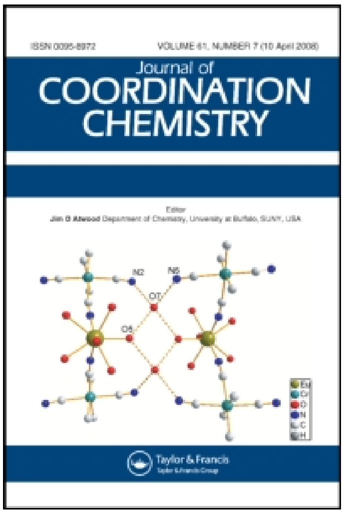

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The first 3-D supramolecular Mn(III) salen complex with 4,4-dicarboxy-2,2-bipyridine: structure and magnetic properties

Ting-Ting Cao[a]; Yue Ma[a]; Chun Yang[a]; Dai-Zheng Liao[a]; Shi-Ping Yan[a]
[a] Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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The first 3-D supramolecular Mn(III) salen complex with 4,4-dicarboxy-2,2-bipyridine: structure and magnetic properties

TING-TING CAO, YUE MA, CHUN YANG,
DAI-ZHENG LIAO* and SHI-PING YAN

Department of Chemistry, Nankai University, Tianjin 300071, P.R. China

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The Mn(III) salen complex $[Mn(salen)(H_2O)_2](dcbp)_{0.5} \cdot H_2O$ (dcbp = 4,4-dicarboxy-2,2-bipyridine, salen = *N*,*N*′-ethylenebis-salicylideneaminato) has been isolated under hydrothermal conditions and is structurally characterized. The complex is formed by three independent units, one $[Mn(salen)(H_2O)_2]$, one H_2dcbp, and one guest water molecule, which are further interconnected by hydrogen-bond interactions to form a 3-D supramolecular architecture. IR spectra, UV-Vis spectra, and variable temperature magnetic susceptibility of the complex have been studied. The magnetic study indicated a weak antiferromagnetic interaction between the $[Mn(salen)(H_2O)_2]$ molecules.

Keywords: Manganese(III); 4,4-Dicarboxy-2,2-bipyridine; Magnetic properties

1. Introduction

Mn(III) in Schiff-base complexes with N_2O_2 basal environments have strong uniaxial magnetic anisotropy created by the Jahn–Teller effect in an octahedral ligand field [1], accelerating investigation of the magnetic properties of Mn(III) salen complexes in molecular superparamagnets, such as single-molecule magnets (SMMs) [2–5] and single-chain magnets (SCMs) [6, 7]. Mn(III) salen complexes with multi-carboxylate ligands [8, 9] show novel structures and magnetic properties. Among the multi-carboxylate ligands, 4,4-dicarboxy-2,2-bipyridine, potentially has a rich coordination chemistry with dual chelating capacity through bipyridine coordination and exodentate carboxylate with hydrogen-bonding capacity [10], making it a good building block for constructing metal complexes. It has been extensively employed with Ru(III) and other rare-earth ions [11–15], while relatively rare as a ligand for first row transition metals [16–20], especially Mn(III).

We synthesized a new Mn(III) salen complex with 4,4-dicarboxy-2,2-bipyridine under hydrothermal conditions. A 3-D supramolecular complex has been obtained and the IR spectra, UV-Vis spectra, and variable temperature magnetic susceptibility of the complex have also been studied. To the best of our knowledge, although a lot of

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*Corresponding author. Email: liaodz@nankai.edu.cn

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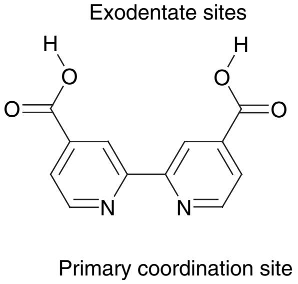
Mn(III) salen complexes have been reported, $[Mn(salen)(H_2O)_2](dcbp)_{0.5} \cdot H_2O$ is the first example of Mn(III) salen complex with 4,4-dicarboxy-2,2-bipyridine.



2. Experimental

2.1. *Materials and methods*

All chemicals were purchased commercially and used without purification, including 4,4-dicarboxy-2,2-bipyridine (Alfa). Elemental analysis was carried out with an Elementar Vario EL III analyzer and IR spectra (KBr pellets) were recorded with a Perkin-Elmer Spectrum One. All the complexes were synthesized by a hydrothermal method under autogenous pressure.

2.2. *Preparation of $[Mn(salen)(H_2O)_2](ClO_4)$*

The tetradentate Schiff base, H_2salen, was prepared by mixing salicylaldehyde and 1,2-ethylenediamine in a 2 : 1 molar ratio in ethanol according to the literature [21]. The $[Mn(salen)(H_2O)]ClO_4$ precursor was prepared by mixing $Mn(OAc)_3 \cdot 2H_2O$, H_2salen, and $NaClO_4$ in methanol/H_2O with the molar ratio of 1 : 1 : 1.5, according to the method reported previously [22].

2.3. *Preparation of $[Mn(salen)(H_2O)_2](dcbp)_{0.5} \cdot H_2O$*

A 15 mL aqueous solution of $[Mn(salen)(H_2O)_2](ClO_4)$ (0.1 mmol), 4,4-dicarboxy-2, 2-bipyridine (0.05 mmol), and Ho_2O_3 (0.4 mmol) were sealed into a bomb equipped with a Teflon liner, reacted at 120°C for four days, and then cooled to room temperature at a rate of $6^{\circ}C\,h^{-1}$. After several days, the resulting brown, plate-like crystalline product was filtered from the solution, washed with distilled water, and dried at ambient temperature. Yield: 59% (based on Mn) $C_{22}H_{23}MnN_3O_7$ (496.37): Calcd (%): C 53.18, H 4.63, O 22.56, N 8.46; Found (%): C 53.10, H 4.69, O 22.48, N 8.53. IR data (KBr, cm^{-1}): 3737 (s), 2361 (m), 1629 (s), 1600 (s), 1542 (w), 1447 (w), 1371 (s), 1286 (w), 1150 (w), 902 (w), 799 (m), 749 (s), 690 (w), 630 (w), 458 (s).

2.4. *X-ray structure determination*

A crystal of the complex was mounted on a glass fiber. Determinations of the unit cell and data collection were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) on a BRUKER SMART 1000 diffractometer equipped with a CCD camera. The ω–φ scan technique was employed. The structure was solved primarily by direct methods followed by Fourier difference techniques and refined by full-matrix least squares. Computations were performed with the SHELXL-97 program [23, 24]. Non-hydrogen atoms were refined anisotropically. Hydrogens were set in calculated positions and refined as riding with a common fixed isotropic thermal parameter.

3. Results and discussion

3.1. *Hydrothermal synthesis*

For the hydrothermal reaction, we chose Mn(III) salen and Ho_2O_3 as the original materials in order to obtain 3d–4f complexes, while only a Mn(III) complex with H_2bpdc ligand was obtained. This might be due to the fact that the Mn(III) complex is thermodynamically favored over the Mn(III)–Ho(III) complex at 120°C [25]. Hydrothermal syntheses carried out under similar experiment conditions without Ho_2O_3 produce no single crystals.

3.2. *Description of crystal structure*

The ORTEP diagram of the independent units of the complex is depicted in figure 1, with data collection and refinement parameters in table 1 and important bond lengths and angles in table 2. As shown in figure 1, the fundamental building unit of the complex is composed of one [Mn(salen)$(H_2O)_2$], one H_2dcbp, and one lattice water molecule. For [Mn(salen)$(H_2O)_2$] molecule, Mn(III) lies in a distorted octahedral

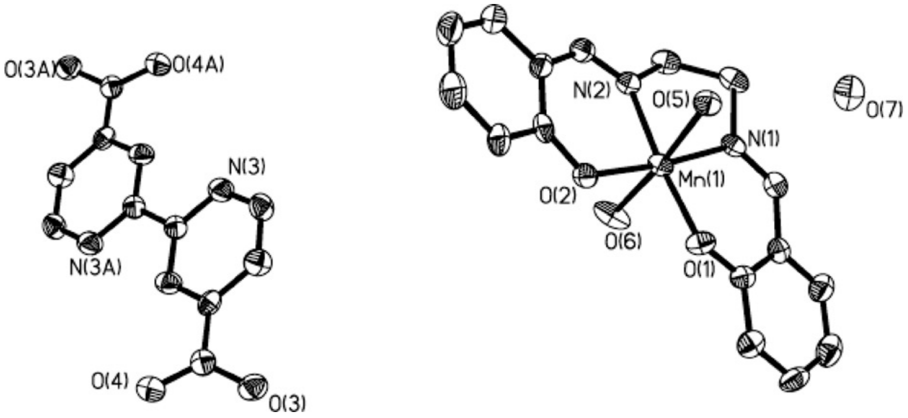


Figure 1. An ORTEP drawing of the coordination environments of independent units in the complex [Mn(salen)$(H_2O)_2$](dcbp)$_{0.5}\cdot H_2O$ with 30% thermal ellipsoids.

Table 1. Crystal structure parameters for the complex.

Formula	$C_{22}H_{23}MnN_3O_7$
Formula weight	496.37
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	24.999(5)
b	11.965(2)
c	14.608(3)
α	90.00
β	94.01(3)
γ	90.00
Volume (Å^3)	4358.7(14)
Temperature (K)	293(2)
D_{calcd} (mg m^{-3})	1.513
F (000)	2056
Reflections collected	12,921
Unique reflections	3844
R(int)	0.1122
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0641$, $wR_2 = 0.1089$
R indices (all data)	$R_1 = 0.1362$, $wR_2 = 0.1283$
Goodness-of-fit on F^2	0.985

Symmetry transformations used to generate equivalent atoms: #1; $-x$, $-y$, $-z+2$.

Table 2. Bond lengths (Å) and angles (°) for the complex.

Mn(1)–O(1)	1.864(3)	Mn(1)–O(6)	2.227(3)
Mn(1)–O(2)	1.883(3)	Mn(1)–O(5)	2.251(3)
Mn(1)–N(1)	1.976(4)	Mn(1)–N(2)	1.986(4)
O(1)–Mn(1)–O(2)	93.89(14)	O(1)–Mn(1)–O(5)	93.26(14)
O(1)–Mn(1)–N(1)	91.49(15)	O(2)–Mn(1)–O(5)	86.97(13)
O(2)–Mn(1)–N(1)	174.42(15)	N(1)–Mn(1)–O(5)	91.24(14)
O(1)–Mn(1)–N(2)	173.25(15)	N(2)–Mn(1)–O(5)	86.72(15)
O(2)–Mn(1)–N(2)	92.84(15)	O(6)–Mn(1)–O(5)	175.29(16)
N(1)–Mn(1)–N(2)	81.77(16)	C(7)–N(1)–Mn(1)	125.4(3)
O(1)–Mn(1)–O(6)	91.08(15)	C(8)–N(1)–Mn(1)	113.0(3)
O(2)–Mn(1)–O(6)	90.89(14)	C(10)–N(2)–Mn(1)	123.5(4)
N(1)–Mn(1)–O(6)	90.50(15)	C(9)–N(2)–Mn(1)	113.4(3)
N(2)–Mn(1)–O(6)	89.19(16)		

Symmetry transformations used to generate equivalent atoms: #1; $-x$, $-y$, $-z+2$.

coordination sphere, with two nitrogens (N1, N2) and two oxygens (O1, O2) from salen in the equatorial plane (with bond lengths of 1.976(4), 1.986(4), 1.864(3), and 1.883(3) Å, respectively) and two oxygens (O5, O6) from two water molecules in the axial positions (with bond lengths of 2.251(3) and 2.227(3) Å). All the bond lengths are similar to those observed in other Mn(III) Schiff-base complexes [26–29]. The bond lengths in the axial positions are much longer than those in the equatorial positions, indicating a distorted octahedral coordination sphere of Mn(III).

In the crystal lattice, there are hydrogen-bonding interactions, as shown in table 3. The crystallographic packing diagram is shown in figure 2, in which there exist intermolecular hydrogen-bonding interactions between oxygen from salen (O2) and coordinated water (O6) (with bond lengths of O2···O6, 2.800 Å), oxygens from coordinated water (O5/O6) and the uncoordinated water (O7) (with bond lengths of

Table 3. Hydrogen bond parameters in the complex.

D–H···A	D–H (Å)	H···A (Å)	∠DHA (°)	D···A (Å)	Symmetry operation
O7–H7A···O3	0.849	2.002	144.02	2.735	$[x, y, z-1]$
O7–H7B···O3	0.851	1.934	156.77	2.737	$[-x+1/2, -y+1/2, -z+1]$
O5–H5C···O4	0.856	1.887	149.95	2.662	$[x, y, z-1]$
O5–H5D···O7	0.845	1.939	159.97	2.748	
O6–H6D···^{v}O2	0.849	1.980	162.06	2.800	$[-x+1/2, -y+1/2, -z+1]$
O6–H6C···O7	0.851	1.871	170.17	2.713	$[-x+1/2, y-1/2, -z+1/2]$

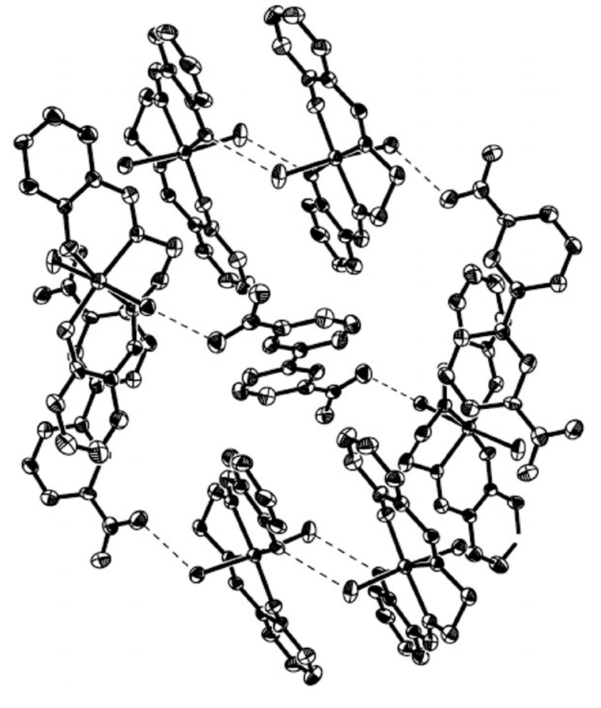


Figure 2. The packing diagram of the complex with hydrogen bonds. All H atoms have been omitted for clarity.

O5···O7, 2.748 Å; O6···O7, 2.713 Å), and also interactions between oxygens from H_2dcbp (O3/O4) and coordinated water (O5/O6) as well as uncoordinated water (O7) (with bond lengths of O3···O7, 2.735(7) Å; O4···O5, 2.662 Å). The combination of all hydrogen-bonding interactions results in the 3-D supramolecular solid-state architecture.

3.3. *IR spectra*

The band at 3737 cm^{-1} is attributable to the O–H stretching and bending of coordinated water or the water of crystallization. Strong absorptions at 1629 cm^{-1} [$\nu_{\mathrm{asym}}(CO_2)$] and 1371 cm^{-1} [$\nu_{\mathrm{sym}}(CO_2)$] are assigned to stretching of the carboxylate [30, 31]. The strong peak at 1600 cm^{-1} may be attributed to C=N stretch of the Schiff base. The phenolic C–O stretch is at 1286 cm^{-1} [32–35].

3.4. *Electronic spectra*

The complex displays two distinct strong absorptions at 236 and 281 nm, attributed to charge transfer from the ligand to Mn(III). As usual, the spectrum shows low-intensity absorptions associated with d–d transitions in the range 490–500 nm [36].

3.5. *Magnetic properties*

The magnetic susceptibility is measured from 2 to 300 K in the applied magnetic field of 2000 Oe, and the plots of χ_M and $\chi_M T$ *versus* T (χ_M is magnetic susceptibility per mole of the complex) are shown in figure 3. At room temperature, the value of $\chi_M T$ is 3.14 cm^3 mol^{-1} K, slightly larger than the spin-only value of 3.0 cm^3 mol^{-1} K for an isolated Mn(III) ($S = 2$, $g = 2$) [37]. Upon cooling, the $\chi_M T$ value decreases slowly from 300 to 22 K and then decreases sharply at lower temperature, reaching a value of 0.30 cm^3 K mol^{-1} at 2.0 K. The plot of χ_M *versus* T shows χ_M increasing upon lowering temperature from 300 to 6 K and reaches a maximum of 0.26 cm^3 mol^{-1} at 6 K, and then decreases sharply to 0.15 cm^3 mol^{-1} at 2 K. The magnetic behavior may be due to the effects of zero-field splitting (ZFS) arising from Mn(III) and/or intermolecular antiferromagnetic interactions between [Mn(salen)(H$_2$O)$_2$] molecules [38].

In order to analyze the magnetism of the complex, we used an approximation model for Mn(III) including both ZFS and intermolecular interactions with the use of the molecular field approximation. The $\chi_M T$ of the complex may be modeled by expression (2) based on Hamiltonian (1) [39]

$$\hat{\mathrm{H}} = D\hat{S}_Z^2 - 2zJ\langle S\rangle\hat{S}_Z, \tag{1}$$

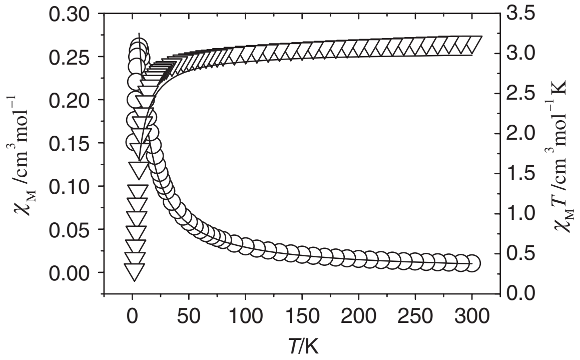


Figure 3. Temperature dependence of χ_M(○) and $\chi_M T$(▽) for the complex in the field of 2000 G. The solid lines represent the theoretical values based on the corresponding equations.

$$\begin{aligned}\chi_{\mathrm{ZFS}} &= \frac{\chi_{\|} + 2\chi_{\perp}}{3},\\ \chi_{\|} &= \frac{2N\beta^2 g_{\|}^2}{KT}\frac{\exp(-D/KT) + 4\exp(-4D/KT)}{1 + 2\exp(-D/KT) + 2\exp(-4D/KT)},\\ \chi_{\perp} &= \frac{2N\beta^2 g_{\perp}^2}{3D}\frac{9 - 7\exp(-D/KT) - 2\exp(-4D/KT)}{1 + 2\exp(-D/KT) + 2\exp(-4D/KT)},\\ \chi &= \frac{\chi_{\mathrm{ZFS}}}{1 - 2zJ\chi_{\mathrm{ZFS}}/N\beta^2 g^2},\end{aligned} \tag{2}$$

where $\langle S_z \rangle$ is the mean value of $\hat{S}_Z$ of the spin operator, zJ the intermolecular interaction parameter between two nearest neighbor magnetic species, and D the axial ZFS parameter. The best agreement between calculated and experimental values of the susceptibility in the range 300–6 K was found with $zJ = -1.40\,\mathrm{cm}^{-1}$, $g = 2.00$, $D = 4.27\,\mathrm{cm}^{-1}$, $R = 5.04 \times 10^{-3}$ ($R = \sum(\chi_{\mathrm{obsd}} - \chi_{\mathrm{cacld}})^2 / \sum(\chi_{\mathrm{obsd}})^2$), indicating a very weak antiferromagnetic interaction between the [Mn(salen)(H_2O)$_2$] molecules.

4. Conclusions

We have successfully isolated a Mn(III) complex with 4,4-dicarboxy-2,2-bipyridine under hydrothermal conditions. The complex has been characterized by elemental analysis, IR spectra, UV-Vis spectra, single-crystal X-ray diffraction, and variable temperature magnetic susceptibility. The complex is formed by three independent molecules, one [Mn(salen)(H_2O)$_2$], one H_2dcbp, and one guest water molecule in the asymmetric unit, which are further interconnected by hydrogen bonds to form a 3-D supramolecular architecture. The magnetic study of the complex indicated a weak antiferromagnetic interaction between [Mn(salen)(H_2O)$_2$] molecules.

Supplementary material

CCDC 735671 for the complex contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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