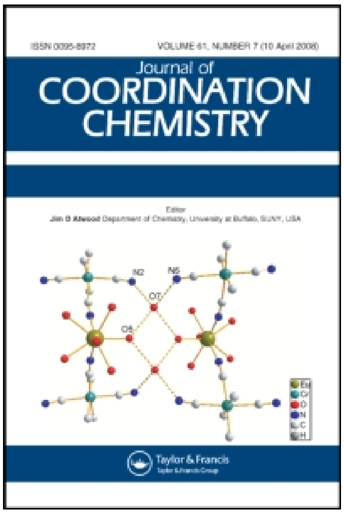

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SYNTHESES AND CHARACTERIZATION OF THREE STRUCTURE TYPES FOR MANGANESE(III) COMPLEXES WITH *N,N'*-ETHYLENE*BIS*(1-PHENYL-3-IMINO-1-BUTANONE)

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SYNTHESES AND CHARACTERIZATION OF THREE STRUCTURE TYPES FOR MANGANESE(III) COMPLEXES WITH *N,N'*-ETHYLENE*BIS*(1-PHENYL-3-IMINO-1-BUTANONE)

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Three manganese(III) complexes with the ligand bzacen^{2-} [bzacen^{2-} = *N,N'*-ethylene*bis* (1-phenyl-3-imino-1-butanonato)], Mn(bzacen) (pyridine)(NCS) (**1**), [Mn_2(bzacen)$_2$ (Me OH)$_2$](ClO_4)$_2$ (**2**) and MnCl(bzacen) (**3**), have been synthesized and characterized by IR, Raman, electronic spectra and cyclic voltammetry. A structure determination of complexes **1** and **2** reveals a octahedral coordination with an N_2O_2 equatorial plane composed of atoms from the Schiff base ligand, while the Mn atom in complex **3** has square pyramidal coordination. The two MnN_2O_4 octahedra in complex **2** are joined by sharing two ketone oxygen atoms (Mn-O 1.910 and 2.493 Å) to form a dinuclear [Mn_2(bzacen)$_2$(MeOH)$_2$]$^{2+}$ cation, the Mn_2O_2 core having an Mn···Mn separation of 3.397 Å and Mn-O-Mn angles of 99.7°. In these three complexes $\nu_{C=O}$ and $\nu_{C=C}$ are shifted to lower frequencies in IR and Raman spectra; π-π^* transitions, d-π^* charge-transfer transitions and d-d* ligand field transitions are observed in electronic spectra.

Keywords: Schiff base; manganese(III) complex; crystal structure; spectroscopy

INTRODUCTION

Manganese(III) Schiff base complexes provide a rich series of structural types that can be used as models for magnetic and structural properties of manganoenzymes such as manganese superoxide dismutase[1], azide-insensitive catalase[2], and photosynthetic oxygen-evolving complexes[3]. New model complexes have appeared over the past ten years[4-6]. A series of manganese complexes

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of a Schiff base ligand, *N,N'*-ethylene*bis*(1-phenyl-3-imino-1-butanone), have recently been studied[7-11]. These complexes form three different structure types: (i) mononuclear six-coordinate complexes Mn(bzacen)(pyrimidine)(NCS)[8] and the title complex (**1**), and five-coordinate complexes Mn(bzacen)(NCS)[7] and the title complex (**3**); (ii) dinuclear bridged complexes $[Mn_2(bzacen)_2(MeOH)_2(\mu\text{-}4,4'\text{-bipy})](ClO_4)_2$[9], $[Mn_2(bzacen)_2(MeOH)_2]$ $(ClO_4)_2{\cdot}2H_2O$[10] and the title complex (**2**); and (iii) the polymeric compound $Mn(bzacen)(CH_3COO)$[11].

EXPERIMENTAL

General Procedures

Some 1.0 g of Mn(bzacen)(NCS) prepared according to the reference[7] was dissolved in 20 cm^3 of methanol, and then 0.5 cm^3 of pyridine was added with stirring. Brown red crystals of complex **1** were obtained by slow evaporation of the resulting solution. Brown red crystals of complex **2** were obtained as an accidental by-product in preparation of $[Mn_2(bzacen)_2$ $(MeOH)_2]$ $(ClO_4)_2{\cdot}2H_2O$[10]. The preparation and crystal structure of complex **3** was reported previously[12].

IR spectra were measured on a Nicolet Magna 750 Fourier transform IR spectrometer using KBr discs. Raman spectra were recorded on a Nicolet Raman 910 Fourier transform spectrometer. Electronic spectra were measured on a Perkin Elmer λ9 spectrometer in methanol and chloroform. Cyclic voltammograms were measured with a BAS 100A electrochemical analyzer. A three-electrode system was employed with a platinum working electrode, an Ag/AgCl reference electrode and a platinum-wire auxiliary electrode, $(Et_4N)ClO_4$ being the supporting electrolyte (0.1M in acetonitrile).

X-Ray Structure Determination

All diffraction data were collected on a Rigaku AFC5R diffractometer at room temperature with graphite-monochromated MoK_α radiation (λ = 0.71069Å), using the ω-2θ scan mode. Cell dimensions were obtained from 25 reflections in the range $20° < 2\theta < 30°$. Details of crystal parameters, data collection and structure refinement are given in Table I. All reflections were corrected for Lp and absorption (DIFABS). Data reduction and structure refinement was performed using the TEXSAN package[13]. The structures were solved by direct methods[14] and refined by full-matrix least-squares procedures. All hydrogen atoms were located by a combination of difference Fourier maps and the HYDROGEN program and added to the structure factor calculation, but their positions were not refined. Positional parameters and equivalent isotropic

TABLE I Crystallographic data for complexes **1** and **2**.

Formula	$C_{28}H_{27}MnN_4O_2S$	$C_{46}H_{52}Cl_2Mn_2N_4O_{14}$
Formula weight	538.45	1065.73
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	11.173(2)	11.025(3)
b (Å)	17.393(3)	12.666(2)
c (Å)	13.702(2)	17.707(4)
β (°)	104.8(2)	94.94(2)
V (Å^3)	2573.8(9)	2464(2)
Z	4	2
D_{calc} (Mg m^{-3})	1.39	1.44
μ (mm^{-1})	0.601	0.666
F (000)	1120	1104
T (K)	298	298
Scan width	1.24 + 0.300 tanθ	1.16 + 0.300 tanθ
Crystal dimensions (mm)	0.50 × 0.35 × 0.30	0.50 × 0.50 × 0.30
Index range h	0 → 15	0 → 14
k	0 → 28	0 → 16
l	−18 → 18	−23 → 23
No. of independent reflections	4231 (R_{int} = 0.058)	5679 (R_{int} = 0.052)
No. of observed reflections	1770 [$I > 3\sigma(I)$]	3500 [$I > 4\sigma(I)$]
No. of variables	325	308
Residual electron density (e·A^{-3})	0.29/−0.26	0.89/−0.52
R	0.046	0.065
R_w	0.054	0.089
GOF	1.212	2.484

$$R = \frac{\sum_{i=1}^{n} |F_o| - |F_c|}{\sum_{i=1}^{n} |F_o|},\ R_w = \left[\frac{\sum_{i=1}^{n} w(|F_o| - |F_c|)^2}{\sum_{i=1}^{n} w|F_o|^2}\right]^{\frac{1}{2}},\ W = \frac{1}{\sigma^2\,(F_o)}.$$

thermal parameters are listed in Table II for **1** and Table III for **2**; selected bond distances and angles are shown in Table IV for **1** and Table V for **2**, respectively.

RESULTS AND DISCUSSION

IR and Raman Spectra

IR and Raman data for free ligand H_2bzacen and three complexes are given with tentative assignments of bands in Table VI. One important features is shift of the strong $\nu_{C=O}$ and $\nu_{C=C}$ bands to lower energies in the title complexes. The $\nu_{C=O}$ and $\nu_{C=C}$ bands in the ligand spectrum are located at 1603 and 1543 cm^{-1} in the IR, at 1596 and 1538 cm^{-1} in the Raman, respectively. In the three complexes, $\nu_{C=O}$ and $\nu_{C=C}$ are shifted approximately 10 cm^{-1} and 35 ~ 40 cm^{-1} in the IR,

TABLE II Fractional atomic coordinates and equivalent isotropic thermal parameters for Mn(bzacen)(pyridine)(NCS); $B_{eq} = (4/3)\ \Sigma_i \Sigma_j\ \beta_{ij}\ \mathbf{a}_i\ \mathbf{a}_j$.

atom	*x/a*	*y/b*	*z/c*	B_{eq}
Mn(1)	0.04853(9)	0.24588(7)	0.45413(8)	2.97(4)
S(1)	0.1062(2)	0.1803(1)	0.1229(2)	5.3(1)
O(1)	−0.0835(4)	0.3160(3)	0.4100(4)	3.4(2)
O(2)	−0.0583(4)	0.1723(3)	0.4868(4)	3.3(2)
N(1)	0.1688(5)	0.3216(4)	0.4335(4)	3.1(3)
N(2)	0.1952(5)	0.1844(3)	0.5123(4)	3.2(3)
N(3)	0.0281(6)	0.2020(4)	0.2973(5)	4.7(3)
N(4)	0.0633(5)	0.2938(3)	0.6245(4)	3.5(3)
C(1)	−0.0787(6)	0.3895(4)	0.3984(5)	2.8(3)
C(2)	0.0284(7)	0.4275(4)	0.4010(6)	3.5(3)
C(3)	0.1481(6)	0.3949(5)	0.4132(5)	3.2(3)
C(4)	0.2493(7)	0.4463(5)	0.3976(6)	4.5(4)
C(5)	0.2885(7)	0.2865(6)	0.4348(7)	5.7(5)
C(6)	0.3092(7)	0.2145(5)	0.4951(7)	4.7(4)
C(7)	0.1989(6)	0.1242(5)	0.5699(5)	3.6(4)
C(8)	0.3200(7)	0.0853(5)	0.6192(6)	5.0(4)
C(9)	0.0914(6)	0.0926(4)	0.5935(5)	3.5(3)
C(10)	−0.0266(6)	0.1166(4)	0.5521(5)	2.8(3)
C(11)	−0.1998(6)	0.4289(4)	0.3818(5)	3.1(3)
C(12)	−0.2195(7)	0.5054(4)	0.3521(6)	3.8(4)
C(13)	−0.3355(8)	0.5370(4)	0.3367(6)	4.4(4)
C(14)	−0.4332(7)	0.4957(5)	0.3502(6)	4.2(4)
C(15)	−0.4160(7)	0.4205(5)	0.3770(7)	4.4(4)
C(16)	−0.3013(6)	0.3877(4)	0.3930(6)	4.1(4)
C(17)	−0.1338(6)	0.0814(4)	0.5832(5)	2.9(3)
C(18)	−0.2381(7)	0.1258(4)	0.5773(6)	4.0(4)
C(19)	−0.3389(7)	0.0947(5)	0.6050(6)	4.6(4)
C(20)	−0.3368(7)	0.0202(5)	0.6368(6)	4.4(4)
C(21)	−0.2340(7)	−0.0244(5)	0.6433(6)	4.2(4)
C(22)	−0.1322(6)	0.0061(5)	0.6166(5)	3.5(3)
C(23)	0.0610(6)	0.1940(4)	0.2244(6)	3.4(3)
C(24)	−0.0398(7)	0.3174(5)	0.6476(6)	4.0(4)
C(25)	−0.0442(7)	0.3412(6)	0.7404(7)	5.5(5)
C(26)	0.0627(8)	0.3419(6)	0.8157(6)	5.9(5)
C(27)	0.1703(7)	0.3181(5)	0.7965(6)	4.8(4)
C(28)	0.1660(7)	0.2947(5)	0.7011(6)	4.1(4)

while $\nu_{C=C}$ is shifted 38 cm^{-1} in the Raman. The $\nu_{C\equiv N}$ bands of NCS$^-$ in **1** appear at 2052 cm^{-1} in the IR and 2050 cm^{-1} in the Raman, respectively, indicating that NCS$^-$ is coordinated to metal atom through its nitrogen atom[15]. The assignment of ClO$_4^-$ bands is complicated by the presence of the ring vibration observed about 1090 cm^{-1} for **2**. Frequencies of coordination bonds observed in the lower frequency region in the Raman are in the normal range for these complexes.

TABLE III Fractional atomic coordinates and equivalent isotropic thermal parameters for $[Mn_2(bzacen)_2(MeOH)_2](ClO_4)_2$; $B_{eq} = (4/3)\ \Sigma_i\Sigma_j\ \beta_{ij}\ \mathbf{a}_i\ \mathbf{a}_j$.

atom	*x/a*	*y/b*	*z/c*	B_{eq}
Mn(1)	0.51403(6)	0.46901(5)	0.09339(4)	3.75(3)
Cl(1)	0.2073(1)	0.4427(1)	0.30383(8)	6.09(7)
O(1)	0.4244(2)	0.4088(2)	0.0068(2)	3.8(1)
O(2)	0.6511(2)	0.3853(2)	0.0813(2)	4.0(1)
O(3)	0.4445(3)	0.3532(3)	0.1733(2)	5.9(2)
O(4)	0.0863(6)	0.4683(7)	0.2851(5)	15.6(5)
O(5)	0.212(1)	0.4029(7)	0.3727(4)	19.4(7)
O(6)	0.2306(6)	0.3665(6)	0.2493(4)	14.4(5)
O(7)	0.2709(7)	0.5312(5)	0.2988(6)	15.9(6)
N(1)	0.3768(4)	0.5601(3)	0.1108(2)	4.6(2)
N(2)	0.6019(3)	0.5543(3)	0.1724(2)	4.1(2)
C(1)	0.3051(4)	0.3898(3)	0.0053(2)	3.9(2)
C(2)	0.2296(4)	0.4482(4)	0.0458(3)	4.5(2)
C(3)	0.2633(4)	0.5394(4)	0.0900(3)	4.4(2)
C(4)	0.1636(5)	0.6090(5)	0.1136(3)	6.1(3)
C(5)	0.4155(5)	0.6584(4)	0.1515(4)	6.2(3)
C(6)	0.5233(5)	0.6328(4)	0.2064(3)	6.2(3)
C(7)	0.7139(4)	0.5396(3)	0.1998(2)	4.1(2)
C(8)	0.7678(5)	0.6099(4)	0.2622(3)	6.0(3)
C(9)	0.7886(4)	0.4605(4)	0.1742(2)	4.1(2)
C(10)	0.7572(4)	0.3882(3)	0.1194(2)	3.5(2)
C(11)	0.2609(4)	0.3010(4)	−0.0425(3)	4.3(2)
C(12)	0.1413(4)	0.2953(5)	−0.0735(3)	5.7(3)
C(13)	0.0995(5)	0.2115(6)	−0.1175(4)	7.0(3)
C(14)	0.1729(7)	0.1335(5)	−0.1336(4)	7.6(4)
C(15)	0.2968(7)	0.1365(6)	−0.1047(5)	10.0(5)
C(16)	0.3362(5)	0.2192(5)	−0.0585(4)	7.0(3)
C(17)	0.8417(4)	0.3034(3)	0.0984(2)	3.3(2)
C(18)	0.7996(4)	0.2213(4)	0.0518(3)	4.4(2)
C(19)	0.8735(5)	0.1399(4)	0.0346(3)	5.6(3)
C(20)	0.9941(5)	0.1388(4)	0.0647(3)	5.4(2)
C(21)	1.0372(4)	0.2175(5)	0.1095(3)	5.3(2)
C(22)	0.9650(4)	0.2999(4)	0.1269(3)	4.4(2)
C(23)	0.4386(6)	0.2430(5)	0.1626(4)	7.7(4)

Electronic Spectra

Data are provided in Table VII. Bands II and III can be related to d-d* ligand field transitions[16]; bands IV, V and VI are considered to be d-π^* charge-transfer transitions; the strong bands VII can be attributed to ligand π-π^* transitions. Ligand field and charge-transfer bands are affected by solvent. The ligand field energy in methanol is lower than in chloroform for the three complexes, but charge-transfer bands are higher ligand bands remain constant.

TABLE IV Selected bond distances (Å) and angles (°) for **1**.

Mn(1)-O(1)	1.890(5)	Mn(1)-O(2)	1.881(5)
Mn(1)-N(1)	1.953(6)	Mn(1)-N(2)	1.948(6)
Mn(1)-N(3)	2.236(7)	Mn(1)-N(4)	2.455(6)
O(1)-Mn(1)-O(2)	91.4(2)	O(1)-Mn(1)-N(1)	91.6(2)
O(1)-Mn(1)-N(2)	172.3(2)	O(1)-Mn(1)-N(3)	91.9(2)
O(1)-Mn(1)-N(4)	86.7(2)	O(2)-Mn(1)-N(1)	174.6(2)
O(2)-Mn(1)-N(4)	92.8(2)	O(2)-Mn(1)-N(3)	94.7(2)
O(2)-Mn(1)-N(4)	84.0(2)	N(1)-Mn(1)-N(2)	83.8(2)
N(1)-Mn(1)-N(3)	89.8(3)	N(1)-Mn(1)-N(4)	91.7(2)
N(2)-Mn(1)-N(3)	94.2(2)	N(2)-Mn(1)-N(4)	87.2(2)
N(3)-Mn(1)-N(4)	178.1(2)		

TABLE V Selected bond distances (Å) and angles (°) for **2**.

Mn(1)-O(1)	1.910(3)	Mn(1)-O(2)	1.873(3)
Mn(1)-O(1a)	2.493(3)	Mn(1)-N(1)	1.948(4)
Mn(1)-N(2)	1.956(3)	Mn(1)-O(3)	2.220(4)
Mn(1)···Mn(1a)	3.387(2)	O(3)···O(6)	2.819(7)
Mn(1)-O(1)-Mn(1a)	99.7(1)	O(1)-Mn(1)-O(1a)	80.3(1)
O(2)-Mn(1)-O(1)	92.8(1)	O(2)-Mn(1)-N(1)	176.7(1)
O(2)-Mn(1)-N(2)	92.3(1)	O(2)-Mn(1)-O(3)	91.5(1)
O(1)-Mn(1)-N(1)	90.5(1)	O(1)-Mn(1)-N(2)	169.9(1)
O(1)-Mn(1)-O(3)	93.7(1)	N(1)-Mn(1)-N(2)	84.4(2)
N(1)-Mn(1)-O(3)	88.6(2)	N(2)-Mn(1)-O(3)	94.9(2)
O(3)-Mn(1)-O(1a)	173.9(6)		

Symmetry code: a, $1-x$, $1-y$, $-z$.

TABLE VI Vibration frequencies (cm^{-1}) in the IR and raman spectra of H_2bzacen and the complexes.

H_2bzacen		**1**		**2**		**3**		
IR	*Raman*	*IR*	*Raman*	*IR*	*Raman*	*IR*	*Raman*	*Assignment*
		2052vs	2050vs					NCS
1603vs	1596vs	1589vs	1599vs	1587vs	1596vs	1589vs	1594vs	C=O
1582vs		1570vs		1570vs		1570vs		
1543vs	1538s	1506vs	1500vs	1503vs	1500vs	1510vs	1502vs	C=C
				1090vs				ClO_4^-
			449m		470m		470m	Mn-O
			399m		400m		400w	Mn-N
			259m		245m		243w	Mn-B(NCS, Cl, O)
			194m					Mn-N(py)

* V = very, s = strong, m = medium, w = weak.

TABLE VII Electronic spectroscopic data for the complexes in methanol.

Complex	$\lambda_{max,nm}$*					
	VII	*VI*	*V*	*IV*	*III*	*II*
1	240 (240)	263 (284)	316 (323)	400 (412)	485 (~480)	
2	242	262	333	403	488	~585
3	241 (241)	262 (269)	316 (317)	400 (408)	485 (~480)	~590

*Data measured in chloroform are given in parentheses.

TABLE VIII Electrochemical redox potentials (V).

Complex	$E_{1/2}$ (ΔE_p)	E_{pa}
1	−0.162 (0.092)	+0.916
2	−0.122	+1.022
3	−0.172 (0.148)	

*$E_{1/2} = (|E_{pa}| + |E_{pc}|)/2$, $\Delta E_p = |E_{pc} - E_{pa}|$.

Cyclic Voltammetry

Redox potentials for the three complexes are summarized in Table VIII. A *quasi*-reversible Mn(III/II) wave is found in complexes **1** and **3**, the half-wave potential $E_{1/2}$ being −0.162 V in **1** and −0.172 V in **3**, respectively. An irreversible Mn(III/IV) oxidation is observed at +0.916 V in **1**, but not in **3**. This phenomenon could be caused by Mn coordination with pyridine whose d-pπ conjugation decreases charge density around the Mn atom. Irreversible Mn(III/IV) oxidation and Mn(III/II) reduction for **2** are found at 1.022 and −0.122 V, respectively.

Description of the structures

The structure of **1** shown in Figure 1 has a distorted octahedral configuration. Two oxygen atoms and two nitrogen atoms from the bzacen^{2-} ligand form the basal plane; two nitrogen atoms (N(3) and N(4)) from the NCS$^-$ and pyridine ligands are in axial sites. The Mn-N(4) bond length of 2.455(6)Å and Mn-N(3) bond length of 2.236(7)Å are much longer than the in-plane Mn-N distances of 1.953(6) and 1.948(6)Å. Mn-N axial elongation of six-coordinate d^4 Mn(III) centres has been reported in a variety of mononuclear Mn(III)[8], dinuclear Mn(III)[9,10], polynuclear Mn(III) species[6] and mixed-valent Mn(III)/Mn(IV) complexes[17]. However, pronounced Mn-N axial elongation is found in only a

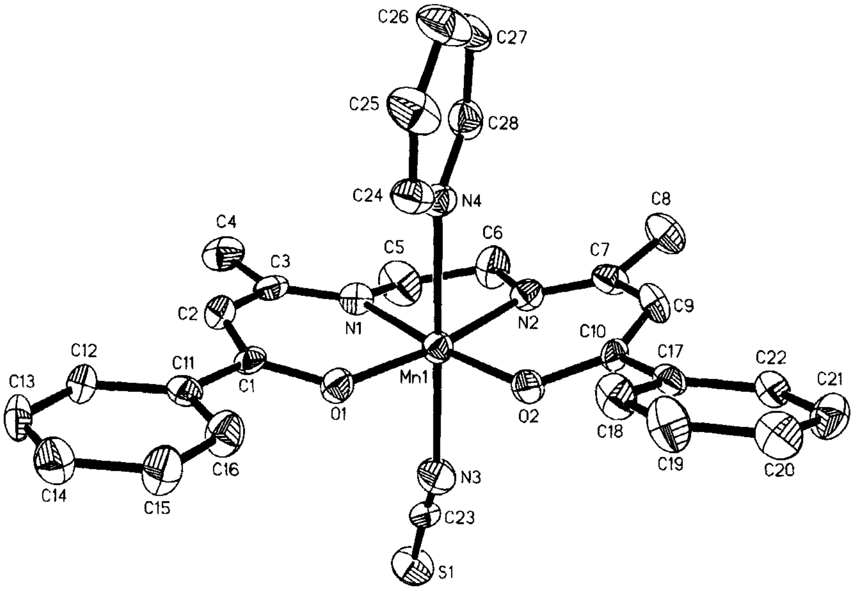

FIGURE 1 Molecular structure of Mn(bzacen)(pyridine)(NCS) showing atom numbering and 30% probability displacement ellipsoids.

few complexes, *e.g.*, Mn-N(4) of 2.455(6) Å in **1** and of 2.504(7)Å in Mn(bzacen)(pyrimidine)(NCS)[8].

The structure of **2** is composed of one dinuclear cation $[Mn_2(bzacen)_2(MeOH)_2]^{2+}$ shown in Figure 2 and two uncoordinated perchlorate anions. The dinuclear cation lies on a crystallographic centre at (1/2, 1/2, 0). The Mn(III) atoms are bridged in pairs by two ketone oxygen atoms of two $beacen^{2-}$ ligands to form the dinuclear cation $[Mn_2(bzacen)_2(MeOH)_2]^{2+}$ with an Mn(1)···Mn(1a) distance of 3.387(2)Å and Mn(1)-O(1)-Mn(1a) angle of 99.7(1)°. In the cation two manganese atoms and two ketone oxygen atoms form an Mn_2O_2 parallelogram core with two short bond lengths (Mn-O 1.910(3)Å) and two long ones (2.493(3)Å). It was reported for Mn Schiff base complexes that bridging oxygen atoms are from the μ_2-O^{2-} anion[18-19], μ_2-phenoxy[20-22], μ_2-alkoxo[19,23] and μ_2-ketoxo[10] groups.

Strong Mn-O axial elongation in the Mn octahedron is seen in complex **2**. This situation is found in a few dinuclear manganese(III) complexes, for example, Mn-O of 2.448(8)Å in $[Mn_2(bzacen)_2(MeOH)_2](ClO_4)_2\cdot 2H_2O$[10], 2.490(3)Å in $[\{Mn(salen)(H_2O)\}_2](ClO_4)_2\cdot H_2O$[20] and 2.627(2)Å in [Mn(L)(TCEA)][22].

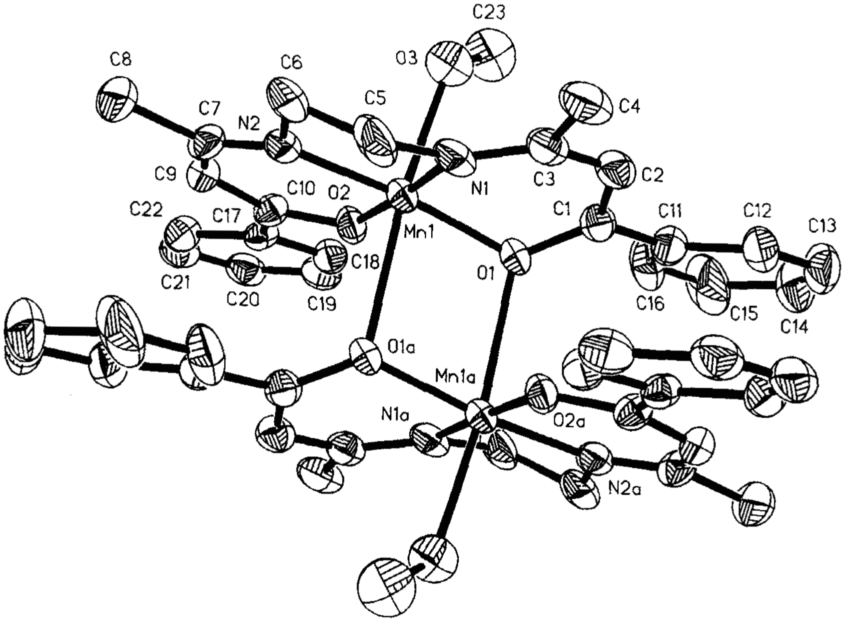

FIGURE 2 Cation structure of $[Mn_2(bzacen)_2(MeOH)_2]^{2+}$ showing atom numbering and 30% probability displacement ellipsoids.

Supplementary Material

Full tables of bond distances and angles for **1** (2 pages) and **2** (2 pages), anisotropic thermal parameter for **1** (2 pages) and **2** (2 pages), structure factors for **1** (13 pages) and **2** (24 pages) are available from the authors upon request.

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