Inorg. Chem. **1985**, *24*, 3265–3270 **3265**

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Reactions of Oxomolybdenum(VI) Hydroxamate and Thiohydroxamate Complexes with Hydrazines. Syntheses and Structures of a Diazenido–Hydrazido(1–) Complex Containing an "End-On"-Bonded Hydrazido(1–) Ligand and of a Diazene–Diazenido(1–) Derivative

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Received January 15, 1985

The reaction of benzoylhydrazine with the molybdenum thiohydroxamate complex $[MoO_2(PhC(S)N(Me)O)_2]$ yields complex I, $[Mo(N_2C(O)Ph)(NHNHC(O)Ph)(PhC(S)N(Me)O)_2]\cdot 0.5H_2O$. Crystals of I ($C_{30}H_{29}MoN_6O_{4.5}S_2$) are monoclinic, space group $P2_1/c$, with $a = 18.968$ (6) Å, $b = 13.900$ (4) Å, $c = 12.629$ (3) Å, $\beta = 107.90$ (2)°, and $Z = 4$. The last blocked-matrix least-squares refinement, when the absorption correction data were used, converged with $R = 0.029$ and $R_w = 0.030$. The complex contains a diazenido group and an "end-on"-bonded hydrazido(1–) group together with two bidentate thiohydroxamate ligands in the coordination sphere around Mo. This is the first structurally characterized end-on hydrazido(1–) complex containing the NH–NH group. Both hydrogens were located in the refinement. Selected dimensions for this group are Mo–N = 1.938 (4) Å, N–N = 1.361 (7) Å, and Mo–N–N = 131.9 (3)°. The corresponding dimensions for the diazenido group are quite different, and they are respectively 1.758 (5) Å, 1.292 (7) Å, and 168.8 (4)°. The ^1H NMR spectrum of I shows coupling between the two hydrogens on the hydrazido(1–) group with doublets centered at 15.85 and 12.51 ppm. When the same dioxomolybdenum thiohydroxamate complex is reacted with thiobenzoylhydrazine, the complex II, $[Mo(NHNC(S)Ph)(N_2C(S)Ph)(PhC(S)N(Me)O)]$, is formed. Complex II of formula $C_{22}H_{19}MoN_5OS_3$ crystallizes in the triclinic space group $P\bar{1}$, with $a = 11.728$ (4) Å, $b = 11.744$ (3) Å, $c = 11.860$ (5) Å, $\alpha = 60.27$ (3)°, $\beta = 60.57$ (3)°, and $\gamma = 64.80$ (3)°. The final blocked-matrix refinement converged with $R = 0.024$ and $R_w = 0.028$. The complex possesses a distorted six-coordinate structure with three different bidentate ligands: diazene, diazenido, and thiohydroxamate. The hydrogen atom of the diazene group was found attached to the nitrogen bonded to Mo. Bond distances in the diazene group include Mo–N = 1.972 (3) Å and N–N = 1.343 (6) Å and for the diazenido group Mo–N = 1.789 (4) Å and N–N = 1.324 (6) Å. Reaction of the corresponding hydroxamate complex $[MoO_2(PhC(O)N(Me)O)_2]$ with thiobenzoylhydrazine led to substitution of all the initial ligands to produce the known trischelated thiobenzoyldiazene species $[Mo(NHNC(S)Ph)_3]$.

Introduction

The synthesis and reactivity of sulfur-containing complexes of molybdenum is currently of much interest from both the bioinorganic[1] and catalytic points of view.[2] In the case of high-valent oxomolybdenum species such as $Mo^{VI}O_2^{2+}$ or $Mo^{V}O^{3+}$ the modes of reactivity of the oxo groups have attracted considerable attention.[3] The present paper deals with the latter aspect. We describe the reaction of *cis*-dioxo chelate complexes of type $[O_2Mo(RC(X)N(R')O)_2]$[4,5] with organohydrazines to produce hydrazido-type products. Structural formulas of the dioxo complexes and various hydrazido, diazenido, etc. moieties are given in Figure 1. One of the primary aims of such a study was to endeavor to systematically investigate the reactivity of the oxo ligands while carefully changing the coligand from hydroxamate {O,O} donor to the analogous thiohydroxamate {S,O} donor.

The pioneering work in this area[3,6–8] has uncovered extremely interesting modes of behavior and structural types, but it appears that the products of reaction can not always readily be predicted from the nature of the coligand attached to the O_2Mo^{2+} moiety. We hoped to clarify this situation by simply changing the donor atom from O to S in otherwise matched pairs of molecules. Our hopes have been partially fulfilled although in some areas frustrated by not always being able to isolate in pure form the desired "partner" of a structurally characterized product that had been prepared by a similar route.

In this paper the products of reaction of $[O_2Mo(PhC(S)N(Me)O)_2]$ and $[O_2Mo(PhC(O)N(Me)O)_2]$ with $PhC(S)NHNH_2$ and $PhC(O)NHNH_2$ are described.[9] The crystal and molecular structures of two of the products are also described.

The diazenido–hydrazido(1–) complex I, $[Mo(N_2C(O)Ph)(NHNHC(O)Ph)(PhC(S)N(Me)O)_2]$, provides the first structurally characterized "end-on"-bonded NHNHR hydrazido(1–)-molybdenum example[41] and is therefore relevant to an understanding of the intermediates formed in the molybdenum-catalyzed reduction of dinitrogen.[6] A number of crystal structures of end-on-bonded hydrazido(1–) complexes have recently been reported, but they generally contain the NHNRR′ group. The structures include those by McCleverty et al.[10] of Mo and W complexes containing the sterically demanding pyrazolylborate group and some Re derivatives by Sutton et al.[11] An orthometalated organoiridium complex containing an end-on-bonded –NHNH– moiety has also been reported by Sutton.[12] There is also a small number of structures now available of "side-on"-bonded (η^2) hydrazido(1–) complexes containing NHNRR′ or NH_2NR groups.[13–18] In fact, it has been proposed that unless steric constraints apply the side-on mode of bonding will be the most stable.[10,13]

The structure of $[Mo(NHNC(S)Ph)(N_2C(S)Ph)(PhC(S)N(Me)O)]$ (II), which contains chelating diazene and diazenido(1–)

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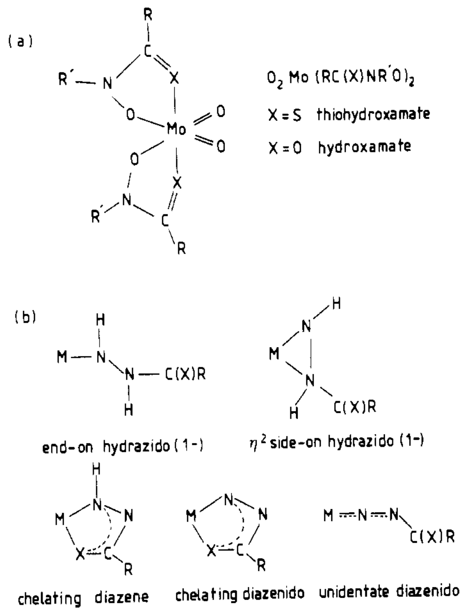

Figure 1. (a) Structural formulas of *cis*-dioxobis(thiohydroxamato)molybdenum(VI) and the related hydroxamato complex. (b) Some coordination modes of benzoyl- and thiobenzoylhydrazido(1−) and related species (X = O and S, respectively).

moieties and only one thiohydroxamate group, shows the greater tendency of the sulfur atom in thioaroylhydrazines to bond to Mo than is the case for the corresponding O atom in aroylhydrazines. Species related to II have previously been reported by Dilworth, Zubieta, et al.[19]

Experimental Section

Hydroxamic acids,[20] thiohydroxamic acids,[21] and thiobenzoylhydrazine[22] were prepared as reported in the literature. Infrared spectra were determined as Nujol mulls with a Jasco IRA-1 spectrometer. ^1H NMR spectra were obtained with a Bruker WH-90 spectrometer while ^{13}C NMR spectra were recorded on a Bruker HX90R spectrometer. They were run as $CDCl_3$ solutions with all shifts reported downfield from Me_4Si.

$[MoO_2(PhC(X)N(Me)O)_2]$ (X = S, O). Methanol solutions of $MoO_2(acac)_2$[23] and 2 mol equiv of the ligand were separately dissolved, filtered, and mixed. The color changed immediately, and the product precipitated as a yellow powder or as microcrystals. These were recrystallized from dichloromethane–methanol to yield the products. *Yellow microcrystals* of $[MoO_2(PhC(S)N(Me)O)_2]$: mp 143 °C; IR (Nujol) 900 s, 860 s cm^{-1} ($\nu(Mo{=}O)$); ^1H NMR ($CDCl_3$) δ 7.48 s (Ph), 3.69 s (Me). Anal. Calcd for $C_{16}H_{16}MoN_2O_4S_2$: C, 41.74; H, 3.50; N, 6.09; S, 13.9. Found: C, 41.60; H, 3.77; N, 5.92; S, 13.7. *Pale yellow crystals* of $[MoO_2(PhC(O)N(Me)O)_2]$: mp 196 °C; IR (Nujol) 940 s, 910 s cm^{-1} ($\nu(Mo{=}O)$); ^1H NMR ($CDCl_3$) δ 7.65–7.53 m (Ph), 3.60 s (Me). Anal. Calcd for $C_{16}H_{16}MoN_2O_6$: C, 44.87; H, 3.77; N, 6.54. Found: C, 44.54; H, 3.47; N, 6.52. A wide range of these chelates were prepared by this route.[24]

$[Mo(N_2C(O)Ph)(NHNHC(O)Ph)(PhC(S)N(Me)O)_2]$ (I). $[MoO_2(PhC(S)N(Me)O)_2]$ (200 mg, 0.43 mmol) and $PhCONHNH_2$ (180 mg, 1.32 mmol) were refluxed in methanol (20 mL) for 3 h. The solution turned red after 5 min, and after 20 min all the solid was taken up into solution. The solution was left to cool to room temperature, yielding red-maroon microcrystals (290 mg, 95%). These were recrystallized as red-maroon crystals from dichloromethane–methanol: mp 118 °C dec (slow); IR (Nujol) 3230 m, 3070 w cm^{-1} ($\nu(N{-}H)$); ^1H NMR ($CDCl_3$) δ 15.85 d (1 H, N—H, J_{H-H} = 10.2 Hz), 12.51 d (1 H, N—H, J_{H-H} = 10.2 Hz), 8.37–8.26 m (2 H, *o*-C_6H_5), 8.18–8.08 m (2 H, *o*-C_6H_5), 7.56–7.37 m (6 H, *m*- and *p*-C_6H_5), 7.47 s (10 H, 2 C_6H_5), 3.75 s (3 H, Me), 3.61 s (3 H, Me); ^{13}C NMR ($CDCl_3$) 178.5 s, 165.7 s, 160.5 s (C═O and C═S), 138.8–128.2 (C_6H_5), 47.2 s (CH_3), 46.1 s (CH_3). Anal. Calcd for $C_{30}H_{28}MoN_6O_4S_2$: C, 51.72; H, 4.05; N, 12.07; S, 9.2. Calcd for $C_{30}H_{28}MoN_6O_4S_2\cdot 0.5H_2O$: C, 51.06; H, 4.14; N, 11.91; S, 9.1. Found: C, 51.49; H, 4.03; N, 11.65; S, 8.8.

$[Mo(NHNC(S)Ph)(NNC(S)Ph)(PhC(S)N(Me)O)]$ (II). The reaction conditions were similar to those in the above reaction. $[MoO_2(PhC(S)N(Me)O)_2]$ (200 mg, 0.43 mmol) and $PhCSNHNH_2$ (200 mg, 1.31 mmol) were refluxed in methanol (30 mL) for 3 h. The reaction solution rapidly changed color from an initial light green solution with a yellow suspension to a very dark green/black solution with all the solid dissolving after 20 min. The reaction solution was left to stand, and the fine dark green/black microcrystals (230 mg, 94%) that formed were filtered off, washed with a little diethyl ether, and dried. The microcrystals were recrystallized from dichloromethane–methanol in the form of large black crystals: mp 143 °C dec (slow); IR (Nujol) 3020 w, br cm^{-1} ($\nu(N{-}H)$); ^1H NMR ($CDCl_3$) δ 9.96 s, br (1 H, N—H), 8.11–7.38 m (15 H, Ph) 3.71 s, 3.57 s (3 H, Me); Anal. Calcd for $C_{22}H_{19}MoN_5OS_3$: C, 47.05; H, 3.41; N, 12.47;S, 17.1. Found: C, 46,96; H, 3.26; N, 12.72; S, 17.0.

Reaction of $[MoO_2(PhC(O)N(Me)O)_2]$ with $PhC(S)NHNH_2$. $[MoO_2(PhC(O)N(Me)O)_2]$ (100 mg, 0.23 mmol) and $PhC(S)NHNH_2$ (100 mg, 0.66 mmol) were stirred in methanol (20 mL) for 1 h. The solution rapidly turned dark green as both reactants dissolved, and dark green crystals formed after 20 min (100 mg, 82%). The crystals were verified as being $[Mo(PhC(S)NNH)_3]$ by comparison with an authentic sample.

Crystal Data. Crystals of the two complexes were mounted on glass fibers with use of cyanoacrylate super glue. In each case, lattice parameters at 22 °C were determined by a least-squares fit to the setting angles of 25 independent reflections, measured and refined by scans performed on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation. The densities were determined by flotation in a solution consisting of a mixture of carbon tetrachloride, 1,2-dibromoethane, and petroleum ether (30–40 °C).

Complex I: $C_{30}H_{29}MoN_6O_{4.5}S_2$; formula weight 705.6; crystal class monoclinic; space group $P2_1/c$; a = 18.968 (6), b = 13.900 (4), c = 12.629 (3) Å; β = 107.90 (2)°; D_{obsd} = 1.45, D_{calcd} = 1.479 g cm^{-3}; U = 3168.6 Å^3; Z = 4; μ(Mo Kα) = 5.43 cm^{-1}; λ(Mo Kα) = 0.7107 Å; $F(000)$ = 1444 electrons.

Intensity data ($\pm h, \pm k, +l$) were collected from a crystal of dimensions 0.10 × 0.24 × 0.16 mm^3 in the range $1.3 < \theta < 20°$ with use of an $\omega-(n/3)\theta$ scan, where n (=1) was optimized by profile analysis of a typical reflection. The ω-scan angles and horizontal counter apertures employed were $(2.15 + 0.35 \tan \theta)°$ and $(2.40 + 0.5 \tan \theta)$ mm, respectively. Three standard reflections, monitored after every 58 min of data collection, indicated that, by completion of the data collection, no decomposition had occurred. Data reduction and application of Lorentz and polarization corrections were performed with use of the program SUSCAD.[25] Absorption corrections were applied with the program ABSORB.[25] Maximum and minimum transmission factors were estimated to be 0.95 and 0.92, respectively. Of the 6557 reflections collected, 2337 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations.

Complex II: $C_{22}H_{19}MoN_5OS_3$; formula weight 561.6; crystal class triclinic; space group $P\bar{1}$; a = 11.728 (4), b = 11.744 (3), c = 11.860 (5) Å; α = 60.27 (3), β = 60.57 (3), γ = 64.80 (3)°; D_{obsd} = 1.55 D_{calcd} = 1.555 g cm^{-3}; U = 1199.1 Å^3; Z = 2; μ(Mo Kα) = 7.75 cm^{-1}; λ(Mo Kα) = 0.7107 Å; $F(000)$ = 568 electrons.

Intensity data ($\pm h, \pm k, +l$) were collected from a crystal of dimensions 0.14 × 0.15 × 0.17 mm^3 in the range $1.5 < \theta < 22°$ with use of an $\omega-(n/3)\theta$ scan, where n (=3) was optimized by profile analysis of a typical reflection. The ω-scan angles and horizontal counter apertures employed were $(1.85 + 0.35 \tan \theta)°$ and $(2.40 + 0.5 \tan \theta)$ mm, respectively. Three standard reflections, monitored after every 66 min of data collection, indicated that, by completion of the data collection, no decomposition had occurred. Data reduction, application of Lorentz and polarization corrections, and absorption corrections were carried out as for complex I. Of the 4867 reflections collected, 2514 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations.

Solution and Refinement of Structures. The molybdenum atom location, in each case, was determined with use of the heavy-atom-method routine of the SHELX[25] program. All other nonhydrogen atoms were located in the Fourier difference maps of successive full-matrix least-

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(25) Programs used included the following: SUSCAD and ABSORB, "Data Reduction Programs for the CAD 4 Diffractometer", by J. M. Guss, University of Sydney, 1979, 1980; SHELX, "Program for Crystal Structure Determination", by G. M. Sheldrick, 1976.

Table I. Atomic Coordinates for Complex I[a]

atoms	*x*	*y*	*z*
Mo(1)	23644 (3)	337 (4)	25634 (4)
S(1)	26886 (8)	−16652 (10)	23203 (11)
S(2)	19841 (8)	14450 (10)	33508 (12)
O(1)	2912 (2)	−412 (3)	4192 (3)
O(2)	1372 (2)	−462 (2)	2818 (3)
O(3)	2990 (3)	1716 (3)	556 (4)
O(4)	1118 (3)	−737 (3)	−976 (3)
O(5)	8333 (4)	2817 (6)	598 (7)
N(1)	3245 (2)	−1273 (3)	4438 (3)
N(2)	966 (2)	141 (4)	3240 (3)
N(3)	3115 (2)	681 (3)	2380 (3)
N(4)	3627 (2)	1285 (3)	2356 (4)
N(5)	1775 (2)	52 (3)	1010 (3)
N(6)	1941 (2)	306 (3)	74 (4)
C(1)	3175 (3)	−1923 (4)	3673 (4)
C(2)	3988 (2)	−3241 (3)	3416 (3)
C(3)	4264 (2)	−4176 (3)	3626 (3)
C(4)	4050 (2)	−4760 (3)	4372 (3)
C(5)	3561 (2)	−4408 (3)	4909 (3)
C(6)	3285 (2)	−3474 (3)	4699 (3)
C(7)	3499 (2)	−2890 (3)	3953 (3)
C(8)	3675 (3)	−1346 (4)	5616 (4)
C(9)	1172 (3)	1024 (4)	3512 (4)
C(10)	322 (3)	−358 (4)	3412 (6)
C(11)	−6 (2)	1925 (3)	3298 (3)
C(12)	−413 (2)	2588 (3)	3702 (3)
C(13)	−91 (2)	3039 (3)	4722 (3)
C(14)	639 (2)	2828 (3)	5339 (3)
C(15)	1046 (2)	2165 (3)	4935 (3)
C(16)	723 (2)	1714 (3)	3914 (3)
C(17)	3518 (3)	1818 (4)	1429 (6)
C(18)	4551 (2)	2907 (3)	2508 (3)
C(19)	5043 (2)	3660 (3)	2535 (3)
C(20)	5055 (2)	4098 (3)	1548 (3)
C(21)	4576 (2)	3782 (3)	533 (3)
C(22)	4085 (2)	3029 (3)	506 (3)
C(23)	4073 (2)	2591 (3)	1493 (3)
C(24)	1602 (3)	−117 (5)	−911 (5)
C(25)	2216 (2)	1001 (3)	−1896 (3)
C(26)	2506 (2)	1188 (3)	−2764 (3)
C(27)	2434 (2)	507 (3)	−3602 (3)
C(28)	2072 (2)	−362 (3)	−3570 (3)
C(29)	1782 (2)	−549 (3)	−2702 (3)
C(30)	1854 (2)	132 (3)	−1864 (3)

[a] Mo, S coordinates ×10^5, others ×10^4.

squares refinements. Methyl and phenyl hydrogen atoms were included at calculated positions (C(Me)–H = 0.97 Å, C(Ph)–H = 1.08 Å), assuming the appropriate geometry about the carbon atoms. The hydrogen atom thermal parameters were refined as a common group factor. The methyl entities and phenyl rings were refined as rigid groups. In complex I, the remaining two hydrogen atoms (bonded to N(5) and N(6)) were located in the last stages of refinement. A constraint was applied so that the two N–H distances were 0.95 Å, with an estimated error of 0.01 Å.

In complex II, H(1) was located in the difference map of the second to last least-squares refinement and then included in the final least-squares refinement at a calculated position of 0.95 Å from N(3).

For both complexes, all of the non-hydrogen atoms were modeled anisotropically in the final blocked-matrix least-squares calculation. Tables I and II, for complexes I and II respectively, give the final least-squares positional parameters. The hydrogen atom parameters and the structure factor amplitudes are supplied in the supplementary tables.

For complex I, the refinement converged with R ($=\sum|(|F_0| - |F_c|)|/\sum|F_0|$) = 0.029 and R_w ($=\sum|(|F_0|-|F_c|)|w^{1/2}/\sum(|F_0|)w^{1/2}$) = 0.030. The weighting scheme employed converged at $w = 1.67/(\sigma^2F_0 + 0.00017F_cF_c)$. The largest peak remaining in the final difference map was 0.3 e Å^{-3} in height.

For complex II, the refinement converged with $R = 0.024$ and R_w = 0.028. The weighting scheme employed converged at $w = 1.87/(\sigma^2F_0 + 0.00012F_cF_c)$. The largest peak remaining in the final difference map was 0.3 e Å^{-3} in height.

All the above calculations were performed with use of the scattering factors for the respective neutral atoms as tabulated in ref 26.

Table II. Atomic Coordinates for Complex II[a]

atoms	*x*	*y*	*z*
Mo(1)	29354 (3)	−45668 (3)	26543 (3)
S(1)	11769 (9)	−38122 (9)	17006 (9)
S(2)	15794 (8)	−60646 (9)	48916 (9)
S(3)	16599 (8)	−25811 (9)	32981 (9)
N(1)	3587 (3)	−5372 (3)	1442 (3)
N(2)	3348 (3)	−5284 (3)	416 (3)
N(3)	4162 (3)	−3341 (2)	1427 (3)
O(1)	4154 (2)	−5533 (2)	3808 (2)
N(4)	4162 (3)	−2311 (3)	1629 (3)
N(5)	3929 (3)	−6640 (3)	4990 (3)
C(1)	3022 (3)	−1896 (3)	2536 (3)
C(2)	1883 (2)	−438 (2)	3953 (2)
C(3)	1800 (2)	650 (2)	4191 (2)
C(4)	2747 (2)	1430 (2)	3280 (2)
C(5)	3777 (2)	1122 (2)	2131 (2)
C(6)	3860 (2)	35 (2)	1892 (2)
C(7)	2912 (2)	−745 (2)	2803 (2)
C(8)	2788 (3)	−6983 (3)	5618 (4)
C(9)	2613 (3)	−8180 (2)	8105 (3)
C(10)	2342 (3)	−9276 (2)	9353 (3)
C(11)	1986 (3)	−10318 (2)	9442 (3)
C(12)	1902 (3)	−10263 (2)	8282 (3)
C(13)	2173 (3)	−9167 (2)	7034 (3)
C(14)	2529 (3)	−8125 (2)	6945 (3)
C(15)	2140 (3)	−4488 (3)	414 (3)
C(16)	2503 (2)	−4706 (3)	−1728 (3)
C(17)	2044 (2)	−4424 (3)	−2745 (3)
C(18)	748 (2)	−3629 (3)	−2701 (3)
C(19)	−88 (2)	−3116 (3)	−1639 (3)
C(20)	371 (2)	−3398 (3)	−622 (3)
C(21)	1667 (2)	−4193 (3)	−666 (3)
C(22)	5137 (4)	−7344 (5)	5362 (5)

[a] Mo, S coordinates ×10^5, others ×10^4.

Results and Discussion

Synthesis and Characterization. The thiohydroxamate complex $[O_2Mo(PhC(S)N(Me)O)_2]$ reacts readily with $PhC(O)NHNH_2$ in refluxing methanol to yield dark red crystals of the mixed diazenido–hydrazido(1−) complex I of formula $[Mo(N_2C(O)Ph)(NHNHC(O)Ph)(PhC(S)N(Me)O)_2]$, both of the initial oxo atoms being removed in the process. In contrast, the hydroxamate complex $[O_2Mo(PhC(O)N(Me)O)_2]$, while reacting readily to form dark-colored solutions, yields only dark-colored insoluble powdery products that display poorly resolved IR spectra. The reaction of the thiohydroxamate complex with $PhC(S)NHNH_2$ again proceeds smoothly to produce green-black crystals of the mixed diazene–diazenido(1−) derivative II of formula $[Mo(NHNC(S)Ph)(N_2C(S)Ph)(PhC(S)N(Me)O)]$. As well as both oxo atoms being removed, one of the thiohydroxamate chelate groups has been displaced by a chelating thiobenzoylhydrazine moiety. The strong donor properties of $PhC(S)NHNH_2$ are also evident in its reaction with $[O_2Mo(PhC(O)N(Me)O)_2]$ at room temperature, in which all the original ligands are displaced to form the known trischelated diazene species $[Mo(NHNC(S)Ph)_3]$.[27,28] Heating this reaction leads to the production of more complicated green-black mixtures. These results show that the hydroxamate ligand, and to a lesser extent the thiohydroxamate counterpart, are labile to substitution and this unfortunately complicates attempts to probe the reactivity of the dioxomolybdenum moiety while keeping the coligands intact.

The ^{1}H and ^{13}C NMR spectra of I are shown in Figure 2. The presence of inequivalent methyl groups is clear from both spectra, which contrasts with the equivalent thiohydroxamate environments found in the precursor dioxo complexes.[4] However, the inequivalence and spatial complexity of the benzoylhydrazine group render the thiohydroxamate groups inequivalent. The NH resonances are observed as an AB pair and are particularly interesting. Both are shifted considerably downfield due to the strong

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(26) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99, 149.

(27) Chatt, J.; Dilworth, J. R. *J. Less-Common Met.* **1974**, *36*, 513.

(28) Dilworth, J. R.; Hyde, J.; Lyford, P.; Vella, P.; Venkatasubramaman, K.; Zubieta, J. A. *Inorg. Chem.* **1979**, *18*, 268.

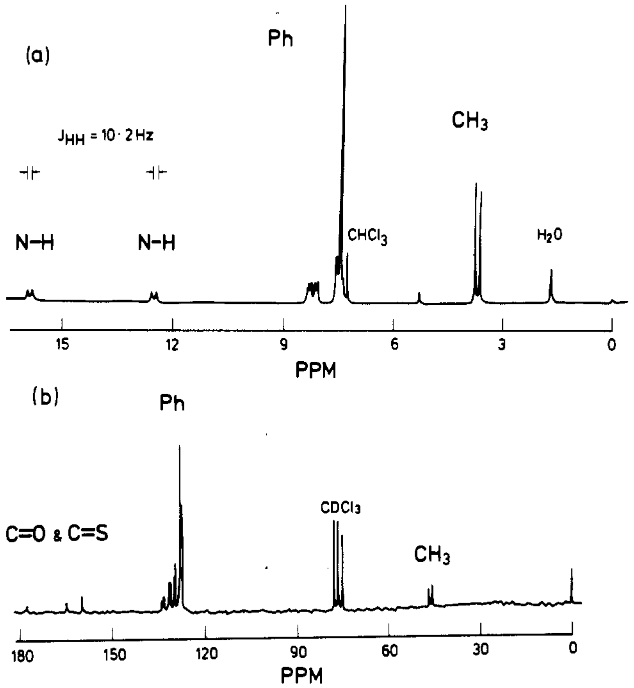

Figure 2. (a) ^1H and (b) ^{13}C NMR spectra of complex I in $CDCl_3$ at 25 °C.

electron-withdrawing property of the Mo atom, the doublet at 15.85 ppm corresponding most likely to the proton closest to Mo. A splitting of 10.2 Hz is observed due to H–H coupling, which is comparable to that in similar M–NHNHR compounds where such coupling could be observed.[10,29] The present large downfield shifts contrast with values of ca. 7[30] and 4 ppm[15,31] observed in η^2 side-bound hydrazido(1–) complexes and a value of 7.16 ppm observed in a chelated Mo–NH_2NR system.[32] Hydrogen bonding of N(6)—H(2) to an adjacent C═O(3) (vide infra) will also influence the size of the downfield shift of this proton in I. In the IR spectrum N–H stretching frequencies are observed at 3230 and 3070 cm^{-1}. From the analytical and spectroscopic data alone it is not possible to unambiguously define the coordination number of the Mo atom. While six-coordination is most likely, a seven-coordinate alternative is possible in which one of the benzoylhydrazine moieties is chelated to the metal ion. Related examples of this type are known.[33-35]

The NH resonance of the chelated diazene in II is observed as a broad line at 9.96 ppm. Other studies of compounds containing the Mo(NHNC(S)Ph) moiety have not been able to locate this resonance.[19,28] The ν(NH) IR frequency can generally be detected, however. It occurs as a weak broad band at 3020 cm^{-1} in contrast to a sharp band of medium intensity at 3240 cm^{-1} observed for $[Mo(PhC(S)NNH)_3]$.[28]

The mechanisms of reactions of the present type are poorly understood. The stoichiometry of the reaction that forms complex I corresponds to loss of two oxygen atoms from MoO_2^{2+} and four hydrogen atoms from 2 mol of $PhC(O)NHNH_2$, giving, formally at least, 2 mol of water. Since the reaction was performed in the air, it is conceivable that the reaction proceeds initially to form bis(diazenido) species, $Mo(N_2COPh)_2^{2+}$, which subsequently pick up two hydrogen atoms, forming the stable product I. The latter can be assigned formal charges of $Mo^{6+}(NHNHC(O)Ph)^-(N_2C(O)Ph)^{3-}(PhC(S)N(Me)O)_2^-$. Alternatively, if the bis(hydrazido(2–)) complex $[Mo(NNHC(O)Ph)_2(PhC(S)N(Me)O)_2]$ is formed initially by simple condensation, it presumably must transfer hydrogens internally to yield the hydrazido(1–)–diazenido species. It is interesting to note that related dimethyldithiocarbamate (dmtc) complexes of formula $[Mo(N_2H_2C(O)OR)(N_2C(O)OR)(dmtc)_2]$, which possess side-bonded hydrazido(1–), could only be made under anaerobic conditions and converted readily to the bis(diazenido) complexes, $[Mo(N_2C(O)OR)_2(dmtc)_2]$, in air.[13,30] This same rearrangement occurs with a tetradentate S_2N_2 coligand.[7] Under similar conditions, however, the mixed hydrazido(1–)–diazenido complex $[Mo(NH_2NC(S)SR)(N_2C(S)SR)(dmtc)_2]$, being similar in stoichiometry to I but containing seven-coordinate Mo and a chelating M–NH_2NR moiety, could be obtained, which, like I, did not convert to the corresponding bis(diazenido) derivative.[32] Clearly, there are many subtle effects involved that are difficult to quantify.

Table III. Atomic Distances (Å) and Angles (deg) and Their Standard Deviations for Complex I

(a) Distances

S(1)–Mo(1)	2.483 (2)	S(2)–Mo(1)	2.408 (2)
O(1)–Mo(1)	2.094 (3)	O(2)–Mo(1)	2.119 (4)
N(3)–Mo(1)	1.758 (5)	N(5)–Mo(1)	1.938 (4)
C(1)–S(1)	1.712 (5)	C(9)–S(2)	1.717 (6)
N(1)–O(1)	1.345 (6)	N(2)–O(2)	1.353 (6)
C(17)–O(3)	1.250 (7)	C(24)–O(4)	1.244 (8)
C(1)–N(1)	1.300 (7)	C(8)–N(1)	1.465 (6)
C(9)–N(2)	1.301 (8)	C(10)–N(2)	1.478 (8)
N(4)–N(3)	1.292 (7)	C(17)–N(4)	1.347 (8)
N(6)–N(5)	1.361 (7)	C(24)–N(6)	1.348 (7)
C(7)–C(1)	1.474 (7)	C(16)–C(9)	1.473 (8)
C(23)–C(17)	1.488 (8)	C(30)–C(24)	1.467 (8)

(b) Angles

S(2)–Mo(1)–S(1)	160.5 (1)	O(1)–Mo(1)–S(1)	76.9 (1)
O(1)–Mo(1)–S(2)	87.5 (1)	O(2)–Mo(1)–S(1)	88.6 (1)
O(2)–Mo(1)–S(2)	79.0 (1)	O(2)–Mo(1)–O(1)	87.2 (1)
N(3)–Mo(1)–S(1)	103.3 (1)	N(3)–Mo(1)–S(2)	89.7 (1)
N(3)–Mo(1)–O(1)	95.9 (2)	N(3)–Mo(1)–O(2)	168.2 (2)
N(5)–Mo(1)–S(1)	88.6 (1)	N(5)–Mo(1)–S(2)	104.8 (1)
N(5)–Mo(1)–O(1)	163.1 (2)	N(5)–Mo(1)–O(2)	84.0 (2)
N(5)–Mo(1)–N(3)	95.7 (2)	C(1)–S(1)–Mo(1)	98.8 (2)
C(9)–S(2)–Mo(1)	99.5 (2)	N(1)–O(1)–Mo(1)	123.1 (3)
N(2)–O(2)–Mo(1)	119.9 (3)	C(1)–N(1)–O(1)	120.9 (4)
C(8)–N(1)–O(1)	111.8 (4)	C(8)–N(1)–C(1)	127.3 (5)
C(9)–N(2)–O(2)	121.8 (5)	C(10)–N(2)–O(2)	111.3 (4)
C(10)–N(2)–C(9)	126.7 (5)	N(4)–N(3)–Mo(1)	168.8 (4)
C(17)–N(4)–N(3)	117.5 (4)	N(6)–N(5)–Mo(1)	131.9 (3)
C(24)–N(6)–N(5)	121.2 (5)	N(1)–C(1)–S(1)	119.8 (4)
C(7)–C(1)–S(1)	119.2 (4)	C(7)–C(1)–N(1)	121.0 (4)
C(2)–C(7)–C(1)	119.5 (4)	C(6)–C(7)–C(1)	120.4 (4)
N(2)–C(9)–S(2)	119.8 (5)	C(16)–C(9)–S(2)	117.0 (4)
C(16)–C(9)–N(2)	123.2 (5)	C(11)–C(16)–C(9)	121.6 (4)
C(15)–C(16)–C(9)	118.4 (4)	N(4)–C(17)–O(3)	124.9 (6)
C(23)–C(17)–O(3)	119.4 (6)	C(23)–C(17)–N(4)	115.6 (5)
C(18)–C(23)–C(17)	121.8 (4)	C(22)–C(23)–C(17)	118.2 (4)
N(6)–C(24)–O(4)	119.7 (6)	C(30)–C(24)–O(4)	122.0 (5)
C(30)–C(24)–N(6)	118.2 (5)	C(25)–C(30)–C(24)	121.0 (4)
C(29)–C(30)–C(24)	118.8 (4)		

Complex II achieves the formal charges shown: $Mo^{6+}(NHNC(S)Ph)^{2-}(N_2C(S)Ph)^{3-}(PhC(S)N(Me)O)^-$. In this compound the extra hydrogen lost from the two reacting $PhC(S)NHNH_2$ molecules presumably has bonded to the displaced thiohydroxamate ligand to yield the free acid. From the stereochemical point of view there seems to be a tendency for the present molecules to achieve six-coordination rather than seven as sometimes found in related dithiocarbamate species.[13,32] This may relate to the "bite" size of these chelating groups and perhaps gives an added stabilizing influence in the present five-membered-ring chelates which would explain some of the differences. Interestingly, complexes of stoichiometry and structure similar to those of II have been reported, of formula $[Mo(NHNC(S)Ph)(N_2C(S)Ph)(PhC(S)NN{=}CMe_2)]$, but prepared by a different route,[19]

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(29) Rigby, W.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 382.

(30) Bishop, M. W.; Butler, G.; Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1843.

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(32) Mattes, R.; Scholand, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 245.

(33) Butcher, A. V.; Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 921.

(34) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Jayaweera, S. A. A.; Quick, A. *J. Chem. Soc., Dalton Trans.* **1979**, 914.

(35) Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Dalton Trans.* **1979**, 1603.

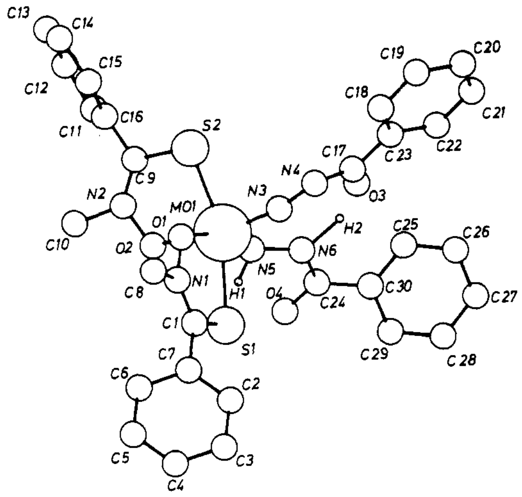

Figure 3. Molecular structure and numbering scheme for complex I. Two waters of crystallization (oxygen O(5)) were found per unit cell and were included in the refinement.

i.e. reaction of [Mo(NHNC(S)Ph)$_3$] with acetone in aerobic acidic medium.

Discussion of Structures. Complex I. A PLUTO diagram[36] showing the positions of the atoms and numbering scheme employed is shown in Figure 3. Pertinent bond distances and angles are given in Table III. Perusal of Figure 3 shows that the coligand geometry remains essentialy as it was in the *cis*-dioxo precursor[4] while the monodentate hydrazine fragments occupy what were the oxo positions. The coordination geometry is that of a distorted octahedron with much of the distortion arising from the restriction of bite size (average 77.95°) of the two bidentate five-membered ligand rings.

Of the two hydrazine moieties, the group containing N(3), N(4) corresponds to a diazenido species while the group containing N(5),N(6) corresponds to a hydrazido(1–) ligand with hydrogens being located on both N(5) and N(6). Hydrogen bonding is evident for N(6)–H(2)···O(3) with a total bond distance of 2.8 Å and bond angle of 153.9°. This is within the accepted range[37] of N–H···O interactions. However, hydrogen bonding is unlikely for N(5)–H(1)···O(4). Although the total bond distance is 3.2 Å, the angle N(5)–H(1)···O(4) deviates 74.2° from a straight line, which is inconsistent with hydrogen-bond formation.[37] The crystallographic parameters for the diazenido and hydrazido(1–) groups are quite distinct and diagnostic. The Mo–N(3) and N(3)–N(4) distances (1.758 (5) and 1.292 (4) Å, respectively) in the Mo–diazenido group are short and comparable to related structures.[3,6] They show significant double bonding and electron delocalization within the essentially linear Mo←N═NR entity (N(3)–Mo–N(4) = 168.8 (4)°). The "end-on" hydrazido(1–) species has bond lengths of Mo–N(5) = 1.938 (4) Å and N(5)–N(6) = 1.361 (7) Å, which are compatible with very little double bonding in the Mo–NHNH framework. The structural parameters are similar to those of known "end-on" hydrazido NHNRR′ complexes[10,11] indicating that substituting R = H does not change the coordination markedly. However, the Mo–N(5) distance is significantly shorter than the values found[13,14,16] in side-bonded hydrazido(1–) species, ca. 2.1–2.2 Å. The Mo–N–N angles are significantly different for the two groups (168.8 (4)° for the diazenido and 131.9 (3)° for the hydrazido(1–)). The diazenido group has a greater trans effect than the hydrazido(1–) as expected. This is reflected in the greater Mo–O distance trans to these groups (diazenido, Mo–O(2) = 2.119 (4) Å; hydrazido, Mo–O(1) = 2.094 (3) Å).

The geometric features of the Mo–NHNHR fragment in I are compared in Figure 4 with those of side-bonded and related hydrazido species. It can be seen that the bond lengths and M–N–N angle are also quite similar to those in a –N$_2$H$_2$– bridged tungsten complex recently described by Schrock[38] and thought to possess some W═N bonding character (see also ref 42).

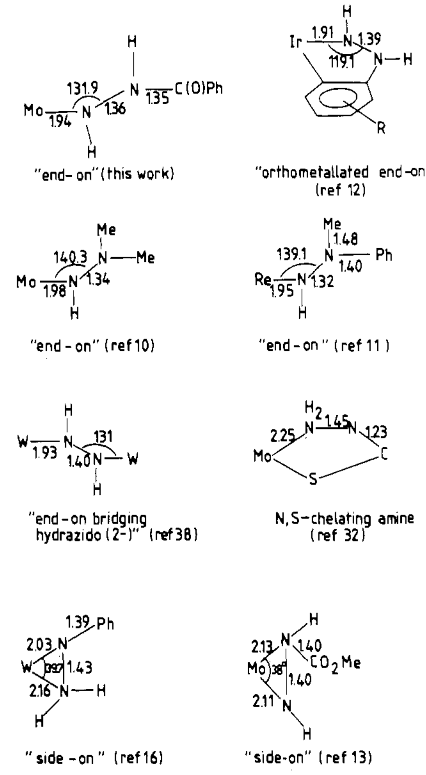

Figure 4. Comparison of pertinent bond lengths and angles in various hydrazido(1–) and related complexes.

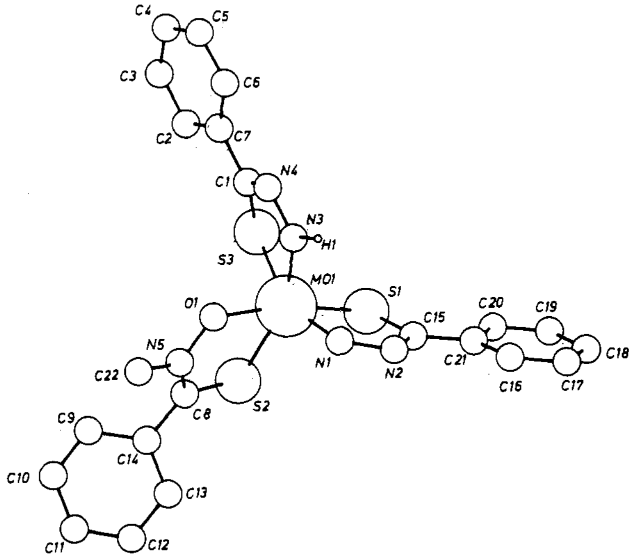

Figure 5. Molecular structure and numbering scheme for complex II.

As indicated earlier, Dilworth and Zubieta[13] have proposed that the side-bonded hydrazido(1–) arrangement will be the stable one unless steric or electronic effects intervene. The only such effect in I that could be responsible for the end-on bonding is the hydrogen-bonding interaction between the NHN*H*COPh and N$_2$*C*OPh ligands described above. However, the same situation exactly could have occurred in the complex [Mo(NHNHC(O)OMe)(N$_2$C(O)OMe)(dmtc)$_2$], which they cite in support of the side-bonded proposal. The only significant differences between the latter complex and I would appear to be the solid angle

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(36) PLUTO, "Plotting Program for Molecular Structures", by W. D. S. Motherwell.

(37) Stout, G. H.; Jensen, L. H. "X-ray Structure Determination-A Practical Guide"; Macmillan: New York, 1968; p 303.

(38) Schrock, R. R.; Blum, R.; Theopold, K. H. *Proc. Int. Conf. Coord. Chem., 23rd* **1984**, 525.

Table IV. Atomic Distances (Å) and Angles (deg) and Their Standard Deviations for Complex II

(a) Distances

S(1)–Mo(1)	2.462 (1)	S(2)–Mo(1)	2.504 (1)
S(3)–Mo(1)	2.436 (1)	N(1)–Mo(1)	1.789 (4)
N(3)–Mo(1)	1.972 (3)	O(1)–Mo(1)	2.051 (3)
C(15)–S(1)	1.726 (4)	C(8)–S(2)	1.701 (4)
C(1)–S(3)	1.724 (4)	N(2)–N(1)	1.324 (6)
C(15)–N(2)	1.325 (4)	N(4)–N(3)	1.343 (6)
N(5)–O(1)	1.358 (3)	C(1)–N(4)	1.317 (4)
C(8)–N(5)	1.299 (5)	C(22)–N(5)	1.462 (7)
C(7)–C(1)	1.477 (6)	C(14)–C(8)	1.467 (4)
C(21)–C(15)	1.471 (6)		

(b) Angles

S(2)–Mo(1)–S(1)	89.9 (1)	S(3)–Mo(1)–S(1)	82.7 (1)
S(3)–Mo(1)–S(2)	92.8 (1)	N(1)–Mo(1)–S(1)	73.3 (1)
N(1)–Mo(1)–S(2)	105.1 (1)	N(1)–Mo(1)–S(3)	149.7 (1)
N(3)–Mo(1)–S(1)	108.5 (1)	N(3)–Mo(1)–S(2)	157.4 (1)
N(3)–Mo(1)–S(3)	77.0 (1)	N(3)–Mo(1)–N(1)	93.0 (1)
O(1)–Mo(1)–S(1)	166.5 (1)	O(1)–Mo(1)–S(2)	76.9 (1)
O(1)–Mo(1)–S(3)	100.6 (1)	O(1)–Mo(1)–N(1)	107.0 (1)
O(1)–Mo(1)–N(3)	85.0 (1)	C(15)–S(1)–Mo(1)	96.9 (2)
C(8)–S(2)–Mo(1)	98.1 (1)	C(1)–S(3)–Mo(1)	95.4 (1)
N(2)–N(1)–Mo(1)	140.3 (2)	C(15)–N(2)–N(1)	110.3 (3)
N(4)–N(3)–Mo(1)	127.1 (2)	N(5)–O(1)–Mo(1)	122.3 (3)
C(1)–N(4)–N(3)	113.5 (3)	C(8)–N(5)–O(1)	121.7 (3)
C(22)–N(5)–O(1)	110.3 (3)	C(22)–N(5)–C(8)	128.0 (3)
N(4)–C(1)–S(3)	121.7 (4)	C(7)–C(1)–S(3)	120.6 (2)
C(7)–C(1)–N(4)	117.5 (3)	C(2)–C(7)–C(1)	120.9 (2)
C(6)–C(7)–C(1)	119.1 (2)	N(5)–C(8)–S(2)	118.9 (2)
C(14)–C(8)–S(2)	120.2 (3)	C(14)–C(8)–N(5)	120.9 (4)
C(9)–C(14)–C(8)	121.8 (4)	C(13)–C(14)–C(8)	118.2 (4)
N(2)–C(15)–S(1)	117.4 (4)	C(21)–C(15)–S(1)	122.3 (2)
C(21)–C(15)–N(2)	120.3 (4)	C(16)–C(21)–C(15)	120.4 (2)
C(20)–C(21)–C(15)	119.6 (3)		

available to the two acylhydrazide groups created by the dithiocarbamate and thiohydroxamate coligands and the different R substituents on the $RC(O)NHNH_2$ group.

Complex II. The molecular structure is shown in Figure 5; bond lengths and angles are given in Table IV. The six-coordinate complex is made up of three five-membered chelating rings, each containing the SC(Ph)NX framework where X = O in the thiohydroxamate ring and N in the diazene and diazenido rings. The chelate containing N(1) and N(2) is a diazenido ligand while the diazene chelate has a hydrogen atom on N(3). The structure of II consists of molecules of a geometry intermediate between octahedral and trigonal prismatic, with S(1), S(2), S(3) and N(1), O(1), N(3) disposed on opposite triangular faces in a facial configuration. These two triangular faces are not perfectly parallel, as shown by the dihedral angle of 6.75° (parallel faces giving an angle of 0°). The occurrence of three S atoms on the same triangular face is a common feature in asymmetric {SX} bidentate systems and probably results from weak S···S interactions.[39]

The average twist angle (defined as the chelate projection angle onto the mean plane defined by the triangular faces) for the complex is 34.4°. This reflects the large distortion from both a regular trigonal-prismatic symmetry (of twist angle 0 °C) and regular octahedral symmetry (of twist angle 60 °C). Presumably, some sources of distortion from regular geometry would include constraints imposed on the geometry of the molecule by the five-membered chelate rings, and the effects of ligating through different donor groups. These and other steric and electronic effects have been discussed in relation to a related Mo complex with similar geometry.[19]

The structural parameters for the diazene and diazenido chelate rings are quite different and distinctive. This is most noticeably reflected in the Mo–N bond distances (diazene, 1.972 (3) Å; diazenido, 1.789 (4) Å). These values are very similar to those in another chelated diazenido–diazene compound, $[Mo(NHNC(S)R)(N_2C(S)R)(RC(S)NNCR'_2)]$, where R = p-ClC_6H_5 and R′ = Me.[19] The diazene parameters are also similar to those in $[Mo(NHNC(S)Ph)_3]$,[28] where $Mo–N_{av}$ = 2.03 Å, while the chelated diazenido Mo–N bond length is similar to that in $[Mo(NH_2NC(S)SR)(N_2C(S)SR)(dtc)_2]$ (Mo–N = 1.77 (1) Å)[32] even though here the diazenido is monodentate. The short bond lengths are indicative of considerable electron delocalization within the chelate rings. The thiohydroxamate geometry is comparable to that in I and in the parent *cis*-dioxo complex.[4]

Conclusions and Prospect

The initial aim of comparing matched pairs of complexes has been thwarted by being unable to obtain appropriate hydroxamate derivatives to compare with the structurally characterized thiohydroxamate derivatives. This results from a combination of lability of the hydroxamate ligand and of a (presumed) lower formation constant compared to that for $PhC(S)NHNH_2$. Thiobenzoylhydrazine is also capable of displacing a thiohydroxamate ligand and shows a pronounced tendency to chelate to Mo, which contrasts with the monodentate coordination mode displayed by $PhC(O)NHNH_2$ in the present derivatives, although there are examples known of chelating benzoylhydrazines.[33]

One of the most significant results of the present study has been the characterization of the first end-on-bonded –NHNHR species in complex I. We are currently investigating the reactivity of this compound toward protonation with particular interest in (i) a comparison of its reactivity with that of the diazenido group and (ii) the characterization of reaction products and intermediates, which hopefully will shed light on the reactivity of the Mo–NHNHR group. It is possible to envisage the formation of Mo=NH or Mo=N moieties together with amines and/or hydrazines. However, rearrangements to produce species such as $Mo{=}N{-}NH_2R^+$ and a source of electrons will be required if the cyclic mechanism for nitrogen reduction by Chatt and Richards[40] is to be realized in these analogs. Deprotonation of the Mo–NHNHR group in I is also of interest.

Acknowledgment. M.R.S. acknowledges support from the Australian Research Grants Scheme.

Registry No. $I{\cdot}2H_2O$, 97751-72-9; I, 97751-73-0; $[MoO_2(PhC(S)N(Me)O)_2]$, 97751-74-1; $[MoO_2(PhC(O)N(Me)O)_2]$, 97806-15-0; $MoO_2(acac)_2$, 17524-05-9; $[Mo(PhC(S)NNH)_3]$, 53449-66-4.

Supplementary Material Available: Listings of atomic coordinates and anisotropic thermal parameters, hydrogen atomic coordinates and isotropic thermal parameters, and structure factor amplitudes for each complex (32 pages). Ordering information is given on any current masthead page.

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(39) Murray, K. S.; Newman, P. J.; Taylor, D. *J. Am. Chem. Soc.* **1978**, *100*, 2251.

(40) Chatt, J.; Richards, R. L. *J. Less-Common Met.* **1977**, *54*, 477.

(41) Since our preliminary description of I (*Proc. Int. Conf. Coord. Chem.*, *23rd* **1984**, 120) the structure of the related rhenium complex $[ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCOPh)]$ has recently been reported: Nicholson, T.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1985**, 367.

(42) Schrock and co-workers have just reported a monomeric "end-on"-bonded hydrazido(1−) complex, $[W(\eta^5\text{-}C_5Me_5)Me_4(NHNH_2)]$, although it is not yet confirmed by crystallography due to instability: Murray, R. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4557.