neutral edge-sharing octahedral nickel dimers **1** and **2**. Complexes of type **1**, with the Sal chelate plane essentially orthogonal to the Ni_2O_2 bridging plane, are ferromagnets, while type **2** complexes, with the Sal chelate plane nearly coplanar with the Ni_2O_2 bridge, are more strongly antiferromagnetic ($J = -9.2\ \mathrm{cm}^{-1}$ for R = *i*-Pr, S′ = dimethylformamide) than the $[Ni_2(PhSal)_4CH_3COO]^-$ ion. Like the type **2** complexes, the acetate bridged dimeric ion has the Sal chelate plane roughly coplanar with the Ni_2O_2 bridging unit, which, however, is itself nonplanar. The Ni–O–Ni superexchange overlap is poorer in $[Ni_2(PhSal)_4CH_3COO]^-$, leading to weaker interaction, though this is mediated somewhat by the availability of the additional exchange path through the carboxylate ligand.

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Registry No. $[pipH][Ni_2(PhSal)_4CH_3COO]$, 79896-46-1.

Supplementary Material Available: A listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Crystal Structure of a New Cesium Manganese Vanadium Oxide, $Cs_3Mn_3V_4O_{16}$

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Single crystals of $Cs_3Mn_3V_4O_{16}$ have been grown by molten salt electrolysis. They are triclinic, space group $P\bar{1}$, with the cell parameters a = 5.1947 (5) Å, b = 7.5017 (7) Å, c = 11.4367 (14) Å, α = 77.70 (1)°, β = 89.72(1)°, γ = 82.62 (1)°, and Z = 1. The crystal structure was determined from single-crystal diffractometer data and refined to R_F = 0.052 for 3167 reflections observed with Mo Kα radiation. The structure contains $(CsMn_3V_4O_{16})_n$ layers parallel to the *ab* plane and two Cs atoms per cell between them. In the layers, edge-sharing MnO_6 octahedra form flat ribbons of formula $(Mn_3O_{10})_n$ extending along *a*, which are bonded together in the *b* direction by two V_2O_7 double tetrahedra per cell, giving a two-dimensional framework with one large cavity per cell occupied by a Cs atom.

Introduction

During a study of the crystal growth of α-MnO_2 by electrolytic oxidation of Mn(II) dissolved in alkali vanadate melts, very different results were obtained according to the nature of the alkali metal.[1] Whereas potassium and rubidium were readily incorporated into the α-MnO_2 phase with a hollandite-type structure, electrolysis from a cesium vanadate melt yielded a new quaternary compound of formula $Cs_3Mn_3V_4O_{16}$. We present here the determination of its structure.

Experimental Section

$Cs_3Mn_3V_4O_{16}$ was formed by electrolysis in a melt of initial molar composition Cs_2CO_3 36.4%, V_2O_5 54.6%, and $MnCO_3$ 9.0% at 420 °C. The crystal growth process is described in detail in ref 1. The anodic deposit contained dark brown needles of a Cs–Mn–V–O compound up to 1 mm long. Preliminary examination using precession photographs indicated that they were single crystals of a new triclinic phase. Qualitative chemical analysis was performed with use of a scanning electron microscope equipped with an X-ray energy spectrometer.

X-ray Diffraction Data. The diffraction intensities of a 0.02 × 0.03 0.4 mm crystal were measured at 24 °C. Graphite-monochromatized Mo Kα radiation generated at 50 kV and 10 mA was used in a $\theta/2\theta$ scan with line-profile analysis.[2] A total of 5369 unique measurements were made up to 2θ = 80°, of which 3167 had $I_{\mathrm{net}} > 3\sigma(I_{\mathrm{net}})$ and were considered to be observed. No absorption correction was performed. The cell parameters were obtained by least-squares refinement of the setting angles of 30 reflections with 2θ > 50°, using λ(Mo Kα) = 0.7107. At 24 °C, they are as follows: a = 5.1947 (5) Å, b = 7.5017 (7) Å, c = 11.4367 (14) Å, α = 77.70 (1)°, β = 89.72 (1)°, γ = 82.62 (1)°. The cell volume is 431.72 Å^3, and the calculated density is 3.936 g cm^{-3}. The periods along *a*, *b*, and *c* were checked by oscillation patterns. The elongation of the needlelike crystals was parallel to the *a* axis.

Solution and Refinement of the Structure. The structure was solved by application of MULTAN[3] to the 200 largest *E* values. The intensity statistics indicated the presence of a center of symmetry, and we considered the space group to be $P\bar{1}$. One manganese and two cesium atoms were found on the *E* map. Two cycles of structure factor calculations followed by Fourier maps revealed all the atomic positions in the structure. All atomic positions were refined with anisotropic thermal motion by full-matrix least squares. An extinction correction was included.[4] The scattering factors for the zerovalent atoms were taken from ref 5.

All the calculations were performed with use of the NRCC PDP8-E system of programs.[6] The final residuals were R_F = 0.052 and wR_F = 0.046. The atomic positional and thermal parameters are listed in Table I. The bond distances and angles are listed in Tables II and III, respectively. The most intense lines of the powder pattern are given in Table IV. The observed powder pattern as well as the measured density were not obtained due to insufficient amounts of material.

Results and Discussion

Description of the Structure. Figures 1 and 2 show projections of the structure along *a* and *b*, respectively. The structure is based on octahedrally oxygen-coordinated manganese and tetrahedrally oxygen-coordinated vanadium atoms. It contains layers approximately 9 Å thick of composition $(CsMn_3V_4O_{16})_n$ parallel to the (001) plane. The layers are bonded in the *c* direction by two cesium atoms per cell (Cs_B in Table II). The layers are made of flat ribbons of formula $(Mn_3O_{10})_n$ bridged by V_2O_7 double tetrahedra, leaving large

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0020-1669/82/1321-0620$01.25/0

Table I. Atomic Parameters x, y, z, B_{iso}, and U Values × 100[a]

	x	y	z	B_{iso},[b] Å^2
Cs_A	0	0	0	1.53 (4)
Cs_B	0.11310 (13)	0.26057 (9)	0.48568 (6)	1.82 (3)
Mn_A	1/2	1/2	0	0.55 (6)
Mn_B	0.01090 (22)	0.44142 (16)	0.13212 (11)	0.62 (5)
V_A	0.5266 (3)	0.13349 (19)	0.23364 (13)	0.70 (5)
V_B	0.4748 (3)	0.32817 (18)	0.76158 (12)	0.73 (5)
O_A	0.8074 (10)	0.6139 (7)	0.0076 (5)	0.68 (22)
O_B	0.3898 (12)	0.6394 (9)	0.3667 (6)	1.9 (3)
O_C	0.6522 (11)	0.1050 (8)	0.3676 (5)	1.3 (3)
O_D	0.3386 (11)	0.6038 (7)	0.1322 (5)	1.1 (3)
O_E	0.6962 (10)	0.2730 (7)	0.1288 (5)	0.85 (24)
O_F	0.2071 (11)	0.2371 (8)	0.2354 (5)	1.1 (3)
O_G	0.1698 (11)	0.4529 (8)	0.7422 (5)	1.2 (3)
O_H	0.4535 (12)	0.0841 (8)	0.8117 (6)	1.7 (3)

	U_{11} (U, Å^2)	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs_A	1.85 (4)	1.38 (3)	2.97 (4)	−0.22 (3)	0.85 (3)	−0.84 (3)
Cs_B	2.67 (3)	2.21 (3)	2.22 (3)	0.142 (23)	0.101 (23)	−0.536 (22)
Mn_A	0.43 (7)	0.75 (7)	1.02 (7)	−0.12 (5)	0.10 (5)	−0.18 (6)
Mn_B	0.59 (5)	0.78 (5)	1.09 (5)	−0.08 (4)	0.12 (4)	−0.14 (4)
V_A	0.69 (6)	0.80 (5)	1.28 (6)	−0.11 (4)	0.05 (5)	−0.15 (4)
V_B	0.82 (6)	0.84 (5)	1.34 (6)	−0.22 (4)	0.14 (5)	−0.40 (5)
O_A	1.01 (25)	0.43 (22)	1.2 (3)	−0.03 (19)	0.05 (20)	−0.09 (19)
O_B	2.1 (3)	3.4 (4)	2.5 (4)	−0.6 (3)	0.7 (3)	−1.2 (3)
O_C	1.2 (3)	1.7 (3)	2.1 (3)	−0.03 (23)	−0.05 (24)	−0.04 (24)
O_D	1.3 (3)	1.3 (3)	1.6 (3)	−0.09 (22)	0.00 (22)	−0.46 (22)
O_E	0.81 (24)	1.1 (3)	1.5 (3)	−0.30 (20)	0.41 (21)	−0.17 (21)
O_F	1.1 (3)	1.5 (3)	1.6 (3)	0.05 (22)	0.03 (22)	0.42 (22)
O_G	1.5 (3)	1.4 (3)	1.7 (3)	−0.25 (23)	−0.08 (23)	−0.37 (23)
O_H	2.4 (3)	1.0 (3)	3.8 (4)	−0.34 (24)	0.7 (3)	−1.3 (3)

[a] Esd's refer to the last digit printed. [b] B_{iso} is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table II. Interatomic Distances (Å) in $Cs_3Mn_3V_4O_{16}$[a]

	O_A	O_B	O_C	O_D	O_E	O_F	O_G	O_H
Mn_A	1.916 (5)^{II}			1.979 (5)^{II}	2.147 (5)^{II}			
Mn_B	1.923 (5) 1.945 (5)			2.217 (6)	2.196 (5)	1.903 (5)	1.964 (6)	
V_A			1.629 (6)		1.732 (5)	1.742 (5)		1.806 (6)
V_B		1.608 (6)		1.754 (6)			1.723 (6)	1.816 (6)
Cs_A	3.168 (5)^{II}			3.314 (5)^{II}	3.048 (5)^{II}	3.759 (6)^{II}		3.215 (6)^{II} 3.481 (7)^{II}
Cs_B		3.372 (7) 3.341 (7) 3.199 (6)	3.290 (6) 3.215 (6) 3.004 (6)			2.940 (6)	3.563 (6) 3.226 (6)	

[a] Numbers in parentheses are estimated standard deviations applying to the last digit. Superscript Roman numerals indicate the bond multiplicity at the cation.

cavities inside the layers, which are occupied by the Cs_A atoms (see Figure 1).

The shape of the $(Mn_3O_{10})_n$ ribbons is shown in Figure 3. It is based on units of three octahedra containing one Mn_A and two Mn_B atoms. The Mn_AO_6 octahedra share one edge with each of the four adjacent Mn_BO_6 octahedra. The latter share a total of three edges (two with Mn_AO_6, one with Mn_BO_6 octahedra). The ribbons, extending along a, are approximately parallel to the (031) plane. The (001) plane is a pseudomirror for the $(CsMn_3V_4O_{16})_n$ layer, but the distribution of the cesium atoms and the stacking of the layers destroy this approximate symmetry.

Discussion. The manganese octahedra in this structure are very distorted. Mn–O distances vary from 1.90 to 2.21 Å and O–Mn–O angles from 80 to 98° (see Tables II and III). Fairly short Mn–O bond lengths are found with the O_A atom, which is shared by three manganese octahedra and one cesium atom. It is the only oxygen atom that has no vanadium neighbor. In the equally distorted V_2O_7 double tetrahedra, the longest V–O distance (1.81 Å) is found with the bridging O_H atom, whereas the O_B and O_C atoms, which are bonded to one vanadium and three cesium neighbors, have very short V–O bond

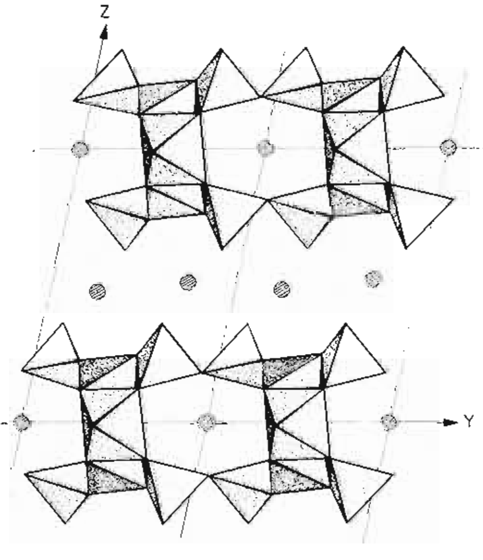

Figure 1. Orthogonal projection of the structure along a. The Mn and V atoms are respectively octahedrally and tetrahedrally coordinated. The cesium atoms are shown as small spheres.

Table III. Bond Angles (Deg) in $Cs_3Mn_3V_4O_{16}$[a]

	Mn Octahedra		
	Mn_AO_6		
O_A-Mn_A-O_A'	180.0	O_D-Mn_A-O_D'	180.0
O_A-Mn_A-O_D	92.6 (2)	O_D-Mn_A-O_E	89.6 (2)
O_A-Mn_A-O_D'	87.4 (2)	O_D-Mn_A-O_E'	90.4 (2)
O_A-Mn_A-O_E	85.7 (2)	O_E-Mn_A-O_E'	180.0
O_A-Mn_A-O_E'	94.3 (2)		
	Mn_BO_6		
O_A-Mn_B-O_A	80.1 (3)	O_A'-Mn_B-O_H	168.9 (3)
O_A-Mn_B-O_D	96.6 (3)	O_D-Mn_B-O_E	177.8 (3)
O_A-Mn_B-O_E	84.1 (3)	O_D-Mn_B-O_F	89.9 (3)
O_A-Mn_B-O_F	168.6 (3)	O_D-Mn_B-O_G	92.9 (3)
O_A-Mn_B-O_G	92.1 (3)	O_E-Mn_B-O_F	89.1 (3)
O_A'-Mn_B-O_D	80.3 (3)	O_E-Mn_B-O_G	89.2 (3)
O_A'-Mn_B-O_F	97.8 (3)	O_F-Mn_B-O_G	97.0 (3)
O_A'-Mn_B-O_G	91.8 (3)		
	V Tetrahedra		
	V_AO_4		
O_C-V_A-O_E	111.2 (3)	O_E-V_A-O_F	109.2 (3)
O_C-V_A-O_F	107.8 (3)	O_E-V_A-O_H	106.1 (3)
O_C-V_A-O_H	110.5 (3)	O_F-V_A-O_H	112.1 (3)
	V_BO_4		
O_B-V_B-O_D	110.7 (3)	O_D-V_B-O_G	111.5 (3)
O_B-V_B-O_G	107.2 (3)	O_D-V_B-O_H	108.1 (3)
O_B-V_B-O_H	108.5 (3)	O_G-V_B-O_H	110.8 (3)

[a] Numbers in parentheses are estimated standard deviations applying to the last digit.

Table IV. Abbreviated Powder Pattern of $Cs_3Mn_3V_4O_{16}$ Calculated from the Single-Crystal Structure Determination[a]

d	*I*	*hkl*	*d*	*I*	*hkl*
11.15	31	001	3.195	74	121
5.583	20	002	3.038	50	113[b]
4.333	20	111	2.9323	56	023
4.008	43	$11\bar{1}$	2.8378	44	$\bar{1}21$
3.828	71	$\bar{1}02$	2.7912	30	004
3.742	82	102[b]	2.7186	22	$11\bar{3}$
3.693	26	021	2.5745	22	200
3.458	36	$\bar{1}12$	2.4429	43	$\bar{1}14$[b]
3.255	100	$02\bar{1}$			

[a] Lines with $I > 20$ only; the complete powder pattern is available as supplementary material. [b] More than one reflection contributes to this line; the indices given are those of the most intense contributor.

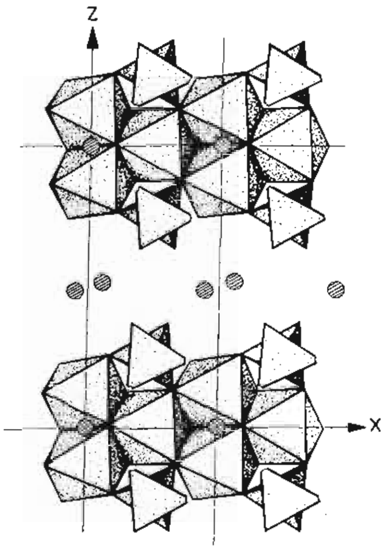

Figure 2. Orthogonal projection of the structure along *b*. The V_2O_7 double tetrahedra link ribbons that correspond through translations along *b* (see Figure 1). Accordingly, the corners of the tetrahedra that attach to the next ribbon have been shown truncated.

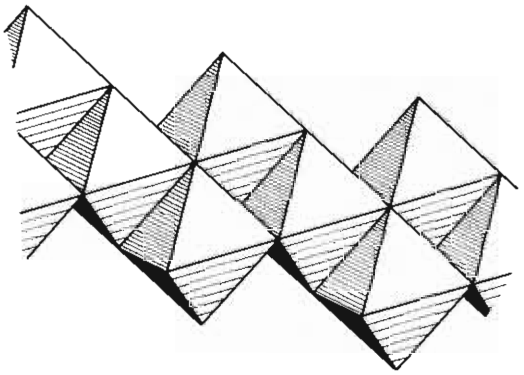

Figure 3. Perspective view of the $(Mn_3O_{10})_n$ ribbon.

lengths (~1.61 Å). The two crystallographically distinct cesium sites have high coordinations. The Cs_A atoms, which are imbedded in the layers, have twelve oxygen neighbors at distances ranging from 3.05 to 3.76 Å whereas the interlayer Cs_B atoms are in ninefold coordination with slightly shorter Cs–O distances (2.94–3.56 Å).

The structural characteristics of manganese and vanadium in $Cs_3Mn_3V_4O_{16}$ and in some typical oxidic compounds of Mn(+3 or +4) and V(+4 or +5) are compared in Table V. The manganese ions are always found with octahedral coordination (for example, Mn^{3+} has one of the highest octahedral

Table V. Structural Characteristics of Some Typical Mn^{3+}, Mn^{4+}, V^{4+}, and V^{5+} Oxidic Compounds[7,8]

ion	compd	struct type	coord no.	av bond length, Å
Mn^{3+}	Mn_2O_3	C-rare earth	6	2.00
	M^IMnO_2	distorted β-$NaFeO_2$	6	2.08 (M = Li)
	$M^{II}Mn_2O_4$	distorted spinel	6	2.00 (M = Mn)
	$M^{III}MnO_3$	distorted perovskite	6	1.97 (M = La)
Mn^{4+}	β-MnO_2	rutile	6	1.89
	$M^{II}MnO_3$	perovskite or ilmenite	6	1.86 (M = Ca)
	$M^{II}Mn_3O_8$	(ribbons, Mn_3O_8)[10]	6	1.89 (M = Co)
Mn in $Cs_3Mn_3V_4O_{16}$		(ribbons, Mn_3O_{10})	6	2.01
V^{4+}	VO_2	distorted rutile	6	1.93
	$M^{II}V_2O_4$	spinel	6	1.88 (M = Mg)
	$M^{II}VO_3$	perovskite or ilmenite	6	1.88 (M = Ca)
V^{5+}	V_2O_5	(layer structure)	5	1.83
	M^IVO_3	(chains, $(VO_3)_n$)	4, 5	1.72 (M = Na)
	$M_2^{II}V_2O_7$	(double tetrahedra, V_2O_7)	4	1.71 (M = Mg)
	$M^{III}VO_4$	scheelite, zircon	4	1.71 (M = La)
V in $Cs_3Mn_3V_4O_{16}$		(double tetrahedra, V_2O_7)	4	1.73

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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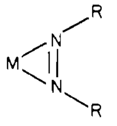
The X-ray crystal and molecular structure of oxobis(dimethyldithiocarbamato)(dibenzoyldiazene)molybdenum–1,2-dichloroethane, $MoO(C_3H_6NS)_2(C_{14}H_{10}N_2O_2) \cdot C_2H_4Cl_2$, was determined from intensity data collected with use of counter methods. The compound crystallizes in the space group $P2_1/c$ 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] (η-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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