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 $Mo_2(2\text{-O-6-Mepy})_4$.[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.

Acknowledgments. We thank the National Science Foundation for financial support and Dr. B. W. S. Kolthammer for assistance with the crystallography.

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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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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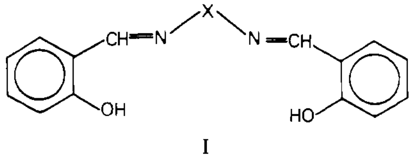
The four compounds [MoO(SALPN)Cl] and [MoOL(MeOH)]Br (H_2L = H_2SALEN, H_2SALPN, H_2SALOPHEN) have been synthesized and characterized in soluble, crystalline form. The crystal structure of the SALEN compound reveals the presence of *trans*-$[MoO(SALEN)(MeOH)]^+$ cations with the Mo atom displaced 0.37 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 exami-



I

nation 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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reactivity[5] properties of the chloro species MoOLCl have been the subject of several recent studies.

Experimental Section

Synthesis. All synthetic manipulations were performed under purified dinitrogen with use of standard Schlenck techniques. Analytical reagent grade solvents were dried and degassed before use. The ligands H_2SALEN, H_2SALPN, and H_2SALOPHEN were synthesized by literature methods.[1] The sources of oxomolybdenum(V) were $(pyH)_2[MoOCl_5]$ and $(pyH)[MoOBr_4]$.[6]

***trans*-[*N*,*N*′-Ethylenebis(salicylideniminato)](methanol)oxomolybdenum(V) Bromide ([MoO(SALEN)(MeOH)]Br).** A solution of NaOMe (0.49 g, 9 mmol) and H_2SALEN (0.81 g, 3 mmol) in MeOH (36 cm^3) was added dropwise to solid $(pyH)[MoOBr_4]$ (1.5 g, 3 mmol), and the resulting red-brown solution and brown precipitate were stirred at room temperature for 2 h. After filtration, the solid was washed with MeOH (3 × 6 cm^3) and the washings were added to the original filtrate. The dark red crystals which appeared in this solution over a period of 3 days at 4 °C were filtered, washed with *i*-PrOH/MeOH (1/1 v/v), and dried under vacuum.

***trans*-[*N*,*N*′-Propylenebis(salicylideniminato)](methanol)oxomolybdenum(V) Bromide ([MoO(SALPN)(MeOH)]Br).** A solution of NaOMe (0.49 g, 9 mmol) and H_2SALPN (0.85 g, 3 mmol) in MeOH (35 cm^3) was added dropwise to $(pyH)[MoOBr_4]$ (1.54 g, 3 mmol), and the resulting red-brown solution and brown precipitate were stirred at room temperature for 4 h, during which time most of the original precipitate redissolved. After filtration, the solution stood at 4 °C overnight, *i*-PrOH (35 cm^3) was added, and the resulting solution was allowed to stand at 4 °C for 24 h. Upon subsequent standing at room temperature for 4 h, dark red crystals appeared, were filtered off, washed with *i*-PrOH/MeOH (3/1 v/v), and dried under vacuum.

***trans*-[*N*,*N*′-*o*-Phenylenebis(salicylideniminato)](methanol)oxomolybdenum(V) Bromide ([MoO(SALOPHEN)(MeOH)]Br).** A solution of NaOMe (0.49 g, 9 mmol) and H_2SALOPHEN (0.95 g, 3 mmol) in MeOH (100 cm^3) was added to $(pyH)[MoOBr_4]$ (1.54 g, 3 mmol) and stirred for 0.5 h at room temperature to produce a red-brown precipitate under a transparent brown solution. After filtration, dimethylformamide (60 cm^3) was added to the solid. The mixture was vigorously stirred, filtered, and allowed to stand overnight. Addition of *i*-PrOH (100 cm^3) produced red-brown crystals after the mixture was allowed to stand for 8 h at room temperature.

[*N*,*N*′-Propylenebis(salicylideniminato)]oxochloromolybdenum(V) ([MoO(SALPN)Cl]). A solution of NaOMe (0.65 g, 12 mmol) and H_2SALPN (0.85 g, 3 mmol) in MeOH (30 cm^3) was added to $(pyH)_2[MoOCl_5]$ (1.35 g, 3 mmol). The red-brown solution and precipitate were stirred at room temperature for 2 h, and the solvent was removed under vacuum. The solid was extracted with MeCN (30 cm^3) at 45 °C, the solution filtered, and the solid residue extracted with more MeCN (20 cm^3) and refiltered. The combined filtrates were heated to 45 °C, and *i*-PrOH was added until incipient precipitation. After the mixture was allowed to cool and stand overnight at 4 °C, the microcrystalline product was filtered off, washed with *i*-PrOH/MeOH (3/1 v/v), and dried under vacuum.

Physical Measurements. Electronic spectra were obtained in matched quartz cells in a Varian Series 634 spectrophotometer. Bulk magnetic susceptibility measurements were measured at room temperature on a Faraday balance constructed from a Newport 4-in. electromagnet fitted with appropriate pole pieces and a Cahn RG electrobalance. $Hg[Co(SCN)_4]$ was the callibrant. A modified Oxford Instruments Faraday balance with superconducting solenoid was employed for the low-temperature study. Measurements were made at fields of 10 and 40 kG, and no field dependence was evident. A gradient field of 100 G cm^{-1} was employed and calibrated with a sample of pure nickel. The temperature was measured by thermocouples (calibrated relative to a GaAs diode) suspended in the sample position.

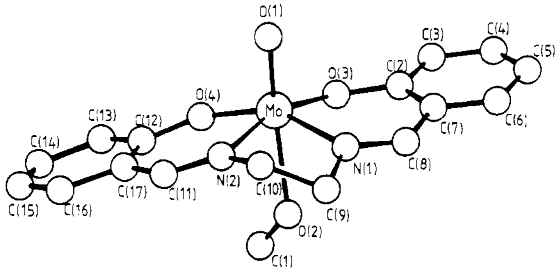

Figure 1. Perspective view of the complex cation (C) with thermal ellipsoids scaled to 50% probability.

X-ray Crystallography. Dark orange-brown prismatic single crystals of $[MoO(C_{16}H_{14}N_2O_2)(CH_3OH)]Br$ were selected directly from recrystallized material. Weissenberg photographs showed that they were triclinic. Accurate unit cell dimensions were determined by a least-squares fit of 2θ values measured for 25 strong reflections centered on a four-circle diffractometer with Mo Kα radiation ($\bar{\lambda}$ = 0.710 69 Å). The density determination by flotation in aqueous $K_2[HgI_4]$ is prone to error due to moisture and/or oxygen sensitivity of the crystals.

Crystal data: asymmetric unit $3C_{17}H_{18}BrMoN_2O_4$; M_r = 491.03; triclinic space group $P\bar{1}$; 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)°; V = 2748.7 Å^3; Z = 6; ρ(obsd) = 1.71, ρ(calcd) = 1.78 g/cm^{-3}; $F(000)$ = 1464; μ(Mo Kα) = 27.9 cm^{-1}. (In view of the unusual situation of three complex cations and three bromide ions in the asymmetric unit, the triclinic system was verified by cell reduction. Refinement confirmed the $\bar{1}$ symmetry).

As the crystals proved to be unstable on prolonged exposure to air, a crystal of dimensions ca. 0.60 × 0.15 × 0.06 mm was sealed in a Lindemann glass tube under dinitrogen for data collection. The intensities were measured on a Rigaku-AFC four-circle diffractometer with Mo Kα radiation (graphite crystal monochromator). The crystal was aligned with its longest dimension (along a) approximately parallel to the diffractometer ϕ axis, and the data were recorded by an ω–2θ scan with a 2θ scan rate of 2° min^{-1}, 10-s stationary background counts, and a scan range ($\Delta\omega$) of 1.2 + 0.5 tan θ. Three reference reflections monitored every 50 reflections showed no significant variation in intensity during the data collection period. Integrated intensities were recorded to a 2θ maximum of 40°, and of the 5343 nonequivalent terms measured, 3454 for which $|F_o| > 3\sigma|F_o|$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors and for absorption (transmission factors ranged between 0.651 and 0.851). No corrections for extinction were made. The scattering factors were taken from Cromer and Mann,[7] and anomalous dispersion corrections were made with the values of Cromer and Liberman.[8]

The structure was solved by the heavy-atom and direct-method procedures. With the assumption of the centrosymmetric space group $P\bar{1}$ an E map calculated with 286 phased terms for which $|E| > 1.60$ contained six large peaks in the asymmetric unit. In a solution consistent with the vector map, three of the peaks were assigned to the sites of Mo and the other three to the sites of Br. As the latter were at least 4.7 Å from any of the Mo sites, it was apparent that the Br was not coordinated to the Mo but was present in the crystal as Br$^-$. The sites of the O, N, and C atoms were located by successive Fourier syntheses. In the refinement, their parameters were refined in three blocks, each block containing parameters of one complex cation. Refinement with anisotropic temperature factors given to the atoms converged to a conventional R of 0.057 and $R_w = (\sum w||F_o| - |F_c||^2/\sum |F_o|^2)^{1/2}$ = 0.057, and the "goodness of fit", defined by $[\sum w||F_o| - |F_c||^2/(m - n)]^{1/2}$ where m is the number observations and n the number of variables, was 1.46. Hydrogen atoms were not included in the analysis. The largest peaks on a final difference map were of height 0.73 and −0.54 e Å^3.

The major calculations were carried out with use of SHELX-76.[9] In the least-squares refinements, the function minimized was $\sum w(|F_o|$

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Table I. Final Atomic Coordinates (×10⁴) with Estimated Standard Deviations for $[Mo^VO(C_{16}H_{24}N_2O_2)(CH_3OH)]^+ Br^{-a}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo(A)	11026 (2)	4060 (1)	1315 (1)	Mo(B)	7874 (2)	8260 (1)	1733 (1)
O(1A)	10593 (11)	4585 (6)	687 (5)	O(1B)	6616 (12)	7339 (6)	1825 (5)
O(2A)	11739 (12)	3431 (6)	2249 (5)	O(2B)	9625 (11)	9514 (6)	1513 (5)
C(1A)	11319 (25)	2593 (12)	2320 (11)	C(1B)	9511 (23)	10341 (11)	1662 (10)
N(1A)	12672 (15)	5012 (7)	2003 (6)	N(1B)	8519 (15)	8031 (7)	680 (6)
O(3A)	12817 (12)	3797 (6)	909 (5)	O(3B)	9907 (11)	8172 (6)	2097 (5)
C(2A)	14364 (19)	4320 (10)	903 (8)	C(2B)	10755 (17)	7739 (9)	1778 (8)
C(3A)	15312 (20)	4075 (9)	408 (8)	C(3B)	11925 (17)	7593 (9)	2252 (7)
C(4A)	16859 (20)	4544 (10)	391 (8)	C(4B)	12909 (18)	7180 (9)	1964 (8)
C(5A)	17550 (18)	5252 (10)	850 (9)	C(5B)	12754 (18)	6929 (9)	1227 (9)
C(6A)	16655 (18)	5484 (9)	1368 (8)	C(6B)	11646 (18)	7072 (9)	764 (8)
C(7A)	15056 (18)	5015 (9)	1382 (8)	C(7B)	10626 (17)	7510 (8)	1053 (8)
C(8A)	14216 (19)	5309 (8)	1953 (7)	C(8B)	9588 (17)	7709 (9)	527 (8)
C(9A)	12052 (15)	5296 (8)	2662 (7)	C(9B)	7703 (17)	8327 (9)	111 (7)
N(2A)	9529 (15)	4336 (7)	2068 (5)	N(2B)	6270 (14)	8667 (7)	1116 (6)
O(4A)	9438 (12)	2978 (6)	1090 (5)	O(4B)	7549 (11)	8931 (6)	2569 (5)
C(10A)	10269 (18)	5168 (8)	2442 (8)	C(10B)	6086 (17)	8374 (10)	324 (8)
C(11A)	8130 (19)	3869 (10)	2201 (8)	C(11B)	5358 (17)	9059 (8)	1364 (8)
C(12A)	7977 (20)	2629 (10)	1335 (9)	C(12B)	6249 (17)	9174 (8)	2685 (9)
C(13A)	7174 (18)	1807 (9)	1062 (7)	C(13B)	5999 (19)	9357 (9)	3394 (9)
C(14A)	5653 (20)	1407 (10)	1301 (9)	C(14B)	4687 (21)	9629 (9)	3529 (9)
C(15A)	4973 (19)	1832 (12)	1760 (11)	C(15B)	3695 (20)	9755 (11)	2981 (10)
C(16A)	5801 (18)	2638 (10)	2066 (8)	C(16B)	3991 (18)	9573 (9)	2264 (9)
C(17A)	7364 (16)	3041 (10)	1843 (8)	C(17B)	5265 (18)	9285 (8)	2118 (8)
Mo(C)	4212 (1)	7464 (1)	4538 (1)	N(2C)	5640 (14)	6840 (7)	4993 (6)
O(1C)	4615 (11)	7336 (6)	3691 (4)	O(4C)	5837 (11)	8488 (5)	4952 (5)
O(2C)	3488 (11)	7468 (6)	5725 (5)	C(10C)	4932 (16)	5947 (9)	4841 (8)
C(1C)	3880 (24)	8158 (13)	6222 (11)	C(11C)	7012 (19)	7166 (9)	5353 (7)
N(1C)	2517 (14)	6307 (6)	4574 (6)	C(12C)	7233 (19)	8652 (9)	5346 (8)
O(3C)	2432 (12)	7895 (6)	4428 (5)	C(13C)	8209 (20)	9481 (10)	5522 (8)
C(2C)	914 (17)	7487 (11)	4167 (7)	C(14C)	9636 (21)	9688 (11)	5949 (10)
C(3C)	25 (19)	7960 (9)	3922 (8)	C(15C)	10202 (19)	9077 (12)	6152 (9)
C(4C)	−1552 (20)	7594 (13)	3623 (8)	C(16C)	9319 (18)	8243 (10)	5939 (9)
C(5C)	−2240 (19)	6734 (12)	3574 (7)	C(17C)	7812 (16)	8030 (10)	5538 (7)
C(6C)	−1401 (18)	6230 (10)	3824 (7)				
C(7C)	236 (17)	6636 (10)	4117 (7)	Br(1)	14934 (2)	4336 (1)	3277 (1)
C(8C)	993 (17)	6074 (8)	4376 (6)	Br(2)	12130 (2)	9625 (1)	389 (1)
C(9C)	3114 (15)	5720 (8)	4922 (8)	Br(3)	208 (2)	6209 (1)	6074 (1)

[a] Atoms of cations A, B, and C are labeled accordingly.

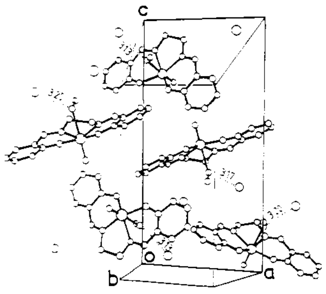

Figure 2. Crystal packing.

$- |F_c|)^2$ with the terms weighted according to $w = (\sigma^2|F_o| + 0.0008|F_o|^2)^{-1}$. The perspective view of the complex cation given in Figure 1, which includes the atom numbering, and the packing diagram in Figure 2 have been prepared from the output of the ORTEP program.[10] Final atomic coordinates are given in Table I, while bond lengths and angles are given in Tables II and III. Listings of observed and calculated structure amplitudes and anisotropic thermal parameters are included with the supplementary material.

Results and Discussion

Synthesis and Characterization. The synthesis employs $[MoOCl_5]^{2-}$ and $[MoOBr_4]^{2-}$ as sources of Mo^VO and halide, NaOMe as base, and MeOH as solvent and avoids heating where possible. Pure complexes (Table IV) can be isolated in the presence of MeOH, *i*-PrOH, and dimethylformamide, but CH_2Cl_2 and MeCN tend to produce mixtures.

Table II. Bond Length (Å) and Angles (Deg) with Estimated Standard Deviations in Parentheses in the MoN_2O_4 Moiety

	cation A	cation B	cation C
Mo–O(1)	1.668 (10)	1.664 (10)	1.666 (8)
Mo–O(2)	2.327 (10)	2.326 (10)	2.362 (10)
Mo–O(3)	1.969 (11)	1.958 (10)	1.973 (11)
Mo–O(4)	1.947 (10)	1.968 (10)	1.957 (9)
Mo–N(1)	2.098 (12)	2.135 (12)	2.100 (11)
Mo–N(2)	2.125 (12)	2.131 (13)	2.123 (12)
O(1)–Mo–O(2)	175.2 (4)	175.7 (4)	172.9 (4)
O(3)–Mo–N(2)	161.2 (5)	158.4 (5)	158.1 (5)
O(4)–Mo–N(1)	153.9 (5)	155.7 (5)	154.7 (4)
O(1)–Mo–O(4)	103.8 (5)	102.4 (5)	105.0 (4)
O(1)–Mo–O(3)	99.5 (5)	101.1 (5)	101.1 (4)
O(1)–Mo–N(1)	100.1 (5)	99.7 (5)	98.2 (5)
O(1)–Mo–N(2)	96.3 (5)	97.9 (5)	98.2 (5)
O(2)–Mo–O(3)	81.1 (4)	79.8 (4)	80.8 (4)
O(2)–Mo–O(4)	80.7 (4)	81.6 (4)	81.5 (4)
O(2)–Mo–N(1)	75.2 (4)	76.0 (4)	75.0 (4)
O(2)–Mo–N(2)	82.0 (4)	80.5 (4)	78.8 (4)
O(3)–Mo–N(1)	89.3 (5)	87.7 (5)	88.4 (4)
O(4)--Mo–N(2)	88.5 (4)	87.9 (4)	88.1 (4)
O(3)–Mo–O(4)	96.8 (4)	97.8 (4)	96.9 (4)
N(1)–Mo–N(2)	78.4 (5)	79.1 (5)	78.5 (5)

We were unable to isolate analytically pure, soluble samples of [MoOLCl] (H_2L = H_2SALEN, H_2SALOPHEN) using the present synthetic approach. In addition, in our hands, the following was true.

(i) Method a of ref 1 ($[MoOCl_3(thf)_2]$ and Li_2L refluxed in EtOH) produced rather insoluble products. Although these

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(10) Johnson, C. K. "ORTEP, Fortran Thermal-Ellipsoid Plot Program"; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table III. Mean Bond Lengths (Å) and Angles (Deg) with Mean Deviations Given in Square Brackets

C(2)-O(3)	1.36 [1]	C(12)-O(4)	1.36 [2]
C(8)-N(1)	1.30 [1]	C(11)-N(2)	1.30 [0]
C(9)-N(1)	1.49 [0]	C(10)-N(2)	1.49 [2]
C(7)-C(8)	1.47 [1]	C(17)-C(11)	1.45 [1]
C(2)-C(3)	1.42 [1]	C(12)-C(13)	1.42 [0]
C(3)-C(4)	1.39 [2]	C(13)-C(14)	1.41 [2]
C(4)-C(5)	1.40 [1]	C(14)-C(15)	1.39 [1]
C(5)-C(6)	1.40 [1]	C(14)-C(16)	1.42 [0]
C(6)-C(7)	1.43 [3]	C(16)-C(17)	1.42 [1]
C(7)-C(2)	1.39 [1]	C(17)-C(12)	1.40 [1]
C(1)-O(2)	1.43 [3]	C(9)-C(10)	1.55 [0]
Mo-O(2)-C(1)	128 [2]		
Mo-O(3)-C(2)	128 [1]	Mo-O(4)-C(12)	131 [2]
Mo-N(1)-C(8)	126 [1]	Mo-N(2)-C(11)	127 [0]
Mo-N(1)-C(9)	116 [1]	Mo-N(2)-C(10)	113 [1]
C(8)-N(1)-C(9)	118 [1]	C(11)-N(2)-C(10)	120 [1]
N(1)-C(9)-C(10)	108 [2]	N(2)-C(10)-C(9)	107 [1]
C(7)-C(8)-N(1)	124 [1]	C(17)-C(11)-N(2)	124 [1]
C(6)-C(7)-C(8)	115 [1]	C(16)-C(17)-C(11)	115 [0]
C(2)-C(7)-C(8)	126 [1]	C(12)-C(17)-C(11)	126 [1]
O(3)-C(2)-C(7)	124 [0]	O(4)-C(12)-C(17)	122 [0]
O(3)-C(2)-C(3)	116 [0]	O(4)-C(12)-C(13)	117 [1]
C(3)-C(2)-C(7)	121 [1]	C(13)-C(12)-C(17)	121 [1]
C(2)-C(3)-C(4)	120 [1]	C(12)-C(13)-C(14)	119 [1]
C(3)-C(4)-C(5)	121 [1]	C(13)-C(14)-C(15)	121 [1]
C(4)-C(5)-C(6)	120 [1]	C(14)-C(15)-C(16)	120 [2]
C(5)-C(6)-C(7)	118 [1]	C(15)-C(16)-C(17)	119 [1]
C(2)-C(7)-C(6)	120 [1]	C(12)-C(17)-C(16)	120 [0]

often analyzed reasonably satisfactorily for C, H, and N, they were invariably low in Cl content and appear to be mixtures. For example, products with H_2L = H_2SALPN could not be *completely* dissolved in dimethylformamide, and the soluble fraction produced electronic spectra similar to those reported by ref 1 for MoO(SALPN)Cl (ϵ_{495} 226 L mol^{-1} cm^{-1}) but much less absorbing than those reported by ref 3 (ϵ_{492} 1970) and this work (ϵ_{495} 1914).

(ii) Method b of ref 1 ([$MoOCl_3(thf)_3$], H_2L and NEt_3 refluxed in MeCN) produced stained (Et_3NH)Cl as the initial product, rather than [MoOLCl] as reported. We have not examined method c of ref 1 ([$MoOCl_3(thf)_3$] and $(SiMe_3)_2L$ in MeCN), and this may well be a viable route to [MoOLCl], as may that of ref 3 ([$MoO(acac)_2Cl$] and LH_2 in MeOH). In both cases, heating is avoided.

The presence of MeOH in the bromo compounds is suggested by microanalysis (Table IV) and the presence of a weak, broad absorption in the range 3000–3300 cm^{-1}, assignable to ν_s(OH). The electron impact mass spectra of the bromo compounds show characteristic[11] peaks for MeOH at mass numbers 31 and 29 at temperatures above 80 °C. Gross thermal decompositions occur in the range 140–160 °C. On the other hand, no ions of mass numbers 31 and 29 are observed for MoO(SALPN)Cl, even during thermal decomposition at 240 °C. The methanol is retained in MoO(SALOPHEN)Br(MeOH) even after recrystallization from dimethylformamide/*i*-PrOH.

Characteristic infrared and electronic spectra features are reported in Table IV, as are room-temperature magnetic moments which fall in the range normally observed for compounds of Mo^VO of lower symmetry (1.6–1.8 μ_B). In addition, the magnetic susceptibilities display Curie–Weiss behavior in the temperature range 4.3–298 K (see, e.g., Figure 3) as expected[6,12] for an octahedral $^2T_{2g}$ term which has been split by a combination of spin–orbit coupling and a strong axial ligand field (derived mainly from the MoO moiety) to yield an orbital singlet as the ground state. Consequently, these compounds are essentially simple $S = {}^1/_2$ paramagnets in the solid state, and any spin–spin interactions are extremely weak.

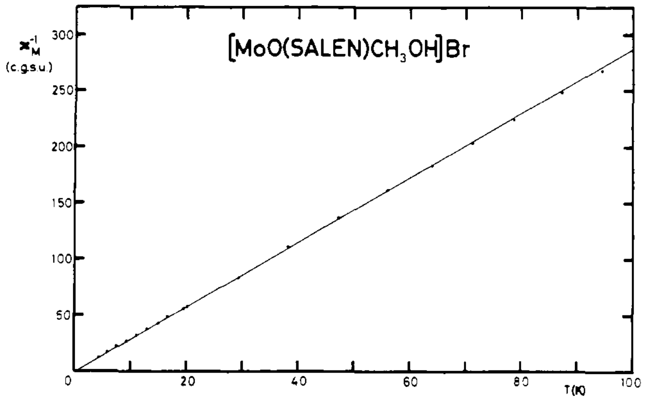

Figure 3. Temperature dependence of the molar susceptibility of [$MoO(SALEN)(CH_3OH)$]Br in the range 0–100 K.

Crystal Structure. The structure consists of *trans*-[MoO(SALEN)(MeOH)]$^+$ cations and bromide anions (Figure 2). The three crystallographically independent complex cations in the asymmetric unit are geometrically similar, and discussion of numerical values will refer to the mean vaues for cations A, B, and C. A perspective view of the cation (Figure 1) shows that the molybdenum atom is six-coordinate with the four ligand atoms of the quadridentate SALEN ligand occupying four equatorial positions and the oxygen atoms O(1) and O(2) of the terminal oxo and methanol ligands, respectively, in trans axial positions.

The four coordinated atoms of the SALEN ligand are slightly displaced from coplanarity (Table V). The molybdenum atom lies 0.37 Å from this mean O_2N_2 plane toward O(1). Although the Mo–N bond lengths (mean 2.119 Å) can be compared with the values 2.094 (3) and 2.136 (6) Å observed[13,14] in the binuclear Mo(V) complexes [$Mo_2O_3(tpp)_2$] ($tppH_2$ = 5,10,15,20-tetraphenylporphyrin) and $(pyH)_3$[$Mo_2O_4(NCS)_4(MeCO_2)$], respectively, and with the value[15] 2.137 (8) Å in [$Mo^{IV}Cl_2L''_2$] ($L''H$ = methylsalicylidenimine), they are considerably shorter than the mean length 2.358 (9) Å observed[16] in [$Mo^{VI}O_2L''_2$]. The equatorial Mo–O bond lengths (mean 1.962 Å) in the present compound lie within the range 1.950 (8)–1.979 (8) Å reported for the two complexes of L'' referred to above. The ethylene bridge of SALEN is in the usual gauche conformation with the torsional angle N(1)–C(9)–C(10)–N(2) = 43.2° and C(9) is much further displaced from the O_2N_2 plane than is C(10)—see Table V. Although the benzene rings are planar within experimental error, the atoms in each salicylaldimine moiety are only approximately coplanar as reflected in the torsion angles given in Table VII. The angles between the perpendiculars to the mean planes through the salicylaldimine moieties range from 8.2 to 12.6° (Table VI), while these planes are inclined to the O_2N_2 planes at angles which range from 6.6 to 7.0° (C(2)–C(9), N(1), O(3)) and from 2.9 to 14.2° (C(10)–C(17), N(2), O(4)). No characteristic trend toward either an umbrella or stepped conformation analogous to that adopted by SALEN in many complexes is evident.[17] The bond lengths and angles within the SALEN ligand given in Table III are

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Table IV. Characterization Data

compd	% yield	microanalysis[a] C	H	N	O	halogen	IR,[b] cm^{-1} ν(MoO)	ν(CN)	ν(CO)	magnetic moment, μ_B[c]	λ,[d] nm (ϵ, M^{-1} cm^{-1})
[MoO(SALPN)Cl]	16	47.61 (47.74)	3.81 (3.77)	6.64 (6.55)	11.00 (11.22)	8.15 (8.29)	930	1617	1551	1.70	497 (1914) 360 sh (6252)
$[MoO(SALPN)(MeOH)]^+Br^-$	55	43.01 (42.88)	3.84 (4.00)	5.86 (5.56)	12.80 (12.69)	15.96 (15.85)	962 968	1602 1612	1555	1.73	503 (777) 365 sh (5005)
$[MoO(SALEN)(MeOH)]^+Br^-$	36	41.92 (41.65)	3.48 (3.70)	6.09 (5.72)	12.92 (13.06)	16.37 (16.30)	960	1605 1612	1551	1.73	533 sh (436) 410 sh (2074)
$[MoO(SALPHEN)(MeOH)]^+Br^-$	39	46.98 (46.86)	3.20 (3.37)	5.52 (5.26)	11.90 (11.89)	15.01 (14.85)	963	1548	1535	1.69	432 br (7007)

[a] Calculated in parentheses. [b] Nujol mulls. [c] Per Mo in solid state at room temperature. [d] DMF solution.

Table V. O_2N_2 Least-Squares Planes and Atom Deviations (Å)[a]

	10^4p	10^4q	10^4r	10^4s
cation A	−3644	5791	−7293	11111
cation B	−3497	−9282	1271	130066
cation C	3177	408	−9473	82715

	cation A	cation B	cation C
O(3)	0.06 (1)	0.03 (1)	0.03 (1)
O(4)	−0.06 (1)	−0.03 (1)	−0.03 (1)
N(1)	−0.07 (1)	−0.03 (1)	−0.03 (1)
N(2)	0.07 (1)	0.03 (1)	0.03 (1)
Mo[b]	0.357 (2)	0.368 (2)	0.381 (2)
O(1)[b]	2.02 (1)	2.03 (1)	2.04 (1)
O(2)[b]	1.97 (1)	−1.95 (1)	−1.98 (1)
C(9)[b]	0.50 (1)	−0.44 (2)	−0.48 (1)
C(10)[b]	0.25 (1)	0.10 (2)	0.21 (1)

[a] The plane equations are in the form $pX + qY + rZ + s = 0$, with X, Y, Z expressed in Å referred to orthogonal axes. Conversion from triclinic to orthogonal coordinates is given by

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & cP \\ 0 & 0 & cP \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

where $P = (\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma$ and $Q = (1 - \cos^2\beta - P^2)^{1/2}$. [b] Atom omitted from plane calculations.

Table VI. Interplanar Angles

plane	atoms in plane	angle	value, deg cation A	cation B	cation C
1	O(3),O(4),N(1),N(2)	1,2	6.5	4.4	6.5
2	C(2)–C(7)	1,3	13.5	7.9	14.2
3	C(12)–C(17)	1,4	7.0	6.6	6.6
4	C(2)–C(9),N(1),O(3)	1,5	12.7	2.9	14.2
5	C(10)–C(17),N(2),O(4)	2,3	13.7	10.5	8.9
		4,5	12.6	8.2	9.7

Table VII. Selected Torsion Angles in the SALEN Ligand (Deg)

O(3)–C(2)–C(7)–C(8)	2.1	−1.0	−4.5
O(4)–C(12)–C(17)–C(11)	1.3	−8.6	0.7
C(2)–C(7)–C(8)–N(1)	10.2	9.3	12.5
C(12)–C(17)–C(11)–N(2)	−1.0	−5.8	1.0
C(7)–C(8)–N(1)–C(9)	−171.8	−170.5	−171.7
C(17)–C(11)–N(2)–C(10)	179.7	−172.0	179.5
C(8)–N(1)–C(9)–C(10)	−156.1	−157.9	−157.8
C(11)–N(2)–C(10)–C(9)	−136.0	−152.7	−140.4
N(1)–C(9)–C(10)–N(2)	−48.3	−37.9	−43.3

similar to those found in other SALEN complexes.[18]

The terminal MoO(1) bond length 1.666 Å falls within the range, 1.60–1.78 Å, previously observed[19] for six-coordinate oxomolybdenum(V) species. The sixth coordination bond length, Mo–O(2) = 2.338 Å, which on average is 0.38 Å longer than the equatorial Mo–O bonds, is similar to the length 2.284 (5) Å reported[20] for Mo–methanol coordination in [Mo(NO)(ttp)(MeOH)] ($ttpH_2$ = *meso*-tetra-*p*-tolylporphyrin) but longer than the range of values 1.7–2.0 Å generally observed[21] for terminal metal–alkoxy bond lengths. The results involving the trans axial Mo–O bond lengths are consistent with the solid-state infrared spectrum: a strong absorption at 960 cm^{-1} and a weak broad one at 3000–3300 cm^{-1} can be assigned[19] to ν(Mo–O) of an oxomolybdenum(V) species and the ν_s(OH) for a methanol ligand, respectively. The ν_b(OH) region of 1600–1700 cm^{-1} is masked by SALEN ligand absorptions.

Table VIII. Intermolecular Contacts Less Than 3.50 Å[a]

Br(1)···O(2A)	3.20 (1)	$O(1C)\cdots C(4B)^I$	3.47 (2)
Br(1)···C(8A)	3.30 (1)	$O(1C)\cdots C(4C)^{II}$	3.30 (2)
Br(2)···O(2B)	3.13 (1)	$O(1C)\cdots C(5C)^{II}$	3.30 (2)
Br(2)···C(8B)	3.42 (2)	$O(4B)\cdots C(4C)^{II}$	3.46 (2)
Br(3)···O(2C)	3.17 (1)	O(4C)···C(13B)	3.42 (2)
Br(3)···C(8C)	3.32 (1)	$O(4A)\cdots C(8B)^{III}$	3.43 (2)
$O(1A)\cdots C(4A)^I$	3.31 (2)	$O(3B)\cdots C(4C)^{II}$	3.33 (2)
$O(1A)\cdots C(5A)^I$	3.30 (2)	$N(2C)\cdots C(5C)^{II}$	3.38 (2)
$O(1B)\cdots C(4B)^I$	3.24 (2)	$C(16B)\cdots C(3B)^I$	3.34 (2)
$O(1B)\cdots C(5B)^I$	3.38 (2)	$C(17B)\cdots C(3B)^I$	3.48 (2)
O(1C)···C(13B)	3.45 (2)	$C(10C)\cdots C(10C)^{IV}$	3.46 (2)

[a] Transformations of the coordinates (x, y, z) are denoted by superscripts: (I) $-1 + x, y, z$; (II) $1 + x, y, z$; (III) $2 - x, 1 - y, -z$; (IV) $1 - x, 1 - y, 1 - z$.

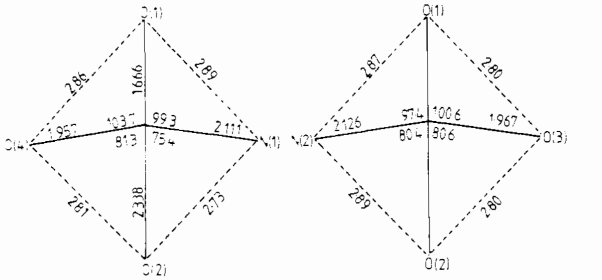

Figure 4. Selected mean dimensions (distances, Å; angles, degrees) within the coordination sphere.

The crystallographic symmetry requires the cations to adopt two configurations in the crystal, i.e., mirror image conformers. Each bromide ion lies close to a methanol oxygen, O(2) (Figure 2), and to C(8) of the same cation. The Br···O(2) distances which range from 3.13(1) to 3.20(1) Å are indicative of hydrogen bonding and suggest that the proton is associated with O(2). The Br(1)···C(8A), Br(2)···C(8B) and Br(3)···C(8C) distances are 3.30 (2), 3.42 (2), and 3.32 (2)Å, respectively. Some short contacts between the cations are included in Table VIII.

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As for other oxomolybdenum(V) and -(VI) species,[22] ligand–ligand repulsion is a major determinant of the geometry of the coordination sphere (Figure 4). The intramolecular contacts between the nitrogen and oxygen atoms of the SALEN ligand and the axial oxygen atoms are nearly equal and only vary between 2.73 and 2.89 Å. This leads to the displacement of the molybdenum from the equatorial O_2N_2 plane and the expansion of the O(1)–Mo–O(SALEN) and O(1)–Mo–N(SALEN) angles to mean values of 102.2 and 98.4°, respectively; the O(2)– Mo–N(SALEN) and O(2)–Mo–O(SALEN) angles suffer a corresponding contraction to 77.9 and 81.0°. The O(1)–Mo– O(2) bond is distorted from linearity by 5.4°.

The presence of six ligand atoms from the first row of the periodic table permits reasonable Mo–oxo, Mo–HOMe, and "nonbonded" intramolecular contacts. The substitution of the methanol by a bromo ligand would require a Mo–Br bond length of >3 Å if a reasonable SALEN–Br contact distance is to obtain. These facts, plus the electrostatic contribution to the lattice energy afforded by the presence of a cation and an anion and the apparent H bonding between Br^- and ligand MeOH, appear to stabilize the observed solid-state structure. The situation contrasts with that[23] of $Ph_4As^+[MoO(SPh)_4]^-$ where the structural and electronic requirement of the benzenethiolate ligands preclude the presence of a sixth ligand such as MeOH.

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Registry No. [MoO(SALEN)(MeOH)]Br, 78891-63-1; [MoO(SALPN)(MeOH)]Br, 78891-62-0; [MoO(SALOPHEN)(MeOH)]Br, 78891-61-9; MoO(SALPN)Cl, 64085-33-2; (pyH)$[MoOBr_4]$, 16925-10-3; $(pyH)_2[MoOCl_5]$, 17871-01-1.

Supplementary Material Available: Listings of anisotropic thermal parameters and observed and calculated structure amplitudes (37 pages). Ordering information is given on any current masthead page.

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Preparation, Solution Properties, and Structure of Iron(III) Porphyrin Oxyanion Complexes. Crystal and Molecular Stereochemistry of a Novel Bidentate Nitrato Complex

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Synthesis and physical characterization are reported for the first iron(III) porphyrin complexes possessing the oxyanionic axial ligands nitrate, sulfate, and toluenesulfonate. Molecular stereochemistry of (nitrato)iron(III) tetraphenylporphyrin, $Fe(TPP)NO_3$, has been determined by X-ray diffraction methods, revealing nitrate coordination in an unsymmetrical, bidentate fashion. The planar nitrate anion is oriented between pyrrole nitrogen atoms in order to minimize steric interactions. Iron–oxygen distances are 2.019 and 2.323 Å. The iron atom is raised 0.60 Å from the mean porphyrin plane. The red-brown monoclinic cyrstals belong to space group $P2_1/n$ with unit cell parameters a = 10.279 (2) Å, b = 16.232 (5) Å, c = 20.951 (4) Å, β = 90.50 (2)°, and Z = 4. The $Fe(TPP)NO_3$ structure was solved by heavy-atom Patterson and Fourier techniques using 4996 unique reflections. Refinement was completed by a full-matrix least-squares method to yield R_1 = 0.065. This is the first example of an iron(III) porphyrin with a bidentate axial ligand. Coordination of nitrate in this manner is associated with unique physical properties apparent in cyclic voltammetric, electronic spectral, and NMR studies. Solution magnetic moment measurements for $Fe(TPP)NO_3$ reveal an $S = {}^5/_2$ spin state for the ferric ion. In contrast, sulfate complexes exhibit a slightly diminished magnetic moment. Physical measurements are consistent with a dimeric structure, $[FeTPP]_2SO_4$, where the sulfate ion is bridging and bidentate to the iron(III) centers. Unlike the μ-oxo dimers, sulfate does not allow extensive electronic interaction of the monomeric units that it bridges. These sulfato complexes exhibit unusually rapid electronic relaxation, which gives rise to very sharp NMR resonances and a silent ESR spectrum at liquid nitrogen temperature.

Introduction

Synthesis and solution study of novel metalloporphyrin compounds continues as an active and challenging research area. The relevance of such work to the structure and function of parent hemoprotein compounds is frequently invoked. An important aspect of iron porphyrin models is based on the observed relationship of coordination number, spin state, and distance of the metal ion from the porphyrin plane.[1,2] In the case of iron(III) porphyrins, these factors are determined predominantly by the nature of the axial ligand. With strong axial ligands such as imidazole or cyanide, a low-spin bisligated species results, where the iron is essentially in the porphyrin plane. High-spin five-coordinate complexes with the iron displaced ~0.5 Å from the mean porphyrin plane are formed with weaker halide anionic ligands. The crystal structures of six-coordinate high-spin iron(III) porphyrins, $[Fe^{III}(TPP)L_2]^+$, where L_2 = tetramethylene sulfoxide, have shown the iron to be centered in the porphyrin plane with concomitant porphyrin core expansion.[3] Recent structural characterization of iron(III) porphyrins with the very weak perchlorate ligand has yielded a quantum mechanical spin admixed, $S = {}^3/_2, {}^5/_2$ complex where the iron is 0.30 Å from the mean porphyrin plane.[4]

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