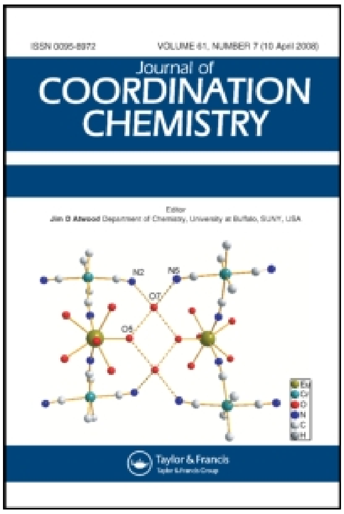

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Crystal structure, thermal and magnetic studies of a dinuclear Mn(II) complex with decadentate picolinate based ligand

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Crystal structure, thermal and magnetic studies of a dinuclear Mn(II) complex with decadentate picolinate based ligand

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The reaction of the decadentate ligand tpmen (H_4tpmen = N,N,N′N′-tetrakis[(6-carboxypyridin-2-yl)methyl]ethylenediamine) with $MnCl_2 \cdot 4H_2O$ in aqueous solution gives a homodinuclear complex $[Mn_2(H_2O)_2(\text{tpmen})] \cdot 16H_2O$, which has been characterized by elemental analysis, thermal gravimetric and single-crystal X-ray diffraction analysis. The complex crystallizes in the orthorhombic system, space group *Cmca*, $a = 28.786(5)$ Å, $b = 11.5033(19)$ Å, $c = 14.437(2)$ Å, $Z = 8$, $R_1 = 0.0432$, $wR_2 = 0.0786$. The tpmen ligand contains four picolinate groups, two of which bind each Mn(II) to form a dinuclear complex. The geometry around the Mn(II) is distorted octahedral with two nitrogen and two oxygen atoms from the picolinate groups and two oxygen atoms from coordinated water. The variable-temperature (2–300 K) magnetic susceptibilities shows an antiferromagnetic interaction between Mn(II) ions.

Keywords: Manganese(II) complex; Tpmen; Crystal structure; Magnetic property

1. Introduction

Both homo- and heterodinuclear transition-metal complexes occupy important positions in modern inorganic chemistry. The impetus for the study of these complexes derives from magnetic exchange interactions and electron transfer between metal ions and from their significance as models for biological systems [1–6]. In particular, there has been considerable interest in the coordination chemistry of manganese involving nitrogen and oxygen donor ligands. These complexes are significant not only for the diversity of their magnetic properties, but also for their redox active role in biochemical processes with increasing recognition of the role of this metal in biological systems [7–15].

For the synthesis of polynuclear metal complexes, carboxylates are interesting ligands because of their wide variety of coordination modes; pyridinecarboxylic acid and derivatives should be good candidate providing nitrogen and oxygen donors at the same time. However, there are only a few reports of mononuclear manganese complexes with pyridine-2,6-dicarboxylic acid and pyridinecarboxylic acid [16, 17]. In this article, a

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flexible decadentate ligand tpmen with four picolinate groups was employed (H_4tpmen = N,N,N′N′-tetrakis[(6-carboxypyridin-2-yl)methyl]) as the bridging ligand to produce a dinuclear Mn(II) complex, $[Mn_2(H_2O)_2(\mathrm{tpmen})] \cdot 16H_2O$, which has been structurally characterized. The spectroscopic, thermal stability and magnetic properties are also presented.

2. Experimental

2.1. *Synthesis*

All reagents were used as received from commercial suppliers without further purification. The decadentate ligand N,N,N′N′-tetrakis[(6-carboxypyridin-2-yl)methyl] ethylenediamine (H_4tpmen) is synthesized in five steps from pyridine-2,6-dicarboxylic acid and ethylenediamine in a yield of 19% according to the literature method [16].

The complex $[Mn_2(\mathrm{tpmen})(H_2O)_2] \cdot 16H_2O$ was prepared by slow diffusion in water, in a U-shaped tube containing silica gel, of $MnCl_2 \cdot 4H_2O$ (19.8 mg, 0.1 mmol) in one side, and H_4tpmen (29.8 mg, 0.05 mmol) at pH 7, adjusted by the addition of KOH (0.1 M), in the other side at room temperature. Two weeks later, well-shaped colorless single crystals suitable for X-ray structure analysis were obtained. Yield: 42%. Anal. Calcd for $C_{15}H_{32}MnN_3O_{14}$: C, 33.78; H, 6.04; N, 7.88. Found: C, 33.63; H, 5.85; N, 7.11%.

2.2. *Physical measurements*

Analyses for C, H and N were carried out on a Perkin-Elmer analyzer. Infrared spectra on KBr pellets were recorded on a Shimadzu IR-408 spectrophotometer in the range 4000–600 $\mathrm{cm^{-1}}$ and electronic spectra on a Jasco-570 spectrophotometer in water. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

2.3. *Crystal structure determination*

A colorless single crystal having approximate dimensions 0.30 × 0.20 × 0.10 mm was mounted on a glass fiber. Determination 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. Cell parameters were determined from a least-squares refinement on the setting angles from 25 well-centered reflections in the range 2.37–29.06° at 223 K. The intensities of the $\pm hkl$ reflections were measured up to $\theta_{\max} = 29.06°$ with the $\omega - 2\theta$ scan technique. The index range is $-38 \le h \le 32$, $-15 \le k \le 15$ and $-13 \le l \le 19$. The structure was solved by direct methods using the program SHELXS-97 [19] and subsequent Fourier difference techniques, and refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Crystal parameters and structure refinements are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of structure*

The molecular structure with atomic numbering of the complex is shown in figure 1. In this complex, two picolinate arms linked to the same amine nitrogen bind one Mn(II) resulting in a dinuclear complex spaced by the ethylenediamine segment. The distance between the two metal centers is 8.333(4) Å. Both of the Mn(II) ions are six-coordinate

Table 1. Crystal data and structure refinement for $[Mn_2(tpmen)(H_2O)_2] \cdot 16H_2O$.

Empirical formula	$C_{15}H_{32}MnN_3O_{14}$
Formula weight	533.38
Crystal system	Orthorhombic
Space group	*Cmca*
Unit cell dimensions (Å)	
a	28.786(5)
b	11.5033(19)
c	14.437(2)
Volume (Å^3)	4780.6(14)
Z	8
Calculated density (Mg m^{-3})	1.482
Absorption coefficient (mm^{-1})	0.624
F(000)	2240
Reflections collected/unique	14933/3059 [R(int) = 0.0177]
θ (°)	2.37–29.06
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3059/0/222
Goodness-of-fit on F^2	1.134
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0358$, $wR_2 = 0.0758$
R indices (all data)	$R_1 = 0.0432$, $wR_2 = 0.0786$
Largest diff. peak and hole (e Å^{-3})	0.324 and −0.231

Table 2. Selected bond lengths (Å) and angles (°).

$[Mn_2(tpmen)(H_2O)_2] \cdot 16H_2O$			
Mn1–O3	2.2173(16)	Mn1–O4	2.2264(17)
Mn1–N2	2.2378(13)	Mn1–O1	2.2437(11)
O1–C7	1.2548(19)	O2–C7	1.2445(19)
N1–C1	1.4741(18)	N1–C8	1.484(3)
Mn1–N2A	2.2378(13)	Mn1–O1A	2.2437(11)
O3–Mn1–O4	174.97(6)	O3–Mn1–N2	93.09(3)
O4–Mn1–N2	85.20(3)	O3–Mn1–O1	87.14(4)
O4–Mn1–O1	96.79(5)	N2–Mn1–O1	71.78(4)
N2–Mn1–N2A	139.41(6)	O3–Mn1–O1A	87.14(4)
O4–Mn1–O1A	96.79(5)	O1–Mn1–O1A	76.90(6)
C7–O1–Mn1	119.84(9)	C1–N1–C8	112.58(10)
C2–N2–C6	119.63(13)	C2–N2–Mn1	122.74(10)

A: $-x+1$, y, z.

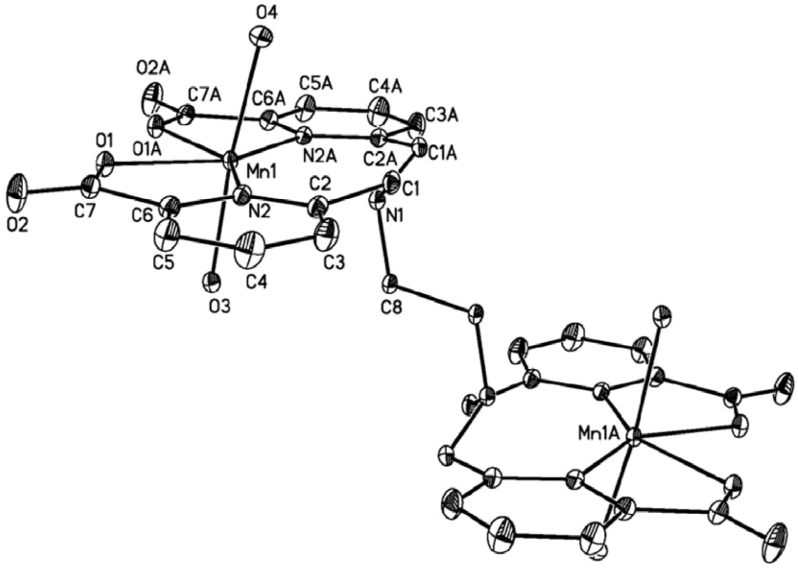

Figure 1. Crystal structure of $[Mn_2(tpmen)(H_2O)_2] \cdot 16H_2O$. Hydrogen atoms and lattice water molecules have been omitted for clarity.

with four oxygen atoms and two nitrogen atoms; two oxygen and two nitrogen atoms are from two picolinate arms of the ligand with Mn–O and Mn–N distances of 2.2437(11) and 2.2378(13) Å, respectively. Two oxygen atoms from coordinated water complete the distorted octahedral geometry of the metal center with average Mn–O distance of 2.2219(16) Å. The O1, O1A, N2 and N2A atoms are in the equatorial plane without deviation. The Mn1 atom deviates from the plane by 0.0496 Å. Oxygen atoms (O3, O4) from coordinated water occupy axial positions with the O3–Mn1–O4 angle of 174.97(6)°. The dihedral angle between two pyridine planes linked to Mn1 is 3.9(2)°. Two equatorial planes in the octahedral geometries of Mn1 and Mn1A are strictly parallel with the perpendicular distance of 3.9289(4) Å. For the decadentate ligand tpmen, each of the four picolinate arms coordinates bidentate to Mn(II) via oxygen and nitrogen donors with the O1–Mn1–N2 angle of 71.78(4)°. Two Mn(II) centers wrapped by four picolinate arms of the decadentate ligand form a chair-like conformation.

The coordinated water molecules in the Mn center form hydrogen bonds with the carboxylic oxygen atoms in the neighboring molecules (O1 ··· H–O3A, O1A ··· H–O3A, O3 ··· H–O1CC, and O3 ··· H–O1B), as shown in figure 2. All the O ··· O distances are 2.785(3) Å. Such hydrogen bonds lead to close contact between Mn atoms in neighboring molecules (Mn1 ··· Mn1B, 5.237(3) Å), much shorter than the intramolecular Mn1 ··· Mn1A distance (8.333(7) Å) in the dinuclear unit.

3.2. *IR and UV-vis spectroscopies*

The IR spectrum of the title complex in KBr disk presents a broad band (3100–3600 cm^{-1}), mainly due to the $\nu(H_2O)$ centered at ca 3420 cm^{-1}. A very strong band appears at 1619 cm^{-1} due to the antisymmetry stretching of carboxylic group, and the symmetrical stretching band of carboxylic group appears at 1408 cm^{-1}.

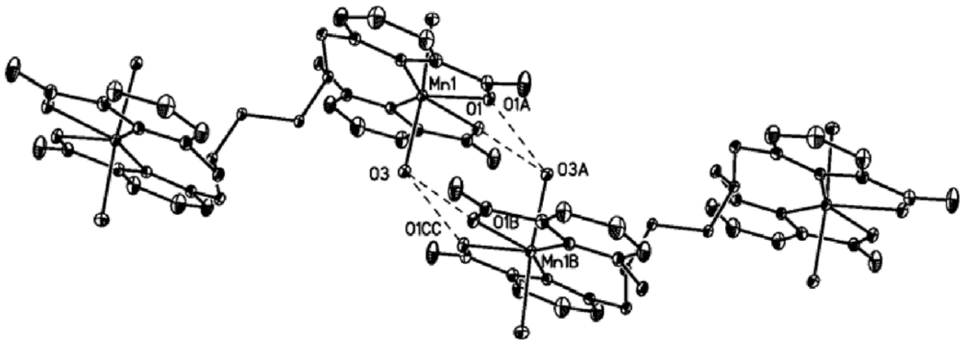

Figure 2. Hydrogen bonds in $[Mn_2(tpmen)(H_2O)_2] \cdot 16H_2O$. Hydrogen atoms have been omitted for clarity.

The difference between the ν_{as} and ν_s is 211 cm^{-1}, indicating monodentate carboxylate, in accord with the X-ray crystal analysis [21]. The bands at ca 1631, 1576, 1477 and 1433 cm^{-1} might be attributed to the vibration modes of ν_{as} and ν_s of C=C/C=N.

The UV-vis spectrum of the title compound was measured in water at a concentration of 1×10^{-5} M. The strong band centered at ca 232 nm can be assigned to charge-transfer transitions in the Mn(II)-tpmen chromophore, and the peak at ca 370 nm may be due to d–d transition of Mn(II) in a distorted octahedral coordination environment.

3.3. *Magnetic property*

Magnetic susceptibilities of the title complex were measured at a field of 5000 Oe in the 2–303 K range (figure 3). The temperature dependence of $1/\chi_M$ obeys the Curie–Weiss law with a negative Weiss constant ($\theta = -5.6$ K), indicating an antiferromagnetic interaction in the binuclear manganese unit. At 303 K, the effective magnetic moment is 8.44 μ_B close to the spin-only value of 8.36 μ_B expected for two uncoupled high-spin Mn^{II} ions. On decreasing temperature μ_{eff} steadily decreases to 7.91 μ_B at 27 K, then decreases rapidly to 1.07 μ_B at 2 K, which confirm antiferromagnetic interaction between the Mn(II) centers. Considering the long intramolecular distance in the dinuclear unit, such antiferromagnetic interaction may result from dipole coupling between the manganese centers in two neighboring molecules through hydrogen bonds. To interpret quantitatively the magnetic data of the complex, we can analyze them in terms of the "dipolar coupling" approach for a dinuclear Mn(II). The expression for the magnetic susceptibility of the manganese(II) dimer is derived from Van Vleck's equation, using the Hamiltonian $H = -2JS_1 \cdot S_2$ with $S_1 = S_2 = 5/2$ [22].

$$\chi = \frac{2Ng^2\beta^2}{kT} \cdot \frac{A}{B} \tag{1}$$

$$A = 55 + 30\exp\left(\frac{-10J}{kT}\right) + 14\exp\left(\frac{-18J}{kT}\right) + 5\exp\left(\frac{-24J}{kT}\right) + \exp\left(\frac{-28J}{kT}\right)$$

$$B = 11 + 9\exp\left(\frac{-10J}{kT}\right) + 7\exp\left(\frac{-18J}{kT}\right) + 5\exp\left(\frac{-24J}{kT}\right) + 3\exp\left(\frac{-28J}{kT}\right) + \exp\left(\frac{-30J}{kT}\right)$$

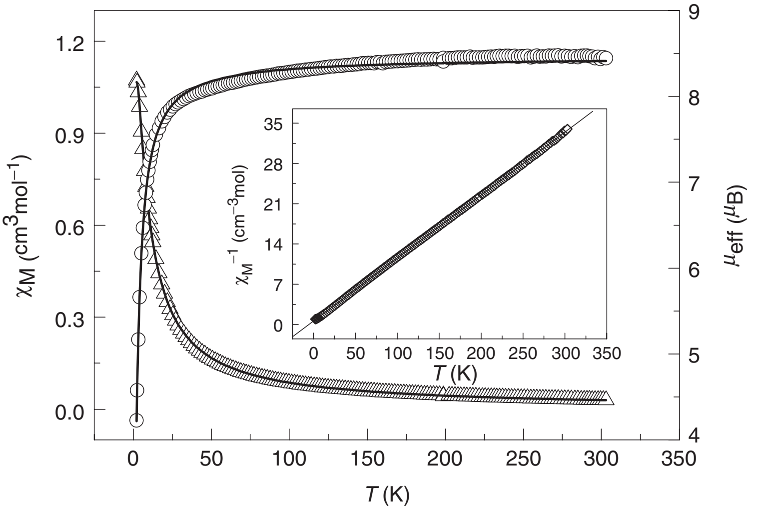

Figure 3. Plots of χ_M (Δ) and μ_{eff} (⊔) *vs.* T for $[Mn_2(tpmen)(H_2O)_2]\cdot 16H_2O$, the solid line represents the theoretical curve with the best-fit parameters. Inset: plots of $\chi_M{}^{-1}$ *vs.* T, the solid line represents the theoretical curve with the best fit parameters.

A molecular field approximation was further used (zJ') giving the final susceptibility equation.

$$\chi_M = \frac{\chi}{[1 - \chi(2zJ'/Ng^2\beta^2)]} \tag{2}$$

The best fit parameters are $J = -0.82\,\text{cm}^{-1}$, $g = 2.0$, $zJ' = -0.11\,\text{cm}^{-1}$ with the agreement factor R of 1.8×10^{-4} ($R = \Sigma[(\chi_M)^{Obs} - (\chi_M)^{Calcd}]^2/[(\chi_M)^{Obs}]^2$). The fitting results further confirm the antiferromagnetic interaction between two Mn(II) centers.

3.4. *Thermal stability*

Thermal gravimetric analysis (TGA) was performed on crystalline samples of the complex in the range 25 to 598°C. The weight loss of 26.51% between 30 and 130°C corresponds to the loss of lattice water molecules (Calcd 27.0%). A second weight loss of 6.01% exists between 130 and 533°C, corresponding to loss of all coordinated water molecules (Calcd 6.75%).

In conclusion, we have synthesized a dinuclear Mn(II) complex with the decadentate ligand tpmen and spectroscopically characterized it. The study of the magnetic properties indicates that the metal centers are antiferromagnetically coupled. The thermal stability of the complex has also been investigated.

Supplementary material

Additional materials, consisting of atomic coordinates and equivalent isotropic displacement parameters, are available from CCDC (Deposit number 638771).

Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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