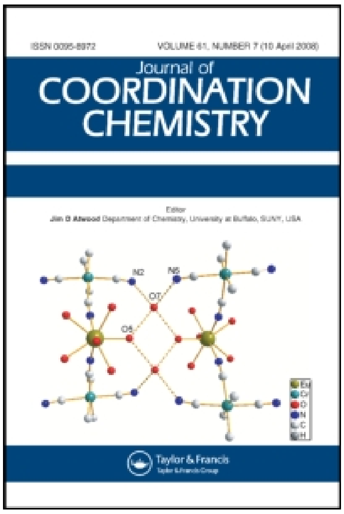

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A novel manganese(II) complex with phen ligands: hydrothermal synthesis, structure and magnetic properties of $[Mn(phen)(H_2O)_4]SO_4{\cdot}2H_2O$

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A NOVEL MANGANESE(II) COMPLEX WITH PHEN LIGANDS: HYDROTHERMAL SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF $[Mn(phen)(H_2O)_4]\ SO_4 \cdot 2H_2O$

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A novel manganese(II) complex, $[Mn(phen)(H_2O)_4]SO_4 \cdot 2H_2O$ (**1**), has been hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction. The manganese(II) complex contains only one phen ligand and four water ligands. By a catalytic test, complex **1** provided direct evidence that phen is a key ligand instead of an auxiliary one in manganese catalase mimics. Magnetic susceptibility measurements for complex **1** have been performed down to 2 K, suggesting paramagnetic behavior for this complex.

Keywords: Hydrothermal syntheses; Crystal structure; Magnetic properties; Manganese complex

INTRODUCTION

Recent work on the synthesis of inorganic compounds with very complicated structures has shown that hydrothermal synthesis is an excellent low-temperature synthetic approach to novel solid-state compounds [1–3]. From our studies of hydrothermal syntheses of several inorganic oxides [4,5], however, we have found that some unusual coordination compounds can also be obtained from hydrothermal reactions. In particular, these complexes generally exhibit novel structures which are very difficult to achieve by other synthetic methods. Here we report a novel complex, $[Mn(phen)(H_2O)_4]SO_4 \cdot 2H_2O$ (**1**) (phen = 1,10-phenanthroline), which was obtained from a hydrothermal reaction. It is well known that manganese-containing enzymes catalyze the disproportionation of hydrogen peroxide to dioxygen and water, an important reaction for cell detoxification [6,7]. To mimic the catalytic activity of manganese catalases, many model multinuclear complexes have been synthesized and their catalase activities investigated [8–11]. Recently, McCann and coworkers studied the ability of manganese complexes containing mixed carboxylate–phenanthroline ligands to function as biomimics for manganese catalases, and suggested that

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$[Mn(phen)_2(H_2O)_2]^{2+}$ might be primarily responsible for the catalytic disproportionation of hydrogen peroxide [12]. Therefore, the role of phen in catalytic disproportionation is significant. Up to now, the structures and properties of mononuclear manganese(II) complexes containing phen have been rarely reported, and direct evidence of the role of phen in catalytic disproportionation has not been found [12]. Therefore, complex **1** with only one phen ligand could give direct evidence that phen is a key ligand rather than an auxiliary one in manganese catalase mimics. In this paper we describe the hydrothermal synthesis, crystal structure, catalytic activity and magnetic properties of complex **1**, showing that hydrothermal synthesis is an effective method to obtain coordination compounds with novel structures.

EXPERIMENTAL

Materials and Methods

All reagents were obtained from commercial sources and used as purchased. The elemental analyses were performed on a PLASMSPE elemental analyzer (American Leeman Labs). IR spectra were recorded on an Alpha Centauri FT-IR spectrophotometer with pressed KBr pellets. A Beckman-DU 8B spectrophotometer was used for UV-Vis spectral measurements. The catalytic test for H_2O_2 disproportionation using complex **1** as catalyst was carried out on a home-built apparatus. Variable-temperature magnetic susceptibility data were obtained on polycrystalline samples in the temperature range of 2–300 K in an applied field of 1 T using a Metronique Ingenierie MS03 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants.

Synthesis

$[Mn(phen)(H_2O)_4]\ SO_4 \cdot 2H_2O$ (*1*) Complex **1** was prepared by a hydrothermal reaction. A mixture of $MnSO_4 \cdot H_2O$ (2.6 mmol), phen (4.3 mmol), HCl (2.2 mmol) and H_2O (14 cm^3)was sealed in a 30-cm^3 Teflon-lined reactor which was kept at 180°C for five days. After slow cooling to room temperature, light green crystals of **1** were separated from the green–yellow mother liquor, yield 64%. Anal. Calcd. for title compound (%): C, 32.8; H, 4.6; N, 6.4. Found: C, 32.7; H, 4.5; N, 6.2. IR (KBr): 3414 s, 1637 m, 1615 s, 1517 w, 1424 m, 1144 s, 858 m, 783 w, 728 m, 620 s, 476 m cm^{-1}.

X-ray Crystallographic Analysis

Crystal determination data for complex **1** were collected with Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K on a Siemens P4 diffractometer using an ω scan technique. The crystal dimensions used for determination were 0.52 × 0.46 × 0.38 mm. The crystallographic data and structure determination parameters are listed in Table I. Final atomic coordinates are listed in Table II. A semi-empirical absorption correction was applied based on ψ-scans for selected reflections. The structure was solved by direct methods and refined by the full-matrix least-squares technique on F^2 using SHELXTL software [13]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps. Selected bond lengths

TABLE I Crystal data and structure refinement for **1**

Formula	$C_{12}H_{20}MnN_2O_{10}S$
M	439.3
Space group	Pbca
Crystal system	Orthorhombic
a (Å)	8.872(2)
b (Å)	18.489(4)
c (Å)	22.077(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3621.4(13)
Z	8
μ (Mo Kα) (cm^{-1})	7.86
D_{calc} (g cm^{-1})	1.612
F(000)	1589
Maximum 2θ (°)	50
Reflections collected	4216
Independent reflections	3189 ($R_{\mathrm{int}} = 0.0205$)
T_{min}, T_{max}	0.64551, 0.67028
Data, restraints, parameters	3141, 0, 235
Goodness of fit on F^2	0.902
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0385, 0.0899
(all data)	0.0693, 0.1194
$(\Delta\rho)_{\mathrm{max}}$, $(\Delta\rho)_{\mathrm{min}}$ (e Å^{-3})	0.520, −2.828

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1**

	x	y	z	U_{eq}
Mn	8651(1)	880(1)	5853(1)	32(1)
S	5899(1)	−1559(1)	5317(1)	34(1)
O(1)	4570(3)	−1173(1)	5537(1)	48(1)
O(2)	5421(3)	−2139(1)	4902(1)	47(1)
O(3)	6879(3)	−1059(1)	4991(1)	48(1)
O(4)	6717(3)	−1876(1)	5830(1)	45(1)
N(1)	7602(3)	297(2)	6638(1)	38(1)
N(2)	9521(3)	1423(2)	6704(1)	38(1)
C(1)	6680(5)	−269(2)	6609(2)	51(1)
C(2)	6175(5)	−632(3)	7121(3)	72(2)
C(3)	6601(6)	−388(3)	7675(2)	71(2)
C(4)	7543(5)	203(3)	7733(2)	54(1)
C(5)	8037(6)	501(4)	8302(2)	76(2)
C(6)	8922(5)	1063(3)	8330(2)	72(2)
C(7)	9462(5)	1413(2)	7800(2)	52(1)
C(8)	10411(6)	2015(3)	7802(2)	66(1)
C(9)	10886(5)	2299(3)	7279(2)	66(1)
C(10)	10434(5)	1994(2)	6734(2)	53(1)
C(11)	9033(4)	1135(2)	7234(2)	38(1)
C(12)	8040(4)	527(2)	7202(2)	40(1)
OW1	7340(3)	366(1)	5118(1)	44(1)
OW2	10237(3)	1464(1)	5292(1)	45(1)
OW3	10142(3)	−53(1)	5752(1)	42(1)
OW4	7134(3)	1798(1)	5751(1)	39(1)
OW5	2056(3)	−2032(2)	5958(1)	61(1)
OW6	550(3)	1313(1)	3702(1)	52(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE III Selected bond lengths (Å) and angles (°) for **1**

Mn–Ow(2)	2.162(2)	Mn–Ow(4)	2.178(2)
Mn–Ow(3)	2.185(2)	Mn–Ow(1)	2.210(3)
Mn–N(1)	2.244(3)	Mn–N(2)	2.265(3)
S–O(1)	1.462(3)	S–O(2)	1.472(3)
N(1)–C(1)	1.330(5)	N(1)–C(12)	1.373(5)
N(2)–C(10)	1.332(5)	N(2)–C(11)	1.357(5)
C(1)–C(2)	1.390(6)	C(4)–C(5)	1.439(7)
Ow(2)–Mn–Ow(4)	87.38(9)	Ow(2)–Mn–Ow(1)	97.90(10)
Ow(4)–Mn–Ow(3)	168.26(9)	Ow(4)–Mn–N(1)	101.37(10)
Ow(2)–Mn–N(1)	162.17(11)	Ow(1)–Mn–N(2)	167.98(11)
N(1)–Mn–N(2)	73.36(11)	C(12)–N(1)–Mn	115.8(2)
O(1)–S–O(2)	109.3(2)	O(3)–S–O(4)	109.8(2)
N(1)–C(12)–C(11)	117.5(3)	C(1)–N(1)–Mn	126.6(3)
N(1)–C(12)–C(4)	122.9(4)	N(2)–C(11)–C(12)	117.6(3)

TABLE IV Atom deviation (Å) from the best least-squares plane for phen

N1	−0.032(3)	N2	0.036(3)	C1	−0.037(4)	C2	0.011(5)
C3	0.022(5)	C4	0.012(5)	C5	0.010(6)	C6	−0.007(5)
C7	−0.015(4)	C8	−0.032(5)	C9	−0.010(5)	C10	0.029(4)
C11	0.010(4)	C12	0.003(4)				

and angles are given in Table III. The best least-squares plane for the phen ligand is calculated by PLATON. Atom deviations from the best least-squares plane of phen are listed in Table IV.

RESULTS AND DISCUSSION

Crystal Structure

Single crystal X-ray diffraction of **1** reveals that it is a mononuclear manganese complex with one phen and four water ligands, besides the presence of a counter sulfate anion and two lattice water molecules. The 2+ oxidation state of manganese in **1** is consistent with the bond valence sum ($BVS = 2.08$) [14]. In the structure of **1**, the geometry about the manganese is a distorted octahedron formed by four oxygen atoms of water molecules and two nitrogen atoms of phen (see Fig. 1). The rigid planar structure of the phen molecule implies that the two nitrogen atoms are always held in juxtaposition, resulting in the formation of a plane consisting of the phen molecule and the manganese atom. However, the plane cannot be considered a symmetrical mirror about the anion of **1** owing to distortion of the octahedron. By comparison, the chelate bond angle of N–Mn–N (73.3°) in **1** is similar to that of N–Mn–N (73.6°) in the complex [Mn(phen)$_2$Cl$_2$] [12]. The crystal packing of **1** viewed along the *a* axis is shown in Fig. 2.

The longer bond distance of Mn–Ow1 (Ow refers to a water oxygen atom) compound to the other three Mn–Ow (H$_2$O) bond distances is related to the formation of a hydrogen bond between the Ow1 oxygen atom of a water molecule and the O3 oxygen atom of a SO_4^{2-} anion, with an Ow1 $\cdots$ O3 distance of 2.68 Å. A multipoint hydrogen-bonding network forms in the crystal structure of **1**, depending on linkages between the oxygen

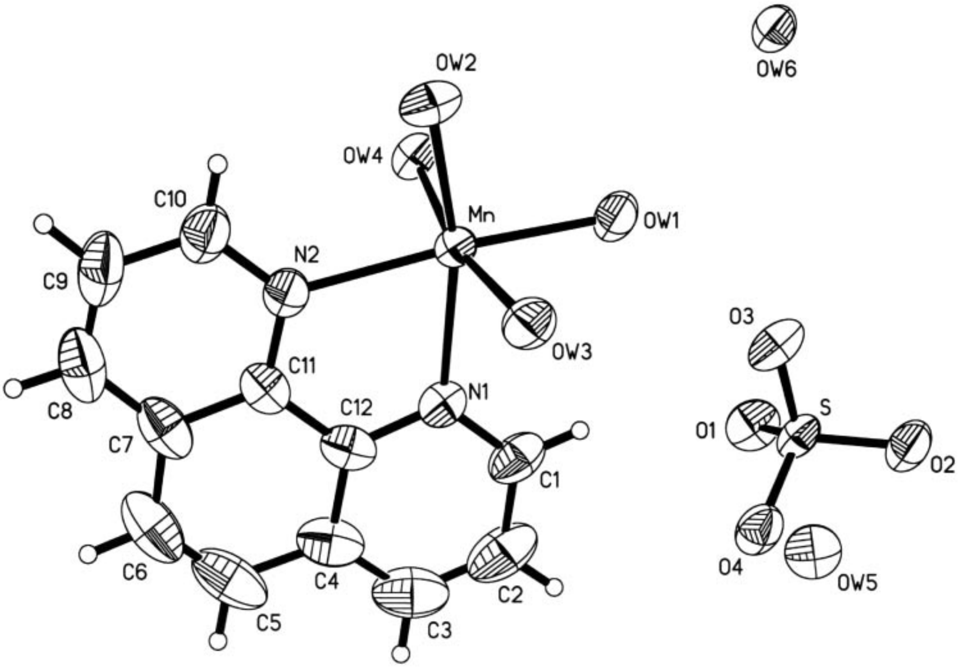

FIGURE 1 Molecular structure of complex **1**.

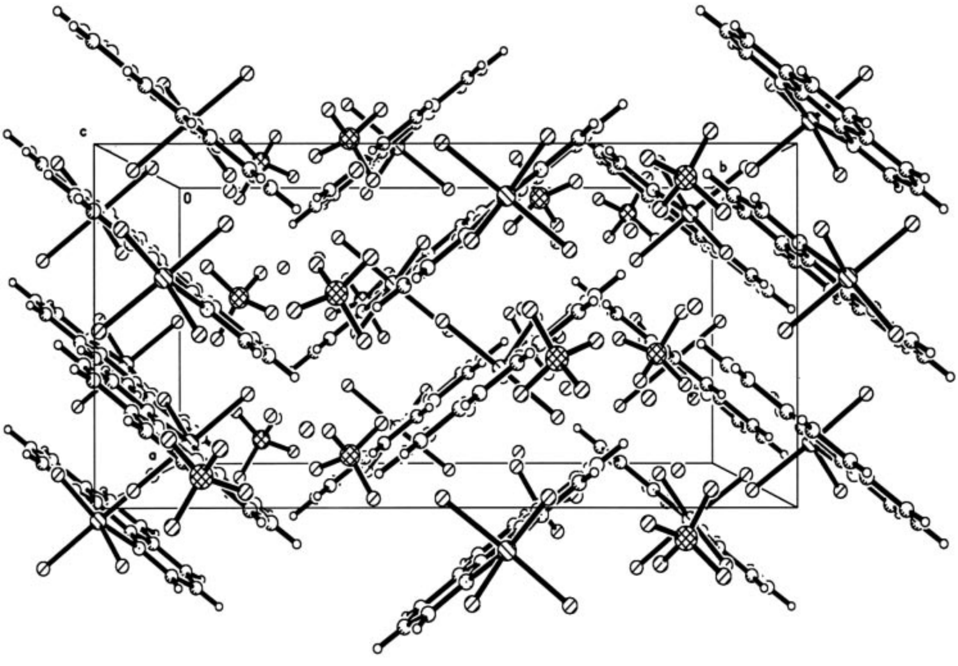

FIGURE 2 Crystal packing of complex **1** viewed along the *c* axis.

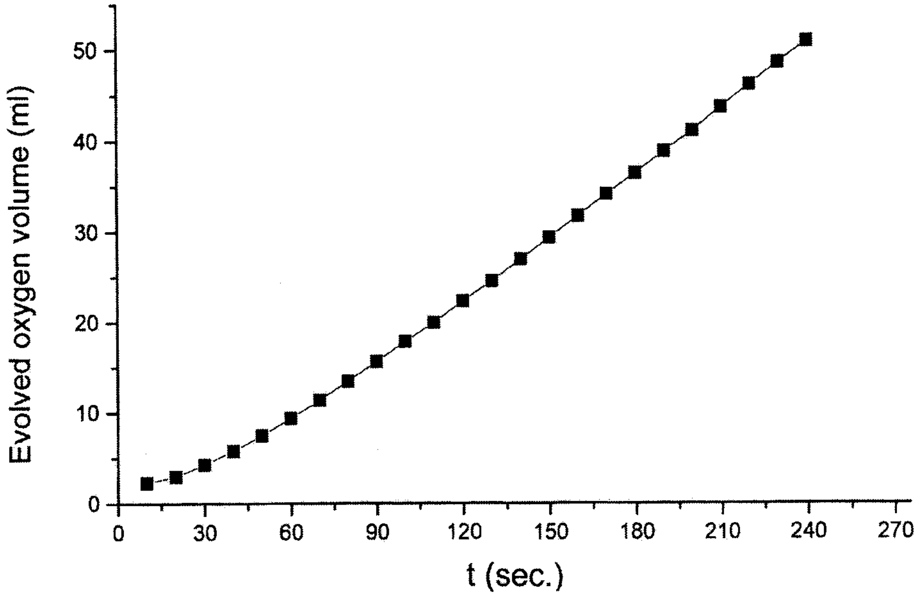

FIGURE 3 Catalytic disproportionation of H_2O_2 by complex **1** at 25°C.

of water molecules from $[Mn(phen)(H_2O)_4]^{2+}$ and the oxygen atoms from SO_4^{2-} anions, as shown by some short distances among these oxygen atoms (for example, Ow2 ··· O2, 2.79 Å; Ow4 ··· O2, 2.76 Å; Ow4 ··· O4, 2.66 Å; Ow1 ··· Ow3, 3.00 Å; etc.). The multipoint hydrogen-bonding network stabilizes the structure. A typical Mn–N bond distance of 2.265(3) Å appears in **1**, as found for $[Mn(bipy)_2Cl_2]$ (2.27 Å) and $[Mn_2(\eta'\eta'\mu_2\text{-oda})(phen)_4(H_2O)_2]\cdot[Mn_2(\eta'\eta'\mu_2\text{-oda})(phen)_4(\eta^1\text{-oda})_2]\cdot 4H_2O$ (2.28 Å) [7,12].

IR and UV Spectra

The IR spectrum for **1** is characterized by the vibration $\nu(\text{–N}=\text{C})$ for phen changing from 1642 to 1618 cm^{-1} and by vibration of the phen ring changing from 1558 to 1517 cm^{-1}. These changes indicate that binding of phen to manganese occurred. Furthermore, complex **1** can be slowly dissolved in water to produce a $[Mn(phen)(H_2O)_4]^{2+}$ cation and an SO_4^{2-}anion; addition of $BaCl_2$ to an aqueous solution of **1** produces an immediate white precipitate of $BaSO_4$. Compared with a mixture of manganese sulfate and phen of the same concentration, complex **1** has a lower molar conductivity ($\Lambda_m = 220\ S\,cm^2\,mol^{-1}$) in aqueous solution, implying the presence of a stable $[Mn(phen)(H_2O)_4]^{2+}$ cation in the aqueous solution. After complex **1** was recrystallized from water, its IR spectrum was the same as the original. UV-Vis spectra for **1** in aqueous solution exhibited three strong absorption bands at 50 000 ($\varepsilon = 3000\ M^{-1}cm^{-1}$), 43 860 ($\varepsilon = 4500\ M^{-1}cm^{-1}$) and 37 600 cm^{-1} ($\varepsilon = 3370\ M^{-1}cm^{-1}$) and a weak absorption at 28 900 cm^{-1}, characteristic of π–π^* transitions for phen. The very weak spin-forbidden d–d transition bands associated with the Mn(II) ion have not been observed.

Catalytic Test

Complex **1** was investigated as a catalyst for H_2O_2 disproportionation. To an aqueous H_2O_2 solution (35% wt/wt, 10 cm^3, 0.114 mol, kept at 25°C) a solid sample of complex **1** (10 mg; 2.28×10^{-5} mol) was added, and the amount of evolved oxygen measured volumetrically. The kinetic curves for the catalytic disproportionation of hydrogen peroxide are shown in Fig. 3. After 3 min, the number of H_2O_2 molecules decomposed by each manganese atom in complex **1** was 131. In comparison with $[Mn(phen)_2Cl_2]$, the catalytic activity of complex **1** for this reaction is relatively low [15]. However, the catalytic activity of complex **1** exhibits direct evidence that phen is a key ligand instead of an auxiliary one in manganese catalase mimics, because complex **1** contains only one phen ligand with four water molecules. For this reason the established crystal structure of complex **1** is significant. Under the same experimental conditions, using the same molar quantity of solid $MnSO_4 \cdot H_2O$ as of complex **1** as catalyst, the disproportionation of hydrogen peroxide did not occur. Considering the electron-transfer mechanism for the catalytic reaction, the conjugating and chelating effect of the phen ligand may facilitate formation and stabilization of the Mn^{3+} intermediate [16].

Magnetic Properties

The variable-temperature magnetic susceptibility of **1** was measured in the temperature range 300–2 K. Figure 4 shows the magnetic behavior of **1** as χ_m *vs.* T and $\chi_m T$ *vs.* T plots, respectively. The $1/\chi_m$ *vs.* T plot of **1** is also given as an inset. At 300 K, the

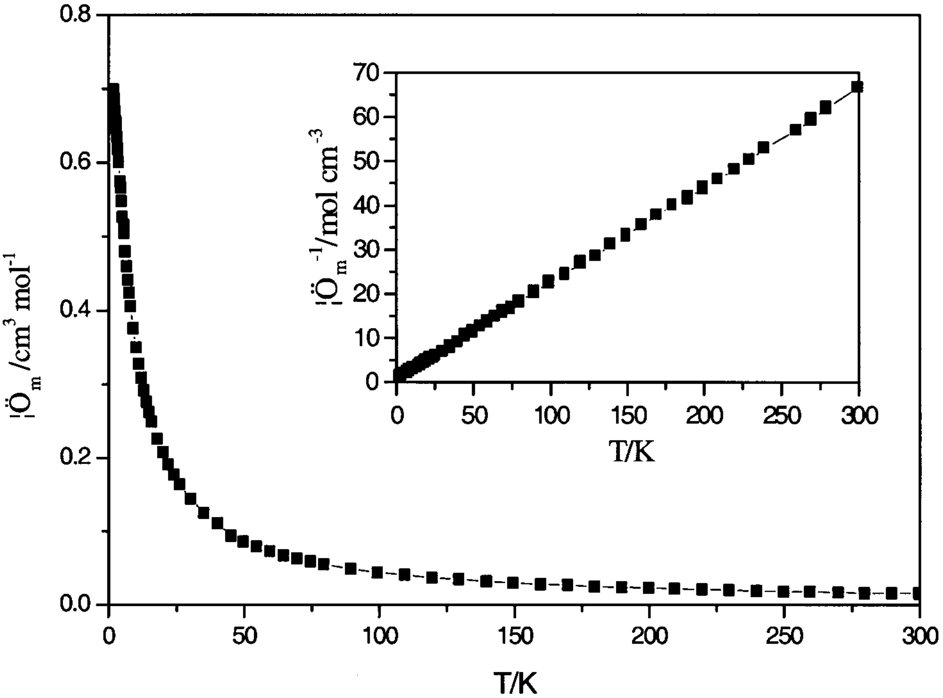

FIGURE 4 Thermal variation of χ_m and $1/\chi_m$ for complex **1**. The solid line corresponds to the best theoretical fit.

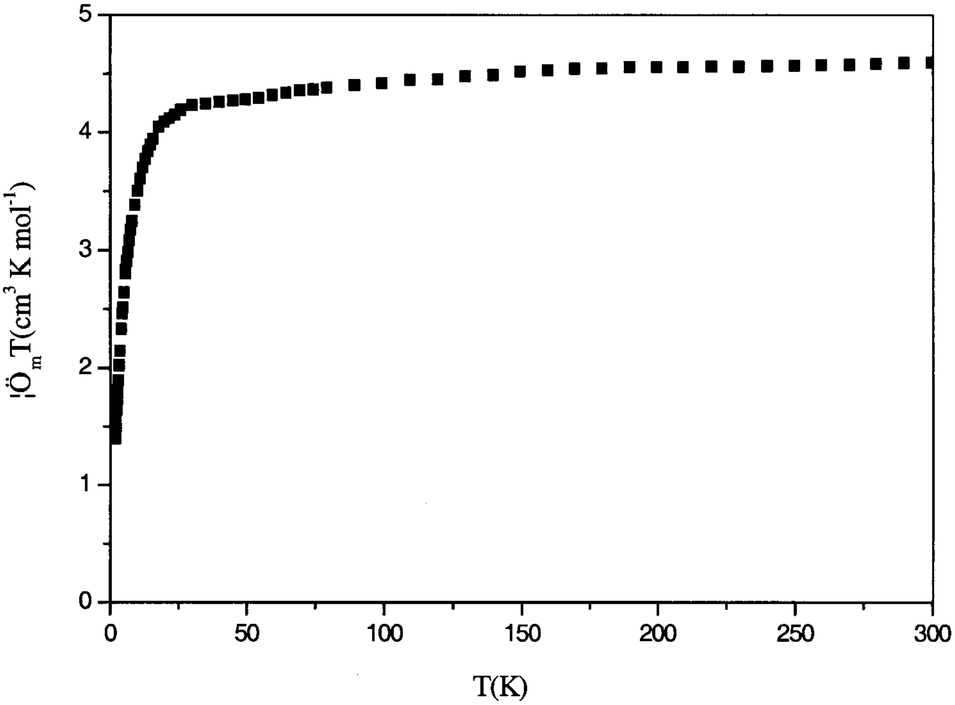

FIGURE 5 Thermal variation of $\chi_m T$ for complex **1**.

magnetic moment (μ_{eff}) per manganese(II) atom, determined from the equation $\mu_{eff} = 2.828(\chi_m T)^{1/2}$, is 6.05 μ_B. The value is in accord with that expected for an isolated high-spin Mn(II) ($3d^5$) center with $S = 5/2$ (μ_{eff} in the range of 5.65–6.10 μ_B) [17]. On cooling from room temperature the value of $\chi_m T$ decreases continuously from 4.60 cm^3 K mol^{-1} at 300 K to 4.21 cm^3 K mol^{-1} ($\mu_{eff} = 5.8\,\mu_B$) at 25 K for the Mn(II) center. At temperatures lower than 25 K, $\chi_m T$ decreases sharply to reach a minimum of 1.40 cm^3 K mol^{-1} ($\mu_{eff} = 3.35\,\mu_B$) at 2 K (see Fig. 5). Considering the structure of complex **1**, there is no possibility of superexchange interactions between these isolated Mn(II) ions. Such magnetic behavior may be attributed to a large zero-field splitting of the single Mn(II) ion in a distorted octahedral environment.

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