Inorg. Chem. **1991**, *30*, 1425–1428

Appendix

The geometry of $Mo_2Cl_8^{4-}$ was constructed by placing a Mo–Mo vector of 2.14 Å in a cube of Cl atoms with a Cl- - -Cl edge distance of 3.38 Å. This provides a Mo–Cl bond length of 2.47 Å and a Mo–Mo–Cl angle of 104.6°. The Walsh diagram was constructed by rotating the Mo–Mo vector through 45° about an axis perpendicular to the Mo–Mo vector. The transition state pictured in V was generated by aligning the Mo–Mo vector along a diagonal defined by two opposite corners of the cube. This results in Mo–Cl distances of 1.85 Å (apical) and 2.76 Å (equatorial). The atomic parameters of $W_2(OH)_6$ were obtained by locating a W–W vector of 2.24 Å inside an octahedron of OH ligands with an O- - -O edge distance of 3.25 Å and an O–H distance of 0.96 Å. With the W–W vector oriented toward the centroid of two opposite faces (D_{3d} symmetry), a W–O distance of 1.89 Å and a W–W–O angle of 98° result. The Walsh diagram was constructed by rotating the W–W vector 36° toward an edge of the octahedron about an axis perpendicular to the W–W vector.

All atomic wave functions were generated by using the method of Bursten, Jensen, and Fenske.[23] Contracted double-ζ representations were used for the Mo 4d, W 5d, Cl 3p, and O 2p AO's. In the basis functions for Mo and W, the following exponents were fixed: Mo 5s and 5p, 2.20; W 6s and 6p, 2.40. All calculations were converged with a self-consistent-field iterative technique using a convergence criteria of 0.0010 as the largest deviation of atomic orbital populations between successive cycles.

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Synthesis and Characterization of the Mixed-Valence Complex $LMo^VOCl(\mu\text{-}O)Mo^{VI}O_2L$ (L = Hydrotris(3,5-dimethyl-1-pyrazolyl)borate)

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Oxo–thio–Mo(VI) complexes are much sought after models of the active site of oxidized, active xanthine oxidase and xanthine dehydrogenase.[1] However, only a restricted number and variety of such complexes have been isolated to date;[2-4] these include the oxothiomolybdates, $[MoO_{4-x}S_x]^{2-}$ (x = 1–3),[2] and the $MoOS(ONR_2)_2$ (R = Et; $R_2 = C_5H_{10}$) complexes reported by Wieghardt and co-workers.[3] These complexes were prepared by the reaction of a sulfiding agent such as H_2S, B_2S_3, or $(Me_3Si)_2S$ with precursor oxo complexes. Faller and Ma[4] recently reported the synthesis of stable $Cp^*MoOS(CH_2SiMe_3)$ ($Cp^* = \eta^5\text{-}C_5Me_5^-$) and Cp^*WOSR (R = Me, CH_2SiMe_3) complexes by a similar methodology, viz., the reaction of Cp^*MO_2R complexes with H_2S. The organometallic dioxo–M(VI) precursors were prepared by reaction of Cp^*MO_2X with the appropriate Grignard reagent in tetrahydrofuran or diethyl ether.[5] Their synthesis parallels the transmetalation reactions employed in the synthesis of other stable organometallic dioxo–Mo(VI) complexes such as $MoO_2Br(R)(bpy)$ (R = Me, Et, CH_2-*t*-Bu, *n*-Pr, *i*-Pr, *t*-Bu; bpy = 2,2′-bipyridine)[6] and $MoO_2(R)_2(bpy)$ (R = Me,[7] Et through C_6H_{11},[8] CH_2Ph,[9] CH_2-*t*-Bu[10]). Our interest in the synthesis of oxo–thio–Mo(VI) complexes of hydrotris(3,5-dimethylpyrazolyl)borate, $HB(Me_2pz)_3^-$, as models of xanthine oxidase and the frequent similarity in the chemistries of Cp^{*-} and $HB(Me_2pz)_3^-$ complexes, led us to contemplate the reaction of $[HB(Me_2pz)_3]MoO_2R$ complexes with H_2S as a route to $[HB(Me_2pz)_3]MoOSR$ complexes. Our initial attempts to prepare the necessary $[HB(Me_2pz)_3]MoO_2R$ precursors focused on the reactions of $[HB(Me_2pz)_3]MoO_2Cl$[11] with Grignard reagents, but in contrast to the chemistry observed in the Cp^{*-} system[5] these reactions resulted in the formation of the mixed-valence complex $[HB(Me_2pz)_3]Mo^VOCl(\mu\text{-}O)Mo^{VI}O_2[HB(Me_2pz)_3]$ (**1**). Mixed-valence compounds now attract considerable interest, and early-transition-metal compounds of this type have been exhaustively reviewed by Young.[12] Dinuclear Mo^VMo^{VI} complexes are in fact rare, and none have been previously isolated or structurally characterized. The synthesis and characterization of complex **1** are reported herein.

Results and Discussion

Reaction of *cis*-$[HB(Me_2pz)_3]MoO_2Cl$ with the Grignard reagent MeMgCl, MeMgI, or $PhCH_2MgBr$ in tetrahydrofuran at −78 or −42 °C produced a deep brown reaction mixture after rapid disappearance of an initial transient green coloration. Examination of the reaction mixture by thin-layer chromatography (silica/CH_2Cl_2) revealed the presence of up to six products depending on the reaction and the conditions used. Intense purple compounds, likely to possess di- or polynuclear structures, are observed along with orange-brown **1** (R_f ca. 0.46). Column chromatography allowed the separation and crystallization of all components, but the small quantities of the byproducts prevented their unambiguous characterization. The formation of **1** is clearly a multistep process, and a possible reaction sequence leading to its formation involves (1) initial reaction of $[HB(Me_2pz)_3]Mo^{VI}O_2Cl$ and RMgX to produce coordinatively unsaturated $[HB(Me_2pz)_3]Mo^VO_2$, MgXCl, and $^1/_2$ R_2 (note, dibenzyl is isolated from reactions involving $PhCH_2MgBr$), (2) reaction of $[HB(Me_2pz)_3]Mo^VO_2$ with $[HB(Me_2pz)_3]Mo^{VI}O_2Cl$ to form $[HB(Me_2pz)_3]Mo^VO_2(\mu\text{-}O)Mo^{VI}OCl[HB(Me_2pz)_3]$, and (3) intramolecular electron transfer to produce the energetically favored class I[13] mixed-valence complex, **1**. The transient green coloration may arise from the presence of the initially formed $[HB(Me_2pz)_3]Mo^VO_2$ complex or the first mixed-valence species. Notably, we have not been able to detect or isolate any organometallic species $[HB(Me_2pz)_3]MoO_2R$ (R = Me, CH_2Ph) in the reactions above. This result contrasts with the isolation of the stable transmetalation products in reactions involving Grignard reagents and analogous dioxo–Mo(VI) species.[5-10]

Orange-brown, air-stable **1** was characterized by elemental analysis, infrared, electronic, and ESR spectroscopy, mass spectrometry, magnetic susceptibility measurements, and X-ray

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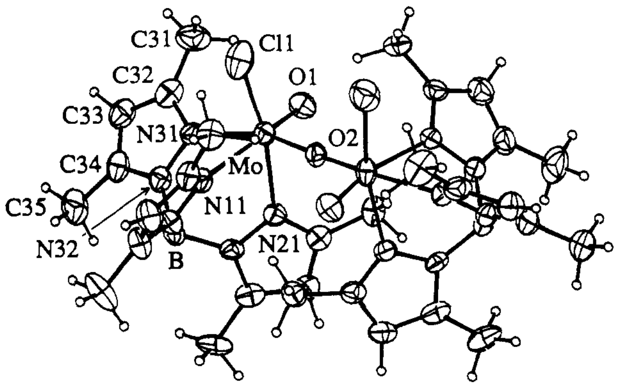

Figure 1. Molecular structure of **1** showing the atom-labeling scheme. The numbering of atoms in the pyrazolyl rings containing N(11) and N(21) parallels that shown for the ring containing N(31). The two halves of the disordered model are related by a C_2 axis. Thermal ellipsoids are plotted at the 50% probability level, and hydrogen atoms are shown by spheres of arbitrary radius.

crystallography. The infrared spectrum of **1** exhibited bands typical of $HB(Me_2pz)_3^-$, along with three ν(Mo=O) bands in the 1000–850-cm^{-1} region. The ν(Mo=O) bands are assigned to Mo^V=O (955 cm^{-1}) and *cis*-$Mo^{VI}O_2$ (925, 895 cm^{-1}) fragments. The presence of the μ-oxo ligand was indicated by a strong, broad ν_{as}(Mo—O—Mo) band at 750 cm^{-1}. Compound **1** exhibited an ESR signal typical of a mononuclear Mo(V) complex. The signal, characterized by $\langle g \rangle$ and $\langle a \rangle(^{95,97}Mo)$ values of 1.935 and 45 × 10^{-4} cm^{-1}, respectively, consisted of a strong central line due to species containing Mo isotopes with $I = 0$ (75% abundant) flanked by six lines due to species containing Mo isotopes with $I = {}^5/_2$ (25% abundant). In the case of **1**, however, the Mo(V) ESR signal is not due to a mononuclear species but instead results from a localized Mo(V) center in a class I mixed-valence complex. The dinuclear complex could be considered a member of the series $[HB(Me_2pz)_3]Mo^VOXY$ (X = Y or X ≠ Y) extensively studied by Cleland et al.;[14a] in the case of **1**, X = Cl and Y = (μ-O)-$MoO_2[HB(Me_2pz)_3]$. Cleland et al.[14a] observed an inverse, ligand-dependent correlation of $\langle a \rangle$ with $\langle g \rangle$ for the complexes $[HB(Me_2pz)_3]MoOXY$. The presence of at least one sulfur-donor ligand generally resulted in a large $\langle g \rangle$ being associated with a small value of $\langle a \rangle$ whereas halides and oxygen- and nitrogen-donor ligands resulted in smaller values of $\langle g \rangle$ associated with larger values of $\langle a \rangle$. The ESR parameters of **1**, viz., a small value of $\langle g \rangle$ and a large value of $\langle a \rangle$, are consistent with the oxo, μ-oxo, and chloro ligation of the $[HB(Me_2pz)_3]Mo^V$ center and support the observations of Cleland et al.[14a] The bulk paramagnetism of **1** was established by solid-state magnetic susceptibility studies which yielded an effective magnetic moment of 1.63 μ_B; due to its paramagnetism the complex was not amenable to NMR studies. The electronic spectrum was characterized by absorptions with λ_{max} (ϵ, M^{-1} cm^{-1}) values of 260 (16 100), 266 (16 200), 273 (15 500), 300 (8000, sh), 450 (580, sh), and 850 nm (115). A band at 485 nm (ϵ_{max} 10 000 M^{-1} cm^{-1}), indicative of the presence of the dinuclear Mo(V) complex $\{[HB(Me_2pz)_3]MoOCl\}_2(\mu\text{-}O)$[11] was not present in the electronic spectrum of **1**. Cleland et al.[14a] have also observed that the electronic spectra of complexes of the type $[HB(Me_2pz)_3]MoOXY$ (X,Y = O donor or halide) exhibit a low-intensity (ϵ < 100) lowest energy band; an analogous band is observed at 850 nm (ϵ 115) in the electronic spectrum of **1**. The mass spectrum of **1** exhibits a cluster of peaks, with appropriate molecular mass and isotope distribution, assignable to the $[\mathbf{1} - Cl]^+$ ion.

An ORTEP drawing of the molecule, along with the atom-labeling scheme, is given in Figure 1. The dinuclear complex is composed of distorted octahedral *fac*-$\{[HB(Me_2pz)_3]Mo^VOCl\}^+$ and *fac*-$\{[HB(Me_2pz)_3]Mo^{VI}O_2\}^+$ moieties linked by a linear oxo ligand bridge (average Mo—O(2) = 1.896 (1) Å). As the molecules are sited on 2-fold rotation axes, the structure is disordered and the complex possesses pseudo-C_2 symmetry. The site labeled Cl(1) is occupied by terminal chloro and terminal oxo ligands each with 0.5 occupancy. Disorder prevents the determination of accurate bond distances and angles; those presented are averages derived from the structurally inequivalent halves of the molecule. Physical and spectroscopic data are not consistent with the presence of the known complexes $\{[HB(Me_2pz)_3]MoOCl\}_2(\mu\text{-}O)$[11] and $\{[HB(Me_2pz)_3]MoO_2\}_2(\mu\text{-}O)$;[15] hence a disordered model involving these species cannot account for the diffraction data. The terminal oxo ligands O(1) exhibit an average Mo—O(1) bond distance of 1.699 (3) Å and are anti disposed. Considering the bond distances in other oxo–Mo complexes of $HB(Me_2pz)_3^-$, it is probable that the Mo^V=O bond is in fact shorter than the two Mo^{VI}=O bonds.[11,14–16] On the Mo(VI) center, oxo ligand O(1) is bound cis to a terminal oxo ligand (at site labeled Cl(1)) and bridging O(2) oxo ligands, while on the adjacent Mo(V) center chloro ligand Cl(1) is bound cis to the terminal O(1) and bridging O(2) oxo ligands. The electron density maximum at the Cl(1) site is 2.142 (2) Å from Mo; Mo—O/Cl distances in the range 2.294 (3) and 2.072 (5) Å have been observed in the disordered structure of $[HB(Me_2pz)_3]MoOCl_2$.[16,17] In the two geometrical isomers of $[(HB(pz)_3)MoOCl]_2(\mu\text{-}O)$[16] the Mo—Cl distances average at 2.348 Å. The $HB(Me_2pz)_3^-$ ligand adopts its usual facial coordination mode at both Mo centers. The Mo—N distances in **1** range from 2.213 (5) to 2.323 (4) Å, the longest being trans to the terminal oxo ligand O(1), as observed in other oxo–Mo complexes of $HB(Me_2pz)_3^-$.[11,14–16] The angles between the cis and trans donor atoms in the coordination sphere are within the ranges 80.1 (2)–97.6 (2)° and 161.0 (2)–169.0 (2)°, respectively. There are no unusually short intermolecular contacts between molecules of **1** or the CH_2Cl_2 molecules of solvation. Close structural relatives to **1** include isovalent $\{[HB(Me_2pz)_3]MoO_2\}_2(\mu\text{-}O)$,[15] the two ($C_i$ and C_2) isomers of $[(HB(pz)_3)MoOCl]_2(\mu\text{-}O)$,[16] and the mixed-valence $W^{IV}W^{VI}$ complex $[HB(Me_2pz)_3]W^{IV}O(CO)(\mu\text{-}O)W^{VI}O_2[HB(Me_2pz)_3]$ recently reported by us.[18] These complexes possesses *syn*-dioxo-*anti*-dioxo, *anti*-dioxo-*anti*-dichloro (C_i), *anti*-dioxo-*syn*-dichloro (C_2), and *syn*-dioxo-*anti*-oxo(carbonyl) core structures, respectively. The structure established for **1** has a close structural similarity to the C_2 isomer of $[(HB(pz)_3)MoOCl]_2(\mu\text{-}O)$.[16] Enantiomeric forms, which are chiral at the Mo(V) center, are predicted for **1**. In the case of $[(HB(pz)_3)MoOCl]_2(\mu\text{-}O)$ the two structurally characterized C_i and C_2 forms are diastereomers. Although the synthesis of $\{[HB(Me_2pz)_3]MoOCl\}_2(\mu\text{-}O)$ has been reported,[11] its structure has not been determined.

Dinuclear Mo^VMo^{VI} complexes are rare, and none have been previously isolated or structurally characterized.[12,19–23] Deep blue $[Mo_2O_4(\mu\text{-}O)(Me_3tcn)_2]^+$ (Me_3tcn = 1,4,7-trimethyl-1,4,7-triazacyclononane), reported by Wieghardt et al.,[19,20] is formed upon chemical[19] or electrochemical[19,20] reduction of $[Mo_2O_4(\mu\text{-}O)(Me_3tcn)_2]^{2+}$. The complex is likely to possess a corner-shared bioctahedral structure similar to **1** and $[Mo_2O_4(\mu\text{-}O)(Me_3tcn)_2]^{2+}$ [19] and exhibits an ESR spectrum consistent with electron delocalization over two equivalent Mo nuclei.[20] A green Mo^VMo^{VI} complex, formulated as $[(gly)(H_2O)MoO(OH)(\mu\text{-}$

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$O)MoO_2(gly)(H_2O)]^+$ (gly = glycinate) has been reported by Chaudhury,[21] and although it remains to be isolated and unambiguously characterized, it too may possess a bioctahedral structure similar to **1**. Kinetic studies of the oxidation of $[Mo_2O_4(edta)]^{2-}$ (edta = ethylenediaminetetraacetate)[22] and $[Mo_2O_4(aq)]^{2+}$[23] reveal that these reactions are likely to proceed via Mo^VMo^{VI} intermediates, which retain the two bridging oxo ligands.

Table I. Crystal Data and Experimental Details for $\mathbf{1}\cdot CH_2Cl_2$

$C_{31}H_{46}B_2Cl_3Mo_2N_{12}O_4$	space group: $C2/c$ (C^6_{2h}; No. 15)
fw = 970.65	T = 292 (1) K
a = 15.211 (1) Å	λ = 1.5418 Å
b = 20.354 (2) Å	ρ_{obsd} = 1.57 (1) g cm^{-3}
c = 13.759 (1) Å	ρ_{calcd} = 1.577 g cm^{-3}
β = 106.32 (1)°	μ = 72.61 cm^{-1}
V = 4088 (1) Å^3	R = 0.053
Z = 4	R_w = 0.050

Experimental Section

Materials and Methods. All reactions were performed under an atmosphere of dinitrogen by using standard Schlenk methods and dried, deoxygenated solvents. Workups were performed in air. Samples of $[HB(Me_2pz)_3]MoO_2Cl$ were prepared by the method of Roberts et al.[11] and were free (by thin-layer chromatographic criteria) of contaminants. Methylmagnesium chloride (3 M in tetrahydrofuran) was purchased from Aldrich Chemical Co.; the other Grignard reagents were prepared in situ by reaction of magnesium and alkyl/aryl halide in tetrahydrofuran. Microanalyses were performed by Atlantic Microlabs. Infrared spectra were obtained on a Perkin-Elmer 1430 ratio recording IR spectrophotometer using pressed KBr disks with polystyrene as reference. Solid-state magnetic susceptibilities were measured by using a Faraday balance calibrated with $[Ni(H_2NCH_2CH_2NH_2)_2](S_2O_3)$. Diamagnetic corrections were based on the experimentally measured diamagnetic susceptibility of $\{[HB(Me_2pz)_3]MoO_2\}_2(\mu\text{-}O)$ ($\chi_g = 380 \times 10^{-6}$ cgsu) appropriately modified by using tabulated Pascal constants.[24] ESR spectra were run on a Varian E-line spectrometer using DPPH as standard reference. Electron impact (70 eV) mass spectra were recorded on a VG TRIO-1 spectrometer with a probe temperature of 200 °C. Column chromatography was performed on a 50-cm column by using Merck Artikel 7734 Kieselgel 60. TLC's were run on Merck Artikel 5735 DC-Plastikfolien Kieselgel 60 F_{254}.

Synthesis and Characterization of 1. A vigorously stirred suspension of finely ground $[HB(Me_2pz)_3]MoO_2Cl$[11] (1.5 g, 3.26 mmol) in tetrahydrofuran (75 mL) was treated dropwise with a solution of MeMgCl (1.63 mmol) in tetrahydrofuran (35 mL) over 1.5 h. Following further stirring for 0.5 h, the solution was filtered in air and the filtrate was evaporated to dryness. Column chromatography (Keiselgel, CH_2Cl_2) resulted in the collection of an intense brown band (band 3) following the elution of minor colored products. The complex was recrystallized from a solution of dichloromethane by addition of methanol. Yield: 0.36 g (25%).

Anal. (Partial loss of CH_2Cl_2 of solvation evident from analytical result. Experimental values best fit $\mathbf{1}\cdot 0.87CH_2Cl_2$) Calcd for $C_{30.87}H_{45.74}B_2Cl_{2.74}Mo_2N_{12}O_4$: C, 38.64; H, 4.80; N, 17.52; Cl, 10.12. Found: C, 38.80; H, 4.75; N, 17.60; Cl, 10.10. Infrared spectrum (KBr): ν(BH) 2550 (m), 1540 (s), 1445 (s), 1410 (s), 1380 (s), 1360 (s), 1200 (s), 1065 (s), 1040 (m) cm^{-1}; ν(MoO) 955 (s) cm^{-1}; $\nu(MoO_2)$ 925 (m), 895 (s), 860 (m), 810 (s) cm^{-1}; ν_{as}(MoOMo) 750 (s, br), 640 (m), 460 (m), 380 (w) cm^{-1}; ν(MoCl) 330 (m), 270 (m) cm^{-1}. Electronic spectrum (CH_2Cl_2), λ_{max} (ϵ, M^{-1} cm^{-1}): 260 (16 000), 266 (16 200), 273 (15 500), 300 (8000, sh), 450 (580, sh), 850 (115). ESR spectrum (CH_2Cl_2): $\langle g \rangle$ 1.935, $\langle a \rangle$ (^{95,97}Mo) 45×10^{-4} cm^{-1}. Mass spectrum, m/e for $[\mathbf{1} - Cl]^+$ (%, within multiplet): 842 (10), 843 (10), 844 (25), 845 (41), 846 (54), 847 (66), 848 (91), 849 (82), 850 (100), 851 (88), 852 (84), 853 (70), 854 (56), 855 (34), 856 (20), 857 (7) (other multiplets due to dinuclear species at m/e 770, 755, and 674).

X-ray Crystallographic Studies. Crystals suitable for X-ray crystallographic studies were grown by slow diffusion of n-pentane into a dichloromethane solution of **1**. Crystal data and experimental details are reported in Table I. Cell constants were obtained from least-squares refinement, using setting angles of 25 reflections in the range $48 \leq 2\theta \leq 75°$. Data were collected at 292 (1) K by using a Rigaku AFC diffractometer and graphite-monochromated Cu Kα radiation (Mo radiation was not available in our laboratory). During data collection three reflections monitored every 50 reflections showed a gradual 5% decrease in intensities; the data were scaled accordingly. The data were corrected for Lorentz and polarization effects and for absorption. Absorption corrections were numerically evaluated by Gaussian integration to a precision of 0.5%.[25a,26] Of the 3387 unique data, 2939 with $I_0 \geq 3\sigma I$ were used for structure solution by Patterson and Fourier methods. The methyl hydrogens were included in their calculated positions and given a common isotropic temperature factor. Those bonded to C(13), C(23), C(33), and B were included at sites derived from difference maps; their positional coordinates were not refined. All non-hydrogen atoms were refined with anisotropic temperature factors. An isotropic extinction correction of the form $F_c = F[1 - (10.1 \times 10^{-8}|F|^2/\sin\theta)]$ was applied to the calculated structure amplitudes. Refinement was carried out with the SHELX-76 program[26] and Figure 1 was prepared from the output of ORTEP-II.[27] Scattering factor curves were taken from refs 26 (H, B, C,

Table II. Final Atomic Coordinates for Non-Hydrogen Atoms in $\mathbf{1}\cdot CH_2Cl_2$ [Mo ($\times10^5$), others ($\times10^4$)] and Equivalent Isotropic Temperature Factors (Å$^2 \times 10^2$), Esd Values in Parentheses

atoms	x/a	y/b	z/c	U_{eq}[b]
Mo(1)	45748 (3)	31568 (2)	86696 (3)	3.67 (1)
Cl(1)[a]	4389 (2)	2115 (1)	8708 (2)	7.2 (1)
O(1)	5535 (2)	3209 (2)	9662 (3)	4.6 (1)
O(2)	5000	3180 (2)	7500	3.7 (2)
N(11)	3124 (3)	3249 (2)	7539 (3)	3.6 (1)
N(12)	2540 (3)	3751 (2)	7614 (3)	3.6 (1)
C(11)	3081 (4)	2284 (3)	6405 (4)	5.1 (2)
C(12)	2689 (4)	2885 (3)	6722 (4)	4.0 (1)
C(13)	1836 (4)	3167 (3)	6272 (4)	5.2 (2)
C(14)	1765 (4)	3698 (3)	6854 (4)	4.7 (2)
C(15)	981 (4)	4192 (4)	6713 (5)	7.3 (2)
N(21)	4491 (3)	4262 (2)	8644 (3)	3.4 (1)
N(22)	3679 (3)	4582 (2)	8549 (3)	3.3 (1)
C(21)	6136 (4)	4536 (3)	8863 (4)	4.6 (1)
C(22)	5148 (4)	4705 (3)	8733 (4)	3.6 (1)
C(23)	4775 (4)	5325 (3)	8673 (4)	4.3 (1)
C(24)	3843 (4)	5235 (3)	8556 (4)	4.1 (1)
C(25)	3106 (5)	5747 (3)	8401 (5)	5.4 (2)
N(31)	3700 (3)	3310 (2)	9692 (3)	3.5 (1)
N(32)	3008 (3)	3771 (2)	9498 (3)	3.7 (1)
C(31)	4359 (5)	2464 (3)	11031 (5)	6.5 (2)
C(32)	3690 (4)	2993 (3)	10553 (4)	4.7 (2)
C(33)	2982 (4)	3256 (3)	10895 (4)	5.1 (2)
C(34)	2576 (4)	3731 (3)	10229 (4)	4.5 (1)
C(35)	1778 (4)	4166 (3)	10237 (5)	6.3 (2)
B(1)	2815 (4)	4203 (3)	8542 (5)	3.6 (1)
Cl(2)	4468 (2)	580 (1)	6460 (3)	15.0 (1)
C(36)	5000	1024 (8)	7500	21.0 (11)

[a] Atom included with occupancy factor 0.50. Site also occupied by an oxygen atom (occupancy factor 0.50). [b] $U_{eq} = {}^1/_3\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i\cdot\mathbf{a}_j$.

Table III. Bond Distances (Å) and Angles (deg) for **1**[a]

	Distances		
Mo–Cl(1)	2.142 (2)	Mo–N(11)	2.323 (4)
Mo–O(1)	1.699 (3)	Mo–N(21)	2.253 (4)
Mo–O(2)	1.896 (2)	Mo–N(31)	2.213 (5)
Mo···Mo	3.793 (1)		
	Angles		
Mo–O(2)–Mo	180.0 (1)	O(1)–Mo–N(21)	89.0 (2)
Cl(1)–Mo–O(1)	97.6 (2)	O(1)–Mo–N(31)	90.9 (2)
Cl(1)–Mo–O(2)	97.1 (1)	O(2)–Mo–N(11)	85.2 (2)
Cl(1)–Mo–N(11)	89.4 (2)	O(2)–Mo–N(21)	89.6 (2)
Cl(1)–Mo–N(21)	169.0 (2)	O(2)–Mo–N(31)	161.0 (2)
Cl(1)–Mo–N(31)	91.0 (2)	N(11)–Mo–N(21)	82.5 (2)
O(1)–Mo–O(2)	105.0 (2)	N(11)–Mo–N(31)	77.7 (2)
O(1)–Mo–N(11)	166.7 (2)	N(21)–Mo–N(31)	80.1 (2)

[a] Site Cl(1) is occupied by terminal chloro and terminal oxo ligands each with 0.50 occupancy. Due to disorder, only the average bond distances and angles of the two structurally inequivalent halves of the molecule are obtainable.

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(24) Figgis, B. N.; Lewis, J. In *Techniques in Inorganic Chemistry*; Jonassen, H. B., Weissberger, A., Eds.; Wiley-Interscience: New York, 1965; Vol. 4, p 137.

(25) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974 (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands): (a) Vol. IV, p 55; (b) Vol. IV, p 99; (c) Vol. IV, p 149.

(26) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.

N, O, Cl) and 25b (Mo), the non-hydrogen atoms being corrected for anomalous dispersion.[25c] Final atomic coordinates for the non-hydrogen atoms are given in Table II. Selected bond distances and angles are given in Table III.

The structural model adopted is for a site-disordered crystal of **1**·CH_2Cl_2. In this model the site labeled Cl(1) is occupied by a terminal chloro ligand and a terminal oxo ligand, each with 0.5 occupancy. Refinement in the noncentric space group *Cc* resulted in wide discrepancies between the bond lengths and angles in the two halves of the molecule, and refinement of the dichloromethane molecule was unsatisfactory.

Acknowledgment. We thank Dr. Keith S. Murray and Ms. Karen Bertoncello for assistance with the susceptibility measurements and Dr. S. Middleton for the mass spectrum. We gratefully acknowledge the financial assistance of the Australian Research Council.

Supplementary Material Available: Complete listings of crystal and experimental data, positional atomic data, thermal parameters, and bond distances and angles (7 pages); a listing of observed and calculated structure amplitudes (30 pages). Ordering information is given on any current masthead page.

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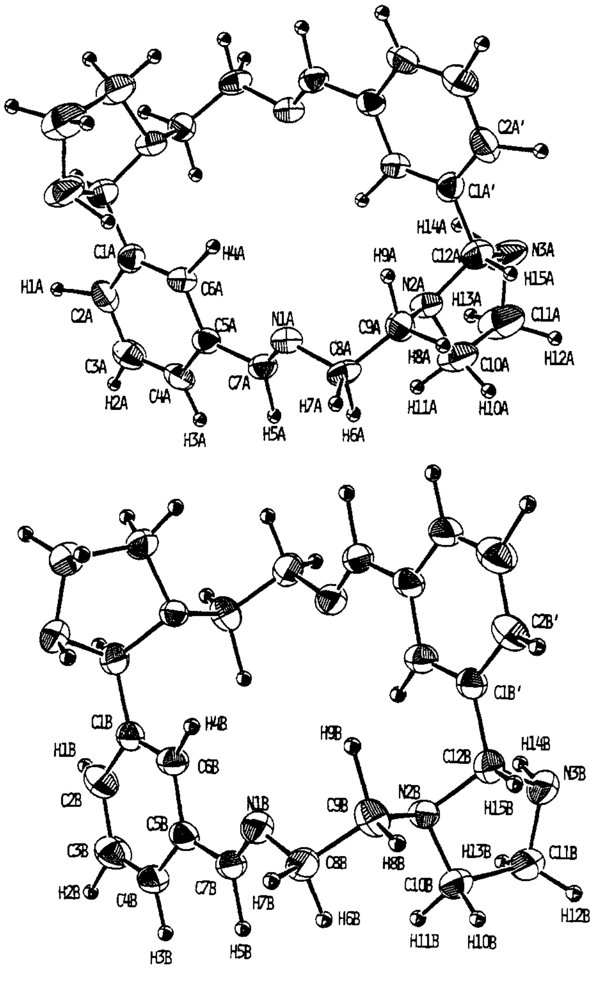
(27) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Additions and Corrections

1990, Volume 29

Rached Menif, Arthur E. Martell,* Philip J. Squattrito, and Abraham Clearfield: New Hexaaza Macrocyclic Binucleating Ligands. Oxygen Insertion with a Dicopper(I) Schiff Base Macrocyclic Complex.

Page 4725. Replace Figure 1 by the following figure. This is necessary in order that the atomic numbering scheme corresponds to the numbers in Tables II–IV.



—Arthur E. Martell