The Chemistry of Molybdenum Oxohydrazido(2—)-complexes; the *X*-Ray Crystal Structure of [MoO(NNMe$_2$)(C$_9$H$_6$NO)$_2$].† A Complex with a Bent Hydrazido(2—)-ligand

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The oxohydrazido-complexes $[MoO(NNR_2)(S_2CNR'_2)_2]$ [R_2 = Me$_2$, MePh, or $(CH_2)_5$; R'_2 = Me$_2$, Et$_2$, or $(CH_2)_5$] react with an excess of acids HX (X = Cl, Br, SPh, $\frac{1}{2}$1,2-$O_2C_6H_4$, or $\frac{1}{2}$2,3-$S_2C_6H_3CH_3$) to give seven-co-ordinate $[MoX_2(NNR_2)(S_2CNR'_2)_2]$. For X = Cl or Br these complexes react with $NaS_2CNR'_2$ to give the cationic seven-co-ordinate $[Mo(NNR_2)(S_2CNR'_2)_3]^+$. The complex $[MoO(NNMe_2)(C_9H_6NO)_2]$ gives NHMe$_2$, NH$_3$, and Me$_2$NNH$_2$ on reaction with HCl and an *X*-ray crystal structure shows a significantly bent NNMe$_2$ ligand with Mo–N–N 155.5°. The Mo–N and N–N distances of 1.800(9) and 1.28(1) Å lie within the range found for other hydrazido(2–)-complexes. The complex crystallises in the space group $P2_1/a$ with a = 19.00(5), b = 14.59(4), c = 7.26(2) Å, and γ = 102.90(6)° for Z = 4. The final conventional error index, R, is equal to 0.087 for 2 747 reflections.

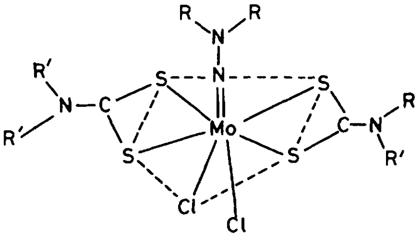
HYDRAZIDO(2—)-complexes are persistent intermediates in the formation of ammonia or ammines from molybdenum tertiary phosphine dinitrogen complexes.[1] However, the detailed mechanism by which these ligands are degraded to reduced nitrogen products is not yet understood. As part of a systematic study of the factors determining the reactivity and structural parameters of the hydrazido(2—)-ligand we here report an investigation of the reactivity of complexes of the type $[MoO(NNR_2)L_2]$ [L = C_9H_6NO (quinolin-8-olate) or dithiocarbamate].

RESULTS AND DISCUSSION

Preparation of Complexes $[MoX_2(NNR_2)(S_2CNR'_2)_2]$.—It was of particular interest to study the reactions of these oxohydrazido(2—)-complexes with acids, to see if the hydrazido(2—)-ligand could be converted into hydrazido(1—) and thence to dialkylamine and ammonia. However, the complexes $[MoO(NNR_2)(S_2CNR'_2)_2]$[2] ($R_2$ = Me$_2$, Ph$_2$, MePh, or C$_5$H$_{10}$; R'_2 = Me$_2$, Et$_2$, MePh, or C$_5$H$_{10}$) react with anhydrous halogen acids in organic solvents at room temperature according to equation (1), X = Cl or Br. The oxo-group is preferentially attacked by acid to generate a series of seven-co-ordinate hydrazido(2—)-complexes. The complexes prepared in this way are summarised in Table 1, together with analytical and spectroscopic data.

$$[MoO(NNR_2)(S_2CNR'_2)_2] + 2HX \longrightarrow [MoX_2(NNR_2)(S_2CNR'_2)_2] + H_2O \quad (1)$$

The dihalidohydrazido(2—)-complexes are pale brown or tan air-stable crystalline solids and are monomeric in 1,2-dichloroethane solution and non-electrolytes in nitrobenzene solution. The dihalido-complexes react rapidly with water to regenerate the oxo-starting material. The far-i.r. spectra of the dichloro-complexes show two strong bands at *ca.* 260 and 290 cm^{-1} assigned to metal–chlorine stretching frequencies. This is consistent with the presence of *cis* chloro-groups and an overall structure (see below) analogous to that of $[MoOCl_2(S_2CNEt_2)_2]$[3] and $[MoCl_2(NPh)(S_2CNEt_2)_2]$.[4] Indeed the reaction with acid parallels that of $[MoO(NPh)(S_2CNEt_2)_2]$ where protic attack also occurs at oxygen rather than at the imido-ligand.[4]



Reactions with Thiophenol, 1,2-Dithiols, and Catechol.—Other acidic substrates such as thiophenol react analogously with $[MoO(NNR_2)(S_2CNR'_2)_2]$ in methanol at room temperature to give $[Mo(SPh)_2(NNR_2)(S_2CNR'_2)_2]$. This reaction contrasts with that of thiophenol with $[MoO_2(S_2CNR'_2)_2]$ where the product is the dimeric, triply bridged species $[(R'_2NCS_2)OMo(\mu\text{-}SPh)_2(\mu\text{-}O)MoO(S_2CNR'_2)]$.[5] Potentially bidentate ligands such as catechol or toluene-2,3-dithiol react similarly to thiophenol to give complexes of the type $[Mo(NNR_2)L'(S_2CNR'_2)_2]$ (L' = $C_6H_4O_2$ or $CH_3C_6H_3S_2$). An excess of catechol gave different rather labile complexes formulated as $[Mo(NNR_2)\{C_6H_4(OH)O\}_2(S_2CNR'_2)_2]$, only stable in the presence of excess of catechol. The presence of hydroxy-groups was indicated by strong i.r. bands at *ca.* 3 400 cm^{-1}.

The physical and spectroscopic data are summarised in Table 1. Although air-stable in the solid state the complexes are only stable in dry deoxygenated solvents or in the presence of excess of ligands. They are monomeric and non-conducting in 1,2-dichloroethane solution. Two equivalent sets of dithiocarbamato-methyl resonances are observed in the ^{1}H n.m.r. spectra, suggesting a structure completely analogous to the dihalido-complexes shown.

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† [*N*,*N*-Dimethylhydrazido(2—)-*N'*]oxobis(quinolin-8-olato)-molybdenum(VI).

TABLE 1

Molybdenum(VI) hydrazido(2—)-complexes

Complex	Colour	Analysis (%) [a]			$\tilde{\nu}$(Mo–Cl)/cm^{-1}	^{1}H N.m.r. data (p.p.m.) [b]	
		C	H	N		Hydrazido	Dithiocarbamate
(1) $[MoCl_2(NNMe_2)(S_2CNMe_2)_2]$	Fawn	20.8 (20.6)	4.2 (3.9)	11.7 (12.0)	260, 292	3.28 (s, 6)	3.15 (s, 12)
(2) $[MoCl_2(NNMe_2)(S_2CNEt_2)_2]$	Fawn	28.2 (27.7)	4.9 (4.9)	10.7 (10.7)	260, 294	3.41 (s, 6)	1.32 (t, 12), 3.75 (q, 8)
(3) $[MoCl_2(NNMe_2)\{S_2CN(CH_2)_5\}_2]$	Tan	31.1 (30.8)	5.3 (4.7)	9.9 (10.1)	245, 285	3.35 (s, 6)	1.75 (s, 12), 3.75 (s, 8)
(4) $[MoCl_2\{NN(CH_2)_5\}(S_2CNMe_2)_2]$	Tan	26.3 (26.1)	4.7 (4.4)	10.9 (11.1)	258, 290	1.8 (m, 6), 3.7 (m, 4)	3.38 (s, 12)
(5) $[MoCl_2(NNMePh)(S_2CNMe_2)_2]$	Orange	29.7 (29.6)	3.9 (3.8)	10.5 (10.6)	265, 294	3.95 (s, 3), 7—7.6 (m, 5)	3.33 (s, 12)
(6) $[MoCl_2(NNPh_2)(S_2CNMe_2)_2]$	Orange	36.3 (36.3)	4.1 (4.1)	9.4 (9.5)	262, 300	7.2—7.6 (m, 10)	3.27 (d, 12)
(7) $[MoBr_2(NNMe_2)(S_2CNMe_2)_2]$	Fawn	17.7 (17.3)	4.0 (3.3)	9.9 (10.1)		3.37 (s, 6)	3.25 (d, 12)
(8) $[MoBr_2(NNMe_2)(S_2CNEt_2)_2]$	Fawn	23.8 (23.6)	4.4 (4.3)	9.1 (9.2)		3.25 (s, 6)	1.28 (m, 12), 3.60 (m, 8)
(9) $[MoBr_2(NNMe_2)\{S_2CN(CH_2)_5\}_2]$	Tan	26.6 (26.5)	4.2 (4.1)	8.7 (8.7)		3.28 (s, 6)	1.65 (m, 12), 3.64 (m, 8)
(10) $[Mo(NNMe_2)(SPh)_2(S_2CNMe_2)_2]$	Brown	39.2 (39.2)	4.5 (4.6)	8.9 (9.1)		2.84 (s, 6)	3.17 (d, 12)
(11) $[Mo(NNMe_2)(C_6H_4O_2)(S_2CNMe_2)_2]$	Purple	34.0 (33.5)	4.8 (4.4)	11.2 (11.2)		3.21 (s, 6)	3.42 (d, 12)
(12) $[Mo(NNMe_2)(C_7H_6S_2)(S_2CNMe_2)_2]$	Black	32.8 (32.8)	4.4 (4.4)	9.7 (10.2)		3.25 (s, 6)	3.35 (m, 12)
(13) $[Mo(NNMe_2)(S_2CNMe_2)_3]BPh_4$	Brown	50.3 (50.4)	5.4 (5.3)	8.4 (8.4)		3.49 (s, 6)	3.18 (q, 18)
(14) $[Mo(NNMe_2)(S_2CNEt_2)_3]BPh_4$	Brown	53.2 (53.6)	6.5 (6.1)	7.6 (7.6)		3.36 (s, 6)	1.25 (m, 18), 3.7 (m, 12)
(15) $[Mo(NNMePh)(S_2CNMe_2)_3]BPh_4$	Brown	54.1 (53.6)	4.9 (5.1)	8.0 (7.8)		3.38 (s, 3), 7—7.6 (m, 5)	3.25 (q, 18)
(16) $[Mo(NNPh_2)(S_2CNMe_2)_3]BPh_4$	Brown	56.4 (56.4)	5.3 (5.0)	7.4 (7.3)		6.8—7.6 (m, 10)	3.17 (q, 18)

[a] Calculated values are given in parentheses. [b] s = Singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Multiplicities and relative intensities are given in parentheses.

Preparation of the Complexes $[Mo(N_2R_2)(S_2CNR'_2)_3]^+$.—The dihalido-complexes $[MoX_2(NNR_2)(S_2CNR'_2)_2]$ react with the sodium dithiocarbamate salts in refluxing methanol to produce the cationic species $[Mo(N_2R_2)(S_2CNR'_2)_3]^+$ which were generally isolated as tetraphenylborate salts. The preparation of analogous compounds by the alkylation of diazenido-complexes $[Mo(N_2R)(S_2CNR'_2)_3]$ has already been reported.[6] The *X*-ray crystal structure of $[Mo(NNMePh)\{S_2CN(CH_2)_5\}_3]BPh_4$[7] revealed that the complexes have pentagonal-bipyramidal structures with the hydrazido-ligand in one of the apical sites.

The ^{1}H n.m.r. spectra of complexes (13)—(16) are summarised in Table 1 together with analytical data. They are entirely consistent with the pentagonal-bipyramidal structure, a sharp 1 : 2 : 1 : 2 quartet being observed in all cases. At higher temperatures (*e.g. ca.* 70 °C in pyridine) the quartet resonances coalesce as the dithiocarbamato-alkyls become equivalent. However, the spectra are independent of solvent in marked contrast to the complexes $[Mo(N_2R)(S_2CNMe_2)_3]$ where the solvents have a strong influence.[8] The reasons for the complex solvent dependence are not at all clear at this stage. Stereochemical rigidity of seven-co-ordinate metal dithiocarbamato-complexes is comparatively unusual. The only other examples are $[Mo(NO)(S_2CNMe_2)_3]$, $[MoN(S_2CNMe_2)_3]$, $[Ti(\eta\text{-}C_5H_5)(S_2CNMe_2)_3]$, and $[Mo(N_2R)(S_2CNMe_2)_3]$. The related complexes $[MoCl(S_2CNR_2)_3]$ are fluxional at room temperature and $[TiCl(S_2CNMe_2)_3]$ remains fluxional down to −90 °C.

Reactions of $[MoO(NNMe_2)(C_9H_6NO)_2]$ *with Hydrogen Halides*.—The reactions of the quinolin-8-olate complex $[MoO(NNMe_2)(C_9H_6NO)_2]$ with anhydrous hydrogen halides in both dichloromethane and methanol follow a quite different course from the dithiocarbamato-analogues. The hydrazido(2—)-ligand is converted into approximately equimolar proportions of dimethylhydrazine, dimethylamine, and ammonia. The Me_2NNH_2 and $NHMe_2$ were estimated by gas–liquid chromatography (g.l.c.) and ammonia by the indophenol colour test. This behaviour contrasts with that of other dialkylhydrazido(2—)-complexes where protonation leads exclusively to hydrazine.[9] In this instance, the reaction is clearly very complex, proceeding through a number of different colour changes and the only isolable metal-containing product is $[MoO_2(C_9H_6NO)_2]$, and this is obtained in *ca.* 10—20% yield. This makes it difficult to assess if the bent geometry of the hydrazido(2—)-complex or a complex decomposition reaction is responsible for the formation of the reduced nitrogen products. Also, the source of the two electrons required to effect reductive cleavage of the hydrazido(2—)-ligand is uncertain as the metal formally has none available.

The Crystal Structure of $[MoO(NNMe_2)(C_9H_6NO)_2]$.—Atomic positional parameters for $[MoO(NNMe_2)(C_9H_6NO)_2]$ are given in Table 2, intermolecular bond distances

TABLE 2

Final positional parameters for $[MoO(NNMe_2)(C_9H_6NO)_2]$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mo	0.215 0(1)	0.280 8(1)	0.152 0(1)
O(1)	0.136 2(3)	0.276 4(5)	0.043 5(10)
O(2)	0.269 4(4)	0.237 4(5)	−0.087 5(11)
O(3)	0.271 0(4)	0.184 3(6)	0.313 1(13)
N(1)	0.134 6(4)	0.208 2(6)	0.379 6(10)
N(2)	0.273 8(4)	0.363 7(6)	0.183 6(12)
N(3)	0.168 9(5)	0.091 6(6)	0.085 4(14)
N(4)	0.155 5(6)	0.001 9(7)	0.088 3(17)
C(1)	0.140 2(6)	0.178 6(9)	0.547 7(16)
C(2)	0.081 4(7)	0.173 2(9)	0.673 0(16)
C(3)	0.081 5(7)	0.194 5(9)	0.614 9(15)
C(4)	−0.049 1(5)	0.256 3(9)	0.360 7(19)
C(5)	−0.045 8(5)	0.291 4(8)	0.189 7(15)
C(6)	0.016 1(5)	0.301 2(7)	0.074 5(16)
C(7)	0.075 7(5)	0.270 6(6)	0.140 9(13)
C(8)	0.073 6(5)	0.234 8(6)	0.317 1(12)
C(9)	0.021 5(5)	0.227 6(7)	0.434 5(14)
C(10)	0.277 2(6)	0.424 0(8)	0.321 0(17)
C(11)	0.322 4(7)	0.514 9(9)	0.316 4(21)
C(12)	0.366 1(7)	0.541 9(9)	0.170 1(20)
C(13)	0.409 2(8)	0.502 0(9)	−0.137 1(22)
C(14)	0.402 4(8)	0.437 3(11)	−0.278 8(24)
C(15)	0.353 4(7)	0.347 7(9)	−0.266 8(18)
C(16)	0.312 3(5)	0.323 2(6)	−0.109 6(14)
C(17)	0.318 9(5)	0.391 9(6)	0.032 3(15)
C(18)	0.365 5(6)	0.480 4(7)	0.019 5(17)
C(19)	0.105 0(10)	−0.054 8(11)	−0.044 1(30)
C(20)	0.193 2(11)	−0.045 5(12)	0.221 6(33)

and angles in Tables 3 and 4 respectively. An ORTEP representation of the molecular structure with the atom-labelling scheme is shown in Figure 1, a stereo view of the packing of the molecules in the unit cell in Figure 2.

TABLE 3

Selected bond lengths (Å) for $[MoO(NNMe_2)(C_9H_6NO)_2]$

Mo–O(1)	2.123(7)	N(3)–N(4)	1.28(1)
Mo–O(2)	2.019(8)	N(4)–C(19)	1.47(2)
Mo–O(3)	1.671(9)	N(4)–C(20)	1.47(3)
Mo–N(1)	2.250(8)		
Mo–N(2)	2.302(8)		
Mo–N(3)	1.800(9)		
O(1)–C(7)	1.34(1)	O(2)–C(16)	1.34(1)
C(7)–C(8)	1.38(1)	C(16)–C(17)	1.42(1)
C(8)–C(9)	1.43(1)	C(17)–C(18)	1.40(1)
C(7)–C(6)	1.39(1)	C(16)–C(15)	1.38(2)
C(6)–C(5)	1.42(1)	C(15)–C(14)	1.43(2)
C(5)–C(4)	1.34(2)	C(14)–C(13)	1.38(2)
C(4)–C(9)	1.43(2)	C(13)–C(18)	1.40(2)
C(9)–C(3)	1.41(2)	C(18)–C(12)	1.41(2)
C(3)–C(2)	1.37(2)	C(12)–C(11)	1.35(2)
C(2)–C(1)	1.43(2)	C(11)–C(10)	1.41(2)
C(1)–N(1)	1.31(1)	C(10)–N(2)	1.32(2)
N(1)–C(8)	1.38(1)	N(2)–C(17)	1.40(1)

Structure-factor amplitudes, thermal parameters, non-bonding contact distances, and dihedral angles are deposited as Supplementary Publication No. 23255 (22 pp.).*

The structure consists of discrete monomers with a single molecule making up the asymmetric unit of the unit cell. The molybdenum exhibits distorted-octahedral co-ordination.

The bond distance between the molybdenum and the terminal oxygen, 1.67 Å, is short, consistent with a significant degree of multiple-bond character. The bond distance is similar to that found for the dioxo-compound[10] and other molybdenum complexes with terminally bonded oxygen ligands.[11,12] The distance between the molybdenum and the hydrazido-nitrogen, 1.800 Å, is also consistent with a significant degree of multiple-bond character as has been reported previously for other molybdenum complexes containing hydrazido-ligands.[2,13]

TABLE 4

Selected interatomic angles (°) for $[MoO(NNMe_2)(C_9H_6NO)_2]$

O(1)–Mo–O(3)	155.1(4)	Mo–N(3)–N(4)	155.5(9)
N(2)–Mo–N(3)	170.1(4)	N(3)–N(4)–C(19)	121.4(12)
O(2)–Mo–N(1)	161.5(3)	N(3)–N(4)–C(20)	119.2(11)
O(1)–Mo–N(1)	73.8(3)	C(19)–N(4)–C(20)	119.4(12)
O(2)–Mo–N(2)	76.5(3)		
O(3)–Mo–N(3)	100.8(4)		
Mo–O(2)–C(16)	118.3(6)	Mo–O(1)–C(7)	117.4(6)
O(2)–C(16)–C(15)	122.0(9)	O(1)–C(7)–C(6)	123.1(9)
O(2)–C(16)–C(17)	120.6(9)	O(1)–C(7)–C(8)	117.8(8)
C(15)–C(16)–C(17)	117.4(9)	C(6)–C(7)–C(8)	119.1(9)
C(14)–C(15)–C(16)	120.1(12)	C(5)–C(6)–C(7)	118.4(10)
C(13)–C(14)–C(15)	121.5(14)	C(4)–C(5)–C(6)	123.4(11)
C(14)–C(18)–C(18)	119.3(11)	C(5)–C(4)–C(9)	119.2(10)
C(13)–C(18)–C(17)	118.9(11)	C(4)–C(9)–C(8)	117.4(9)
C(12)–C(18)–C(17)	116.7(10)	C(3)–C(9)–C(8)	117.0(10)
C(11)–C(18)–C(18)	120.4(10)	C(2)–C(3)–C(9)	120.4(11)
C(10)–C(11)–C(12)	119.9(12)	C(1)–C(2)–C(3)	120.2(11)
N(2)–C(10)–C(11)	122.4(11)	N(1)–C(1)–C(2)	119.5(11)
C(10)–N(2)–C(17)	117.5(8)	C(1)–N(1)–C(8)	122.4(9)

The hydrazido-ligand occupies a position *cis* to the terminal oxo-ligand as anticipated from the strong π interactions of both these ligands with the molybdenum atom.

The crystallographically distinct quinolin-8-olate (oxinate) ligands are in a *cis,cis* configuration. That

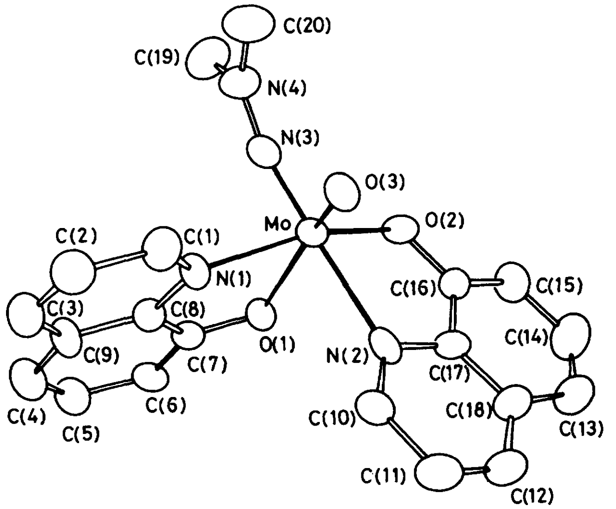

FIGURE 1 Molecular structure of $[MoO(NNMe_2)(C_9H_6NO)_2]$. ORTEP representation; thermal ellipsoids are shown at 40% probability

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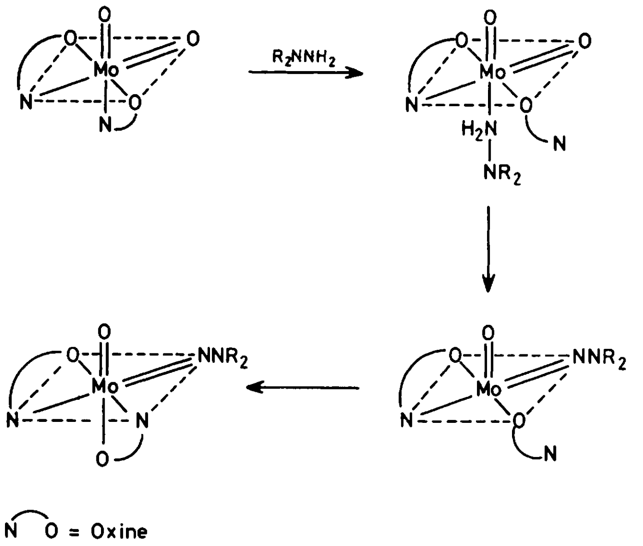
* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

is, the nitrogen-donor atoms occupy relative *cis* positions and the oxygen-donor atoms occupy relative *cis* positions in the co-ordination polyhedron. This arrangement places an oxinate nitrogen-donor atom *trans* to the hydrazido-ligand and an oxinate oxygen-donor atom *trans* to the terminal oxo-group. This contrasts with the dioxo-compounds with oxine [10] and quinolin-8-thiolate [11] in which the oxinate ligands are found in a *cis,trans* configuration with the oxygen atoms occupying relative *trans* positions. In this arrangement, both of the oxinate nitrogen-donor atoms are *trans* to the two terminal oxo-groups. The change in geometry on conversion of an oxo-group into a hydrazido(2—)-group is unexpected and implies a five-co-ordinate intermediate. The oxinate nitrogens are probably weakly bound and the initial reaction with the hydrazine may involve displacement of one of these. Subsequent proton transfer from hydrazine to oxygen and elimination of water generates a five-co-ordinate intermediate (Scheme). Rearrangement and rebinding of the oxinate nitrogen generates the final product.

The Mo–O(1) bond distance, 2.123 Å, is significantly greater than the Mo–O(2) bond distance of 2.019 Å, consistent with a structural *trans* influence on O(1) from the multiply bonded terminal oxygen, O(3). Atom O(2) is *trans* to a singly bonded oxinate nitrogen donor, N(1), and the bond distance to the molybdenum is similar to that found in the dioxo-complex in which the two singly bonded oxinate donor oxygens occupy *trans* positions.



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Similarly, the Mo–N(2) bond distance, 2.302 Å, is significantly greater than the Mo–N(1) bond distance of 2.250 Å, consistent with a structural *trans* influence from the multiply bonded hydrazido-group. In this case, the Mo–N(2) distance is similar to that found in the dioxo-compound in which the two oxinate donor nitrogens are *trans* to the multiply bonded terminal oxygens. Atom N(1) is in a position *trans* to the O(2) oxinate donor oxygen and has a bond distance similar to that expected for a singly bonded nitrogen *trans* to a singly bonded donor atom. The *trans* influence is seen to be weaker for the nitrogen-donor atom than for the oxygen-donor atom, reflecting the relative strengths of the bond between the molybdenum and these donor atoms.

The oxinate rings are planar within the estimated standard deviation, and the molybdenum atom falls outside the plane of the rings, 0.35 Å for ring I and 0.17 Å for ring II, Table 5. The dihedral angle between the two ligand planes is 86.6°, compared to 89.2° for the parent dioxo-compound.[10] The hydrazido-ligand is significantly bent with the Mo–N(3)–N(4) angle, 155.5°, considerably smaller than has been found previously in other hydrazido(2—)-complexes (Table 6). The Mo–N(3) and N(3)–N(4) distances are similar to those reported for hydrazido-complexes (Table 6). The only other reported complex to contain a bent hydrazido(2—)-ligand is $[W(\eta\text{-}C_5H_5)_2(NNHC_6H_4F\text{-}p)]$. Here linearity of the hydrazido(2—)-ligand would impose a formal 20-electron configuration on the metal and this situation is apparently relieved by bending of the Mo–N–N system. Our oxine complex can similarly be regarded as a 20-electron complex if the oxo-ligand is formally a four-electron donor, and the distortion of the hydrazido(2—)-ligand may be the response to this situation. However, in the isoelectronic complex $[MoO(NNMe_2)(S_2CNMe_2)_2]$ the hydrazido(2—)-ligand is rigorously linear (Table 6). Clearly simple electron counting does not provide an explanation and calculations are currently in progress to shed further light on the factors dictating the geometries adopted by the hydrazido(2—)-ligand.

TABLE 5

Deviations (Å) of atoms from selected least-square planes *

O(1)	0.016	O(2)	−0.049	N(3)	0.004
N(1)	−0.042	N(1)	−0.018	N(4)	−0.012
C(1)	0.004	C(10)	−0.004	C(19)	−0.004
C(2)	0.062	C(11)	−0.002	C(20)	0.004
C(3)	0.004	C(12)	0.008	Mo *	0.108
C(4)	−0.029	C(13)	0.037	σ	0.008
C(5)	0.013	C(14)	−0.009	*P*	14.440
C(6)	0.046	C(15)	−0.048	*Q*	−2.125
C(7)	−0.004	C(16)	−0.012	*R*	−4.716
C(8)	−0.039	C(17)	0.001	*S*	1.837
C(9)	−0.030	C(18)	0.007		
Mo *	−0.348	Mo *	0.116		
σ	0.034	σ	0.026		
P	2.987	*P*	15.745		
Q	12.707	*Q*	−7.781		
R	2.419	*R*	3.127		
S	4.012	*S*	2.072		
O(1)	0.087	O(1)	−0.214	O(2)	−0.117
O(2)	−0.076	O(3)	−0.243	N(1)	−0.090
O(3)	0.079	N(2)	0.228	N(2)	0.098
N(1)	−0.090	N(3)	0.229	N(3)	0.109
Mo *	−0.193	Mo *	0.092	Mo *	0.215
σ	0.096	σ	0.264	σ	0.120
P	4.421	*P*	10.565	*P*	14.817
Q	12.490	*Q*	−1.899	*Q*	−7.155
R	2.026	*R*	−6.035	*R*	3.886
S	4.055	*S*	0.866	*S*	2.070

* Atoms marked with asterisks were not included in the calculation of the planes. σ Is the standard deviation of the defining atoms from the plane. *P*, *Q*, *R*, and *S* are the variables for the normal form of the equation of a plane, $Px + Qy + Rz = S$, in direct space.

TABLE 6

Comparison of structural parameters of hydrazido-ligands in molybdenum or tungsten complexes

Complex	Mo–N/Å	N–N/Å	Mo–N–N/°	Ref.
$[MoO(NNMe_2)(C_9H_6NO)_2]$	1.800(9)	1.28(1)	155.5(9)	*a*
$[Mo(NNPh_2)_2(S_2CNMe_2)_2]$	1.790(8)	1.31(1)	169.9(8)	13
$[Mo(NNPhMe)_2(S_2CNMe_2)_2]$	1.790(9)	1.30(1)	172.6(8)	13
$[MoO(NNMe_2)(S_2CNMe_2)_2]$	1.799(8)	1.29(1)	168.0(7) [b]	2
$[Mo(NNPhEt)\{S_2CN(CH_2)_5\}_3]^+$	1.715(6)	1.37(2)	170(2)	7
$[W(\eta\text{-}C_5H_5)_2H(NNHC_6H_4F\text{-}p)]^+$	1.838	1.31	146.3	*c*

[a] This work. [b] Hydrazido-group is bent away from the terminal oxygen ligand. [c] T. Jones, A. J. Hanlan, F. W. B. Einstein, and D. Sutton, *J. Chem. Soc., Chem. Commun.*, 1980, 1078.

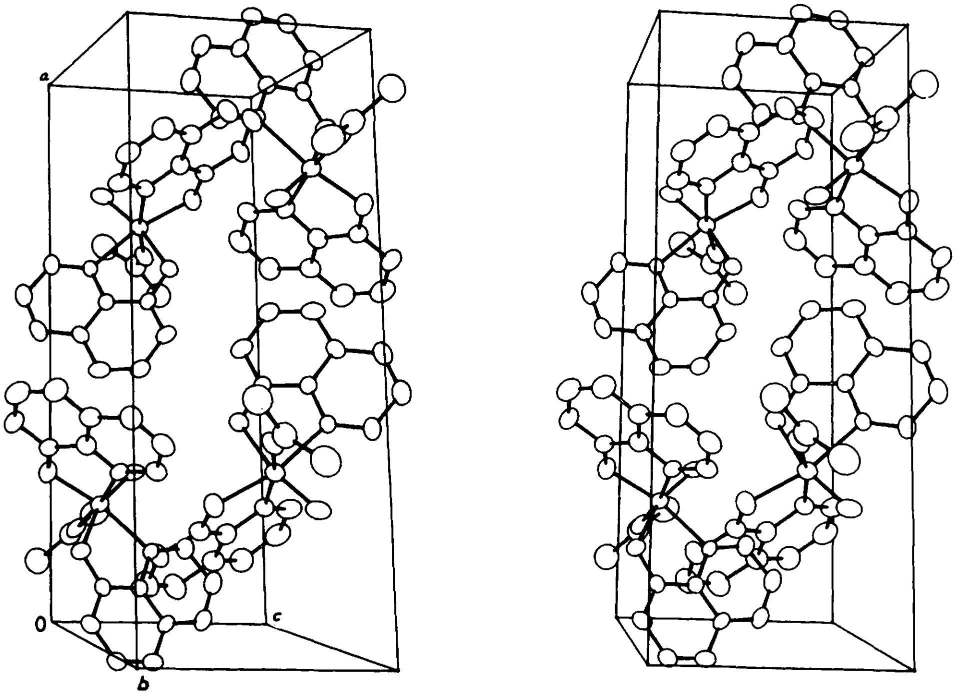

FIGURE 2 Stereoscopic view of the molecular packing in the unit cell

TABLE 7

Geometrical parameters for $[MoO(NNMe_2)(C_9H_6NO)_2]$

(*a*) Dihedral angles/°

O(1), O(2), O(3), N(1) plane; ring I	5.3
O(1), O(2), O(3), N(1) plane; ring II	88.9
O(1), O(2), N(3) face; N(1), N(2), O(3) face	11.0
ring I, ring II	86.6

(*b*) Trigonal twist angles/°

ϕ_{I}	59.7
ϕ_{II}	45.6
ϕ_{III}	50.4

The hydrazido-group is bent towards the terminal oxygen ligand, in a similar fashion to the bis(disubstituted hydrazido)complexes.[13] In contrast, the complex $[MoO(NNMe_2)(S_2CNMe_2)_2]$ exhibits a hydrazido-group which is bent away from the terminal oxygen ligand.[2] It is not clear at this stage of the investigation if this observation reflects an electronic effect or is merely a consequence of steric constraints imposed by crystal packing.

The compound displays distorted-octahedral coordination geometry with pseudo-trigonal faces generated by the O(1),O(2),N(3) and the N(1),N(2),O(3) atoms. These planes are not perfectly parallel due to the short Mo–O(3) and Mo–N(3) bond lengths, defining a dihedral angle of 11°, Table 7. The trigonal twist angle is defined as the dihedral angle between these trigonal faces and is measured from the projections of the lines generated from points defined by the centroid of each trigonal face and each vertex in turn, Figure 3. The twist angles for an ideal octahedron are 60°. They are constrained by steric interactions and chelate bite distances. If the compound is treated like a tris(bidentate) complex, the expected twist angles can be estimated from the ratio of the bond lengths between the metal atom and the donor atoms and the chelate bite distance.[14] This gives a value of *ca.* 40°. The twist angle defined by oxinate ring I is 60° and that defined by oxinate ring II is 46°. The twist angle defined by the N(3),O(3) planes, for which no chelate bite constraints are imposed, is 50°, Table 7. The difference in the twist angles is consistent with a large degree of distortion as required by the presence of non-equivalent donor groups.

The square planes are very distorted and only the

O(1),O(2),O(3),N(1) atoms form a good plane (Table 5). The dihedral angles between the square planes range from 83.8 to 89.5°.

Although the oxinate rings do not stack in a parallel fashion as found in the dioxo-complex [10] and the analogous quinolin-8-thiolate complexes,[11] the oxinate rings are folded towards adjacent unidentate ligands in a similar fashion to the folding reported for those complexes. The dihedral angles formed between the oxinate rings and the respective co-ordination planes are compared in Table 7. This folding has been attributed to intermolecular repulsions between oxinate rings which stack in the solid state.[10] The absence of any stacking interaction in the hydrazido-complex suggests that the presence of folding would better be attributed to the minimisation of intramolecular interactions which are subsequently modified by the stacking and other intermolecular interactions. The shortest intermolecular contact distance of 3.14 Å is found between C(2) and O(1) in an adjacent molecule related by one unit-cell translation along the *c* axis. This interaction forces oxinate ring II towards the hydrazido-group, thus, the folding is found to be significantly greater for this ligand.

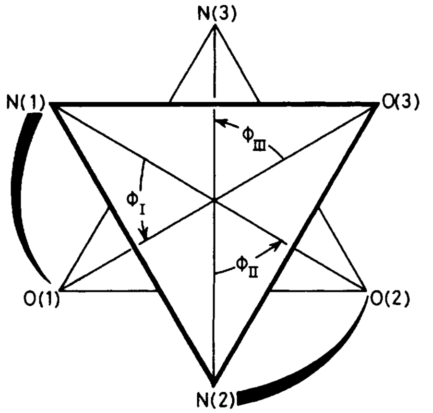

FIGURE 3 Diagram illustrating the trigonal twist angles

EXPERIMENTAL

All manipulations were carried out in conventional Schlenk apparatus under dinitrogen using dry solvents. Carbon, hydrogen, and nitrogen analyses were performed by Mr. and Mrs. A. Olney at the University of Sussex. Infrared spectra were recorded in the range 200—4 000 cm^{-1} as Nujol or hexabutadiene mulls using a Pye–Unicam SP2000 spectrophotometer. Proton n.m.r. spectra were recorded at 100 MHz using a JEOL PS100 spectrometer with tetramethylsilane as standard. Molecular weights were determined in 1,2-dichloroethane solution with a Hitachi–Perkin-Elmer model 115 osmometer.

The complexes [MoO(NNR$_2$)(S$_2$CNR'$_2$)$_2$] were prepared by the literature method,[2] and other reagents were used as purchased without further purification.

Dichlorobis(dimethyldithiocarbamato)[N,N-*dimethylhydrazido*(2−)]*molybdenum*(VI), (1).—The complex [MoO(NNMe$_2$)(S$_2$CNMe$_2$)$_2$] (0.5 g) in dichloromethane (40 cm^3) was treated with a stream of HCl gas for 5 min. The resulting brown solution was evaporated to *ca.* 5 cm^3 at 10^{-2} mmHg * and the complex precipitated as a fawn solid by the addition of diethyl ether (40 cm^3). The product was recrystallised as brown plates from dichloromethane–diethyl ether in 88% yield.

Alternatively the anhydrous HCl can be generated *in situ* by employing methanol as solvent and the addition of chlorotrimethylsilane to give the product in similar yield. Use of aqueous acid yields a product contaminated with bis(oxo)-species.

Complexes (2)—(9) were prepared analogously using the appropriate acids and oxohydrazido(2−)-complexes.

Bis(dimethyldithiocarbamato)[N,N-*dimethylhydrazido*-(2—)]*bis(thiophenolato)molybdenum*(VI), (10).—Thiophenol (1.0 g) was added to a suspension of [MoO(NNMe$_2$)(S$_2$CNMe$_2$)$_2$] (0.5 g) in ethanol (40 cm^3) and the mixture stirred for 1 h at room temperature. The product precipitated as a golden brown crystalline material. Yield 0.6 g, 80%.

Catecholatobis(dimethyldithiocarbamato)[N,N-*dimethylhydrazido*(2−)]*molybdenum* (VI), (11).—The complex [MoO(NNMe$_2$)(S$_2$CNMe$_2$)$_2$] (0.7 g) and catechol (0.2 g) were stirred in methanol (30 cm^3) at room temperature for 0.5 h to precipitate the product as a purple microcrystalline solid in 87% yield. Use of excess of catechol gave an unstable bright red product containing two catecholato-moieties.

Complex (12) was prepared analogously to (11) in 60% yield using toluene-2,3-dithiol.

Tris(dimethyldithiocarbamato)[N,N-*dimethylhydrazido*-(2−)]*molybdenum*(VI) *Tetraphenylborate*, (13).—The complex [MoCl$_2$(NNMe$_2$)(S$_2$CNMe$_2$)$_2$] (0.7 g) and NaS$_2$CNMe$_2$·3H$_2$O (1.0 g) were heated under reflux in methanol (60 cm^3) for 1 h to give a clear yellow solution. A solution of NaBPh$_4$ (0.5 g) in methanol (10 cm^3) was added to the cooled solution to precipitate the complex as a pale yellow solid, recrystallised as small brown prisms from dichloromethane–methanol. Yield 1.0 g, 80%.

Complexes (14)—(16) were prepared in an analogous manner.

The X-*Ray Crystal Structure of* [MoO(NNMe$_2$)(C$_9$H$_6$NO)$_2$].—Orange crystals of [MoO(NNMe$_2$)(C$_9$H$_6$NO)$_2$] in the form of rectangular columns were obtained from a solution of the compound in dichloromethane which was cooled to 4 °C. A crystal of dimensions 0.09 × 0.34 × 0.09 mm was used in the structure determination. The density was determined by the flotation method using a mixture of CCl$_4$ and toluene.

Approximate cell dimensions were obtained from Weissenberg and precession photographs of the crystal using Cu-K_α (λ = 1.5418 Å) radiation. These were used to generate angular co-ordinates for reflections with $8 \leqslant 2\theta < 32°$. Fourteen independent reflections within this range were centred manually in the window of a Siemens AED automatic diffractometer. A least-squares procedure was used to obtain a best fit between the observed and calculated values for the angular co-ordinates of these reflections and the unit-cell parameters were calculated.†

Crystal data. C$_{14}$H$_{24}$MoN$_4$O$_3$, M = 458.33, a = 19.00(5), b = 14.59(4), c = 7.26(2) Å, γ = 102.90(6)°, U = 1 962

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

† The programs used in solving the structure are part of the 'X-RAY' system, revised 1974, from the University of Maryland, U.S.A.

(4) Å^3, $D_m = 1.564(3)$ g cm^{-3}, $Z = 4$, $D_c = 1.552$ g cm^{-3}, $F(000) = 1\,024$, $\mu(\text{Mo-}K_\alpha) = 6.85$ cm^{-1}.

The Weissenberg and precession photographs showed systematic absences indicating the non-conventional space group $P2_1/a$ (c axis unique).

Intensity data were collected using Mo-K_α ($\lambda = 0.710\,73$ Å) radiation with a coupled θ(crystal)—2θ(counter) scan; scan range $4 \leqslant 2\theta \leqslant 54°$. A variable scan rate with a range of 1—10° min^{-1} was used to measure the reflections. Reflections were measured for $\pm h,+k,+l$. The intensity of a single check reflection was measured every 35 reflections during data collection. 2 747 Reflections with $I \geqslant 2.58\sigma(I)$ were used in the solution of the structure. Lorentz and polarisation corrections were applied.

Solution and refinement of the structure. The molybdenum atom was located from a three-dimensional Patterson function. All other non-hydrogen atoms were located from subsequent difference-Fourier maps. No hydrogen atoms were located. Blocked full-matrix least-squares refinement was performed with anisotropic thermal parameters for all atoms. Scattering factors for neutral C, O, N, and Mo were used.[15] The scattering factors for molybdenum were corrected for both the real and imaginary components of anomalous dispersion.[15] An absorption correction was made,[15] approximating the shape of the crystal by a 5 × 16 × 5 grid. The final error index, R, was equal to 0.087 and the final weighted error index, R', was 0.122, where the weighting function was $\sigma(I_{\text{obs}})^{-1}$.

In the final cycle of least-squares refinement, all shifts in atomic positional parameters were less than 0.03 of their estimated standard deviations (e.s.d.s) and all shifts in the anisotropic thermal parameters were less than 0.13 of their e.s.d.s except for the molybdenum atom for which the maximum change was 0.65 of the e.s.d.

The final difference-Fourier map showed a maximum excursion of electron density of approximately 1 e Å^{-3} located near the molybdenum position.

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