site preference energy in spinels[9]). Mn^{3+} and Mn^{4+} compounds differ by the occurrence of strong Jahn–Teller distortions in the former, due to the d^4 electronic configuration of Mn^{3+}. Whereas the six Mn^{4+}–O bond lengths are nearly equal in β-MnO_2 (1.88–1.91 Å), the Mn^{3+} ions in Mn_2O_3 have four oxygen neighbors at ~1.96 Å and two oxygen neighbors at 2.06 or 2.25 Å.[7] A very similar distortion occurs in $Cs_3Mn_3V_4O_{16}$, with four "short" Mn–O distances (1.90–1.98 Å) and two "long" Mn–O distances at 2.15–2.22 Å (see Table II). The structural features of V^{4+} and V^{5+} are very different from each other. V^{4+} is usually octahedrally coordinated, whereas V^{5+} is found mostly with coordination numbers 4 or 5. The double tetrahedron (V_2O_7) occurs in the structure of several mixed oxides with the formula $M_2^{II}V_2O_7$.[8] Thus it can be seen from Table V that $Cs_3Mn_3V_4O_{16}$ exhibits structural characteristics of Mn^{3+} (average bond length, Jahn–Teller distortion) and of V^{5+} (bond length, coordination). The charge distribution is most probably $(Cs^+)_3(Mn^{3+})_3(V^{5+})_4(O^{2-})_{16}$, as expected from the crystal growth process, which was based on oxidation in a medium containing Mn^{2+} and V^{5+} ions.

The structure of $Cs_3Mn_3V_4O_{16}$, characterized by ribbons of $(Mn_3O_{10})_n$ bridged by V_2O_7 double tetrahedra, is new. Apart from oxide solid solutions (Mn, V)O_2, no mixed oxides containing both Mn(3+ or 4+) and V(4+ or 5+) are known. Most manganese complex oxides belong to structural types derived from close-packed arrays of oxygen anions. Ribbons of edge-sharing (MnO_6) octahedra have been found in the Mn^{4+} compounds $Co_2Mn_3O_8$ and $Cu_2Mn_3O_8$,[10] but with a different spatial arrangement leading to a ribbon composition $(Mn_3O_8)_n$. A ribbon $(A_3O_{10})_n$ with the same architecture as in $Cs_3Mn_3V_4O_{16}$ occurs in lindgrenite, a copper(II) hydroxomolybdate of formula $2CuMoO_4 \cdot Cu(OH)_2$, with ribbon composition $[Cu_3O_8(OH)_2]_n$.[11]

Other Properties. The magnetization in $Cs_3Mn_3V_4O_{16}$ was measured in the range 4.2–60 K with use of a vibrating-sample magnetometer in a field of 20 kOe. There was no evidence of magnetic ordering, and the sample appeared to be paramagnetic down to 4.2 K. The Curie constant could not be determined due to the very small amounts of substance available (~0.3 mg).

Finally, the Mn–Mn distances between adjacent Mn_A and Mn_B atoms in the ribbons is 2.98 Å. Comparison of this value with the critical distance R_c defined by Goodenough[12] as a criterion for localized vs. collective electron transport behavior indicates that no collective (metallic) electronic properties should be expected in this material ($R_c[Mn^{3+}]$ = 2.72 Å).

Acknowledgment. We thank Dr. S. P. McAlister for the magnetic measurements and Dr. L. D. Calvert for pointing out the similarity with the ribbons in the lindgrenite structure.

Registry No. $Cs_3Mn_3V_4O_{16}$, 80105-64-2.

Supplementary Material Available: A listing of calculated and observed structure factors and complete listing (100 lines for 2θ(Cu Kα) up to 58°) of the calculated powder pattern (36 pages). Ordering information is given on any current masthead page.

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Contribution from the Charles F. Kettering Research Laboratory, Yellow Springs, Ohio 45387,
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Structure of Oxobis(dimethyldithiocarbamato)(dibenzoyldiazene)molybdenum–1,2-Dichloroethane, $MoO(PhCONNCOPh)(S_2CNMe_2)_2 \cdot C_2H_4Cl_2$

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The X-ray crystal and molecular structure of oxobis(dimethyldithiocarbamato)(dibenzoyldiazene)molybdenum–1,2-dichloroethane, $MoO(C_3H_6NS)_2(C_{14}H_{10}N_2O_2) \cdot C_2H_4Cl_2$, was determined from intensity data collected with use of counter methods. The compound crystallizes in the space group $P2_1/c$ with the parameters a = 10.035 (2) Å, b = 16.360 (8) Å, c = 18.649 (6) Å, β = 104.00 (2)°, V = 2970.7 (18) Å^3, and Z = 4; d_{calcd} = 1.54 g/mL, d_{obsd} = 1.55 g/mL, and conventional R value = 0.058. The crystal structure contains discrete monomers. The approximate stereochemistry about the molybdenum atom is pentagonal bipyramidal. The four sulfur atoms of the dithiocarbamate ligands and N1 of the benzoyldiazene ligand occupy the equatorial positions. The axial sites are occupied by the terminal oxo group and O1 of the diazene ligand. The bidentate diazene ligand coordinates to Mo through N1 and O1 to form a five-membered chelate ring. The angle between the trans oxygen atoms is 166.0°, N1–N2 = 1.418 (14) Å, C1–N2 = 1.295 (10) Å, Mo–O = 1.685 (10) Å, and $(Mo–S)_{av}$ = 2.525 (14) Å. The dichloroethane of crystallization is disordered.

Introduction

The stereochemistry of transition-metal complexes of diazenes is of interest because several postulated mechanisms for the reduction of coordinated dinitrogen to ammonia involve η^2-diazenes (I) as intermediates or transition states.[2–4] There are relatively few well-documented η^2 complexes of diazenes and other reduced nitrogen ligands. Some examples include the azobenzene[5] and diazofluorene[6] complexes of nickel(0), the η^2-hydrazine complex[7] $(\eta\text{-}C_5H_5)Mo(NO)I(N_2H_3Ph)$, and the η^2-hydrazido(1−) complexes[8] $(\eta\text{-}C_5H_5)_2W(N_2H_2Ph)^+$ and

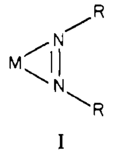

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Table I. Crystallographic Data for the Title Compound

mol formula	$MoO(C_3H_6NS_2)_2(C_{14}H_{10}N_2O_2)\cdot C_2H_4Cl_2$
mol wt	689.60
color	dark purple
cryst size, mm	0.20 × 0.20 × 0.20
radiation, Å	0.710 69 (Mo K$\bar{\alpha}$)
range 2θ reflctn array, deg	4.5–25.5
a, Å	10.035 (2)
b, Å	16.360 (8)
c, Å	18.649 (6)
β, deg	104.00 (2)
V, Å	2970.7 (18)
Z	4
space group	$P2_1/c$ (No. 14)[a]
d_{calcd}, g/mL	1.54
d_{obsd}, g/mL	1.55
scan mode	θ:2θ
variable scan rate range, deg/min	3.91–29.3
scan width, deg	$(K\alpha_1 - 1.0)$–$(K\alpha_2 + 1.0)$
total bkgd time/scan time	0.5
2θ range, deg	4.0–50.0
μ, cm^{-1}	9.13
no. of unique data	5642
no. of data $F_o^2 > 3\sigma(F_o^2)$	2706
NV	215
final R_1	0.058
final R_2	0.060
esd of observn of unit wt (GOF)	1.83

[a] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965; Vol. 1.

Table II. Selected Interatomic Bond Distances (Å) for $MoO(C_3H_6NS_2)_2(C_{14}H_{10}N_2O_2)\cdot C_2H_4Cl_2$

	Coordination Sphere		
Mo–S11	2.511 (4)	Mo–S22	2.499 (11)
Mo–S12	2.569 (18)	Mo–S21	2.520 (17)
Mo–O	1.685 (10)	Mo–N1	2.119 (18)
Mo–O1	2.054 (14)		
	Diazene Ligand		
N1–N2	1.418 (14)		
N1–C1′	1.384 (11)	N2–C1	1.295 (10)
C1′–O2	1.219 (16)	C1–O1	1.314 (11)
C1′–C2′	1.470 (15)	C1–C2	1.477 (17)
C2′–C3′	1.431 (13)	C2–C3	1.380 (14)
C3′–C4′	1.405 (16)	C3–C4	1.402 (18)
C4′–C5′	1.307 (21)	C4–C5	1.360 (15)
C5′–C6′	1.420 (16)	C5–C6	1.371 (15)
C6′–C7′	1.406 (17)	C6–C7	1.410 (17)
C7′–C2′	1.390 (19)	C7–C2	1.417 (13)
	Dimethyldithiocarbamato Ligand		
S11–C11	1.710 (9)	S22–C21	1.699 (11)
S12–C11	1.706 (15)	S21–C21	1.698 (16)
N11–C11	1.321 (12)	N21–C21	1.344 (12)
N11–C12	1.445 (13)	N21–C22	1.429 (13)
N11–C13	1.468 (17)	N21–C23	1.509 (18)

$Mo(NNMePh)(NHNMePh)(S_2CNMe_2)_2^+$. Several years ago it was shown that bis(dithiocarbamato)oxomolybdenum(IV) complexes react with diazenes to form 1:1 adducts.[9] In the case of $(EtO_2C)_2N_2$ an intense purple is initially observed and a yellow complex can be later isolated. For dibenzoyldiazene, $(PhCO)_2N_2$, an isolable purple compound is formed with the stoichiometry $MoO(dtc)_2$(diazine). In order to determine if this intensely colored compound had η^2 coordination of the diazine, we carried out a crystal structure determination. The structure determination shows the complex to be a pentagonal-bipyramidal molecule with the dibenzoyldiazene ligand coordinated through a carbonyl oxygen atom and one of the nitrogen atoms to form a five-membered chelate ring. Details of the structure are described herein.

Experimental Section

Single crystals were obtained by inert atmosphere vapor diffusion of reagent grade diethyl ether into a saturated solution of $MoO(C_3H_6NS_2)_2(C_{14}H_{10}N_2O_2)$ (**1**), prepared as previously described,[9] in freshly distilled and degassed 1,2-dichloroethane. Suitable crystals formed after 18 h. For the X-ray structure determination a large uniform crystal was cut to approximately equal dimensions (0.2 mm/side), encased in a bead of epoxy, and mounted on a quartz fiber.

Data Collection and Reduction. The crystal was transferred to a full-circle Syntex P2$_1$ autodiffractometer controlled by a NOVA 1200 series computer. Twenty reflections were machine-centered,[10] and adequate crystal mosaicity was verified by several ω scans having widths of less than 0.20° at half-peak height. The orientation matrix and unit cell parameters were determined from indexing and least-squares routines. The systematic absences ($h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$) indicated the centrosymmetric, uniquely determined space group $P2_1/c$. A unique quadrant of data was collected, and the 3 standard reflections monitored every 97 reflections showed no significant deviations. Additional details concerning data collection appear in Table I.

An empirical absorption correction was applied to the data with use of eight ψ scans with 2θ values ranging from 8.7 to 41.6°. The lowest transmission factor was 0.83, and the calculated linear absorption coefficient is 9.13 cm^{-1} (Mo Kα). Intensities were assigned, the data were reduced, and Lp corrections were applied as previously described.[11]

Structure Solution and Refinement. Standard crystallographic heavy-atom methods were used to determine the structure. Neutral-atom scattering factors for all nonhydrogen atoms were used in structure factor calculations;[12] the values tabulated by Stewart, Davidson, and Simpson[13] were applied to hydrogen atoms. The Mo, S, and Cl contributions were corrected for the real and imaginary components of anomalous dispersion.[14]

Residual (R_1) and weighted residual (R_2) indices were defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2}$ (where $w = 4F_o^2/(\sigma^2(F_o^2) + (pF_o^2)^2)$ and $p = 0.03$), respectively. The "goodness of fit" parameter was determined by the equation $(\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV}))^{1/2}$ where NO is the number of observed reflections and NV is the number of variables refined.

In the final stages of refinement several hydrogen atoms were located in a difference electron density map. In subsequent cycles of refinement all the H atoms were included as fixed contributors to the structure factors at idealized positions (C–H = 0.95 Å, *B* set at 1.0 Å^2 greater than the isotropic temperature factor of the C to which it is bonded).

The 1,2-dichloroethane molecule of crystallization is disordered; this is apparent from the anomalously large temperature factors of the CSOLV atoms. The five highest peaks (~0.65 e/Å^3) of the final difference map were near the solvent molecule, but no set of partial atoms would successfully refine. The final refinement yielded a C–C distance of 1.2 Å for the dichloroethane molecule. The H atoms were not located.

Description of the Structure

Selected interatomic distances and angles for the molecular structure are given in Tables II and III; the final atomic positional and thermal parameters are presented in Tables

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Table III. Selected Interatomic Angles (Deg) for $MoO(C_3H_6NS_2)_2(C_{14}H_{10}N_2O_2) \cdot C_2H_4Cl_2$

	Coordination Sphere		
S11-Mo-S12	67.6 (7)	S21-Mo-S22	68.4 (5)
S11-Mo-O	97.5 (5)	S22-Mo-O	102.6 (5)
S12-Mo-O	87.6 (8)	S21-Mo-O	93.5 (7)
S11-Mo-O1	87.3 (7)	S22-Mo-O1	91.4 (3)
S12-Mo-O1	82.1 (7)	S21-Mo-O1	91.5 (8)
S12-Mo-N1	75.6 (2)	S21-Mo-N1	77.4 (4)
S11-Mo-S22	70.3 (8)	O-Mo-O1	166.0 (3)
		O-Mo-N1	95.5 (4)
		O1-Mo-N1	72.8 (2)
	Diazene Ligand		
Mo-O1-C1	117.1 (6)		
Mo-N1-N2	116.6 (5)	Mo-N1-C1′	126.8 (9)
N1-N2-C1	109.8 (10)	N2-N1-C1′	116.6 (11)
N2-C1-O1	121.8 (11)	N1-C1′-O2	118.6 (11)
N2-C1-C2	118.4 (10)	N1-C1′-C2′	119.3 (12)
O1-C1-C2	119.8 (8)	O2-C1′-C2′	122.1 (9)
C1-C2-C3	121.5 (9)	C1′-C2′-C3′	116.9 (13)
C1-C2-C7	119.0 (9)	C1′-C2′-C7′	125.6 (9)
C3-C2-C7	119.6 (12)	C3′-C2′-C7′	118.3 (12)
C2-C3-C4	120.5 (11)	C2′-C3′-C4′	119.3 (13)
C3-C4-C5	119.8 (12)	C3′-C4′-C5′	120.5 (12)
C4-C5-C6	121.5 (14)	C4′-C5′-C6′	123.6 (15)
C5-C6-C7	120.2 (11)	C5′-C6′-C7′	116.5 (14)
C6-C7-C2	118.5 (10)	C6′-C7′-C2′	121.7 (10)
	Dimethyldithiocarbamato Ligand		
Mo-S11-C11	91.0 (9)	Mo-S21-C21	89.3 (4)
Mo-S12-C11	89.1 (6)	Mo-S22-C21	90.0 (8)
S11-C11-S12	111.7 (8)	S21-C21-S22	112.3 (7)
S11-C11-N11	123.8 (10)	S21-C21-N21	124.5 (8)
S12-C11-N11	124.6 (7)	S22-C21-N21	123.3 (10)
C11-N11-C12	120.8 (11)	C21-N21-C22	121.6 (12)
C11-N11-C13	121.5 (8)	C21-N21-C23	121.5 (9)
C12-N11-C13	117.7 (10)	C22-N21-C23	116.9 (10)

Table IV. Final Atomic Coordinates for Anisotropically Refined Atoms

atom	x	y	z
Mo	−0.20789 (8)	0.07593 (5)	0.18157 (4)
Cl1	−0.4853 (7)	0.3443 (4)	0.1620 (4)
Cl2	−0.2399 (8)	0.3702 (5)	0.3769 (6)
S11	0.02320 (25)	0.12622 (17)	0.17144 (14)
S12	−0.09453 (25)	0.17020 (16)	0.28922 (13)
S21	−0.38768 (25)	−0.02528 (16)	0.11865 (14)
S22	−0.14446 (29)	0.00914 (18)	0.07397 (14)
O	−0.3003 (6)	0.1573 (4)	0.1424 (3)
O1	−0.1061 (5)	−0.0123 (3)	0.25229 (29)
O2	−0.5226 (6)	0.1099 (4)	0.2022 (4)
N1	−0.3214 (7)	0.0558 (4)	0.2621 (4)
N2	−0.2565 (7)	0.0085 (5)	0.3245 (4)
N11	0.1361 (8)	0.2407 (5)	0.2702 (4)
N21	−0.3220 (8)	−0.1050 (5)	0.0054 (5)

Table V. Final Atomic Positional and Isotropic Thermal Parameters

atom	x	y	z	B, Å^2
C11	0.0363 (9)	0.1873 (6)	0.2473 (5)	3.11 (18)
C12	0.1421 (12)	0.2895 (7)	0.3355 (7)	5.94 (28)
C13	0.2436 (11)	0.2534 (7)	0.2302 (6)	5.49 (26)
C21	−0.2898 (9)	−0.0481 (6)	0.0587 (5)	3.48 (20)
C22	−0.4441 (12)	−0.1530 (8)	−0.0049 (6)	6.03 (28)
C23	−0.2319 (13)	−0.1201 (8)	−0.0474 (7)	7.2 (3)
C1	−0.1456 (9)	−0.0243 (5)	0.3137 (5)	2.65 (17)
C2	−0.0640 (8)	−0.0777 (6)	0.3719 (5)	3.07 (17)
C3	−0.0945 (10)	−0.0854 (7)	0.4399 (6)	5.06 (23)
C4	−0.0179 (13)	−0.1380 (8)	0.4936 (7)	6.6 (3)
C5	0.0870 (11)	−0.1820 (7)	0.4785 (6)	5.44 (26)
C6	0.1218 (10)	−0.1751 (7)	0.4121 (6)	4.95 (24)
C7	0.0478 (10)	−0.1220 (6)	0.3571 (5)	4.07 (21)
C1′	−0.4518 (9)	0.0846 (6)	0.2605 (5)	3.53 (18)
C2′	−0.5000 (9)	0.0847 (6)	0.3289 (5)	3.93 (20)
C3′	−0.6424 (10)	0.0675 (7)	0.3219 (6)	4.78 (22)
C4′	−0.6957 (11)	0.0714 (8)	0.3849 (7)	6.20 (27)
C5′	−0.6177 (14)	0.0936 (8)	0.4487 (8)	7.7 (3)
C6′	−0.4766 (13)	0.1140 (8)	0.4598 (7)	7.0 (3)
C7′	−0.4203 (10)	0.1069 (6)	0.3979 (6)	4.52 (23)
CSOLV	−0.3934 (27)	0.3270 (18)	0.2599 (16)	16.9 (9)
CSOLV	−0.339 (4)	0.3799 (26)	0.2799 (24)	23.3 (17)

IV–VI (Table VI is presented in the supplementary material). The numbering scheme for the atoms is shown in Figure 1.

The compound $MoO(C_3H_6NS_2)_2(C_{14}H_{10}N_2O_2) \cdot C_2H_4Cl_2$ crystallizes as discrete monomers with one disordered dichloroethane per asymmetric unit. The bidentate diazene ligand coordinates to Mo through N1 and O1, forming a five-membered chelate ring (Figure 1). The stereochemistry of the coordination sphere of Mo approaches pentagonal-bipyramidal geometry. The four sulfur atoms and N1 of the benzoyldiazene ligand occupy the equatorial positions. The axial sites are occupied by the terminal oxo group and O1 of the diazene ligand.

Minor distortions away from idealized pentagonal-bipyramidal geometry occur. The Mo atom is 0.12 Å above the plane defined by the four dithiocarbamato sulfur atoms whereas N1 of the diazene moiety is 0.42 Å below this well-defined plane (Table VII, supplementary material). This distortion can be attributed to the restrictions of the five-membered chelate ring. The chelate ring also causes the trans O–Mo–O1 angle to contract to 166°. No symmetry is imposed upon the molecule by the space group. The approximate coordination symmetry at the molybdenum atom is C_s, but significant differences occur between chemically equivalent angles (Table III).

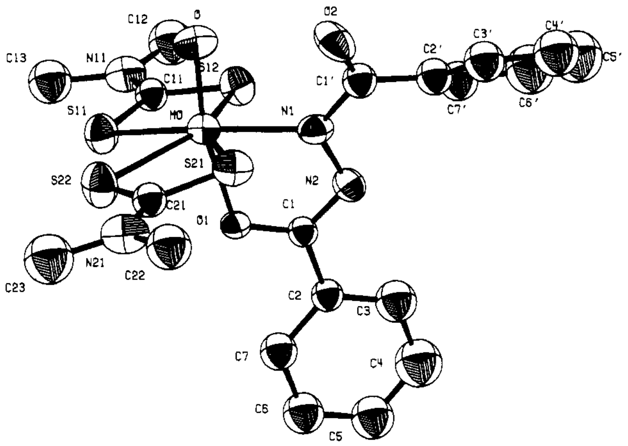

Figure 1. Perspective of the molecular structure of **1**. Hydrogen atoms and $C_2H_4Cl_2$ solvate molecule have been omitted for clarity.

The parameters determined for the chelated benzoyldiazene ligand are not significantly different from those reported by Ittel and Ibers[15] for this ligand chelated to bis(triphenylphosphine)platinum. Extended electron delocalization is manifested in the intermediate nature of the bond lengths, which lie between those for single and double bonds. The solid-state conformations of the uncoordinated benzoyl fragment of the diazene ligand differ for the two compounds. In the platinum complex the uncoordinated benzoyl fragment is approximately coplanar with the chelate ring. In **1** the uncoordinated benzoyl fragment makes a dihedral angle of 53° with the chelate ring (Figure 1).

The average Mo–S distance in **1** of 2.525 Å is similar to the average equatorial Mo–S distance in related seven-coordinate pentagonal-bipyramidal complexes containing dithiocarbamate ligands: $MoO(S_2CNEt_2)_3^+$, Mo–S = 2.486 Å;[16]

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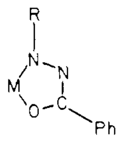
Table VIII. Comparison of the Metrical Details of the Chelate Rings



no.	compd	R	M-N, Å	M-O, Å	N-N, Å	C-N, Å	C-O, Å	ref
1	$MoO(S_2CNMe_2)_2(PhCONNCOPh)$	C(O)Ph	2.119 (18)	2.054 (14)	1.418 (14)	1.295 (10)	1.314 (11)	this work
2	$Mo(NC_6H_4CH_3)Cl_2(PMe_2Ph)(PhCONNC_6H_4CH_3)$	$C_6H_4CH_3$	1.984 (8)	2.110 (7)	1.38 (1)	1.30 (1)	1.30 (1)	18
3	$Mo(NNCOPh)Cl(PMe_2Ph)_2(PhCONNH)$	H	1.945 (8)	2.131 (7)	1.41 (1)	1.33 (1)	1.27 (1)	19
4	$[MoOCl_3(Cl\text{-}PhCONNPh)]^-$	Ph	2.030 (17)	2.159 (12)	1.38 (2)	1.35 (3)	1.24 (3)	21
5	$ReOCl_2(PPh_3)(PhCONN{=}C(CH_3)_2)$	$C(CH_3)_2$	2.127 (10)	2.013 (7)	1.41 (1)	1.31 (2)	1.32 (1)	20
6	$Pt(PPh_3)_2(PhCONNCOPh)$	C(O)Ph	2.047 (6)	2.016 (5)	1.401 (9)	1.286 (10)	1.318 (10)	15

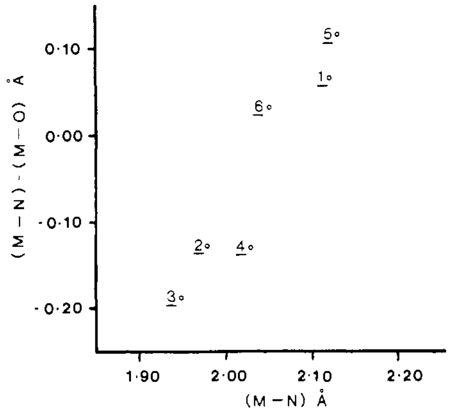


Figure 2. Plot of (M–N) – (M–O) vs. M–N distances for compounds that contain O,N-coordinated benzoyldiazene ligands.

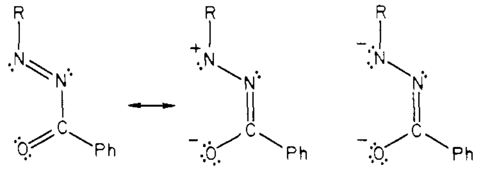
$Mo(N_2Ph)(S_2CNMe_2)_3$, Mo–S = 2.514 Å;[17] $Mo(N_2\text{-}3\text{-}C_6H_4(NO_2))(S_2CNMe_2)_3$, Mo–S = 2.515 Å.[17]

Discussion

Compound **1** can alternatively be described as a diazene complex of Mo(IV) or as a Mo(IV) complex of the enol form of a hydrazido(2–) ligand.[15] Recently several molybdenum and rhenium complexes related to **1** have been prepared from various benzoylhydrazines.[18,19] Structure determinations for several of these complexes[18–21] show that all contain the same chelate ring found in **1** but have the exo benzoyl group replaced by other functionalities. Pertinent structural details for the complexes are summarized in Table VIII.

Comparison of the C–O, C–N, and N–N distances shows that within the limits of the precision of the determinations there are no statistically significant differences among the compounds. However, large and significant variations do occur in the M–N and M–O distances. For example, **1** has Mo–N > Mo–O by 0.065 Å (4σ) whereas **2–4** have Mo–O > Mo–N by 0.13–0.19 Å (16–20σ). A plot of (M–N) – (M–O) vs. M–N (Figure 2) shows the correlation between these parameters for the compounds of Table VIII, which involve three different metals, a range of ancillary ligands, and three different coordination numbers (4, 6, and 7).

Some insight into these correlated variations in Mo–N and M–O distances is provided by valence bond structures II, III, and IV. Structure II is the usual representation of a diazene; III is a dipolar diazene structure, which has a C=N double bond and N—N and C—O single bonds. Structure IV is the enol form of a hydrazido(2–) ligand.



II III IV

Structure III can be stabilized by multiple bonding with an electron-rich center such as Mo(IV). Structure IV can be stabilized by multiple bonding to an electron-poor center such as Mo(VI).[18] However, the charges on the nitrogen atoms in structures III and IV can also be stabilized by multiple bonding with the R group, and multiple N–R bonding will occur at the expense of M–N multiple bonding. Consistent with this view, the shortest M–N distance occurs for **3**, where R is H and N–R multiple bonding is not possible. The longest M–N distance occurs for **5**, which contains an $-N{=}C(CH_3)_2$ double bond. We conclude that the nature of the R group on the coordinated N atom directly affects the degree of M–N multiple bonding, which in turn leads to correlated variations in the M–O distance (Figure 2).

The dependence of the M–N distance on the nature of the R group attached to N is similar to the dependence of the M–C distances of metal carbene complexes upon the nature of the substituents on the carbene ligand.[22]

Structures III and IV also account for the lack of significant variation in the N–N, C–N, and C–O distances in the chelate rings. In molecular orbital terms III is related to the lowest unoccupied molecular orbital of the diazene ligand, which is C–N bonding and N–N and C–O antibonding. In IV this orbital is completely filled. Whether **1** is regarded as a Mo(IV) complex of a diazene (π-acceptor ligand) or a Mo(VI) complex of a hydrazido(2–) (π-donor ligand) is partly a matter of semantics.

Finally, it is of interest to compare the structure of **1** to other seven-coordinate pentagonal-bipyramidal complexes containing a $MoO(dtc)_2$ fragment. The structure of **1** is similar to that of $MoOCl_2(S_2CNEt_2)_2$, which has the sulfur atoms in the equatorial plane and the oxo group and one chlorine atom in trans axial positions.[23] On the other hand, in the structure of $MoO(S_2CNMe_2)_2(DTA)$, where DTA is ditoluoylacetylene,

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the equatorial plane of the pentagonal bipyramid is occupied by the two carbon atoms of coordinated acetylene and three sulfur atoms, whereas the axial positions are taken up by the terminal oxo group and a sulfur atom from a dtc ligand.[24] The same stereochemistry is adopted[25] by $MoO(S_2CNPr_2)_2(TCNE)$, where TCNE is tetracyanoethylene. For DTA and TCNE the latter structure is favored both by the small bite angle of the bidentate ligand and by the π-acceptor character of these ligands.

Summary

X-ray structure determination shows that the deep purple complex $MoO(S_2CNMe_2)_2(PhCONNCOPh)$ contains an O,N-coordinated dibenzoyldiazene ligand with a five-membered chelate ring. The same stereochemistry is observed for other complexes of substituted benzoyldiazene ligands,[18-21] as predicted by Ittel and Ibers.[15]

The initial purple material formed from the reaction of bis(dithiocarbamato)oxomolybdenum(IV) compounds with $(EtO_2C)_2N_2$ probably has the same stereochemistry as **1**. This leaves unanswered the stereochemistry of the final yellow product with the formula $MoO(S_2CNMe_2)_2(EtO_2CNNCO_2Et)$. Attempts to obtain suitable crystals of this yellow product for structure determination have been unsuccessful.

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Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, hydrogen positional parameters (Table VI), and least-squares planes (Table VII) (15 pages). Ordering information is given on any current masthead page.

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Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 20.[1] Crystal Structure and NMR Spectra of $(\mu\text{-}H)_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$

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The heteronuclear species $(\mu\text{-}H)_2Os_3Co(CO)_{10}(\eta^5\text{-}C_5H_5)$, synthesized from $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $(\eta^5\text{-}C_5H_5)Co(CO)_2$, has been examined via NMR spectroscopy and a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ [C_{2h}^5, No. 14] with $a = 8.193$ (2) Å, $b = 14.641$ (3) Å, $c = 16.341$ (5) Å, $\beta = 90.98$ (2)°, $V = 1960.0$ (8) Å^3, and $\rho(\text{calcd}) = 3.31$ g cm^{-3} for $Z = 4$ and mol wt 976.75. Diffraction data were collected with a Syntex P2$_1$ diffractometer, and the structure was refined to $R_F = 3.5\%$ for 1837 reflections with $3° < 2\theta < 40°$ (Mo Kα radiation). The molecule contains a tetrahedral heterometallic Os_3Co core. Each osmium atom is linked to three terminal carbonyl ligands, while the cobalt atom is bonded to an η^5-cyclopentadienyl ring. The structure is completed by an asymmetric bridging carbonyl ligand on the Os(1)–Co edge [Co–C(41) = 1.789 (14) Å, Os(1)–C(41) = 2.208 (13) Å] and bridging hydride ligands across the Os(1)–Os(2) and Os(2)–Os(3) edges. The nonbridged metal–metal distances are normal [Os(1)–Os(3) = 2.778 (1) Å, Os(2)–Co = 2.672 (2) Å, Os(3)–Co = 2.680 (2) Å], while the carbonyl-bridged metal–metal bond is slightly shortened [Os(1)–Co = 2.645 (2) Å] and the hydrido-bridged metal–metal bonds are lengthened [Os(1)–Os(2) = 2.940 (1) Å, Os(2)–Os(3) = 2.870 (1) Å] relative to the normal values for a tetrahedral cluster. The bridging hydride ligands were each located directly in the analysis; their disposition about their tetrahedral edges is discussed in detail.

Introduction

Mixed-metal clusters have previously been prepared from the formally unsaturated hydrido–osmium cluster $(\mu\text{-}H)_2Os_3(CO)_{10}$ by procedures that exploit its Lewis acid character.[4-7]

It has recently been shown[8] that $(\mu\text{-}H)_2Os_3(CO)_{10}$ can also function as an apparent Lewis base. A specific example of the two possibilities is provided by alternative routes to $(\mu\text{-}H)_2Os_3Fe(CO)_{13}$.

Equation 1 shows $(\mu\text{-}H)_2Os_3(CO)_{10}$ acting as a Lewis acid in the route discovered by Geoffroy and Gladfelter,[9] while eq 2 shows the Lewis base route.[8]

$$(\mu\text{-}H)_2Os_3(CO)_{10} + [Fe(CO)_4{}^{2-}] \rightarrow (\mu\text{-}H)_2Os_3Fe(CO)_{13} \tag{1}$$

$$(\mu\text{-}H)_2Os_3(CO)_{10} + Fe_2(CO)_9 \rightarrow (\mu\text{-}H)_2Os_3Fe(CO)_{13} \tag{2}$$

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[1] For recent previous publications in this series see the following: (a) Part 17: Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1580. (b) Part 18: Churchill, M. R.; Wasserman, H. J. *Ibid.* **1981**, *20*, 2905. (c) Part 19: Churchill, M. R.; Hollander, F. J. *Ibid.* **1981**, *20*, 4124.

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