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Reactions of Dioxomolybdenum(VI) Hydroxamate and Thiohydroxamate Complexes with Organohydrazines. Structures of Oxohydrazido(2−) Complexes $[MoO(N_2Ph_2)(PhC(X)N(Me)O)_2]$, where X = O and S, and of the Bis-diazenido Complex $[Mo(N_2Ph)_2(PhC(S)N(Me)O)_2]$

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Abstract

The six-coordinate *cis*-oxohydrazido(2−) molybdenum(VI) complexes $[MoO(N_2Ph_2)(PhC(S)N(Me)O)_2]$ (**1**) and $[MoO(N_2Ph_2)(PhC(O)N(Me)O)_2]$ (**3**) were prepared by reaction of *N*,*N*-diphenylhydrazine with the appropriate *cis*-dioxomolybdenum(VI) precursor. The thiohydroxamato and hydroxamate coligands differ only in their S- and O-donor atoms. A bis-hydrazide(2−) complex, $[Mo(N_2Ph_2)_2(PhC(S)N(Me)O)_2]$ (**2**) and a bis-diazenido complex $[Mo(N_2Ph)_2(PhC(S)N(Me)O)_2]$ (**4**) were also prepared. Crystal data are as follows: **1**: monoclinic, $P2_1/c$, $a = 12.182(2)$, $b = 11.238(1)$, $c = 20.035(2)$ Å, $\beta = 90.75(1)°$, $U = 2742.5$ Å^3, $Z = 4$. $R = 0.038$ and $R_w = 0.041$ for 3945 observed reflections. **3**: triclinic, $P\bar{1}$, $a = 12.060(4)$, $b = 17.795(7)$, $c = 14.025(5)$ Å, $\alpha = 93.67(2)$, $\beta = 108.35(2)$, $\gamma = 91.41(2)°$, $U = 2847.8$ Å^3, $Z = 4$. $R = 0.062$ and $R_w = 0.084$ for 5056 observed reflections. **4**: monoclinic, $C2/C$, $a = 24.775(12)$, $b = 9.030(5)$, $c = 14.322(7)$ Å, $\beta = 109.72(8)°$, $U = 3016.2$ Å^3, $Z = 4$. $R = 0.059$ and $R_w = 0.056$ for 1731 observed reflections. The geometries of the *cis*-$MoO(N_2Ph_2)$ fragment in **1** and **3** are similar and indicative of multiply bonded oxo and hydrazide(2−) groups, disposed some 103° relative to each other. The C=O oxygen donor in **3** and C=S sulfur donor in **1** are not in the same configuration with respect to the *cis*-$[MoO(N_2Ph_2)]$ fragment. In the *cis*-bis-diazenido complex (**4**) the two multiply bonded N_2Ph groups have an essentially linear Mo–N–N geometry and an angle of 92.2° between them. The two thiohydroxamate sulfur atoms are *trans* to each other and 2.469(2) Å from the Mo atom.

Preliminary attempts to obtain $[(PhN_2)_2MoL_2]$ bis-diazenido species led to the isolation of partially characterized products which probably contain μ-ethoxo bridged $(PhN_2)_2Mo$ fragments, cocrystallized in the case of L = $PhC(O)N(Ph)O^-$, with benzanilide, PhC(O)N(Ph)H. These observations led to the production of benzanilide from *N*-phenylbenzohydroxamic acid by reaction with phenylhydrazine or hydrazine in the presence of trace quantities of $[MoO_2(acac)_2]$.

Introduction

The structures and reactivities of oxo–metal species are currently of much interest [1–3]. The present paper complements our earlier study on the reactions of *cis*-dioxomolybdenum(VI) hydroxamate and thiohydroxamate complexes with aroyl- and thioaroylhydrazines which yielded a rare example of an end-on bonded hydrazido(1−) complex [4, 5]. In the present study substituted hydrazines such as Ph_2NNH_2 and $PhNHNH_2$ have been employed and have led to condensation of one or both of the oxo groups to form oxohydrazido(2−), bis(hydrazido-(2−)) or bis-diazenido derivatives. Reactions of this kind had been pioneered by Chatt [6], Leigh [7], Dilworth [8], Zubieta [9] and coworkers. It seemed that the nature of the product in such reactions could not always be predicted with any degree of certainty. To try and remedy, and perhaps understand, this situation various aspects of the precursor dioxo complexes such as overall geometry and the make up of the donor atom set in the coligands where controlled, in order to see if this influenced the nature of the products. In a separate paper the results of reactions involving five-coordinate precursors of type $[MoO_2(\text{tridentate Schiff base})]$ will be described, while this paper describes reactions involving a matched pair of six-coordinate precursors $[MoO_2(PhC(X)N(Me)O_2]$, where X = O and S, and which contain two hydroxamate or thiohydroxamate coligands.

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Experimental

General Information

Infrared spectra were determined as Nujol mulls using a Jasco IRA-1 spectrophotometer. ^{1}H NMR spectra were obtained using either a Perkin-Elmer (90 MHz) or a Bruker WH90 spectrometer. They were determined on $CDCl_3$ or $(CD_3)_2SO$ solutions, with all shifts reported downfield from internal Me_4Si. Microanalyses were determined at the Australian Microanalytical Service, Melbourne. Unless otherwise specified solvents were of laboratory grade and were purified and dried by standard methods. The reactions were carried out in air. The dioxomolybdenum(VI) hydroxamate and thiohydroxamate complexes were prepared as described previously [4]. *N,N*-phenylhydrazine in methanol [10] was obtained from the hydrochloride (2.2 g, 0.01 mol) by dissolving the latter in dry degassed methanol (10 ml) and adding to it under nitrogen, a solution of sodium (0.23 g, 0.01 mol) dissolved in dry methanol (5 ml). After standing it in an ice-bath the solution was filtered from sodium chloride. Dilution to 18 ml yielded a solution containing 100 mg of Ph_2NNH_2 per 1 ml. This dry methanolic solution was sealed under nitrogen with a Suba seal and aliquots were syringed out when needed.

Synthesis

[1,1-diphenylhydrazido(2−)-N^2]bis(N-methylbenzothiohydroxamato)oxomolybdenum(VI), [$MoO(N_2Ph_2)(PhC(S)N(Me)O)_2$ (1)

A small scale method involved reacting a suspension of $[MoO_2(PhC(S)N(Me)O)_2]$ (100 mg, 0.22 mmol), diphenylhydrazine hydrochloride (140 mg, 0.63 mmol) and Et_3N (0.09 ml, 0.65 mmol) for 3 h in refluxing methanol (40 ml). Upon leaving the reaction solution to slowly evaporate at room temperature for several days the product crystallized as red–orange cyrstals (110 mg, 80%) suitable for an X-ray crystal structure determination.

A larger scale method involved refluxing a suspension of $[MoO_2(PhC(S)N(Me)O)_2]$ (400 mg, 0.86 mmol) and diphenylhydrazine (2 ml of methanol solution, 1.08 mmol), in dichloromethane (40 ml) until all the initial yellow solid had dissolved ($4\frac{3}{4}$ hours). After filtration of a small amount of light grey powder from the reaction solution, the filtrate was evaporated to a residue. This was then redissolved in a small amount of dichloromethane. A small amount of unreacted $MoO_2(PhC(S)N(Me)O)_2$ (60 mg) was insoluble and so was filtered off. An orange fraction, which contained the product as an orange powder (220 mg, 41%), was isolated by chromatography using a small alumina column (activity I, 0.063–0.2 mm; 15 X 2 cm) and dichloromethane/methanol ($9\frac{1}{2}:\frac{1}{2}$) as the eluent; melting point (m.p.) 130 °C (v. slow decomp.). *Anal.* Found: C, 53,6; H, 4.2; N, 8.8; S, 10.5. Calc. for $C_{28}H_{26}MoN_4O_3S_2$: C, 53.6; H, 4.1; N, 8.9; S, 10.2%. Characteristic infrared peaks (Nujol and HCB): 1585m, 1480m, (N_2Ph_2), 885s (Mo=O). ^{1}H NMR ($CDCl_3$): 7.49–7.33m, 20H(Ph), 3.80s, 3H(Me), 2.97s, 3H(Me).

Bis[1,1-diphenylhydrazido(2−)-N^2]bis(N-methylbenzothiohydroxamato)molybdenum(VI), [$Mo(N_2Ph_2)_2(PhC(S)N(Me)O)_2$] (2)

A suspension of $[MoO_2(PhC(S)N(Me)O)_2]$ (200 mg, 0.43 mmol) and diphenylhydrazine (3 ml of methanol solution, 1.62 mmol) was refluxed in dichloromethane (20 ml) for 3 h. A small amount of light grey by-product was filtered from the dark red solution. The filtrate was evaporated to 5 ml, methanol added and the solution cooled in an ice bath. The yellow powder (300 mg, 87%) which precipitated was filtered and washed with methanol and ether to remove some purple colour. The product was recrystallized from dichloromethane/methanol as yellow flaky crystals which darkened appreciably when left to stand for several weeks; m.p. 132 °C (slow decomp.). *Anal.* Found: C, 60.8; H, 4.9; N, 10.4; S, 7.4. Calc. for $C_{40}H_{36}MoN_6O_2S_2$: C, 60.5; H, 4.5; N, 10.6; S, 8.1%. Characteristic infrared peaks (Nujol and HCB): 1590m, 1550m, 1485s, (N_2Ph_2). ^{1}H NMR ($CDCl_3$): 7.42–6.84m, 30H(Ph), 3.06s, 6H(Me).

[1,1-diphenylhydrazido(2−)-N^2]bis(N-methylbenzohydroxamato)oxomolybdenum(VI), [$MoO(N_2Ph_2)(PhC(O)N(Me)O)_2$] (3)

$[MoO_2(PhC(O)N(Me)O)_2$ (100 mg, 0.23 mmol) and diphenylhydrazine (1 ml of methanol solution, 0.54 mmol) were refluxed in dry methanol (15 ml) for 2 h. The reaction solution was evaporated to 5 ml and the addition of ether caused the precipitation of a small amount of white by-product which was filtered off. Leaving the filtrate to stand overnight allowed the product to form as orange crystals (120 mg, 86%). Single crystals suitable for an X-ray crystal structure determination, which contained half a mole of methanol, were slowly recrystallized from methanol; m.p. 109 °C (v. slow decomp.). *Anal.* Found: C, 56.1; H, 4.6; N, 9.5. Calc. for $C_{28}H_{26}MoN_4O_5\cdot\frac{1}{2}CH_4O$: C, 56.0; H, 4.6; N, 9.1%. Characteristic infrared peaks (Nujol and HCB): 1590s, 1570sh, s, 1565s, 1500s, 1485s (N_2Ph_2), 900s (Mo=O). ^{1}H NMR ($CDCl_3$): 7.68–7.11m, 20H(Ph), 3.57s, 3H(Me), 3.47s, 3H(Me).

Bis(phenyldiazenido)bis(N-methylbenzothiohydroxamato)molybdenum, [$Mo(N_2Ph)_2(PhC(S)N(Me)O_2$] (4)

A suspension of $[MoO_2(PhC(S)N(Me)O)_2]$ (200 mg, 0.43 mmol), phenylhydrazine (0.2 ml, 2.03 mmol) and triethylamine (0.3 ml, 2.16 mmol) was refluxed in methanol (20 ml) for 1 h. The solution was filtered hot and the filtrate cooled to reveal the product as dark red microcrystals (53 mg, 19%). A dark purple oil remained in the methanol. The crystals were recrystallized from dichloromethane/methanol to yield large dark red crystals suitable for an X-ray structure determination; m.p. 181 °C (violent decomp.). *Anal.* Found: C, 52.3; H, 4.1; N, 13.4; S, 10.1. Calc. for $C_{28}H_{26}MoN_6O_2S_2$: C, 52.6; H, 4.1; N, 13.1; S, 10.0%. Characteristic infrared peaks (Nujol and HCB): 1635m, 1600m, 1580sh,s, 1560br,s, 1520sh,s, 1510s, 1470sh,2, 1460s $(PhN_2)_2$. ^1H NMR ($CDCl_3$, 300 MHz): 7.77–7.08m, 20H(Ph), 3.55s, 6H(Me). λ_{max} (MeOH) = 520 nm.

Preliminary studies of the reaction of $PhNHNH_2$ with dioxomolybdenum(VI) hydroxamate and thiohydroxamate complexes without added base

A wide variety of conditions were employed using dried or undried ethanol or methanol as solvents; these included stirring at 0 °C, room temperature or at reflux temperature, generally in air but also under a nitrogen atmosphere. The ratio of $[MoO_2(PhC(O)N(Ph)O)_2]$ or $[MoO_2(PhC(S)N(Me)O)_2]$ to $PhNHNH_2$ was generally 1:3. On the basis of some thirty reactions the following general observations were made: (i) the hydroxamate complexes react more quickly than the thiohydroxamates and a gas is generally evolved from the suspension of the hydroxamate (and sometimes from the thiohydroxamate) complex as $PhNHNH_2$ is added; (ii) a colour change from brown to a red/maroon solution proceeds even at room temperature but more quickly at reflux; (iii) high melting maroon/purple microcrystalline products containing $(PhN_2)_2Mo$ moieties are generally obtained on reflux; the carbon analysis of these products is always much lower than that observed in complex **4**; (iv) room temperature reaction of the thiohydroxamate complexes leads to partial recovery of the starting material; (v) the hydroxamate reactions yield benzanilide as clear crystals or as maroon coloured (doped) crystals at room temperature or at reflux especially on prolonged reaction.

Some typical procedures were as follows.

(a) Reaction of $[MoO_2(PhC(S)N(Me)O)_2]$ with $PhNHNH_2$ in boiling ethanol. Phenylhydrazine (0.15 ml, 1.5 mmol) was added dropwise into a yellow suspension of $MoO_2(PhC(S)N(Me)O)_2$ (0.22 g, 0.5 mmol) in absolute ethanol (20 ml). After a few minutes the reaction began and bubbles of gas were evolved from the suspension while the colour changed first to dark brown and then to dark maroon. After refluxing for 3 h and cooling, fine maroon/purple microcrystals were deposited. These were filtered, washed with cold ethanol and dried; m.p. $\approx$ 180 °C. *Anal.* Found: C, 34.8; H, 3.2; N, 10.9; S, 9.1% (see calc. values for **4**). NB. Repeat preparations of this material yielded samples with similar IR spectra but with variable C, H, N figures although in no case was C higher than 45%. Melting points of some samples were greater than 250 °C. Selected IR bands (Nujol) 1641m, 1610m, 1580sh, 1570m, 1520s,br: $(PhN_2)_2$; 840m,br(?). ^1H NMR ($CDCl_3$, 90 MHz) 7.5–6.7m (Ph), 4.4m, J = 7 Hz and 1.6m, J = 7 Hz (OEt), 3.55s (Me). λ_{max} (acetone) 520 nm.

(b) Reaction of $[MoO_2(PhC(O)N(Ph)O)_2]$ with $PhNHNH_2$. Cold reaction: $[MoO_2(PhC(O)N(Ph)O)_2]$ (0.27 g, 0.5 mmol) was stirred with $PhNHNH_2$ (0.15 ml, 1.5 mmol) in absolute ethanol (20 ml) under a nitrogen atmosphere. Bubbles of gas formed and the solution turned first brown and then maroon within 5 min. After 6 h stirring dark maroon crystals were deposited (0.05 g, m.p. > 250 °C) and these were filtered and washed with ethanol. Concentration of the filtrate yielded other mauve coloured crystals (0.11 g, m.p. 161 °C) which under the microscope appeared to be colourless crystals coated with mother liquor. Chromatographic separation of clear and mauve coloured bands (CH_2Cl_2/EtOH on silica) enabled the colourless product to be crystallized and identified as benzanilide, PhC(O)NH(Ph), by comparison of its m.p. (163 °C), infrared and mass spectra to those of an authentic sample. In particular the ν(CO) and ν(NH) bands at 1670 and 3360 cm^{-1} could be distinguished from those of the ν(NN) bands in the 1640–1500 cm^{-1} region of $(PhN_2)_2$ Mo-containing products such as the initial maroon coloured product.

This cold reaction proceeds the same way in dry methanol. Use of Me_2NNH_2 in chloroform also yielded benzanilide.

Hot reaction: The conditions were as above except that the solution was refluxed for 3 h. On cooling, the deep red coloured solutions deposited fine maroon crystals; m.p. > 250 °C. Selected IR bands (Nujol): 1640m, 1610m, 1580sh, 1570m, 1520s,br: $(Ph_2N_2)_2$; 800–900s,br(?). ^1H NMR ($CDCl_3$, 90 MHz) 7.3–6.8m(Ph), 4.5m, J = 7 Hz and 1.6m, J = 7 Hz (OEt). *Anal.* Found: C, 38.7; H, 4.0; N, 11.2%. NB. Repeat preparations gave some variation in these figures. On standing the filtrate yielded coated crystals of benzanilide which were again purified by chromatography.

(c) Reaction of PhC(O)N(Ph)OH with $PhNHNH_2$ in the presence of catalytic quantities of $[MoO_2(acac)_2]$. To a solution of PhC(O)N(Ph)OH (0.21 g, 1 mmol) and $PhNHNH_2$ (0.15 ml, 1.5 mmol) in ethanol (20 ml) was added $[MoO_2(acac)_2]$ (0.006 g, 0.02 mmol) with stirring under nitrogen. Over the weekend the solution turned a dark red colour and on evaporation crystals of benzanilide were obtained; m.p. 163 °C. A blank run without $(MoO_2(acac)_2]$ added gave back the hydroxamic acid; m.p. 122 °C.

A similar production of benzanilide was effected on refluxing in dry methanol using the above, or 1:1, stoichiometric ratio in the presence of small quantities of $[MoO_2(acac)_2]$ or $[VO(acac)_2]$. Other hydrazines can be substituted for phenyl hydrazine such as $N_2H_4 \cdot H_2O$.

Crystallography

Complexes [MoO(N₂Ph₂)(PhC(S)N(Me)O)₂] (1) and [MoO(N₂Ph₂)(PhC(O)N(Me)O)₂] 0.5MeOH (3) (J.M.F., ERTT, Adelaide)

Parameters for **1** are given in parentheses after those for **3**. Intensity data for 5758 (5324) reflections were collected at room temperature on an Enraf-Nonius CAD4-F diffractometer fitted with Mo Kα (graphite monochromator) λ 0.71073 Å. No significant decomposition of a crystal of **3** occurred during the data collection however for **1**, the net intensity values of three standard reflections decreased to *c.* 60% of their initial values and the data set was scaled accordingly. Corrections were applied for Lorentz and polarization effects [11] and for absorption [12]. Crystal data are summarized in Table 1.

The structure of **3** was solved with the use of the direct-methods routine in SHELX [13] and **1** was solved from the interpretation of the Patterson. Both structures were refined by a full-matrix least-squares method [13]. For **3**, phenyl-group carbon atoms were refined as hexagonal rigid groups with individual isotropic thermal parameters and all remaining non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically for **1**. A weighting scheme, $w = k/[\sigma^2(F) + g|F|^2)$, was introduced and hydrogen atoms included in both models their calculated positions. A difference map for **3** calculated at this stage showed the presence of two separate electron-density peaks centred about two centres of inversion. These peaks were assigned to the presence of methanol. At the convergence of the refinements R 0.062 and R_w 0.084 (0.038 and 0.041). The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 1.40 e Å^{-3} located in the vicinity of one of the phenyl rings for **3** and 0.67 e Å^{-3} in the vicinity of a methyl group for **1**.

The scattering factors for neutral Mo were those from ref. 14; the values being corrected for $\Delta f'$ and $\Delta f''$. Scattering factors for all remaining atoms were those incorporated in the SHELX program [13].

Complex [Mo(N₂Ph)₂(PhC(S)N(Me)O)₂] (4) (G.D.F., Monash)

Crystal data are summarized in Table 1. Cell parameters were determined from 24 accurately centered reflections and were calculated by the standard Philips program. A representative transparent dark red prismatic crystal of dimensions (0.20 X

TABLE 1. Crystal data for $[MoO(N_2Ph_2)(PhC(S)N(Me)O)_2]$ (1), $[MoO(N_2Ph_2)(PhC(O)N(Me)O)_2 0.5MeOH]$ (3) and $[Mo(N_2Ph)_2$-$(PhC(S)N(Me)O)_2]$ (4)

Complex	1	3	4
Formula	$C_{28}H_{26}N_4O_3S_2Mo$	$C_{28.5}H_{30}N_4O_{5.5}Mo$	$C_{28}H_{26}N_6O_2S_2Mo$
Molecular weight	626.59	610.49	638.7
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ (C_{2h}^5, No. 14)	$P\bar{1}$ (C_i^1, No. 2)	$C2/C$
a (Å)	12.182(2)	12.060(4)	24.775(12)
b (Å)	11.238(1)	17.795(7)	9.030(5)
c (Å)	20.035(2)	14.025(5)	14.322(7)
α (°)	90	93.67(2)	90
β (°)	90.75(1)	108.35(2)	109.72(8)
γ (°)	90	91.41(2)	90
U (Å^3)	2742.5	2847.8	3016.2
d_x (d_m^{a}) (Mg/m^3)	1.518	1.424(1.44)	1.41(1.39)
Z	4	4	4
μ (mm^{-1})	0.616	0.461	0.56
$F(000)$	1280	1216	1303.7
Data collected	$12. < \theta < 18$	$1.4 < \theta < 20$	$3 < \theta < 30$
Omega scan angle (°)	$(0.99 + 0.35 \tan \theta)$	$(1.90 + 0.35 \tan \theta)$	$(1.3 + 0.3 \tan \theta)$
Horizontal counter Apertures (mm)	$(2.40 + 0.5 \tan \theta)$	$2.40 + 0.5 \tan \theta)$	
Unique data, $I > 2.5\sigma(I)$	4502, 3945	5758, 5056	4408, 1731
k	2.5	1.0	1.0
g	0.0003	0.0037	0

[a] Aqueous zinc bromide solution.

0.23 X 0.25 mm) was used for data collection. Intensity measurements were made on a Philips PW1100 diffractometer with graphite monochromated Mo Kα radiation. Three standard reflections monitored every 6 h showed no significant variation in intensity over the data collection period.

Intensity data were processed as described previously [15]. A numerical absorption correction was applied, the maximum and minimum transmission factors being 0.943 and 0.933 respectively. The atomic scattering factors for neutral atoms were taken from ref. 14 and were corrected for anomalous dispersion by using values from ref. 14. All calculations were performed on a VAX 11/780 computer. The program used for least-squares refinement was that due to Sheldrick [13].

The structure was solved by conventional Patterson and Fourier techniques. Full-matrix least-squares refinement employing anisotropic thermal parameters for Mo and S and isotropic thermal parameters for all other atoms, with hydrogen in geometrically idealized positions (C–H, 1.08 Å) and a common thermal parameter, reduced R and R_w to 0.059 and 0.056 rescpectively at convergence, where $R_w = \Sigma w^{1/2}(||F_o| - |F_c||)/\Sigma w^{1/2}|F_o|$ and $w = \sigma^2(F)$. Final atomic parameters for complexes **1**, **3** and **4** are given in Tables 2–4. Figures 1–3 show the atomic labelling scheme used.

TABLE 2. Fraction atomic coordinates for **1**[a]

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.79422(3)	0.56496(3)	0.35837(2)
S(1)	0.83706(8)	0.36887(9)	0.31613(5)
S(2)	0.69441(9)	0.73067(9)	0.41818(6)
O(3)	0.8484(2)	0.4748(2)	0.4474(1)
O(4)	0.6409(2)	0.4855(2)	0.3942(1)
O(5)	0.9132(2)	0.6445(2)	0.3591(1)
N(1)	0.8867(3)	0.3640(3)	0.4433(2)
N(2)	0.5533(3)	0.5560(3)	0.4047(2)
N(3)	0.7289(2)	0.6133(3)	0.2832(1)
N(4)	0.6833(2)	0.6561(3)	0.2288(2)
C(1)	0.8851(3)	0.3030(3)	0.3884(2)
C(2)	0.9384(3)	0.3227(4)	0.5077(2)
C(3)	0.9931(2)	0.1411(2)	0.3358(1)
C(4)	1.0231(2)	0.0217(2)	0.3304(1)
C(5)	0.9806(2)	- 0.0620(2)	0.3746(1)
C(6)	0.9082(2)	−0.0263(2)	0.4241(1)
C(7)	0.8783(2)	0.0931(2)	0.4295(1)
C(8)	0.9207(2)	0.1768(2)	0.3853(1)
C(9)	0.5650(3)	0.6705(4)	0.4139(2)
C(10)	0.4515(4)	0.4886(4)	0.4117(3)
C(11)	0.3860(2)	0.7425(3)	0.3678(1)
C(12)	0.2973(2)	0.8209(3)	0.3691(1)
C(13)	0.2893(2)	0.9046(3)	0.4202(1)
C(14)	0.3700(2)	0.9098(3)	0.4702(1)
C(15)	0.4587(2)	0.8314(3)	0.4690(1)
C(16)	0.4667(2)	0.7478(3)	0.4178(1)
C(17)	0.5036(2)	0.6949(2)	0.1775(1)
C(18)	0.3984(2)	0.6561(2)	0.1598(1)
C(19)	0.3656(2)	0.5404(2)	0.1750(1)
C(20)	0.4380(2)	0.4635(2)	0.2080(1)
C(21)	0.5432(2)	0.5023(2)	0.2258(1)
C(22)	0.5760(2)	0.6179(2)	0.2105(1)
C(23)	0.7968(2)	0.8335(2)	0.2296(1)
C(24)	0.8531(2)	0.9230(2)	0.1960(1)
C(25)	0.8524(2)	0.9253(2)	0.1264(1)
C(26)	0.7955(2)	0.8382(2)	0.0903(1)
C(27)	0.7392(2)	0.7488(2)	0.1240(1)
C(28)	0.7398(2)	0.7464(2)	0.1936(1)

[a] For anisotropic thermal parameters see 'Supplementary Material'.

Results and Discussion

Synthesis

[$MoO_2(PhC(S)N(Me)O)_2$] reacts with a small excess of Ph_2NNH_2HCl and Et_3N in methanol, or, preferably with free Ph_2NNH_2 in methanol/dichloromethane to yield the orange coloured oxohydrazido(2–) complex [$MoO(N_2Ph_2)(PhC(S)N(Me)O)_2$] (**1**). Care had to be taken that the *N,N*-diphenylhydrazine was pure and that solutions of it were stored under nitrogen otherwise intense purple solutions were obtained. Use of a larger excess of Ph_2NNH_2 led to the formation of yellow crystals of the bis-hydrazido(2–) complex [$Mo(N_2Ph_2)_2(PhC(S)N(Me)O)_2$ (**2**) the colour of which darkened slowly on exposure to air. The hydroxamate complex [$MoO(N_2Ph_2)(PhC(O)N(Me)O)_2$] (**3**) was obtained in an analogous way to the thiohydroxamate. The oxohydrazido(2–) pair of complexes was characterized by a ν(Mo=O) band at ~900 cm^{-1} and N_2Ph_2 bands at 1480 and 1585 cm^{-1} in their IR spectra together with two inequivalent methyl resonances in the ^{1}H NMR spectra (see 'Experimental'), the latter feature being compatible with the crystal structures (*vide infra*).

Deep red coloured crystals of the bis-diazenido complex [$Mo(N_2Ph)_2(PhC(S)N(Me)O)_2$] (**4**) were obtained in low yield by refluxing the dioxo complex with excess phenylhydrazine and triethylamine in methanol. An unidentified purple oil remained in the methanol solution. IR bands in the region 1460–1635 cm^{-1} were characteristic of *cis*-bisphenyldiazenido group being present in **4**. This grouping is chemically quite robust and has now been characterized in a number of mononuclear complexes containing S-donor chelators [16–19] also, more recently in binuclear μ-alkoxo species [20, 21], and in some tetra- and octamolybdate frameworks [9, 22]. Interestingly, we first tried the reaction of phenylhydrazine with dioxomolybdenum hydroxamate and thiohydroxamate complexes in ethanol as an undergraduate exercise in 1979 [23] with the aim of following up related studies on S-donor

TABLE 3. Fractional atomic coordinates for 3[a]

Atom	Molecule A			Molecule B		
	x/*a*	*y*/*b*	*z*/*c*	*x*/*a*	*y*/*b*	*z*/*c*
Mo	0.26064(5)	0.51116(4)	0.25739(5)	0.74469(5)	1.1202(4)	0.24155(5)
O(1)	0.2803(4)	0.6051(3)	0.3660(4)	0.7368(4)	1.1113(3)	0.1593(4)
O(2)	0.0845(4)	0.5047(3)	0.2797(4)	0.9245(4)	1.0191(3)	0.2248(4)
O(3)	0.3254(4)	0.4686(3)	0.3934(4)	0.6852(4)	0.9737(3)	0.0944(4)
O(4)	0.1467(4)	0.5722(3)	0.1510(4)	0.8549(4)	1.0717(3)	0.3697(4)
O(5)	0.3761(4)	0.5441(3)	0.2230(4)	0.6247(4)	1.0364(3)	0.2731(4)
N(1)	0.3478(5)	0.5199(3)	0.4762(5)	0.6626(5)	1.0279(4)	0.0262(5)
N(2)	0.0301(5)	0.5547(3)	0.1339(5)	0.9729(5)	1.0649(3)	0.3849(5)
N(3)	0.2306(5)	0.4177(3)	0.1993(5)	0.7657(5)	0.9186(3)	0.2762(5)
N(4)	0.2024(5)	0.3461(3)	0.1708(5)	0.7689(5)	0.8464(3)	0.2912(5)
C(1)	0.3237(6)	0.5900(4)	0.4573(6)	0.6956(7)	1.0982(5)	0.0634(7)
C(2)	0.3756(8)	0.4825(5)	0.5687(7)	0.5977(8)	0.9980(5)	−0.0747(7)
C(3)	0.4539(4)	0.6569(3)	0.6194(4)	0.6716(6)	1.2322(3)	0.0357(5)
C(4)	0.4783(4)	0.7190(3)	0.6899(4)	0.6734(6)	1.2944(3)	−0.0195(5)
C(5)	0.3996(4)	0.7764(3)	0.6790(4)	0.6915(6)	1.2850(3)	−0.1129(5)
C(6)	0.2965(4)	0.7718(3)	0.5975(4)	0.7078(6)	1.2133(3)	−0.1511(5)
C(7)	0.2722(4)	0.7098(3)	0.5270(4)	0.7060(6)	1.1510(3)	−0.0960(5)
C(8)	0.3508(4)	0.6523(3)	0.5379(4)	0.6879(6)	1.1604(3)	−0.0026(5)
C(9)	0.0025(7)	0.5221(4)	0.2057(6)	1.0042(7)	1.0388(4)	0.3070(7)
C(10)	−0.0454(8)	0.5817(5)	0.0403(6)	1.0453(8)	1.0960(5)	0.4826(7)
C(11)	−0.1416(4)	0.4321(3)	0.2245(5)	1.1831(5)	0.9667(3)	0.3520(6)
C(12)	−0.2538(4)	0.4094(3)	0.2227(5)	1.3005(5)	0.9589(3)	0.3601(6)
C(13)	−0.3450(4)	0.4583(3)	0.1935(5)	1.3634(5)	1.0172(3)	0.3354(6)
C(14)	−0.3241(4)	0.5300(3)	0.1660(5)	1.3090(5)	1.0834(3)	0.3026(6)
C(15)	−0.2119(4)	0.5527(3)	0.1677(5)	1.1916(5)	1.0912(3)	0.2945(6)
C(16)	−0.1206(4)	0.5038(3)	0.1970(5)	1.1287(5)	1.0329(3)	0.3192(6)
C(17)	0.0278(5)	0.2706(4)	0.1570(3)	0.9148(5)	0.8285(3)	0.2075(4)
C(18)	−0.0458(5)	0.2367(4)	0.2029(3)	1.0088(5)	0.7904(3)	0.1935(4)
C(19)	−0.0159(5)	0.2414(4)	0.3076(3)	1.0486(5)	0.7277(3)	0.2471(4)
C(20)	0.0875(5)	0.2800(4)	0.3666(3)	1.0088(5)	0.7904(3)	0.1935(4)
C(21)	0.1610(5)	0.3139(4)	0.3207(3)	0.9148(5)	0.8285(3)	0.2075(4)
C(22)	0.1311(5)	0.3092(4)	0.2159(3)	0.8605(5)	0.8040(3)	0.2750(4)
C(23)	0.3326(5)	0.3503(2)	0.0699(5)	0.6388(5)	0.8573(3)	0.3928(4)
C(24)	0.3886(5)	0.3143(2)	0.0078(5)	0.5527(5)	0.8263(3)	0.4275(4)
C(25)	0.3712(5)	0.2367(2)	−0.0158(5)	0.5079(5)	0.7528(3)	0.3945(4)
C(26)	0.2979(5)	0.1950(2)	0.0229(5)	0.5492(5)	0.7104(3)	0.3267(4)
C(27)	0.2419(5)	0.2310(2)	0.0850(5)	0.6353(5)	0.7414(3)	0.2920(4)
C(28)	0.2592(5)	0.3087(2)	0.1085(5)	0.6801(5)	0.8149(3)	0.3250(4)
Sol(1)[b]	0.0122(29)	0.0402(10)	−0.0009(14)	0.9713(28)	0.5384(11)	0.4966(12)

[a] For anisotropic thermal parameters see 'Supplementary Material'. [b] Sol = methanol.

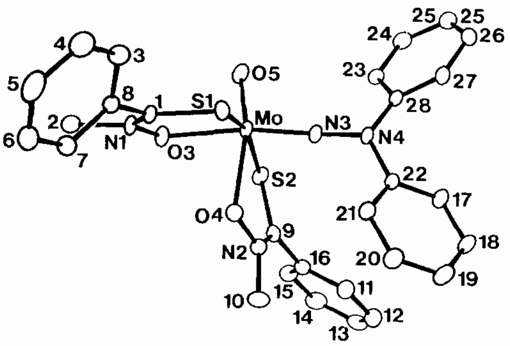

Fig. 1. Molecular structure and numbering scheme for [MoO(N_2Ph_2)(PhC(S)N(Me)O)$_2$] (1).

chelates by Otsuka *et al.* [16]. Very small maroon coloured crystals were obtained in both cases, the exact constitution of which from analytical data was not clear although ^{1}H NMR spectra were indicative of the presence of OEt$^-$ (or EtOH), PhN$_2$ and chelate group, while the visible band at 520 nm and IR bands at 1460–1640 cm^{-1} were characteristic of the *cis*(PhN$_2$)$_2$Mo goup. A broad band at ~850 cm^{-1} was the main distinguishing feature from the spectrum of 4. Unfortunately the crystals could never be grown big enough for X-ray studies. It would appear from recent structural work by Jeannin *et al.* [20, 21] and Zubieta *et al.* [9, 21, 22] that we had probably obtained binuclear μ-ethoxo

TABLE 4. Fractional atomic coordinates for 4

Atom	x	y	z	U_{iso}
Mo	0	0.1929(1)	1/4	*
S	−0.0986(1)	0.1377(2)	0.2449(1)	*
N(1)	0.0210(2)	0.3331(6)	0.3475(4)	0.047(1)
N(2)	0.0344(2)	0.4214(6)	0.4167(4)	0.050(1)
N(3)	−0.0307(2)	−0.0585(6)	0.3627(4)	0.046(1)
O	0.0144(2)	0.0189(5)	0.3551(3)	0.053(1)
C(1)	0.0894(3)	0.4890(8)	0.4504(5)	0.046(2)
C(2)	0.1266(3)	0.4848(9)	0.3969(6)	0.064(2)
C(3)	0.1801(4)	0.5528(9)	0.4371(6)	0.077(3)
C(4)	0.1952(5)	0.6231(11)	0.5290(8)	0.098(3)
C(5)	0.1563(4)	0.6302(10)	0.5798(7)	0.085(3)
C(6)	0.1030(3)	0.5623(9)	0.5384(6)	0.062(2)
C(7)	−0.0837(3)	−0.0142(7)	0.3199(5)	0.045(2)
C(8)	−0.1305(3)	−0.0942(8)	0.3398(5)	0.048(2)
C(9)	−0.1372(3)	−0.0817(9)	0.4326(6)	0.068(2)
C(10)	−0.1827(4)	−0.1555(9)	0.4474(7)	0.080(3)
C(11)	−0.2201(4)	−0.2389(10)	0.3763(7)	0.082(3)
C(12)	−0.2140(4)	−0.2545(11)	0.2849(7)	0.091(3)
C(13)	−0.1678(3)	−0.1776(10)	0.2672(6)	0.075(2)
C(14)	−0.0120(3)	−0.1937(9)	0.4208(6)	0.064(2)

Starred items: anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

Atom	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
Mo	0.0471(6)	0.0450(5)	0.0388(5)	0	0.0211(4)	0
S	0.050(1)	0.057(1)	0.054(1)	0.007(1)	0.022(1)	0.014(1)

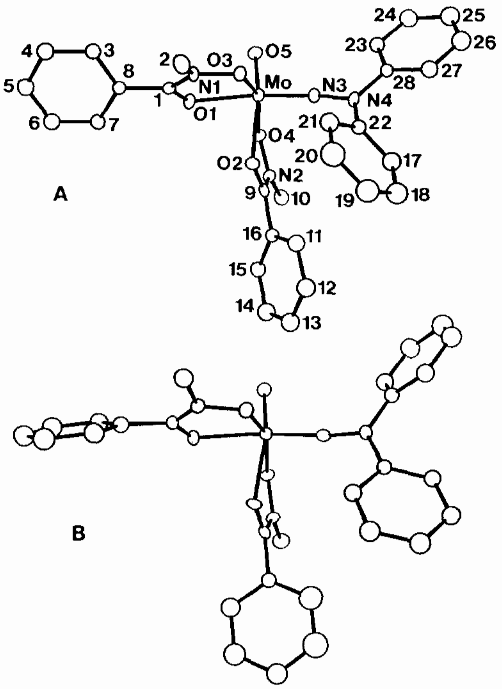

Fig. 2. Molecular structure and numbering scheme for the two structurally distinct molecules (A and B) for $[MoO(N_2Ph_2)(PhC(O)N(Me)O)_2]$ (3).

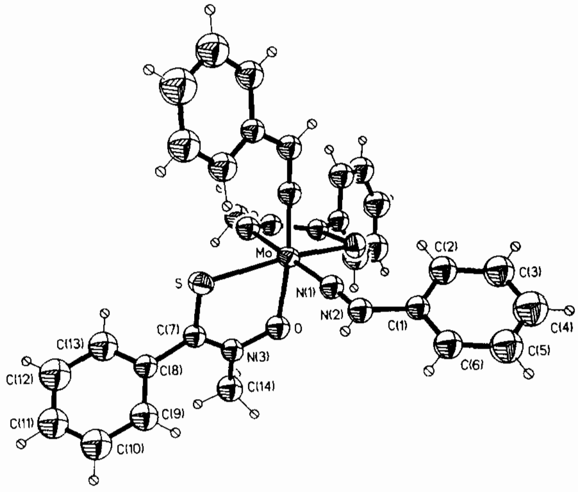

Fig. 3. Molecular structure and numbering scheme for $[Mo(N_2Ph)_2(PhC(S)N(Me)O)_2]$ (4). The molecule has a centre of symmetry at Mo. Thermal ellipsoids are drawn at 40% probability level except hydrogen which are drawn as spheres of arbitrary radius.

bridged bisphenyldiazenidomolybdenum species. These workers have also noted that subtle changes in reaction conditions such as (in the present case) changing from ethanol to methanol, and adding triethylamine, can lead to different types of *cis*-{$(PhN_2)_2$Mo(coligand)} complexes being precipitated. It is not immediately obvious what, for instance, is the precise role of Et_3N in the production of **4**, since the by-products in the methanol solution are probably water and excess $PhNHNH_2$. In view of the likely production of Mo(OEt) groups when Et_3N is not present we propose that $PhNHNH_2$ itself acts as a base causing deprotonation of EtOH, a phenomenon known to occur in methanol solutions, e.g. in the production of $[VO(acac)(OMe)]_2$ from reaction of $PhNHNH_2$ with $VO(acac)_2$ [24] or in the production of $[Mo_4O_{10}(OMe)_6]^{2-}$ from a methanol soluble $[Mo_8O_{26}]^{4-}$ salt in the presence of $Ph(Me)NNH_2$ [22]. Triethylamine therefore could be a sacrificial base needed, as suggested by Zubieta *et al.* [9], to deprotonate intermediate {PhNH=N=Mo} species.

In the absence of triethylamine we also discovered complications of an organic kind. As well as the depositions of the tiny maroon crystals described above, reaction of, for instance $[MoO_2(PhC(O)N(Ph)O)_2]$ with three mole equivalents of $PhNHNH_2$ in ethanol led first to evolution of a (unidentified) gas and to coprecipitation of clear crystals of benzanilide, PhC(O)N(Ph)H, derived from the hydroxamate ligand. The latter could be separated chromatographically from the maroon solid, and identified by IR and mass spectrum (M^+ = 197) and melting point (163 °C). We soon discovered that Me_2NNH_2 acted as well as $PhNHNH_2$ in this reductive process and, further, that the conversion of PhC(O)N(Ph)OH to PhC(O)N(Ph)H went smoothly in the presence of $PhNHNH_2$ and catalytic amounts of $MoO_2(acac)_2$ (or $VO(acac)_2$!). A related published method for producing benzanilide from a Mo hydroxamate precursor used H_2S instead of a hydrazine [25]. We note that Otsuka *et al.* [16] observed reductive cleavage of $Mo(N_2Ph)_2$ groups to yield aniline in the presence of excess $PhNHNH_2$. It would also be interesting to know if Jeannin *et al.* detected any amide by-product in their recent synthesis of $[(PhN_2)_2Mo(PhC(O)N(H)O)_2]$ in which they used a 1:6 ratio of $[MoO_2(PhC(O)N(H)O)_2]$ to $PhNHNH_2$ dissolved in cold ethanol [21]. In summary it can be seen that the reactions of phenylhydrazine with dioxomolybdenum(VI) complexes are complicated and still not fully understood. While considerable advances have been made in defining crystalline products there is still uncertainty in our knowledge of total product analysis and in mechanism of reaction.

Description of the Structures

The structures of $[MoO(N_2Ph_2)(PhC(S)N(Me)O)_2]$ (**1**) and $[MoO(N_2Ph_2)(PhC(O)N(Me)O)_2]$ (**3**) are shown in Figs. 1 and 2. Complex **3** contains two structurally unique molecules, labelled A and B, which differ chiefly in the relative orientation of the phenyl rings of the hydroxamate ligands. Bond distances and angles are given in Tables 5 and 6. The oxo and hydrazido(2–) groups are *cis* to each other in both **1** and **3** as anticipated. The oxygen atoms of the thiohydroxamate ligands in **1** are *trans* to the oxo and hydrazido(2–) groups as was the case in a related $MoO_2(RC(S)N(R')O)_2$ precursor [26]. Consequently the sulfur atoms are *trans* to each other. Frustratingly, from the comparative point of view, the carbonyl oxygen atoms of the hydroxamate ligands in **3** turn out to be *trans* to the oxo and hydrazido(2–) groups. This was also the case in related precursor dioxo structures [27, 28]. Since oxo groups are known to exert a strong *trans* effect it is possible that the differences just mentioned relate to the weakest π-bonding atom being situated *trans* to the oxo group. The $Ph_2N_2^{2-}$ group exerts a weaker *trans* effect than does the oxo group in **1** and **3** as evidenced by longer Mo–ligand bond distances *trans* to the oxo groups.

Relevant structural parameters for **1** and **3** and for some other $[MoO(N_2R_2)(coligand)]$ and related $Mo(N_2R_2)_2$ complexes are given in Table 7. The geometric features of the *cis*-$[MoO(N_2R_2)]$ moiety are remarkably constant, irrespective of the nature of the coligand. **1** has the most linear Mo–N–N band of the known examples, which together with the Mo–N and N–N bond lengths, is indicative of extensive electron delocalization along the Mo=N–NR_2

TABLE 5. Selected bond distances (Å) for 3 (X = O) and 1 (X = S)

Atoms	Distances		
	3 (Molecule A)	3 (Molecule B)	1
Mo–X(1)	2.145(5)	2.159(5)	2.420(1)
Mo–X(2)	2.244(5)	2.255(5)	2.534(1)
Mo–O(3)	2.025(5)	2.026(5)	2.148(3)
Mo–O(4)	2.070(5)	2.075(5)	2.199(3)
Mo–O(5)	1.713(5)	1.699(5)	1.703(3)
Mo–N(3)	1.781(6)	1.763(6)	1.779(3)
X(1)–C(1)	1.270(9)	1.282(10)	1.722(4)
C(1)–C(8)	1.484(9)	1.474(10)	1.484(4)
C(1)–N(1)	1.314(9)	1.326(10)	1.296(5)
N(1)–C(2)	1.444(11)	1.443(11)	1.501(5)
N(1)–O(3)	1.382(8)	1.373(8)	1.333(4)
X(2)–C(9)	1.250(9)	1.269(10)	1.716(4)
C(9)–C(16)	1.478(9)	1.464(10)	1.482(5)
C(9)–N(2)	1.318(9)	1.326(10)	1.307(5)
N(2)–C(10)	1.461(10)	1.439(10)	1.462(6)
N(2)–O(4)	1.374(7)	1.380(7)	1.347(4)
N(3)–N(4)	1.314(8)	1.315(8)	1.309(4)
N(4)–C(22)	1.392(8)	1.421(8)	1.420(4)
N(4)–C(28)	1.415(8)	1.418(8)	1.419(4)
Sol(1)–Sol(1)[a]	1.542(44)	1.455(35)	

[a] Sol = methanol.

TABLE 6. Bond angles (°) for 3 (X = O) and 1 (X = S)

Atoms	Angles		
	3 (Molecule A)	3 (Molecule B)	1
X(1)–Mo–X(2)	79.9(2)	78.0(2)	160.3(1)
X(1)–Mo–O(3)	74.7(2)	74.9(2)	78.2(1)
X(1)–Mo–O(4)	88.8(2)	89.6(2)	86.1(1)
X(1)–Mo–O(5)	91.9(2)	91.1(2)	107.1(1)
X(1)–Mo–N(3)	160.4(3)	161.3(3)	94.5(1)
X(2)–Mo–O(3)	87.3(2)	86.9(2)	95.6(1)
X(2)–Mo–O(4)	71.3(2)	72.5(2)	74.3(1)
X(2)–Mo–O(5)	160.2(2)	160.5(2)	91.4(1)
X(2)–Mo–N(3)	88.0(2)	90.4(2)	87.9(1)
O(3)–Mo–O(4)	155.1(2)	156.6(2)	77.9(1)
O(3)–Mo–O(5)	108.1(2)	106.0(2)	89.3(1)
O(3)–Mo–N(3)	89.5(2)	90.0(2)	167.5(1)
O(4)–Mo–O(5)	90.6(2)	91.5(2)	159.6(1)
O(4)–Mo–N(3)	101.9(2)	101.0(2)	91.6(1)
N(3)–Mo–O(5)	104.1(3)	103.8(3)	102.6(1)
Mo–X(1)–C(1)	114.9(4)	114.0(5)	99.8(1)
X(1)–C(1)–C(8)	119.2(6)	119.9(7)	118.2(2)
X(1)–C(1)–N(1)	118.3(7)	118.3(7)	119.2(3)
C(8)–C(1)–N(1)	122.4(7)	121.7(8)	122.7(3)
C(1)–N(1)–C(2)	131.4(7)	130.7(7)	124.5(3)
C(1)–N(1)–O(3)	116.2(6)	116.3(6)	123.0(3)
C(2)–N(1)–O(3)	111.4(6)	112.8(6)	112.3(3)
N(1)–O(3)–Mo	115.8(4)	116.0(4)	119.6(2)
Mo–X(2)–C(9)	114.1(5)	113.0(4)	97.7(1)
X(2)–C(9)–N(2)	117.6(7)	118.4(6)	119.5(3)
C(16)–C(9)–N(2)	121.3(7)	119.0(8)	119.8(3)
C(9)–N(2)–C(10)	129.9(7)	129.1(7)	125.9(4)
C(9)–N(2)–O(4)	116.8(6)	117.3(6)	121.1(3)
C(10)–N(2)–O(4)	113.1(6)	113.2(6)	112.6(3)
N(2)–O(4)–Mo	115.0(4)	115.2(4)	119.3(2)
Mo–N(3)–N(4)	169.4(6)	172.2(5)	176.2(3)
N(3)–N(4)–C(22)	117.2(6)	119.6(5)	118.8(3)
N(3)–N(4)–C(28)	118.4(5)	117.4(5)	118.3(3)
C(22)–N(4)–C(28)	123.6(5)	123.0(5)	122.7(3)

group. The geometries of the thiohydroxamate and hydroxamate chelating group are unexceptional and similar to those in the dioxo precursors [26–28].

The structure of the bis-phenyldiazenido complex 4 is shown in Fig. 3. Only half of the molecule is labelled since it possesses a C_2 axis. Bond distances and angles are given in Table 8 and a comparison to related complexes is given in Table 9. As in complex

TABLE 8. Selected bond distances (Å) and angles (°) for 4

Atoms	*d* (Å)	Atoms	*d* (Å)
Mo–S	2.469(2)	C(5)–C(6)	1.393(11)
Mo–N(1)	1.825(5)	O–N(3)	1.353(8)
Mo–O	2.121(5)	N(3)–C(7)	1.310(8)
S–C(7)	1.704(7)	N(3)–C(14)	1.462(9)
N(1)–N(2)	1.227(8)	C(7)–C(8)	1.473(11)
N(2)–C(1)	1.421(8)	C(8)–C(9)	1.399(12)
C(1)–C(2)	1.383(12)	C(9)–C(13)	2.393(12)
C(1)–C(6)	1.362(11)	C(9)–C(10)	1.386(13)
C(2)–C(3)	1.395(11)	C(10–C(11)	1.351(11)
C(3)–C(4)	1.394(14)	C(11)–C(12)	1.374(15)
C(4)–C(5)	1.393(17)	C(12)–C(13)	1.431(14)
Bond angles			
S–Mo–S′		156.7(1)	
S–Mo–N(1)′		95.4(2)	
S–Mo–N(1)		100.7(2)	
S–Mo–O		78.4(1)	
S–Mo–O′		84.3(1)	
N(1)–Mo–O′		173.1(2)	
N(1)–Mo–O		92.0(2)	
N(1)–Mo–N(1)′		92.2(3)	
O–Mo–O′		84.4(3)	
Mo–N(1)–N(2)		176.3(5)	
N(1)–N(2)–C(1)		121.4(7)	

′= $-x, y, 0.5 - z$.

TABLE 7. Pertinent bond parameters for $MoO(N_2Ph_2)(PhC(X)N(Me)O)_2$; X = O, S and related six-coordinate hydrazido(2–) complexes

Compound	Mo–S (av.) (Å)	Mo–oxo (Å)	Mo–N (Å)	N–N (Å)	Mo–N–N (°)	O–Mo–N (°)	Reference
$MoO(N_2Ph_2)(PhC(S)N(Me)O)_2$	2.47	1.703(3)	1.779(3)	1.309(4)	176.2(3)	102.6(1)	this work
$MoO(N_2Ph_2)(PhC(O)N(Me)O)_2$[a]		1.713(5)	1.781(6)	1.314(8)	169.4(6)	104.1(3)	this work
$MoO(N_2Ph_2)(PhC(O)N(Me)O)_2$[b]		1.699(5)	1.763(6)	1.315(6)	172.2(5)	103.8(3)	
$MoO(N_2Me_2)(S_2CNMe_2)_2$	2.48	1.708(6)	1.799(8)	1.288(10)	168.0(7)	10.4(3)	29, 30
$MoO(N_2Me_2)(oxine)_2$[c]		1.671(9)	1.800(9)	1.28(1)	155.5(9)	100.8(4)	31
$MoO(N_2Ph_2)(C_8H_{18}N_2S_2)$[d]	2.44	1.696(2)	1.778(3)	1.309(4)	172.9(2)	105.9(1)	18
$Mo(N_2Ph_2)_2(S_2CNMe_2)_2$	2.49		1.790(8)	1.31(1)	169.9(8)	107.5(3)[e]	32, 33
$Mo(N_2PhMe)_2(S_2CNMe_2)_2$	2.49		1.790(9)	1.30(1)	172.6(8)	107.2(5)[e]	33
$MoO_2(p\text{-}MeC_6H_4C(S)N(Me)O)_2$	2.46	1.706(5) 1.713(5)				103.7(2)[f]	26

[a] Molecule 1. [b] Molecule 2. [c] Oxine ≡ 8-hydroxyquinoline. [d] Tetradentate $\{S_2N_2\}$ ligand. [e] N–Mo–N. [f] O–Mo–O.

TABLE 9. Mo–diazenido geometry in **4** and in related mononuclear and polynuclear species

Compound	Mo–N (Å)	N–N (Å)	N–C (Å)	Mo–N–N (°)	N–N–C (°)	N–Mo–N (°)	Reference
$Mo(N_2Ph)_2(PhC(S)N(Me)O)_2$	1.825(5)	1.227(8)	1.421(8)	176.3(5)	121.4(7)	92.2(3)	this work
$[Mo(N_2Ph)_2(PhC(ON(H)O)(\mu\text{-}OEt)]_2$	1.817(8)	1.24(1)		171.6(7)	118.3(8)		21
	1.841(8)	1.26(1)		175.7(7)	118.2(9)		
$[Mo_4O_8(OCH_3)_2(N_2Ph)_4]^{2-}$ [a]	1.823(9)	1.227(12)	1.412(12)	173.5(7)	117.5(7)	93.1(6)	9, 34
$[Mo_8O_{20}(N_2Ph)_6]^{4-}$	1.83(2)	1.23(3)		174.8(17)		90.1(5)	9, 35
	1.82(2)	1.19(3)		177.3(17)			
$Mo(N_2C_6H_4OCH_3\text{-}p)_2\,(C_8H_{18}N_2S_2)$ [b, c]	1.81(1)	1.28(2)	1.51(2)	170.4(17)	113.8(17)	95.5(4)	18
	1.81(1)	1.20(3)	1.38(2)	168.3(19)	119.6(17)		
$MoF(N_2C_6H_4Me\text{-}p)_2\,\{HB(Me_2pz)_3\}$	1.832(3)	1.217(4)	1.418(4)	176.1(2)	118.2(3)	90.8(1)	36
	1.832(3)	1.226(3)	1.421(4)	175.2(2)	118.2(2)		
$Mo(N_2Ph)(S_2CNMe_2)_3$	1.781(4)	1.233(6)	1.417(7)	171.5(4)	120.5(5)		17
$Mo(N_2C(S)SEt)(NH_2NC(S)SEt)(S_2CNMe_2)_2$	1.77(1)	1.21(1)	1.36(1)	178(1)	120(1)		37

[a] Average. [b] Tetradentate $\{S_2N_2\}$. [c] See also a related sterically bulky S_2N_2 example [19].

1 the two sulfur atoms are *trans* to each other. The two PhN_2 groups are in the expected *cis* arrangement at almost right angles (N–Mo–N, 92.2(3)°) to each other. This contrasts with the larger angles observed between *cis*-dioxo or *cis*-oxo-hydrazido(2–) groups such as in **1** and **3** on account of the greater repulsion between these electron rich, strongly π-bonded groups. The goemetry of the PhN_2–Mo fragments in **4** and in related mononuclear and polynuclear *cis*-diazenido species (Table 9) are similar and indicative of extensive electron delocalization throughout the Mo–N–N–unit.

Conclusions

Reactions of O,O-chelated (hydroxamate) and S,O-chelated (thiohydroxamate) dioxomolybdenum(VI) complexes with Ph_2NNH_2 or $PhNHNH_2$ generally proceed rather similarly, and, except for subtle differences, also proceed similarly to other O,N-, S,N- and S,S-chelated systems. The spectral and geometric features of the resulting oxohydrazido(2–) and bis-diazenido compounds are likewise generally similar, irrespective of the coligand present. Clearly the *cis*-bonded $MoO(N_2R_2)^{2+}$ and $Mo(N_2Ph)_2{}^{2+}$ fragments dominate the bonding in these classes of compounds. Specifically, we noted configurational differences of the hydroxamate and thiohydroxamate chelating groups in relation to the $MoO(N_2Ph_2)$ group in **1** and **3**. In the bis-phenyldiazenido chemistry, carried out in the absence of triethylamine, we observed complicated reactions which, in the case of the precursor $[MoO_2(PhC(O)N(Ph)O)_2]$, yielded quantities of the organic amide, benzanilide.

Supplementary Material

Tables of positional coordinates for hydrogen atoms, all bond lengths and angles, mean plane data (**1** and **3**), dihedral angles (**1** and **3**), anisotropic thermal parameters (**1** and **3**), observed and calculated structure factors are available on request to Dr K. S. Murray.

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