SBu^n	SBu^n	45.7 (45.9)	6.9 (6.7)	16.0 (16.3)	10.4 (10.7)		620 (602)
SPh	SPh	50.9 (50.6)	4.8 (5.0)	15.6 (15.3)	10.3 (10.0)		661 (642)
SBu^n	NHMe	43.9 (44.3)	6.8 (6.5)	20.6 (20.7)	6.2 (5.9)		560 (542)
SBu^n	NHEt	45.2 (45.3)	6.9 (6.7)	20.4 (20.1)	6.0 (5.8)		533 (556)
SBu^n	$NHPr^n$	46.6 (46.2)	6.9 (7.1)	19.9 (19.6)	5.3 (5.6)		
SBu^n	$NHBu^n$	47.0 (47.3)	7.1 (7.1)	19.3 (19.2)	5.5 (5.5)		551 (584)
SPh	NHMe	46.6 (46.0)	5.7 (5.6)	19.9 (19.9)	5.3 (5.7)		
SPh	NHEt	47.8 (47.9)	5.7 (5.8)	19.4 (19.4)	5.7 (5.6)		559 (576)
SPh	$NHPr^n$	48.5 (48.8)	5.9 (6.0)	19.0 (19.0)	5.8 (5.4)		577 (590)
SPh	$NHBu^n$	49.4 (49.7)	6.0 (6.2)	18.8 (18.5)	5.1 (5.3)		
SBu^n	OMe	44.3 (44.2)	6.0 (6.3)	17.8 (18.1)	6.2 (5.9)		
SBu^n	OEt	45.5 (45.5)	6.2 (6.5)	17.7 (17.6)	6.1 (5.8)		581 (557)
SPh	OMe	46.8 (46.9)	5.5 (5.4)	17.4 (17.4)	5.8 (5.7)		
SPh	OEt	47.6 (47.9)	5.8 (5.6)	17.2 (17.0)	5.9 (5.6)		558 (577)

* Calculated values are in parentheses.

ethanol to afford the *complex* as a grey-purple powder. Yield 0.38 g, 63%.

[Mo{HB($Me_2pz)_3$}(NO)($SBu^n)_2$].—A mixture of [Mo{HB($Me_2pz)_3$}(NO)I(SBu^n)] (0.3 g), n-butanethiol (0.2 cm^3), and silver acetate (0.1 g) in n-heptane (20 cm^3) was refluxed overnight. The reaction mixture became deep brown and was filtered through Kieselguhr. The filtrate was reduced to *ca.* 5 cm^3 and cooled to −5 °C when the *complex* formed as green crystals. Yield 0.13 g, 45%. [Mo{HB($Me_2pz)_3$}(NO)($SPh)_2$] was prepared similarly. Yield 0.20 g, 67%.

[Mo{HB($Me_2pz)_3$}(NO)(SBu^n)(NHMe)].—To a solution of [Mo{HB($Me_2pz)_3$}(NO)I(SBu^n)] (0.3 g) in dichloromethane (20 cm^3) was added methylamine solution (1 cm^3, 40% in ethanol). The mixture was stirred at room temperature for 2 h, during which time it became homogeneous and orange. The bulk of the solvent was evaporated *in vacuo* to *ca.* 5 cm^3 and ether was added causing the precipitation of a white solid ($[NH_3Me]^+I^-$?). This was filtered off and the filtrate re-evaporated to *ca.* 5 cm^3 and n-hexane added until crystallisation began. After cooling at −5 °C, the *complex* was formed as orange crystals, and was collected by filtration. Yield 0.21 g, 84%.

The complexes [Mo{HB($Me_2pz)_3$}(NO)(SBu^n)(NHR)] (R = Et, Pr^n, and Bu^n) and [Mo{HB($Me_2pz)_3$}(NO)(SPh)(NHR)] (R = Me, Et, Pr^n, and Bu^n) were obtained similarly and were isolated as orange or red crystals in yields greater than 70%.

[Mo{HB($Me_2pz)_3$}(NO)(SBu^n)(OMe)].—A suspension of [Mo{HB($Me_2pz)_3$}(NO)I(SBu^n)] (0.3 g) and silver(I) acetate (0.1 g) in methylcyclohexane (20 cm^3) was stirred for 2 h. After this time, methanol (5 cm^3) was added and the stirring was continued for a further 3 h, during which time the solution became brown. After filtration through Kieselguhr, the filtrate was reduced *in vacuo* until crystallisation began, and the solution allowed to cool at −5 °C overnight. The *complex* was obtained as dark brown crystals which were collected by filtration. Yield 0.16 g, 64%.

The complexes [Mo{HB($Me_2pz)_3$}(NO)(SBu^n)(OEt)] and [Mo{HB($Me_2pz)_3$}(NO)(SPh)(OR)] (R = Me or Et) were obtained similarly in yields greater than 58%.

Crystallographic Studies.—[Mo{HB($Me_2pz)_3$}(NO)I(SC_6H_{11})]. This complex crystallises from chloroform–hexane as dark brown crystals.

Crystal data. $C_{21}H_{33}BIMoN_7OS$, M = 665.3, Monoclinic, a = 14.39(3), b = 13.82(3), c = 17.90(2) Å, β = 118.16(15)°, U = 3 137(11) Å^3, D_m = 1.44, Z = 4, D_c = 1.41 g cm^{-3}, space group $P2_1/c$ (no. 14, C^5_{2h}), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 14.7 cm^{-1}, $F(000)$ = 1 328.

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer by the omega-scan method. 1 284 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects; a correction was made for 20% intensity loss during data collection based on the monitoring of the (20$\bar{2}$) reflection. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were detected in electron-density difference syntheses and were placed in calculated positions [C−H 0.95, B−H, 1.12 Å, C−C−H(methyl) 110°]; their contributions were included in structure factor calculations (B = 10.0 Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0775 with allowance for anomalous scattering and anisotropic thermal motion of iodine, molybdenum, and sulphur atoms: isotropic thermal vibrational parameters were refined for all other non-hydrogen atoms. Table 3 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from ref. 8; unit weights were used throughout the refinement. Computer programs formed part of the Sheffield *X*-ray system.

Results and Discussion

Synthetic Studies.—The complexes (1; X = I, Y = SR; R = Bu^n, C_6H_{11}, $C_{16}H_{33}$, CH_2Ph, Ph, and C_6H_4Me-*p*) were obtained by direct reaction of the appropriate thiol with (1; X = Y = I). The ethanethiolate (1; X = I, Y = SEt), however, could only be obtained cleanly from (1; X = Y = I) using NaSEt, but we were unable to obtain (1; X = I, Y = SMe) by either method, or by reaction of (1; Y = Y = I) with MeSH in a Carius tube. There was apparently no significant reaction between (1; X = Y = I) and either H_2S or naphthalene-2-thiol.

The complexes were isolated as brown or black crystalline solids (analytical data are in Table 1). They are, in general, soluble in chloroform, dichloromethane, acetone, acetonitrile, and dimethyl sulphoxide, slightly soluble in toluene, but insoluble in alcohols and ethers. An exception to this is (1; X = I, Y = SCH_2Ph) which is insoluble in all of these solvents except Me_2SO. The alkanethiolates are slightly soluble in alkanes whereas their aryl thiolato-analogues were insoluble.

The bis-thiolato-complexes (1; X = Y = SR; R = Bu^n or Ph) were prepared from a mixture of (1; X = Y = I), AgO_2CMe, and RSH. The compounds are isolated as dark green solids which are slightly more soluble in organic solvents than their mono-thiolato-analogues. We note that in reactions of (1; X = Y = I) with large excesses of RSH only (1; X = I, Y = SR) was formed, in contrast to the behaviour of (1; X = Y = I) in alcohols, where prolonged refluxing afforded mixtures of (1; X = I, Y = OR) and (1; X = Y = OR).

The mixed-ligand complexes (1; X = SR, Y = NHR′; R = Bu^n, R′ = Me, Et, Pr^n, or Bu^n; R = Ph, R′ = Me, Et, Pr^n, or Bu^n) were obtained by reaction of (1; X = I, Y = SR) with a two-fold excess of the appropriate amine in the cold. During this reaction, $[NH_3R']I$ was formed as a by-product. Attempts to prepare the mixed amido–thiolato-complex by reaction of (1; X = I, Y = NHR′) with RSH afforded only the mono-thiolato-species (1; X = I, Y = SR). These complexes were isolated as orange or red crystals with solubility characteristics similar to those of (1; X = Y = SR). We were unable to obtain mixed amido–thiolato-complexes containing NHPh.

In refluxing alcohols, (1; X = I, Y = SR) was converted to (1; X = I, Y = OR), and if the latter was treated with RSH, then replacement of OR by SR occurred. The bis-alkoxides (1; X = OR, Y = OR′) were obtained [2] by reaction of (1; X = I, Y = OR′) with AgO_2CMe in ROH. Using a similar procedure with (1; X = I, Y = SR), only (1; X = Y = OR) was produced. However, if (1; X = I, Y = SR) was treated with AgO_2CMe in a methylcyclohexane suspension, and ROH was added some 2 h later, the desired mixed alkoxy–thiolato-complexes (1; X = OR, Y = SR) were obtained. These complexes were formed as green-brown or dark brown crystals.

We have proposed [9] a general mechanism for the formation of the species (1; X = I, Y = OR, NHR, NHNRR′, and SR) which involves prior reduction of $[Mo\{HB(Me_2pz)_3\}(NO)I_2]$ to the paramagnetic species $[Mo\{HB(Me_2pz)_3\}(NO)I_2]^-$. This anion dissociates I^- affording solvated $[Mo\{HB(Me_2pz)_3\}(NO)I]$ which, we suggest, reacts with the radical Y giving the final product. On the basis of our preliminary electrochemical studies, this proposal seems reasonable for the formation of (1; X = I, Y = SR), since RSH can act as an effective reducing agent under the conditions of reaction described. Oxidation of the thiol to disulphide may be expected, and the subsequent reaction of $[Mo\{HB(Me_2pz)_3\}(NO)I]$ with RSSR as well as RS and/or RSH may also account in part for the rather slower formation of the mono-thiolate in contrast to (1; X = I, Y = NHR). However, we are not completely satisfied that the proposed mechanism fully describes the situation, and further electrochemical and mechanistic studies are in progress. In the reactions of (1; X = Y = I) with AgO_2CMe, in the formation of (1; X = Y = SR), (1; X = SR, Y = OR or NHR), we imagine that the silver acetate affords the intermediate (1; X = SR, Y = O_2CMe). We know from previous work [2-4] that such acetato-intermediates are useful in the formation of bis-substituted and mixed-ligand species, and we presume that this is because of the effectiveness of acetic acid as a leaving group. However, the behaviour of (1; X = Y = I) and related species with Ag^I salts is very complicated,[10] and we are not yet able to define the reaction mechanism.

All of the complexes described herein react with HCl, HBr, or HI affording the appropriate species (1; X = Y = Cl, Br, or I), with loss of RSH and NHR or OR, as appropriate. They are, however, stable to aerial oxidation and hydrolysis by water, and all are monomeric (Table 1).

Spectroscopic Studies.—The i.r. spectra of the new complexes exhibit the expected absorptions due to the $HB(Me_2pz)_3$ ligand [*ca.* 2 500 cm^{-1} due to $\nu(BH)$ and 1 400 cm^{-1}, associated with the pyrazolyl ring]. These complexes containing NHR groups exhibited a single $\nu(NH)$ near 3 280 cm^{-1}. The NO stretching frequencies of (1; X = I, Y = SR) occurred in the range 1 663—1 690 cm^{-1} in chloroform, the lowest absorption being due to (1; X = I, Y = SCH_2Ph) (measured in Me_2SO). There seems to be only a small substituent effect, $\nu(NO)$ being generally a little higher for the arenethiolato-complexes than for the alkanethiolato-species. This would appear to be true also for the bis-thiolato-species (1; X = Y = SR), where $\nu(NO)$ for R = Ph is 23 cm^{-1} higher than that for R = Bu^n. The NO stretching frequencies for the mixed amido–thiolato-species (1; X = SR, Y = NHR′) occurred in the range 1 638—1 664 cm^{-1} without any significant correlation between $\nu(NO)$ and the substituents R and R′. The related alkoxy–thiolato-species exhibited $\nu(NO)$ in the range 1 650—1 664 cm^{-1} ($CHCl_3$ solution).

We are now in a position to make a general comparison of $\nu(NO)$ for the complete range of complexes of the type $[Mo\{HB(Me_2pz)_3\}(NO)XY]$. Thus the NO stretching frequencies (average values in KBr discs) decrease in the following order: X,Y (average frequency in cm^{-1}, ± 5 cm^{-1}) I,SR (1 679) > I,OR (1 675) > SR,SR (1 667) > I,NHR (1 656) > SR,OR (1 651) > OR,OR (1 646) > SR,NHR (1 635) > OR,NHR (1 632); data taken from refs. 1—5. While this correlation between X,Y and $\nu(NO)$ is of necessity rather unsophisticated, it nevertheless reveals a trend which is broadly consistent with the donor capacities of the various donor atoms in X and Y. Thus, in general, the SR groups are less powerful donors than the corresponding alkoxy and amido-groups, while NHR is the most powerful donor of all the groups involved. We consider it unlikely that the SR groups are functioning as π-acceptors, since $\nu(NO)$ is significantly lower than that in (1; X = Y = halogen), where the halogen groups are electron withdrawing and $\nu(NO)$ occurs above 1 700 cm^{-1}.[1,7] Furthermore, the metal is formally co-ordinatively unsaturated and will clearly be seeking some compensatory electron donation which can only be obtained from SR. Preliminary electrochemical studies indicate that X and Y have a significant influence on the oxidation–reduction behaviour of $[Mo\{HB(Me_2pz)_3\}(NO)XY]$ and we will describe these results in full shortly.

The ^1H n.m.r. spectra of the new complexes are summarised in Table 2. The spectra are characterised by resonances in the region near δ 2.3 and 5.7 p.p.m. due to the pyrazolyl methyl protons and the C^4–H group. In addition, resonances are detected due to the substituents of X and Y. For the species (1; X = I, Y = SR), (1; X = NHR, Y = SR), and (1; X = OR, Y = SR) the C^4-H signals appear as three singlets which is consistent with the expected six-co-ordinate geometry of the complexes, and the lack of a plane of sym-

Table 2. Spectroscopic data obtained for selected complexes $[\mathrm{Mo\{HB(Me_2pz)_3\}(NO)XY}]$

		ν(NO) (cm^{-1})		^{1}H n.m.r. data			
X	Y	KBr	CHCl$_3$	δ/p.p.m.	*A* [a]		Assignment
I	SEt	1 677	1 681	5.99	1	(s)	$\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				5.80	1	(s)	
				5.77	1	(s)	
				4.78	2	(m)	$\mathrm{SC}\mathit{H}_2\mathrm{CH_3}$ [b]
				2.67	3	(s)	$\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.49	3	(s)	
				2.46	3	(s)	
				2.34	6	(s)	
				2.16	3	(s)	
				1.75	3	(t)	$\mathrm{SCH_2C}\mathit{H}_3$, *J*(HH) 8.0 Hz
I	SBu^n	1 669	1 681				
I	$\mathrm{SC_{16}H_{33}}$	1 685	1 680				
I	$\mathrm{SC_6H_{11}}$	1 672	1 677				
I	$\mathrm{SCH_2Ph}$	1 672	1 663 [c]	7.5—7.3	5	(m)	$\mathrm{SCH_2C_6}\mathit{H}_5$
				5.98	1	(s)	$\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				5.84	1	(s)	
				5.80	1	(s)	
				5.52	2		AB pair, δ(A) 5.88, δ(B) 5.16, *J*(AB) 15.0 Hz
				2.59	3	(s)	$\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.50	6	(s)	
				2.37	6	(s)	
				2.20	3	(s)	
I	SPh	1 689	1 690	8.06	2	(d)	*o*-H, $\mathrm{SC_6}\mathit{H}_5$, *J*(HH) 10.0 Hz
				8.50	3	(m)	*m* and *p*, $\mathrm{SC_6}\mathit{H}_5$
				6.01	1	(s)	$\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				5.81	1	(s)	
				5.73	1	(s)	
				2.64	3	(s)	$\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.50	3	(s)	
				2.48	3	(s)	
				2.34	3	(s)	
				2.32	3	(s)	
				1.93	3	(s)	
I	$\mathrm{SC_6H_4Me}$-*p*	1 692	1 684	7.66	4		AA′BB′, ‘ δ(A) ’ 7.96, ‘ δ(B) ’ 7.36, ‘ *J*(AB) ’ 10.0 Hz
				5.87	1	(s)	$\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				5.83	1	(s)	
				5.75	1	(s)	
				2.51	3	(s)	$\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.62	6	(s)	
				2.36	6	(s)	
				1.95	3	(s)	
				2.27	3	(s)	$\mathrm{SC_6H_4C}\mathit{H}_3$
SBu^n	SBu^n	1 653	1 658				
SPh	SPh	1 681	1 681				
SBu^n	NHMe	1 625 1 636	1 647	10.13	1	(br)	$\mathrm{N}\mathit{H}\mathrm{Me}$
				5.87	1	(s)	$\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				5.74	2	(s)	
				4.09	3	(d)	$\mathrm{NH(C}\mathit{H}_3)$, *J*(HH) 7.0 Hz
				3.45	2	(m)	$\mathrm{SC}\mathit{H}_2\mathrm{Pr}^n$
				2.57	18	(s)	$\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.54		(s)	
				2.38		(s)	
				2.30		(s)	
				1.63	2		quintet, $\mathrm{SCH_2C}\mathit{H}_2\mathrm{Et}$, *J*(HH) 7.0 Hz
				1.45	2		sextet, $\mathrm{S(CH_2)_2C}\mathit{H}_2\mathrm{Me}$, *J*(HH) 7.0 Hz
				0.89	3	(t)	$\mathrm{S(CH_2)_3C}\mathit{H}_3$, *J*(HH) 7.0 Hz
SBu^n	NHEt	1 625	1 638				
SBu^n	NHPr^n	1 634	1 663				
SBu^n	NHBu^n	1 643	1 648				
SPh	NHMe	1 624 1 635	1 652	10.80	1	(br)	$\mathrm{N}\mathit{H}\mathrm{Me}$
				ca. 7.18	5	(m)	$\mathrm{SC_6}\mathit{H}_5$
				5.80	3	(s)	$\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				4.32	3	(d)	$\mathrm{NHC}\mathit{H}_3$, *J*(HH) 9.0 Hz
				2.47	18	(s)	$\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.45		(s)	
				2.35		(s)	

Table 2 (*continued*)

X	Y	ν(NO) (cm^{-1})		^{1}H n.m.r. data		
		KBr	$\mathrm{CHCl_3}$	δ/p.p.m.	*A* [a]	Assignment
SPh	NHEt	1 630	1 641			
SPh	$\mathrm{NHPr^n}$	1 652	1 664			
SPh	$\mathrm{NHBu^n}$	1 637	1 652			
$\mathrm{SBu^n}$	OMe	1 649	1 655	5.80	1	(s) $\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				5.74	1	(s)
				5.71	1	(s)
				5.45	3	(s) $\mathrm{OC}\mathit{H}_3$
				3.43	2	(m) $\mathrm{SC}\mathit{H}_2\mathrm{Pr^n}$
				2.52	18	(s) $\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.38		(s)
				2.36		(s)
				2.30		(s)
				2.25		(s)
				1.65	2	(m) $\mathrm{SCH_2C}\mathit{H}_2\mathrm{Et}$, *J*(HH) 8.0 Hz
				1.45	2	sextet, $\mathrm{S(CH_2)_2C}\mathit{H}_2\mathrm{Me}$, *J*(HH) 8.0 Hz
				0.89	3	(t) $\mathrm{S(CH_2)_3C}\mathit{H}_3$, *J*(HH) 8.0 Hz
$\mathrm{SBu^n}$	OEt	1 643	1 650			
SPh	OMe	1 658	1 664	*ca.* 7.2	5	(m,br) $\mathrm{SC_6}\mathit{H}_5$
				5.82	1	(s) $\mathrm{C_3N_2}\mathit{H}\mathrm{Me_2}$
				5.75	1	(s)
				5.72	1	(s)
				5.45	3	(s) $\mathrm{OC}\mathit{H}_3$
				2.50	18	(s) $\mathrm{C_3N_2H(C}\mathit{H}_3)_2$
				2.38		(s)
				2.28		(s)
				2.23		(s)
SPh	OEt	1 653	1 660			

[a] Relative area (multiplicities in parentheses.) [b] Complex, not resolved. [c] Measured in $\mathrm{Me_2SO}$.

metry in the system. In the spectra of the bis-thiolato-complexes (1; X = Y = SR), where a plane of symmetry does exist, the C^4-H signals appear as two resonances, of relative intensity 2 : 1. The spectra of complexes of the type (1; X = I, Y = $\mathrm{SCH_2R'}$) are characterised by low-field shifts of the methylene protons relative to uncomplexed $\mathrm{R'CH_2SH}$, and those signals appear as AB multiplets. The former phenomenon is associated with the high electronegativity of the $\mathrm{Mo\{HB(Me_2pz)_3\}(NO)}$ group, which we have observed and have described previously,[1] and the latter is due to the lack of symmetry in the complexes and restricted rotation about the Mo–S and S–C bonds. We also noted that the chemical shifts of the *o*-, *m*-, and *p*-protons in the arenethiolato-complexes were at frequencies lower than those in the free ligand, again presumably due to the electron-withdrawing properties of the metal. The spectra of the mixed ligand complexes (where measured) were entirely consistent with their formulation and exhibit the same features as described for related amido and alkoxy complexes.

Crystal Structure of $\mathrm{[Mo\{HB(Me_2pz)_3\}(NO)I(SC_6H_{11})]}$.—The structure is illustrated in the Figure with the atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are given in Table 4. The co-ordination geometry of the molybdenum atom is distorted octahedral; the molybdenum–nitrosyl fragment is linear with conventional bond lengths and the length of the molybdenum–iodine bond suggests some small degree of π-donor bonding. The pyrazolyl rings are each planar but the inter-ring angles vary markedly, reflecting the bulk of the adjacent unidentate ligand. The molybdenum–nitrogen bond lengths reflect the competitive π-bonding of the *trans* ligand, being long *trans* to the strong π-accepting nitrosyl and short *trans* to the essentially σ-bonding iodide. The molybdenum–sulphur bond to the terminal cyclohexanethiolato-ligand is apparently intermediate in length between single and

Table 3. Atomic positional parameters for the non-hydrogen atoms with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I	0.310 6(3)	0.192 3(2)	0.040 8(2)
Mo	0.270 5(3)	0.388 8(3)	0.035 8(2)
S	0.092 7(8)	0.386 7(9)	−0.003 0(6)
O	0.222 1(21)	0.394 4(20)	−0.142 4(16)
N(1)	0.245 1(26)	0.394 4(25)	−0.069 6(20)
N(2)	0.299 5(21)	0.376 7(21)	0.171 8(17)
N(3)	0.378 4(23)	0.436 1(22)	0.230 1(18)
N(4)	0.443 1(21)	0.408 6(18)	0.089 9(17)
N(5)	0.497 8(24)	0.451 8(23)	0.165 1(19)
N(6)	0.284 0(20)	0.544 2(18)	0.060 6(15)
N(7)	0.366 3(23)	0.576 1(21)	0.138 3(18)
C(1)	0.170(3)	0.256(3)	0.172(3)
C(2)	0.259(3)	0.327(3)	0.213(2)
C(3)	0.307(3)	0.348(3)	0.293(3)
C(4)	0.380(3)	0.418(3)	0.304(3)
C(5)	0.462(4)	0.472(4)	0.387(3)
C(6)	0.481(3)	0.337(3)	−0.023(3)
C(7)	0.513(3)	0.385(3)	0.064(2)
C(8)	0.611(3)	0.415(3)	0.119(2)
C(9)	0.601(3)	0.454(3)	0.187(2)
C(10)	0.683(3)	0.496(3)	0.268(2)
C(11)	0.142(3)	0.615(3)	−0.073(2)
C(12)	0.234(3)	0.620(3)	0.012(2)
C(13)	0.282(3)	0.701(3)	0.062(2)
C(14)	0.366(3)	0.674(3)	0.146(2)
C(15)	0.443(3)	0.734(3)	0.217(3)
C(16)	0.015(4)	0.370(4)	−0.111(3)
C(17)	−0.095(4)	0.406(4)	−0.137(3)
C(18)	−0.179(5)	0.392(5)	−0.239(4)
C(19)	−0.180(4)	0.285(4)	−0.251(3)
C(20)	−0.074(5)	0.244(4)	−0.232(4)
C(21)	0.008(4)	0.260(3)	−0.130(3)
B	0.441(4)	0.511(3)	0.204(3)

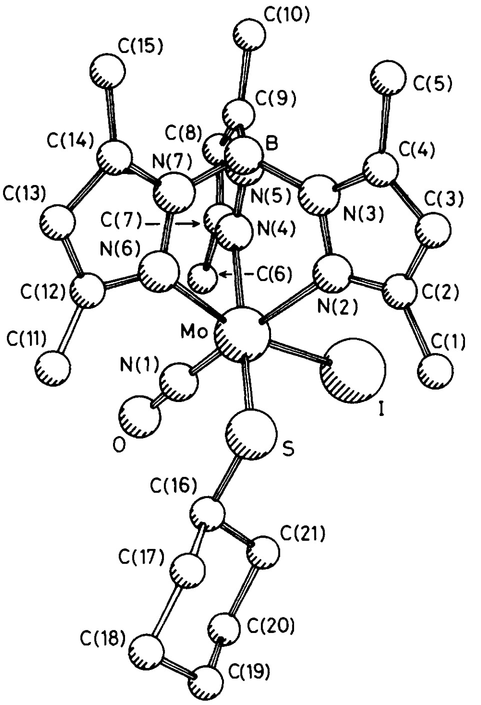

Figure. Molecular structure of $[Mo\{HB(Me_2pz)_3\}(NO)I(SC_6H_{11})]$ with the atom labelling

double (see below). The Mo–S–C angle is much smaller than in comparable alkoxy compounds,[1,2] as might be expected for a second-period donor atom; however, the approximate eclipsing of molybdenum–nitrosyl and sulphur–carbon bonds about the molybdenum–sulphur bond [torsion angle N(1)–Mo–S–C(16) is +10.4°] suggests a similar mode of bonding to that found in the alkoxy compounds. The cyclohexyl group has a chair conformation with the sulphur as an equatorial substituent; the bond lengths and angles are within 3σ of 1.54 Å and 110°. The steric crowding around the molybdenum atom would not permit the cyclohexanethiolato-ligand to adopt its more familiar bridging (μ-SR) role.

In (1; X = I, Y = SC_6H_{11}), the Mo-S distance (2.31 Å) is 0.34 Å shorter than that calculated from covalent radii. Systems formally containing Mo=S bonds exhibit interatomic distances in the range 1.94—2.08 Å.[11] It is difficult to make a meaningful comparison of the Mo-S distances reported here with species containing authentic Mo-S single bonds because of the problem of formulating the oxidation state on (1; X = I, Y = SR), which could be +2, +3, or +4 depending on the formal charge allocated to the NO group. A difficulty also arises because of the possibility of Mo-S $d_\pi \rightarrow d_\pi$ bonding when the metal is in a lower oxidation state. Most formal Mo-S single bond distances appear to fall within the range 2.33—2.55 Å, the lowest occurring in $[Mo(S_2C_2H_2)_3]$,[12] a dithiolene complex which formally contains Mo^{VI} (although this oxidation state formalism is not especially meaningful [13]), and the highest in $[MoCl(CO)_3(MeSCH_2CH_2SMe)(SnCl_3)]$, a complex of Mo^{II}.[14] In the dithiolene complex, whatever the actual oxidation state of the metal some $S \rightarrow Mo(p_\pi \rightarrow d_\pi)$ bonding might be expected, and consequently we suggest that the short molybdenum–sulphur distance in (1; X = I, Y = SC_6H_{11}) is best explained in terms of the normal σ-bond interaction supplemented by donation of p-electrons from S to the metal to compensate for the co-ordinative unsaturation of the metal and its powerful electron-withdrawing properties.

Table 4. Selected bond lengths (Å) and bond angles (°) with estimated standard deviations in parentheses

Mo–N(2)	2.27(3)	C(16)–C(17)	1.51(8)
Mo–N(4)	2.22(3)	C(17)–C(18)	1.67(9)
Mo–N(6)	2.18(3)	C(18)–C(19)	1.49(9)
Mo–I	2.769(5)	C(19)–C(20)	1.51(9)
Mo–N(1)	1.74(4)	C(20)–C(21)	1.66(8)
N(1)–O	1.18(5)	C(21)–C(16)	1.55(7)
Mo–S	2.313(12)		
S–C(16)	1.73(5)		
N(3)–B–N(5)	107(3)	I–Mo–S	100.5(3)
N(3)–B–N(7)	110(3)	I–Mo–N(1)	90.8(12)
N(5)–B–N(7)	108(4)	I–Mo–N(2)	87.9(8)
Mo–N(1)–O(1)	176(3)	I–Mo–N(4)	86.2(8)
Mo–S–C(16)	111.9(18)	I–Mo–N(6)	163.9(7)
S–C(16)–C(17)	109(4)	S–Mo–N(1)	92.2(12)
S–C(16)–C(21)	109(4)	S–Mo–N(2)	86.5(8)
C(17)–C(16)–C(21)	108(4)	S–Mo–N(4)	170.1(8)
C(16)–C(17)–C(18)	114(5)	S–Mo–N(6)	93.1(8)
C(17)–C(18)–C(19)	103(5)	N(1)–Mo–N(2)	177.9(14)
C(18)–C(19)–C(20)	114(5)	N(1)–Mo–N(4)	95.0(14)
C(19)–C(20)–C(21)	108(5)	N(1)–Mo–N(6)	97.4(14)
C(20)–C(21)–C(16)	108(4)	N(2)–Mo–N(4)	86.5(11)
		N(2)–Mo–N(6)	84.3(10)
		N(4)–Mo–N(6)	79.4(10)

Acknowledgements

We are grateful to the S.E.R.C. for support of this work (to J. M. A. S.) and for funds to purchase the diffractometer, to Climax Molybdenum (AMAX) for a gift of molybdenum hexacarbonyl, and to Mr. Alan Jones for technical assistance.

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Received 29th *March* 1982; *Paper* 2/530