Reactions of Molybdenum Oxo-complexes with Substituted Hydrazines. Part 3.[†] The Preparation and Crystal and Molecular Structure of an Oxo-[dimethylhydrazido(2−)]-complex [‡]

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The oxo-complexes $[MoO_2L_2]$ [L = oxinate, S_2CNMe_2, S_2CNEt_2, $S_2CN(CH_2)_5$, or S_2CNPh_2] react with the hydrazines R_2NNH_2 [R_2 = Me_2, $(CH_2)_5$, or Ph_2] to give the hydrazido(2−)-complexes $[Mo(NNR_2)OL_2]$. The crystal and molecular structure of $[Mo(NNMe_2)O(S_2CNMe_2)_2]$ has been determined by single-crystal *X*-ray diffraction methods. The complex crystallises in the monoclinic system, space group $P2_1/c$ with a = 7.897, b = 13.854, c = 15.517 Å, β = 103.1°, and Z = 4. The molecule has a distorted octahedral configuration with the hydrazido-ligand bonded linearly in a position *cis* to the oxo-group. The Mo–N and N–N distances of 1.799 and 1.288 Å are consistent with a mode of bonding closer to the representation $\overset{-}{\text{Mo}}{=}\text{N}{=}\overset{+}{\text{N}}\text{R}_2$ than $\text{Mo}{\equiv}\text{N}{-}\text{NR}_2$.

THE chemistry of hydrazido(2−)-complexes is currently of interest since they have been identified as intermediates in the protonation of co-ordinated dinitrogen to ammonia.[1] Dialkylhydrazido(2−)-complexes of the type $[MX(NNR_2)(Ph_2PCH_2CH_2PPh_2)_2]^+$ [$R_2 = Me_2$, $(CH_2)_4$, or $(CH_2)_5$; X = Cl or Br; M = Mo or W] can be generated from co-ordinated dinitrogen by reaction of $[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W) with methyl iodide or the dihalides $Br[CH_2]_nBr$ (n = 4 or 5).[2] 1,1-Dialkylhydrazines have also been used to prepare hydrazido(2−)-complexes and react with copper(II) bromide in aqueous solution to give complexes of stoicheiometry $[Cu_3Br_3(NNR_2)_2]$, but unknown structure.[3] Reaction of $[\{Mo(\eta\text{-}C_5H_5)I_2(NO)\}_2]$ with 1,1-dialkylhydrazines gives unusual complexes with hydrazido(2−)-ligands asymmetrically bridging two molybdenum atoms.[4] We now report the full details [5] of the preparation of oxomolybdenum 1,1-disubstituted hydrazido(2−)-complexes, by the reaction of dioxomolybdenum complexes with 1,1-disubstituted hydrazines, and the crystal and molecular structure of an oxo[dimethyl hydrazido(2−)]-complex.

RESULTS AND DISCUSSION

The complexes $[MoO_2L_2]$ [L = oxinate, S_2CNMe_2, S_2CNEt_2, $S_2CN(CH_2)_5$, or S_2CNPh_2] react with the hydrazines R_2NNH_2 [$R_2 = Me_2$ or $(CH_2)_5$] to give the oxo[hydrazido(2−)]-complexes $[Mo(NNR_2)OL_2]$ in yields of 60—80%. Even the use of a large excess of hydrazine and high-boiling solvents did not cause replacement of the residual oxo-group. In the case of $R_2 = Ph_2$ and L = S_2CNMe_2 a yellow product apparently containing two Ph_2NN moieties is obtained and the properties and structure of this complex will be discussed elsewhere. The complexes prepared in this manner are summarised in Table 1.

Properties.—The oxo[hydrazido(2−)]-complexes are air-stable crystalline pink to orange compounds which are monomeric and non-conducting in 1,2-dichloroethane. The i.r. spectra (see Table 1) show strong

TABLE 1

Molybdenum hydrazido(2−)-complexes

No.	Complex	Colour (m.p., θ_c/°C) [a]	M [b]	ν(Mo=O) [c] cm^{-1}	^{1}H N.m.r. data [d]		Analysis (%) [b]			
					Hydrazido-protons	Dithio-carbamato-protons	C	H	N	S
(1)	$[Mo(NNMe_2)O(S_2CNMe_2)_2]$	Pink (220—222)	432 (410)	889	3.76(s, 6)	3.39(s, 12)	23.4 (23.4)	4.6 (4.4)	13.5 (13.7)	31.3 (31.2)
(2)	$[Mo(NNMe_2)O(S_2CNEt_2)_2]$	Pink (165—167)	487 (466)	885	3.76(s, 6)	1.29(t, 12) 3.5 4.0(m, 8)	30.1 (30.8)	5.5 (5.6)	11.9 (12.0)	
(3)	$[Mo(NNMe_2)O\{S_2CN(CH_2)_5\}_2]$	Red (196—198)	528 (490)	892	3.78(s, 6)	1.70(br s, 12) 3.98(br s, 8)	33.8 (34.3)	5.4 (5.3)	11.0 (11.4)	
(4)	$[Mo(NNMe_2)O(S_2CNPh_2)_2]$	Red (204—206)		894	3.71(s, 6)	7.2—7.4(m, 20	50.8 (51.0)	4.2 (4.0)	8.5 (8.5)	19.7 (19.5)
(5)	$[Mo\{NN(CH_2)_5\}O(S_2CNMe_2)_2]$	Red (193—195)	510 (450)	887	1.63(br s, 6) 3.97(br s, 4)	3.34(s, 12)	29.2 (29.3)	5.1 (4.9)	12.0 (12.4)	
(6)	$[Mo(NNPh_2)O\{S_2CN(CH_2)_5\}_2]$	Orange (209—211)	640 (614)	877	7.0—7.3(m, 10)	1.69(br s, 12) 3.93(br s, 8)	46.8 (46.9)	4.9 (4.9)	9.4 (9.1)	
(7)	$[Mo(NNMe_2)O(oxinato)_2]$	Orange (268—271)		897	3.74(s, 6)		51.9 (52.4)	3.9 (3.9)	12.0 (12.2)	
(8)	$[Mo\{NN(CH_2)_5\}O(oxinato)_2]$	Orange (260—262)	530 (498)	893	1.58(br s 6) 4.01(br s, 4)		55.1 (55.4)	4.5 (4.4)	11.3 (11.2)	

[a] With decomposition. [b] Calculated values are given in parentheses. [c] As Nujol mulls. [d] In CD_2Cl_2 solution.

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[‡] Bis(dimethyldithiocarbamato)[*N*,*N*-dimethylhydrazido(2−)-*N*′]oxomolybdenum(VI).

bands in the 880—900 cm^{-1} region assigned to ν(Mo=O). The ^{1}H n.m.r. spectrum of complex (1) in CD_2Cl_2 at room temperature (Table 1) shows singlets for both the hydrazido(2—)- and dithiocarbamate methyls at 3.76 and 3.39 p.p.m. respectively. The dithiocarbamate methyls are presumably rendered equivalent by exchange processes and the dynamics of this process and those in other molybdenum dithiocarbamato-complexes are under investigation and will be reported in a subsequent publication, together with the reactions of the hydrazido(2—)-complexes with acids, bases, and electrophiles.

Crystal-structure Analysis of (1).—The analysis showed that molecules of (1) have a distorted octahedral configuration with both dithiocarbamates chelating, and that the oxo- and hydrazido(2—)-moieties are mutually *cis*. A view of one molecule is given in Figure 1 and bond lengths and angles are listed in Table 2.

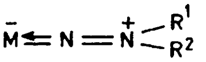
TABLE 2

Selected bond lengths (Å) and angles (°) for $[Mo(N_2Me_2)O(S_2CNMe_2)_2]$ with estimated standard deviations in parentheses

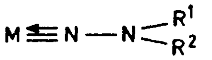
Mo–O	1.708(6)	Mo–S(2)	2.576(2)
Mo–N(1)	1.799(8)	Mo–S(3)	2.519(3)
Mo–S(1)	2.433(3)	Mo–S(4)	2.720(2)
N(1)–Mo–O	104.4(3)	S(1)–Mo–S(4)	86.2(1)
S(1)–Mo–S(2)	70.9(1)	S(3)–Mo–S(1)	151.0(1)
S(3)–Mo–S(4)	67.4(1)	S(4)–Mo–S(2)	80.0(1)
S(3)–Mo–S(2)	92.2(1)		
S(1)–C(1)	1.742(9)	N(3)–C(5)	1.506(13)
S(2)–C(1)	1.743(10)	N(3)–C(6)	1.524(13)
C(1)–N(3)	1.300(12)		
S(1)–C(1)–S(2)	113.1(6)	C(1)–N(3)–C(5)	120.1(9)
C(1)–N(3)–C(6)	120.6(9)	C(5)–N(3)–C(6)	119.3(9)
S(3)–C(2)	1.721(10)	N(4)–C(7)	1.491(13)
S(4)–C(2)	1.700(9)	N(4)–C(8)	1.464(12)
C(2)–N(4)	1.349(11)		
S(3)–C(2)–S(4)	115.7(5)	C(2)–N(4)–C(8)	122.1(9)
C(2)–N(4)–C(7)	120.9(8)	C(7)–N(4)–C(8)	116.9(8)
N(1)–N(2)	1.288(10)	N(2)–C(4)	1.529(12)
N(2)–C(3)	1.485(13)		
Mo–N(1)–N(2)	168.0(7)	N(1)–N(2)–C(4)	117.3(9)
N(1)–N(2)–C(3)	121.9(8)	C(3)–N(2)–C(4)	120.8(9)

A number of other substituted hydrazido(2—)-complexes have already been studied crystallographically,[6] and their bonding characteristics briefly discussed. There seems to be an indication that variation of the substituents on the co-ordinated hydrazido(2—)-ligands has little effect on the M–N and N–N bond lengths but that the nature of the other ligands on the metal (or the metal itself) is probably more important in determining which of the two canonical forms (A) and (B) makes the greatest contribution to the structure.[7] Thus, in the complex cation $[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]^+$,[6] the Re–N and N–N distances are 1.75(1) and 1.28(2) Å indicating a predomination of form (A), whereas in the species $[WCl(N_2H_2)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$),[8] with W–N 1.73(1) and N–N 1.37(2) Å, $[WBr(N_2HMe)(dppe)_2]^+$,[7] with W–N 1.77(1) and N–N 1.32(2) Å and $[Mo(N_2EtPh)\{S_2CN(CH_2)_5\}_3]^+$,[7] with Mo–N 1.72(2) and N–N 1.37(2) Å, the structure is intermediate or approaches form (B).

The presence of the strongly π-bonding oxo-function on our molecule represents a significant change from the types of molybdenum and tungsten complexes previously studied and the geometry of the Mo–N–NMe$_2$ unit reflects this. In fact the Mo–N and N–N distances indicate a structure in which (A) predominates, with dimensions similar to those in the rhenium complex. The lower bond order of the Mo–N linkage is also reflected in the Mo–N–N angle of 168°, which shows a greater deviation from linearity than previously found. The accurate planar co-ordination about N(2) (maximum deviation of any atom from the N_2C_2 plane is 0.001 Å) is yet another indication of significant contributions from (A).



(A)



(B)

The explanation for the adoption of this particular bonding pattern in our complex is presumably the presence of the oxo-function, which being a strong π-donating ligand fills up metal orbitals which could otherwise have been utilised in multiple bonding to the NNMe$_2$ ligand. The net result is that the NNMe$_2$ ligand adopts an electronic configuration approximating that of form (A) rather than (B), the latter requiring an additional metal orbital. Viewed in this manner, our results would certainly fit in with the proposals of Mason *et al.*[6]

The greater *trans* effect exerted by the oxo-relative to the hydrazido(2—)-ligand is revealed by the lengthening of Mo–S(4) [2.720(2) Å] compared to Mo–S(2) [2.576(3) Å]. These values compare with unperturbed Mo–S distances of 2.433(3) and 2.519(3) Å for Mo–S(1) and Mo–S(3) respectively. The asymmetric dithiocarbamate ligand *trans* to the oxo-group has a considerably longer C–N distance of 1.344(11) Å compared to 1.300(12) Å in the other dithiocarbamate, reflecting a lower electron

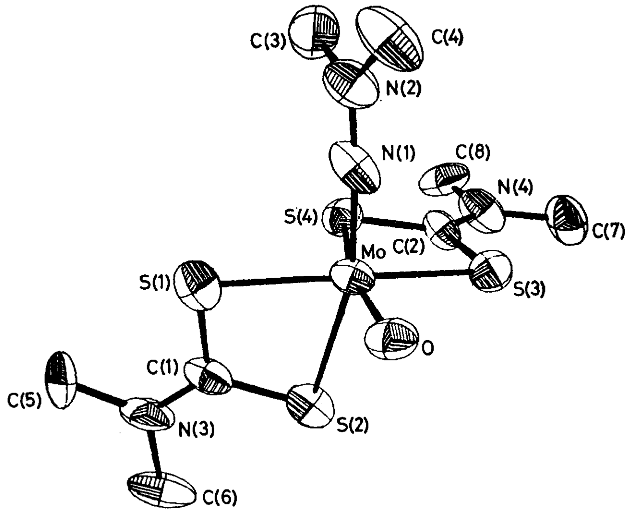


FIGURE 1 The molecular structure of $[Mo(N_2Me_2)O(S_2CNMe_2)_2]$

density on the ligating sulphurs in the less symmetrically bonded dithiocarbamate. Surprisingly there are only relatively small differences in C–S bond lengths between the two dithiocarbamate ligands.

A view of the unit-cell contents is given in Figure 2.

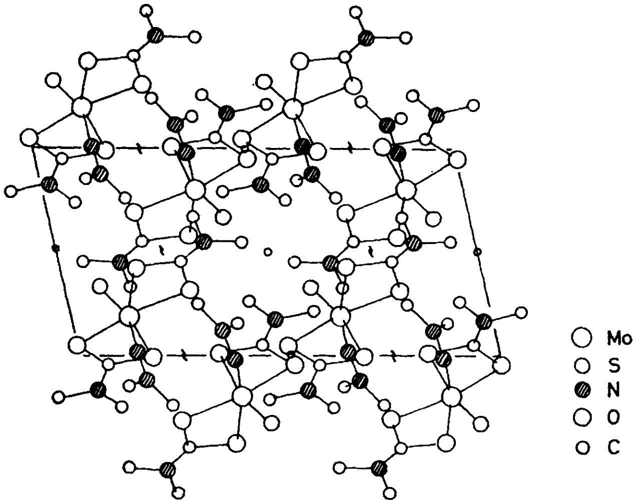


FIGURE 2 Packing diagram of [Mo(N_2Me_2)O(S_2CNMe_2)$_2$] molecules viewed along the b axis

There are no intermolecular contacts less than 3.6 Å, and it is therefore most unlikely that packing forces have any influence on the molecular geometry.

EXPERIMENTAL

Preparations.—All reactions were carried out under dinitrogen, using dry distilled solvents, but recrystallisations were carried out using reagent grade solvents. The hydrazines were purchased from commercial sources. Infrared spectra were recorded on Pye–Unicam SP 1200 and SP 2000 spectrophotometers (Nujol mulls, 200—4 000 cm^{-1}). Varian HA 100 and JEOL PS 100 instruments were used to obtain ^{1}H n.m.r. spectra in $CDCl_3$ or CD_2Cl_2 with tetramethylsilane as internal reference. Molecular-weight determinations were made on a Hitachi–Perkin-Elmer osmometer and microanalyses were performed by A. G. Olney at the University of Sussex.

Bis(dimethyldithiocarbamato)[N,N-*dimethylhydrazido*(2—)-N′]*oxomolybdenum*(VI), (1). Bis(dimethyldithiocarbamato)-dioxomolybdenum(VI) (0.5 g, 1.29 mmol) and 1,1-dimethylhydrazine (0.5 g, 8.3 mmol) were stirred in methanol (30 cm^3) at room temperature for 6 h. The *complex* precipitated as a pinkish solid which was recrystallised as pink needles from dichloromethane–hexane (0.42 g, 75%).

The following complexes were prepared analogously in similar yields using the appropriate oxo-complexes and hydrazines: *bis(diethyldithiocarbamato)*[N,N-*dimethylhydrazido*(2—)-N′]*oxomolybdenum*(VI), (2); [N,N-*dimethylhydrazido*(2—)-N′]*oxobis(pentamethylenedithiocarbamato)molybdenum*(VI), (3); [N,N-*dimethylhydrazido*(2—)-N′]*bis(diphenyldithiocarbamato)oxomolybdenum*(VI), (4); *bis(dimethyldithiocarbamato)oxo*[N,N-*pentamethylenehydrazido*(2—)-N′]-*molybdenum*(VI), (5); [N,N-*diphenylhydrazido*(2—)-N′]*oxobis(pentamethylenedithiocarbamato)molybdenum*(VI), (6); [N,N-*dimethylhydrazido*(2—)-N′]*bis(oxinato)oxomolybdenum*(VI), (7); * *bis(oxinato)oxo*[N,N-*pentamethylenehydrazido*(2—)-N′]*molybdenum*(VI), (8).

X-*Ray Crystallography*.—*Crystal data*. $C_8H_{18}MoN_4OS_4$, $M = 404.2$, Monoclinic, $a = 7.897(5)$, $b = 13.854(8)$, $c = 15.517(8)$ Å, $\beta = 103.1(1)°$, $U = 1\,653.4$ Å^3, $D_m = 1.66$, $Z = 4$, $D_c = 1.69$ g cm^{-3}, $F(000) = 832$, μ(Mo-K_α) = 11.77 cm^{-1}, space group $P2_1/c$.

Intensity data were recorded from a crystal mounted about a^* on a General Electric XRD6 manual diffractometer, using Mo-K_α radiation, in a manner described in detail previously.[9] Of the 1 616 intensities measured, 905 were considered observed [$I > 3\sigma(I)$] and used in the analysis. The structure was solved by the standard heavy-atom technique and refined by full-matrix least squares to a final R value of 0.045. Programs, computers, and procedures were also the same as those described in ref. 9, and the median F^* value used in the Hughes-type weighting scheme was on an absolute scale. The final atomic fractional co-ordinates are given in Table 3. Lists of observed and calculated structure factors are available as Supplementary Publication No. SUP 22557 (5 pp.).†

TABLE 3

Final positional parameters (× 10^4) with estimated standard deviations in parentheses

Atom	X	Y	Z
Mo	1 955(2)	3 106(1)	1 370(1)
S(1)	3 124(6)	3 164(4)	2 961(3)
S(2)	4 256(6)	1 769(3)	1 810(3)
S(3)	467(6)	2 214(3)	−9(3)
S(4)	−92(6)	1 641(3)	1 711(3)
O	3 282(15)	3 735(8)	843(9)
N(1)	815(20)	3 919(10)	1 385(10)
N(2)	−1 212(21)	4 351(11)	1 470(11)
N(3)	5 509(18)	1 790(12)	3 568(11)
N(4)	−1 697(19)	784(11)	209(11)
C(1)	4 464(23)	2 182(12)	2 889(14)
C(2)	−562(22)	1 468(11)	597(12)
C(3)	−2 413(29)	3 915(17)	1 971(14)
C(4)	−1 593(27)	5 342(14)	1 034(16)
C(5)	5 492(27)	2 121(15)	4 490(13)
C(6)	6 728(25)	975(15)	3 442(17)
C(7)	−2 138(27)	661(15)	−771(14)
C(8)	−2 602(25)	518(14)	718(15)

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* oxinate = Quinolin-8-olate.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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