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Preparation and Structural Characterization of the Fully Chelated Dimolybdenum(II) Complex Tetrakis[2-((dimethylamino)methyl)phenyl]dimolybdenum(II)

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Dimolybdenum tetraacetate reacts with Li[o-$Me_2NCH_2C_6H_4$] in tetrahydrofuran to give dark red, crystalline (o-$Me_2NCH_2C_6H_4)_4Mo_2$. The crystalline compound is very air-sensitive. It was identified and structurally characterized by an X-ray crystallographic structure determination. Crystals belong to space group $P2_1/n$ with the following unit cell dimensions: $a = 13.516$ (1) Å, $b = 13.154$ (3) Å, $c = 21.447$ (5) Å, $\beta = 92.15$ (1)°, $V = 3810$ (2) Å^3 and $Z = 4$. The crystal structure consists of a van der Waals packing of discrete molecules. Each molecule consists of a quadruply bonded Mo_2^{4+} core, with an Mo–Mo bond length of 2.145 (1) Å, with two $C_6H_4CH_2NMe_2$ ligands chelated to each metal atom in a cis fashion. There is an approximate twofold rotation axis bisecting the Mo–Mo bond. The Mo–Mo–X angles are quite disparate, with two slightly acute Mo–Mo–C angles (mean 86.5 (1)°), two obtuse Mo–Mo–C angles (mean 109.6 (10)°), and two kinds of Mo–Mo–N angles (mean values 126.1 (1) and 111.6 (1)°). The rotational conformation about the Mo–Mo bond deviates slightly (11°) from being eclipsed. The large distortions are evidently due to the steric requirements of chelate ring formation as well as intramolecular repulsions between ligands on different metal atoms.

Introduction

Recently we reported the first structural evidence for a molecule containing only chelating ligands bonded to a quadruply bonded M_2^{n+} unit, namely $(Et_2B(pz)_2)[Et_2B(pz)(OH)]Mo\overset{4}{-}Mo[Et_2B(pz)(OH)](Et_2B(pz)_2)$ (pz = 2-pyrazolyl).[1] This turned out, from crystallographic data, to be the true identity of a compound that had previously been thought to contain four identical chelating ligands, namely $(Et_2B(pz)_2)_2Mo\overset{4}{-}Mo(Et_2B(pz)_2)_2$. Thus, although the existence of an entirely chelated compound had been established, there was still no structural evidence for the most obvious type, $M_2(LL)_4$, in which all four bidentate ligands are the same. In this paper we describe the preparation and structural characterization of such a molecule, in which the ligand is the 2-((dimethylamino)methyl)phenyl group. It is found that there are some very unusual stereochemical features to the structure.

Experimental Section

All manipulations were carried out under an atmosphere of dry argon. Solvents were dried over Na-K alloy, distilled immediately before use, and transferred by syringe.

Preparation of Tetrakis(*N*,*N*-dimethylbenzylamine)dimolybdenum. 5.0 g (36 mmol) of LiC_6H_4-o-$CH_2N(CH_3)_2$[2] was dissolved in 150 mL of THF. Dimolybdenum tetraacetate[3] (3.89 g, 9 mmol) was added and the resulting dark red solution stirred overnight. Filtration removed the amorphous precipitate of lithium acetate, and the filtrate was reduced in volume to ca. 50 mL and stored at −10 °C for several days. Large dark-red, crystalline blocks were formed in as high as 82% yield. The solvent was removed by syringe, and the very air-sensitive crystals were washed with hexane and dried under vacuum.

Collection and Reduction of X-ray Data. A few crystals obtained in the manner indicated above were transferred to a Vacuum Atmospheres drybox and mounted under nitrogen in capillary tubes, which were subsequently sealed with use of a hot wire and proved adequate for X-ray crystallographic investigation. Data were collected on two approximately equidimensional crystals. An exchange of crystals two-thirds of the way through data collection was deemed necessary by the signficant decomposition of the first. The two sets of data were matched on the basis of three intensity standards [8,3,−1; 9,3,−4; 9,4,0], and the successful refinement of structure indicated the reliability of the method used. Intensity data were collected at room temperature on an Enraf-Nonius CAD-4 automated diffractometer where automatic location and centering of 25 reflections (26° ≤ 2θ ≤ 36°) provided the unit cell parameters presented in Table I.

Table I. Crystallographic Data and Data Collection Prodecures

formula	$Mo_2N_4C_{36}H_{48}$	β, deg	92.15 (1)
mol wt	728.29	Z	4
space group	$P2_1/n$	ρ_C, g/cm^3	1.270
a, Å	13.516 (1)	μ(Mo Kα), cm^{-1}	6.744
b, Å	13.154 (3)		
c, Å	21.447 (5)		
V, Å^3	3810 (2)		

crystal size, mm	0.65 × 0.5 × 0.5 (**1**); 0.65 × 0.5 × 0.45 (**2**)
diffractometer	Enraf-Nonius CAD-4
radiation	graphite-monochromated Mo Kα ($\lambda\alpha$ = 0.710 73 Å)
collection range	$+h,+k,\pm l$, $0 < 2\theta \leqslant 50°$
aperture width	1.50 + 1.0 tan θ
prescan rejctn limit	2.0
max counting time, s	30
prescan acceptance limit	0.02
X-ray exposure time, h	43 (**1**); 24 (**2**)
cryst dec	50% (**1**); 10% (**2**)
no. of unique data	7337
no. of data, $I \geqslant 3\sigma(I)$	4358
p	0.05
no. of variables	379
R_1	0.054
R_2	0.075
esd	2.070
largest shift	0.28
largest peak, e/Å^3	0.85

A preliminary survey of the intensity data established systematic absences in $h0l$ for $h + l = 2n$ and $0k0$ for $k = 2n$, indicating the space group $P2_1/n$. The intensity data were collected to $2\theta = 50°$ by using the ω–2θ method and a scan range determined by $\Delta\omega = (0.80 + 0.35 \tan\theta)°$ with a 25% extension at either end for background determination. Standard data collection procedures have been previously summarized,[4] and the specific CAD-4 operating parameters used here are presented in Table I. Of the 7337 symmetry-independent reflections measured, all those with intensities $I \geq 3\sigma(I)$ (4358) were used in subsequent calculations. Standard deviations were estimated from counting statistics. Data were reduced to unscaled, observed structure factor amplitudes after correction for Lorentz and polarization factors. With $\mu = 6.744$ cm^{-1} no absorption correction was deemed necessary.

Solution and Refinement of the Structure. The structure was solved by Patterson and Fourier methods and refined[5] by full-matrix least

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(1) Cotton, F. A.; Kolthammer, B. W. S.; Mott, G. N. *Inorg. Chem.* **1981**, *20*, 3890.

(2) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068.

(3) Birgnole, A. B.; Cotton, F. A. *Inorg. Synth.* **1972**, *13*, 87.

(4) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(5) All crystallographic computing was performed on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, using a modified version of the Enraf-Nonius structure determination package.

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Table IIA. Positional Parameters and Their Estimated Standard Deviations for Tetrakis(*N*,*N*-dimethylbenzylamine)dimolybdenum[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo(1)	0.23503 (5)	0.33650 (5)	0.37679 (3)	C(27)	0.0336 (6)	0.3892 (6)	0.3084 (4)
Mo(2)	0.19200 (5)	0.21374 (5)	0.43574 (3)	C(28)	0.0390 (7)	0.4850 (6)	0.4040 (4)
N(1)	0.3549 (5)	0.4708 (5)	0.4046 (3)	C(29)	0.1283 (6)	0.5414 (6)	0.3180 (4)
N(2)	0.0985 (5)	0.4499 (5)	0.3530 (3)	C(31)	0.0356 (6)	0.2282 (6)	0.4523 (4)
N(3)	0.1111 (5)	0.0797 (5)	0.3769 (3)	C(32)	−0.0095 (6)	0.2693 (6)	0.5034 (4)
N(4)	0.3035 (5)	0.1035 (5)	0.4974 (3)	C(33)	−0.1113 (7)	0.2654 (7)	0.5099 (4)
C(11)	0.3795 (6)	0.2631 (6)	0.3748 (3)	C(34)	−0.1700 (7)	0.2232 (8)	0.4661 (5)
C(12)	0.4087 (7)	0.1715 (7)	0.3475 (4)	C(35)	−0.1296 (6)	0.1779 (7)	0.4138 (4)
C(13)	0.5024 (7)	0.1346 (7)	0.3479 (4)	C(36)	−0.0292 (6)	0.1817 (6)	0.4081 (4)
C(14)	0.5774 (7)	0.1890 (8)	0.3761 (5)	C(37)	0.0191 (6)	0.1283 (6)	0.3540 (4)
C(15)	0.5568 (6)	0.2813 (7)	0.4026 (4)	C(38)	0.1624 (7)	0.0404 (7)	0.3233 (4)
C(16)	0.4602 (6)	0.3174 (6)	0.4031 (4)	C(39)	0.0876 (7)	−0.0080 (6)	0.4149 (4)
C(17)	0.4391 (6)	0.4157 (6)	0.4346 (4)	C(41)	0.2482 (6)	0.3070 (6)	0.5141 (3)
C(18)	0.3870 (6)	0.5049 (7)	0.3436 (4)	C(42)	0.2109 (6)	0.3971 (6)	0.5380 (4)
C(19)	0.3331 (7)	0.5601 (7)	0.4422 (4)	C(43)	0.2489 (7)	0.4475 (7)	0.5888 (4)
C(21)	0.1911 (6)	0.3057 (6)	0.2800 (3)	C(44)	0.3316 (8)	0.4087 (8)	0.6195 (4)
C(22)	0.2506 (7)	0.2747 (6)	0.2334 (4)	C(45)	0.3733 (7)	0.3190 (8)	0.5985 (4)
C(23)	0.2193 (7)	0.2795 (6)	0.1695 (4)	C(46)	0.3315 (6)	0.2697 (7)	0.5478 (4)
C(24)	0.1271 (7)	0.3121 (7)	0.1530 (4)	C(47)	0.3761 (6)	0.1732 (7)	0.5253 (4)
C(25)	0.0663 (6)	0.3448 (7)	0.1976 (4)	C(48)	0.2402 (8)	0.0649 (7)	0.5461 (4)
C(26)	0.0973 (6)	0.3427 (6)	0.2601 (4)	C(49)	0.3561 (7)	0.0162 (7)	0.4708 (5)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

squares. The positions of the two molybdenum atoms were obtained through a three-dimensional Patterson synthesis. Three cycles of isotropic least-squares refinement gave values of $R_1 = 0.29$ and $R_2 = 0.40$ where the R_i are defined as

$$R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$$

Subsequent least-squares cycles and difference Fourier maps located all 42 nonhydrogen atoms, and after anisotropic refinement the discrepancy indices were $R_1 = 0.055$ and $R_2 = 0.077$. Hydrogen atoms were then included at calculated positions and their contributions included in F_c values, but they were not refined. Inclusion of these atoms in the refinement gave convergence at $R_1 = 0.054$ and $R_2 = 0.075$. The error in an observation of unit weight was 2.070, and the largest shift/error ratio in the final cycle was 0.02. A final difference synthesis showed random fluctuations not exceeding ±0.85 e/Å^3.

Final positional parameters of nonhydrogen atoms are given in Table IIA. The thermal parameters are listed in Table IIB, which is available as supplementary material. Table IIC (also supplementary material) gives parameters for hydrogen atoms. Values of F_o vs. F_c for the 4358 observed data are available as supplementary material.

Results

The crystal structure consists of a packing of $Mo_2(C_6H_4CH_2NMe_2)_4$ molecules with normal contact distances. The entire molecule constitutes the asymmetric unit and is not subject to any crystallographically imposed symmetry. The molecule is depicted in Figure 1, where the atom numbering scheme used in all the tables is defined. The bond distances and angles are listed in Table III, and some planes and dihedral angles are given in Table IV.

The molecule has approximate C_2 symmetry, with the C_2 axis of rotation bisecting the Mo–Mo bond and also bisecting imaginary lines from C(11) to C(41) and N(2) to N(3). In Figure 1, this C_2 axis is a vertical line lying approximately in the plane of the figure.

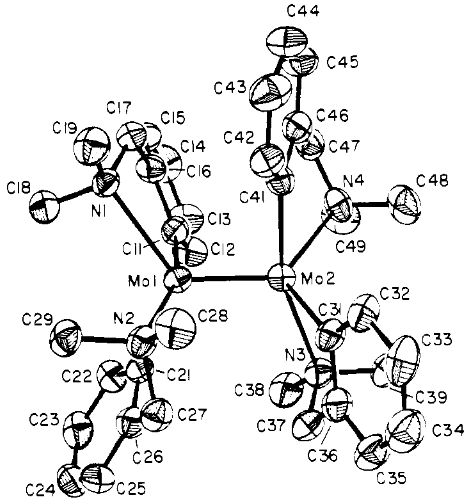
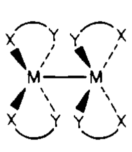


Figure 1. The $Mo_2(C_6H_4CH_2NMe_2)_4$ molecule, computer-drawn with use of the ORTEP program. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 40% of the electron density.

Discussion

The Mo–Mo distance of 2.145 (1) Å is typical for a quadruple bond when no bridging groups are present. It may be compared, for example, with the bond length of 2.156 (1) Å in $Mo_2(Et_2B(pz)_2)[Et_2B(pz)(OH)]_2$.[1] There are two possible arrangements for a pair of unsymmetrical chelating ligands, XY, in an approximately planar or slightly pyramidal arrangement about a metal atom, namely, cis and trans. In this case the cis arrangement is adopted on each metal atom. The two ends of the molecule are then related in such a way that chelate rings are face to face but with orientations reversed, as shown schematically in **1**. This arrangement is potentially capable of having symmetry as high as C_{2h}, where the C_2 axis would be vertical and the σ_h horizontal with respect to the orientation shown in 1. However, because of distortions in the chelate ring conformations and in the M′–M–L angles, there is no horizontal symmetry plane. A C_2 axis is effectively (though not rigorously) present, however.



1

The rotational conformation about the Mo–Mo bond is described by the four torsional angles of the C–Mo–Mo–N type listed in Table IV. Two of these are close to zero, while the other two are ca. 20°, and all of them represent twists in the same helical sense. Thus, there is a net average deviation from the eclipsed conformation of 11°. As noted previously, however, a small deviation such as this does not significantly decrease the strength of the δ component of the quadruple bond.[6]

The title compound therefore clearly belongs to the class of quadruply bonded $X_4M\overset{4}{-}MX_4$ species, which in their simplest, idealized form have D_{4h} symmetry. It was only to be expected that when the X_4 set of ligand atoms is replaced by two unsymmetrical chelate ligands, XY, distortions would occur. However, in this case, some of the distortions are remarkable for either their qualitative character or their magnitude. It appears likely that these distortions have their origins mainly in the conformational requirements of the five-membered chelate rings and in the repulsive forces between ligand atoms on opposite ends of the molecule.

The chelate rings are all fairly similar and deviate appreciably from planarity. One way of stating this nonplanarity is presented in Table IV, where the deviations of the two remaining carbon atoms from the plane defined by the C–Mo–N set of atoms are given. In each case, these two carbon atoms deviate in the same direction but by different amounts. In each case, these carbon atoms are displaced towards the other end of the molecule. Alternatively, it may be said that each nitrogen atom is displaced from the mean plane of the molybdenum atom, and the three carbon atoms are displaced in a direction away from the other end of the molecule.

Each $N(CH_3)_2$ group is opposite to a phenyl ring on the other molybdenum atom, and thus the displacement of the nitrogen atom away from the other end of the molecule lessens the contact between $N(CH_3)_2$ and the phenyl group. However, it appears that additional measures are necessary to reduce such contacts to a tolerable level, and thus the Mo′–Mo–N angles are all unusually large. Two of them are about 126° and two about 112°. Also, two of the Mo′–Mo–C angles are somewhat larger than usual for M′–M–X angles in molecules of this kind, namely, about 110°.

Curiously, however, the other two Mo′–Mo–C angles are slightly acute being about 85.5°. This is the first time an acute M′–M–X angle has been observed except in some cases where there are bridging RCO_2^- ligands, or sterically similar ones, reaching across relatively long M–M bonds, as for example, in several recently reported structures of dirhodium compounds.[7]

The rather large angular distortions and irregularities around the molybdenum atoms are at first sight surprising, but not unreasonable when the properties of the quadruply bonded Mo_2^{4+} unit and the steric demands of the ligands are taken into account. The steric demands are such that the maintenance of a regular $X_4M\overset{4}{-}MX_4$ configuration is not possible. Since the force constants for various kinds of angle deformations are not large, it is reasonable that angle deformations provide the principal means of relieving internal strain caused by nonbonded repulsions. None of the individual angle deformations are in themselves unprecedented except for the larger (ca. 126°) Mo′–Mo–N angles. However, the entire set of angle deformations exhibited here does provide a striking and unprecedented demonstration of the ability of a quadruply bonded dimetal unit to tolerate deviations from the idealized D_{4h} symmetry of a $X_4M\overset{4}{-}MX_4$ moiety and still retain the short M–M distance characteristic of the quadruple bond.

Another interesting feature of this structure is the very large value of the mean Mo–N bond length, 2.430 Å. The mean Mo–C bond length is much smaller, viz., 2.179 Å. This mean Mo–C distance is similar to that in $Mo_2(2,6\text{-}(OMe)_2Ph)_4$,[8] 2.16 Å, where a phenyl carbon atom is also involved although in that case the plane of the phenyl group is parallel to the Mo–Mo bond while in the present compound the phenyl plane is turned 90° about the Mo–C bond. It is interesting that in

Table III. Bond Distances (Å) and Bond Angles (Deg) with Esd's

Distances

Mo(1)–Mo(2)	2.145 (1)	C(14)–C(15)	1.374 (9)
–N(1)	2.456 (4)	C(15)–C(16)	1.390 (8)
–N(2)	2.412 (5)	C(16)–C(17)	1.491 (8)
–C(11)	2.180 (6)	C(21)–C(22)	1.369 (8)
–C(21)	2.176 (5)	C(21)–C(26)	1.409 (8)
Mo(2)–N(3)	2.408 (4)	C(22)–C(23)	1.420 (8)
–N(4)	2.444 (5)	C(23)–C(24)	1.353 (9)
–C(31)	2.165 (6)	C(24)–C(25)	1.354 (9)
–C(41)	2.193 (5)	C(25)–C(26)	1.390 (8)
N(1)–C(17)	1.477 (7)	C(26)–C(27)	1.502 (8)
–C(18)	1.464 (7)	C(31)–C(32)	1.383 (8)
–C(19)	1.461 (7)	C(31)–C(36)	1.406 (8)
N(2)–C(27)	1.502 (7)	C(32)–C(33)	1.389 (9)
–C(28)	1.459 (7)	C(33)–C(34)	1.329 (10)
–C(29)	1.483 (7)	C(34)–C(35)	1.399 (10)
N(3)–C(37)	1.466 (7)	C(35)–C(36)	1.369 (8)
–C(38)	1.457 (7)	C(36)–C(37)	1.524 (8)
–C(39)	1.455 (7)	C(41)–C(42)	1.393 (8)
N(4)–C(47)	1.456 (8)	C(41)–C(46)	1.406 (8)
–C(48)	1.466 (8)	C(42)–C(43)	1.361 (8)
–C(49)	1.475 (8)	C(43)–C(44)	1.374 (10)
C(11)–C(12)	1.402 (8)	C(44)–C(45)	1.389 (10)
C(11)–C(16)	1.420 (8)	C(45)–C(46)	1.370 (8)
C(12)–C(13)	1.357 (9)	C(46)–C(47)	1.493 (9)
C(13)–C(14)	1.364 (10)		

Angles

Mo(2)–Mo(1)–N(1)	126.1 (1)	Mo(1)–C(11)–C(12)	130.9 (4)
–N(2)	111.6 (1)	–C(16)	116.3 (4)
–C(11)	86.6 (2)	C(12)–C(11)–C(16)	112.8 (5)
–C(21)	110.6 (1)	C(11)–C(12)–C(13)	125.6 (6)
N(1)–Mo(1)–N(2)	95.7 (2)	C(12)–C(13)–C(14)	119.5 (6)
–C(11)	74.9 (2)	C(13)–C(14)–C(15)	119.2 (6)
–C(21)	121.3 (2)	C(14)–C(15)–C(16)	120.7 (6)
N(2)–Mo(1)–C(11)	161.5 (2)	C(11)–C(16)–C(15)	122.1 (6)
–C(21)	74.6 (2)	–C(17)	118.3 (5)
C(11)–Mo(1)–C(21)	96.4 (2)	C(15)–C(16)–C(17)	119.6 (5)
Mo(1)–Mo(2)–N(3)	111.7 (1)	N(1)–C(17)–C(16)	112.7 (5)
–N(4)	126.2 (1)	Mo(1)–C(21)–C(22)	127.3 (4)
–C(31)	108.6 (2)	–C(26)	115.8 (4)
–C(41)	86.4 (1)	C(22)–C(21)–C(26)	115.3 (5)
N(3)–Mo(2)–N(4)	96.2 (2)	C(21)–C(22)–C(23)	122.0 (6)
–C(31)	73.9 (2)	C(22)–C(23)–C(24)	120.2 (6)
–C(41)	161.7 (2)	C(23)–C(24)–C(25)	119.6 (6)
N(4)–Mo(2)–C(31)	123.3 (2)	C(24)–C(25)–C(26)	120.4 (6)
–C(41)	74.3 (2)	C(21)–C(26)–C(25)	122.3 (6)
C(31)–Mo(2)–C(41)	97.9 (2)	C(21)–C(26)–C(27)	117.6 (5)
Mo(1)–N(1)–C(17)	104.1 (3)	C(25)–C(26)–C(27)	119.8 (5)
–C(18)	102.6 (3)	N(2)–C(27)–C(26)	108.6 (4)
–C(19)	124.6 (4)	Mo(2)–C(31)–C(32)	128.7 (4)
C(17)–N(1)–C(18)	106.8 (4)	–C(36)	116.0 (4)
C(17)–N(1)–C(19)	108.8 (4)	C(32)–C(31)–C(36)	115.0 (5)
C(18)–N(1)–C(19)	108.6 (5)	C(31)–C(32)–C(33)	122.2 (6)
Mo(1)–N(2)–C(27)	103.3 (3)	C(32)–C(33)–C(34)	120.8 (6)
–C(28)	118.4 (4)	C(33)–C(34)–C(35)	120.3 (6)
–C(29)	112.9 (3)	C(34)–C(35)–C(36)	118.3 (6)
C(27)–N(2)–C(28)	108.7 (4)	C(31)–C(36)–C(35)	123.4 (6)
–C(29)	105.8 (4)	–C(37)	116.1 (5)
C(28)–N(2)–C(29)	106.9 (5)	C(35)–C(36)–C(37)	120.4 (6)
Mo(2)–N(3)–C(37)	102.6 (3)	N(3)–C(37)–C(36)	109.2 (5)
–C(38)	116.9 (4)	Mo(2)–C(41)–C(42)	129.7 (4)
–C(39)	113.0 (3)	–C(46)	116.6 (4)
C(37)–N(3)–C(38)	108.3 (5)	C(42)–C(41)–C(46)	113.7 (5)
–C(39)	109.5 (5)	C(41)–C(42)–C(43)	125.3 (6)
C(38)–N(3)–C(39)	106.3 (5)	C(42)–C(43)–C(44)	118.6 (7)
Mo(2)–N(4)–C(47)	104.0 (3)	C(43)–C(44)–C(45)	119.5 (6)
–C(48)	103.1 (4)	C(44)–C(45)–C(46)	119.9 (6)
–C(49)	123.3 (4)	C(41)–C(46)–C(45)	122.9 (6)
C(47)–N(4)–C(48)	109.1 (5)	C(41)–C(46)–C(47)	117.2 (5)
–C(49)	108.8 (5)	C(45)–C(46)–C(47)	120.0 (6)
C(48)–N(4)–C(49)	108.0 (5)	N(4)–C(47)–C(46)	113.2 (5)

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(6) Cotton, F. A.; Fanwick, P. E.; Fitch, J. W.; Glicksman, H. D.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *100*, 1752. An 11° rotation causes a 7% decrease in the δ–δ overlap.

(7) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 584.

(8) Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2087.

Table IV. Planes,[a] Dihedral Angles, and Torsional Angles for Tetrakis(*N*,*N*-dimethylbenzylamine)dimolybdenum

A. Chelate Ring Planes

coeff in eq of plane		other atoms	displacement, Å
	Plane P_1: N(1)-Mo(1)-C(11)		
$A = 0.0968$	$C = -0.9662$	C(16)	−0.312
$B = 0.2389$	$D = -6.4667$	C(17)	−0.686
	Plane P_2: N(2)-Mo(1)-C(21)		
$A = 0.6525$	$C = -0.2984$	C(26)	−0.351
$B = 0.6966$	$D = 2.5488$	C(27)	−0.820
	Plane P_3: N(3)-Mo(2)-C(31)		
$A = -0.0771$	$C = -0.7886$	C(36)	0.439
$B = 0.6100$	$D = -5.8229$	C(37)	0.872
	Plane P_4: N(4)-Mo(2)-C(41)		
$A = 0.7861$	$C = -0.5427$	C(46)	0.325
$B = 0.2958$	$D = -2.4723$	C(47)	0.700
	Angles between Planes, Deg		
P_1/P_4	47.8	P_2/P_3	52.4

B. Torsional Angles, Deg

N(1)-Mo(1)-Mo(2)-C(41)	19.9	N(2)-Mo(1)-Mo(2)-C(31)	2.2
C(11)-Mo(1)-Mo(2)-N(4)	21.0	C(21)-Mo(1)-Mo(2)-N(3)	0.8

[a] The equations of the planes are of the form $Ax + By + Cz - D = 0$.

two compounds with Mo–C bonds to aliphatic carbon atoms, viz., $Mo[(CH_2)_2P(CH_3)_2]_4$[9] and $[Mo_2(CH_3)_8]^{4-}$,[10] the Mo–C distances are somewhat longer, the mean values being 2.31 and 2.29 Å, respectively. For Mo–N bonds to $Mo\overset{4}{-}Mo^{4+}$ units, the only previous data involve nitrogen atoms belonging to π systems as in $Mo_2(PhN_3Ph)_4$,[11] $Mo_2(PhNCPhNPh)_4$[12] and $Mo_2(2\text{-}O\text{-}6\text{-}Mepy)_4$.[13] In all of these, the Mo–N distances are in the range of 2.14–2.17 Å. Even if there should be an increase similar to that just cited for carbon on going from the aromatic to aliphatic type of ligand, the Mo–N distance might have been expected to be only about 2.30 Å, rather than the 2.43 Å observed. It is possible that this lengthening of the Mo–N bonds may, at least in part, be still another consequence of the repulsive forces within the molecule. However, we have no reference structure containing the Mo–N(aliphatic) bond under unstrained conditions, so our conclusions concerning the Mo–N bonds in the present case must be purely speculative.

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Registry No. $(o\text{-}Me_2NCH_2C_6H_4)_4Mo_2$, 78804-47-4; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of observed and calculated structure factors, thermal parameters (Table IIB), and hydrogen atom parameters (Table IIC) (25 pages). Ordering information is given on any current masthead page.

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(9) Cotton, F. A.; Hanson, B. E.; Ilsley, W. H.; Rice, G. W. *Inorg. Chem.* **1979**, *18*, 2713.

(10) Cotton, F. A.; Troup, J. M.; Webb, T. R.; Williamson, D. H.; Wilkinson, G. *J. Am. Chem. Soc.* **1974**, *96*, 3824.

(11) Cotton, F. A.; Rice, G. W.; Sekutowski, J. C. *Inorg. Chem.* **1979**, *18*, 1143.

(12) Cotton, F. A.; Inglis, T.; Kilner, M.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 2023.

(13) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

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Quadridentate Schiff Base Complexes of Oxomolybdenum(V). Crystal and Molecular Structure of *trans*-[*N*,*N*′-Ethylenebis(salicylideniminato)](methanol)oxomolybdenum(V) Bromide

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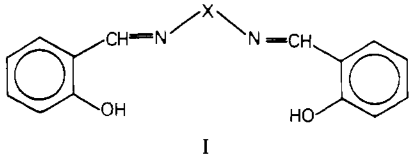
The four compounds [MoO(SALPN)Cl] and [MoOL(MeOH)]Br (H_2L = H_2SALEN, H_2SALPN, H_2SALOPHEN) have been synthesized and characterized in soluble, crystalline form. The crystal structure of the SALEN compound reveals the presence of *trans*-$[MoO(SALEN)(MeOH)]^+$ cations with the Mo atom displaced 0.37 Å from the basal plane defined by the SALEN ligand atoms. The Mo–oxo and –O(methanol) bond lengths are 1.666 and 2.338 Å, respectively. Intramolecular contacts between the axial and equatorial ligand atoms are a major determinant of the coordination geometry. Significant close contacts occur between each cation and an attendant bromide anion. Crystal data are as follows: a = 8.891 (7) Å, b = 17.491 (11) Å, c = 18.862 (11) Å, α = 95.35 (6)°, β = 93.02 (6)°, γ = 109.11 (4)°, $P\bar{1}$, Z = 6.

Introduction

The intention of the study was to synthesize the series of compounds $[Mo^VOLX]$ (H_2L = H_2SALEN, H_2SALPN, H_2SALOPHEN; X = Cl, Br) (I) for detailed ESR examination following the initial report[1] that the chloro compounds exhibited geometric isomerism and our observation[2] of Br superhyperfine coupling in *cis*-$[MoOL'_2Br]$ (L′H = 8-mercaptoquinoline and 8-hydroxyquinoline). However, synthesis and characterization has not been straightforward as the compounds are labile in solution, and we have isolated only the four crystalline compounds MoO(SALPN)Cl and MoOLBr(MeOH) in *recrystallizable*, *soluble* form. An X-ray crystallographic study allows formulation of the SALEN-bromo compound as *trans*-[MoO(SALEN)(MeOH)]Br where a methanol ligand is trans to oxo and significant close contracts occur between the complex cation and the bromide anion. The solution properties of the four compounds are being examined in detail by an integrated ESR and electrochemical study which will be reported subsquently. Synthetic,[3] ESR,[1,4] and



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(1) Dilworth, J. R.; McAuliffe, C. A.; Sayle, B. J. *J. Chem. Soc., Dalton Trans.* **1977**, 849.

(2) Boyd, I. W.; Hanson, G. R.; Wedd, A. G., unpublished observations.