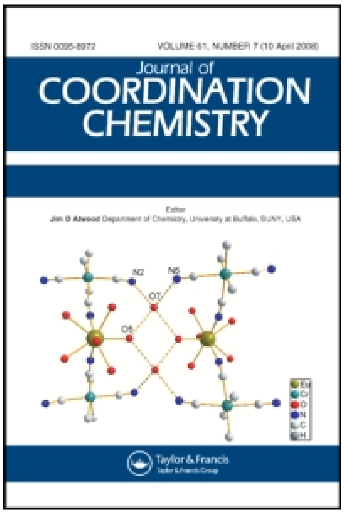

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A new terephthalato-bridged binuclear manganese(II) complex $[Mn_2(dmptacn)_2($<i>p</i>$-bdc)](ClO_4)_2$: synthesis, structure and properties

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A new terephthalato-bridged binuclear manganese(II) complex [$Mn_2(dmptacn)_2(p\text{-bdc})](ClO_4)_2$: synthesis, structure and properties

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A binuclear manganese complex, [$Mn_2(dmptacn)_2(p\text{-bdc})$] ($ClO_4)_2$ [dmptacn = 1,4-*bis*(2-pyridylmethyl)-1,4,7-triazacyclononane, *p*-bdc = terephthalate] has been synthesized and characterized. The complex crystallizes in triclinic space group $P\bar{1}$, with $a = 9.0325(7)$, $b = 11.2851(8)$, $c = 11.9907(9)$ Å; $\alpha = 90.7900(10)$, $\beta = 101.3700(10)$, $\gamma = 103.5040(10)^\circ$. IR, UV–Vis, element analysis, interaction with DNA and magnetic property of the complex has been studied. The magnetic susceptibility measured over the range 2–300 K showsthat there is a very weak antiferromagnetic interaction with $J = -0.035\,\mathrm{cm}^{-1}$, $g = 1.98$.

Keywords: Binuclear Mn(II); Terephthalate; 1,4,7-Triazacyclononane; Interaction with DNA

1. Introduction

The past three decades have witnessed a rapid expansion in the coordination chemistry of 1,4,7-triazacyclononane (tacn). It has been extensively recognized that tacn and its derivatives are excellent ligands in supporting mono- and bi-metallic complexes containing labile coordination sites. Hence, many tacn, and its N-substituted complexes, are found to be both structural and functional models of metalloenzymes [1–6]. One of the tacn derivatives, 1,4-*bis*(2-pyridylmethyl)-1,4,7-triazacyclononane (dmptacn), synthesized by Leone Spiccia *et al.*, and its complexes have so far focused on mononuclear compounds [7–12], with only one binuclear example [13]. Herein we present the synthesis and crystal structure of a binuclear complex bridged by terephthalate with the ligand dmptacn [$Mn_2(dmptacn)_2(p\text{-bdc})$] ($ClO_4)_2$, together with the spectroscopy properties, magnetic behavior and interaction with DNA. This long bridging ligand with a separation of 11–12 Å has proven to be a very interesting

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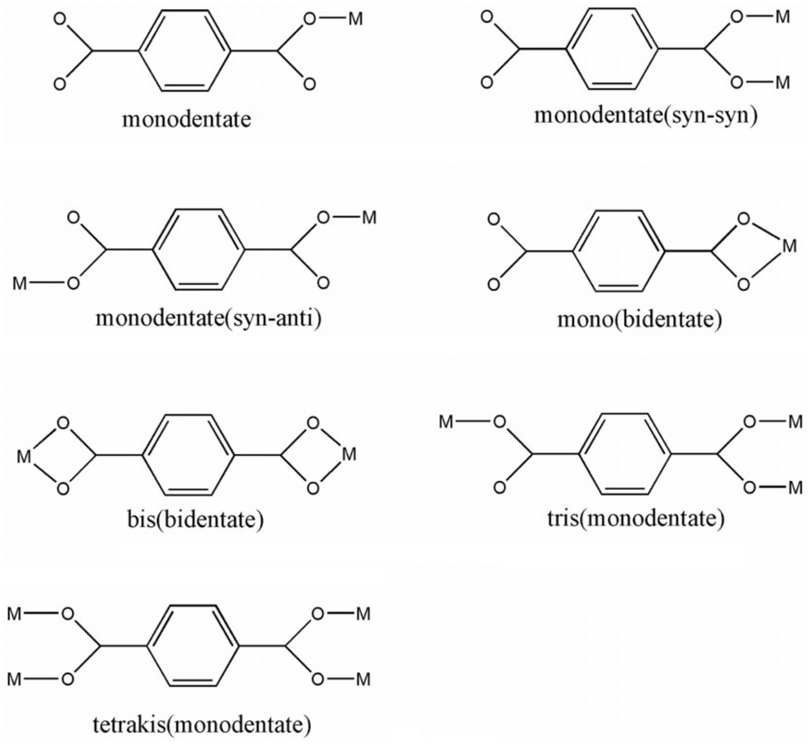

Scheme 1. The seven coordination mode of *p*-bdc.

magnetic system between the paramagnetic centers and its ability to mediate exchange coupling, going from 4 to $-140\,\mathrm{cm}^{-1}$, needs further studies [14–16]. There are seven coordination models for terephthalate listed in scheme 1 and the bridging model of terephthalate of the title compound is *bis*(monodentate)(*syn*-*anti*) [17–21].

2. Experimental

2.1. *Materials and general methods*

1,4,7-Triazacyclononane (tacn) was prepared according to the previous procedure [22] and the ligand dmptacn was prepared according to the literature [7]. All starting materials and solvents were of analytical purity. Elemental analyses for carbon, hydrogen and nitrogen were carried out on Model 240 Perkin-Elmer instrument. IR spectra were measured using KBr disks in a Bruker Tensor 27 FTIR spectrophotometer in the 400–4000 cm^{-1} region. The UV–Vis spectra were measured on Jasci V-570 UV–Vis spectrophotometer in the 200–2000 nm region. Fluorescence spectra were measured at room temperature in DMSO solution excited at 526 nm in a Cary Eclipse spectrophotometer. Magnetic properties were measured using the SQUID MPMS XL-7 magnetometer.

2.2. *Synthesis of [Mn_2(dmptacn)$_2$(p-bdc)](ClO_4)$_2$*

The compound $MnCl_2 \cdot 4H_2O$ (0.48 g, 2.4 mmol) was added to a solution of dmptacn (0.76 g, 2.4 mmol) in methanol (125 mL) and stirred for 15 min before adding $NaClO_4$ (1.0 g). Storage of the solution at 4°C overnight gave a pale yellow precipitate which was filtered off and washed with ethanol, and afforded [Mn(dmptacn)(H_2O)](ClO_4)$_2$ (73% yield) [23]. The solution of terephthalic acid (0.084 g, 0.5 mmol) in water (5 mL) (adjust pH = 6 by triethylamine) was added to the solution of [Mn(dmptacn) (H_2O)](ClO_4)$_2$ (0.528 g, 1 mmol) in methanol (15 mL). The mixed solution was stirred under reflux for 1 h and placed at room temperature for a few weeks, and then pale brown crystals suitable for X-ray analysis were obtained. Anal. Found: C, 48.30; H, 5.02; N, 12.73%. Calcd for $C_{44}H_{54}Cl_2Mn_2N_{10}O_{12}$: C, 48.23; H, 4.97; N, 12.78%. IR (KBr, cm^{-1}): 3432 (H_2O), 3238 (NH), 1607 (py), 1589 (*p*-bdc), 1492 (py), 1442 (*p*-bdc), 1099 (ClO_4^-), 622 (ClO_4^-).

2.3. *Crystallographic studies*

A crystal of the title complex was mounted on a Bruker Smart 1000 X-ray diffractometer. The determination of unit cell parameters and the data collection were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined on F^2 by full matrix least-squares methods using SHELXTL-97 [24]. The H atoms were treated as riding on their attached atoms, refined and placed at calculated positions. The crystal parameters and details of the data collection and refinement for the complexes are listed in table 1 (CCDC: 608847).

Table 1. Crystal data and structure refinement for [Mn_2(dmptacn)$_2$(*p*-bdc)](ClO_4)$_2$.

Empirical formula	$C_{44}H_{54}C_{12}Mn_2N_{10}O_{12}$
Formula weight	1095.75
Temperature (K)	293(2)
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.0325(7)
b	11.2851(8)
c	11.9907(9)
α	90.7900(10)
β	101.3700(10)
γ	103.5040(10)
Volume (Å^3)	1162.83(15)
Z	1
Calculated density (Mg m^{-3})	1.562
Absorption coefficient (mm^{-1})	0.733
F(000)	566
Crystal size (mm^3)	0.32 × 0.30 × 0.24
θ range for data collection (°)	1.74–25.03
Limiting indices	$-10 \le h \le 10$, $-13 \le k \le 3$, $-11 \le l \le 14$
Reflections collected/unique	6346/4063 [*R*(int) = 0.0126]
Max. and min. transmission	1.000000 and 0.828025
Data/restraints/parameters	4063/0/316
Goodness-of-fit on F^2	1.091
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0452$, $wR_2 = 0.1292$
R indices (all data)	$R_1 = 0.0520$, $wR_2 = 0.1331$

2.4. *Spectroscopic studies on DNA interaction*

The compound was dissolved in the mixed solvent of DMSO and tris–Na_2EDTA buffer (1 mM Na_2EDTA, 10 mM tris, pH 7.50) in 1 : 3 ratio and incubated with DNA for 1 h before measurement.

2.4.1. Electronic spectroscopy. The concentration of CT-DNA per base was determined by recording the UV–Vis absorption at 260 nm using the molar absorption coefficient of $6600\,M^{-1}\,cm^{-1}$. The UV–Vis absorbance at 260 and 280 nm of the CT-DNA solution in tris–Na_2EDTA buffer gives a ratio of 1.87, indicating that the DNA was sufficiently free of protein. The concentration of the compound was 2.0×10^{-5} M.

2.4.2. Fluorescence spectroscopy. Fluorescence spectra were recorded at room temperature with excitation wavelength at 526 nm. The experiment was carried out by titrating the compound (2.0×10^{-3} M) into samples containing 1×10^{-4} M DNA and 2.5×10^{-5} M EB.

3. Results and discussions

3.1. *Crystal structure of [$Mn_2(dmptacn)_2(p\text{-}bdc)$]($ClO_4$)$_2$*

A perspective drawing of the unit of [Mn_2(dmptacn)$_2$(*p*-bdc)]$^{2+}$ is shown in figure 1. Selected bond distances and angles are shown in table 2. The terephthalato dianion acts as a *bis*(monodentate) ligand which is bound on each side to two manganese atoms through the one carboxylate oxygen in syn-anti configuration. The dimer lies about a crystallographic center, which is located at the middle of the phenyl ring of the

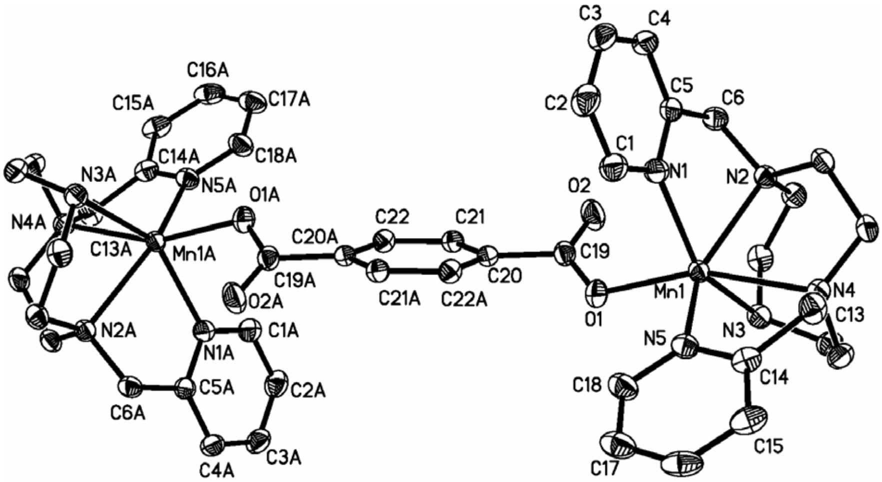

Figure 1. Thermal ellipsoid diagram of [Mn_2(dmptacn)$_2$(*p*-bdc)]$^{2+}$ with the ellipsoids drawn at the 30% probability level.

terephthalate ligand. The intermolecular distance of the two Mn(II) ions is 11.217 Å, which is slightly shorter than that of [Mn_2(phen)$_4$(H_2O)$_2$(ta)](ClO_4)$_2$ (11.456 Å) [15], [Mn(4-methylpyrazole)$_3$(H_2O)(tp)]$_\mathrm{n}$ (11.581 Å) and [Mn(4-methylpyrazole)$_4$(tp)]$_n$ (11.449 Å) [11]. The local geometry around each Mn(II) is pseudo-trigonal-prismatic geometry, involving five nitrogen atoms [N(1), N(2), N(3), N(4) and N(5)] from dmptacn and one oxygen atom [O(1)] from carboxylate. The Mn–O bond distance [2.073(2) Å] is somewhat shorter than Mn–N [2.241(3)–2.361(2) Å] but is similar to that observed in [Mn_2(phen)$_4$(H_2O)$_2$(ta)](ClO_4)$_2$ [Mn–O: 2.120(3) Å and Mn–N: 2.256(4)–2.291(4)] [15].

The average dihedral angle of the carboxylate groups [C(19), O(1), O(2)] and benzene rings [C(20), C(21), C(22)] is 29.45°. The puckering of the five-membered chelate rings are formed by the pyridyl arms [Mn(1)–N(2)–C(6)–C(5) and Mn(1)–N(4)–C(13)–C(14) torsion angles = 47.2(3) and 42.2(3)°]. The two 2-pyridylmethyl pendant arms adopt a Δ configuration, and, in contrast to those of the Cu(II) analogue [25], they are perpendicular (the dihedral angel of two pyridyl is 80.29°) rather than parallel to one another. The angles subtended by the tacn nitrogens (average 75.74°) are much smaller than those subtended by the tacn ligand in the binuclear Ni(II) complex of tmpdtnb (average 84.6°) [26], which has a more regular octahedral geometry. The degree of pseudo-trigonal-prismatic geometry can be quantified by the trigonal twist angle (ϕ), which is a measure of the rotation of the two N donors on the pyridyl arms and the oxygen ligand on *p*-bdc relative to the tacn nitrogen donor atoms (figure 2). For a trigonal-prismatic geometry, ϕ is 0°, while for an octahedral arrangement, ϕ is 60°. The observed value of ϕ for the title compound is 21.3° confirms a geometry that it is intermediate between trigonal prismatic and octahedral but which is slightly closer to the former, as was found for [Mn(tmptacn)](ClO_4)$_2$ ($\phi = 19.6°$) [27] and [Mn(dmptacn)Cl][ClO_4] ($\phi = 23.4°$) [8].

3.2. *Spectroscopic discussion on DNA interaction*

The numerous biological experiments performed so far suggest that DNA is the primary intracellular target of an anticancer complex because the interaction between

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

Mn(1)–N(5)	2.241(3)	Mn(1)–N(1)	2.257(3)
Mn(1)–N(3)	2.293(3)	Mn(1)–N(2)	2.326(2)
Mn(1)–N(4)	2.361(2)	Mn(1)–O(1)	2.073(2)
O(1)–Mn(1)–N(5)	89.38(10)	O(1)–Mn(1)–N(1)	88.58(9)
N(5)–Mn(1)–N(1)	95.24(10)	O(1)–Mn(1)–N(3)	100.80(9)
N(5)–Mn(1)–N(3)	115.87(10)	N(1)–Mn(1)–N(3)	147.35(10)
O(1)–Mn(1)–N(2)	125.45(9)	N(5)–Mn(1)–N(2)	141.58(9)
N(1)–Mn(1)–N(2)	72.57(9)	N(3)–Mn(1)–N(2)	76.63(9)
O(1)–Mn(1)–N(4)	158.42(9)	N(5)–Mn(1)–N(4)	73.80(9)
N(1)–Mn(1)–N(4)	106.01(9)	N(3)–Mn(1)–N(4)	75.59(9)
N(2)–Mn(1)–N(4)	74.97(9)	C(19)–O(1)–Mn(1)	121.4(2)
C(5)–N(1)–Mn(1)	116.0(2)	C(1)–N(1)–Mn(1)	125.5(2)
C(6)–N(2)–Mn(1)	104.96(17)	C(7)–N(2)–Mn(1)	105.86(17)
C(12)–N(2)–Mn(1)	110.25(17)	C(11)–N(3)–Mn(1)	102.44(18)
C(10)–N(3)–Mn(1)	112.95(19)	C(13)–N(4)–Mn(1)	105.96(19)
C(9)–N(4)–Mn(1)	102.91(18)	C(8)–N(4)–Mn(1)	112.02(18)
C(14)–N(5)–Mn(1)	117.3(2)	C(18)–N(5)–Mn(1)	123.6(2)

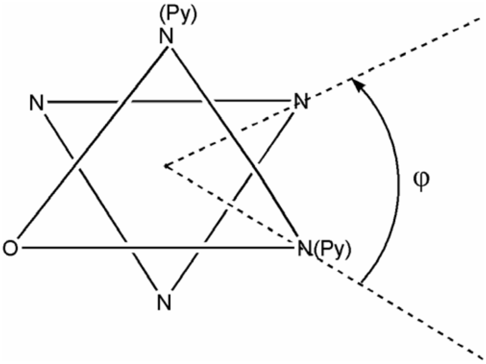

Figure 2. Definition of the trigonal twist angle (ϕ).

these molecules and DNA can cause DNA damage in cancer cells, blocking the division of cancer cells and resulting in cell death [28]. The complex is bound to DNA through three noncovalent modes: intercalation, groove binding and external static electronic effects. Among these interactions, intercalation is one of the most important DNA binding modes, related to the antitumor ability of the complex. The intercalative binding affinities had to be significantly increased for intercalation to dominate as the mode of interaction. There has been considerable interest in DNA binding properties of transition metal complexes that are capable of binding to DNA by intercalation [29].

In order to investigate whether DNA was the biological target of the compound, its interactions with Calf-thymus DNA (CT-DNA) were determined by UV–Vis and fluorescence spectroscopy. The absorption spectra of the compound in the absence and presence of CT-DNA at various concentrations are given in figure 3. Free dmptacn does not have any absorption band in the ultraviolet region because of the high energy gap between LUMO and HOMO. However, manganese binding lowered the gap and thus caused the transition occurring at 257 nm. All bands showed a hypochromism with the increasing ratio of [DNA]/[compound], the LMCT band decreased about 39.5% in intensity when the ratio increased from 0.0 to 0.5. The DNA-EB system was used to further probe the DNA binding mode of the compound. Ethidium bromide (EB) is an intercalator that gives a significant increase in fluorescence emission when bound to DNA and its displacement from DNA results in decrease in fluorescence intensity [30]. Fluorescence titration spectra are shown in figure 4. The emission intensity decreased with the increase of the concentration of the compound, which suggests that the compound can replace EB from CT-DNA and intercalate into the DNA double helix.

3.3. *Magnetic property*

Magnetic susceptibility of the complex was measured throughout the temperature range 2–300 K. At 300 K, the effective magnetic moment value is 8.34 BM, very similar to that expected for two non-interacting Mn(II) ions (8.37 BM). With temperature decrease in the range 300–2 K, the μ_{eff} value slightly decreases and then rapidly decreases and reaches a value of 7.82 BM at 2 K. Because the *p*-bdc bridge results in a long $\mathrm{Mn} \cdots \mathrm{Mn}$

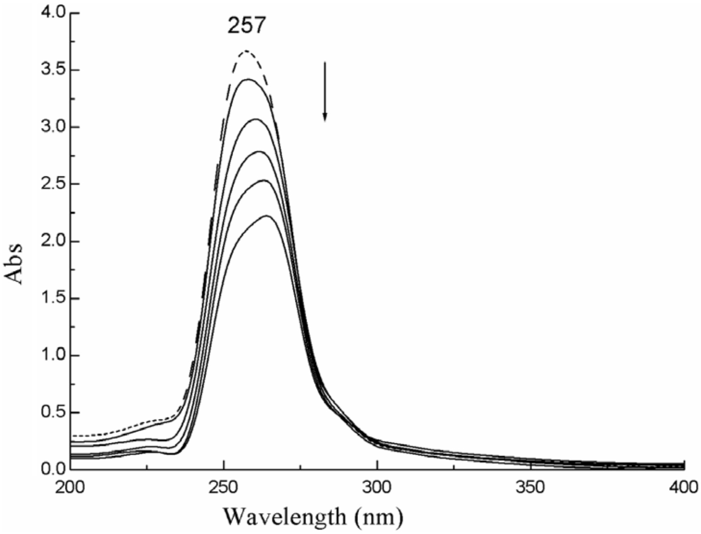

Figure 3. UV–Vis absorption spectra of the compound in 1 : 3 mixed solution of DMSO and buffer (buffer = 10 mM tris, 1 mM Na_2EDTA, pH 7.50) with increasing concentration of CT-DNA. The concentration of the compound is 2.0×10^{-5} M, r = [CT-DNA]/[compound] = 0, 0.1, 0.2, 0.3, 0.4, 0.5.

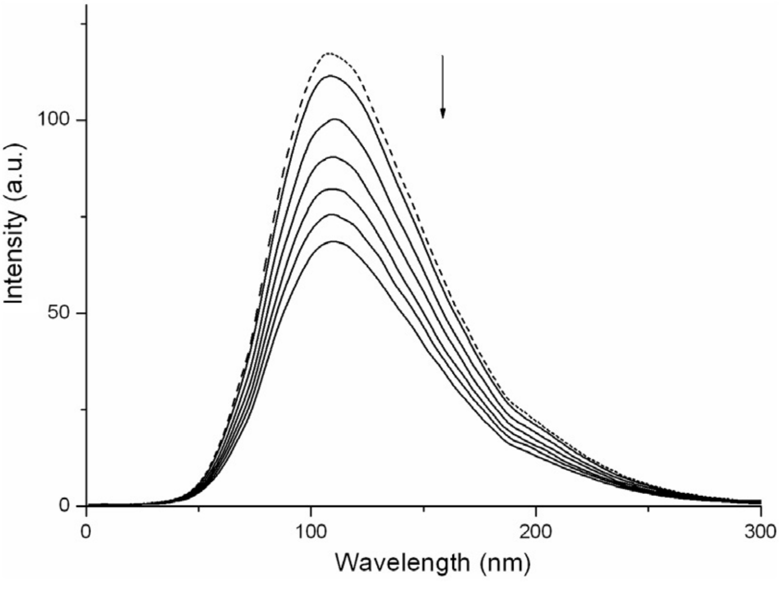

Figure 4. Fluorescence emission spectra (excited at 526 nm) of the EB-CTDNA system (2.5×10^{-5} M EB, 1×10^{-4} M DNA) in the absence (dotted line) and presence (solid line) of $[Mn_2(dmptacn)_2(p\text{-bdc})](ClO_4)_2$ (2.0×10^{-3} M, 10 μL per scan).

separation, it is believed that the two Mn(II) ions undergo only very weak magnetic exchange interaction with the exchange integral *J*. This behavior is characteristic of an antiferromagnetic interaction between the two high-spin Mn(II) ions (figure 5). The following equation (1) was used for calculating the susceptibilities of the compound.

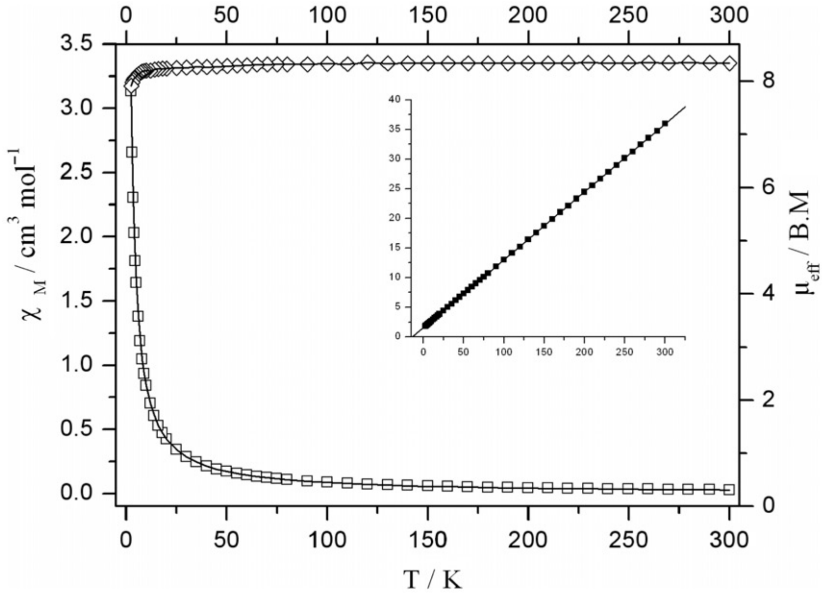

Figure 5. The temperature variation of magnetic susceptibility and magnetic moment of $[Mn_2(dmptacn)_2(p\text{-}bdc)](ClO_4)_2$.

The susceptibility data for the complex were treated by the isotropic Heisenberg $S_A = S_B = 5/2$ spin-coupled dimer model ($\hat{H} = 2J\hat{S}_A \cdot \hat{S}_B$) and the computed curves match very well the experimental data with $J = -0.035\,\text{cm}^{-1}$, $g = 1.98$ and the agreement factor defined by $R[R = \Sigma(\chi^i_{obs} - \chi^i_{cald})^2 / \ \Sigma(\chi^i_{obs})^2 = 3.28 \times 10^{-5}$. The magnetic property of the title complex is similar to that of $[Mn_2(phen)_4(H_2O)2(ta)](ClO_4)_2$ ($J = -0.065\,\text{cm}^{-1}$, $g = 1.99$) [15] and $(salen)_2Mn_2(\mu\text{-phth})$ ($J = -0.0295\,\text{cm}^{-1}$, $g = 2.02$) [31].

$$\chi_M = \frac{2N\beta^2 g^2}{KT}\left[\frac{A}{B}\right]$$
$$A = 55 + 30\exp\left(\frac{-10J}{KT}\right) + 14\exp\left(\frac{-18J}{KT}\right) + 5\exp\left(\frac{-24J}{KT}\right) + \exp\left(\frac{-28J}{KT}\right)$$
$$B = 11 + 9\exp\left(\frac{-10J}{KT}\right) + 7\exp\left(\frac{-18J}{KT}\right) + 5\exp\left(\frac{-24J}{KT}\right) + 3\exp\left(\frac{-28J}{KT}\right) + \exp\left(\frac{-30J}{KT}\right) \tag{1}$$

In equation (1), χ_M indicates the magnetic interaction between two Mn(II) atoms in the binuclear unit through *p*-bdc. The complex obeys the Curie-Weiss law through the temperature range of 2–300 K, with a Curie constant of $7.73\,\text{cm}^3\,\text{K}\,\text{mol}^{-1}$ and a Weiss temperature, θ, of -0.63 K. This is consistent with the μ_{eff} *versus* T curve. It has been proved that the coplanarity of the terephthalate and the magnetic orbital (the dihedral degree is defined as α) was a prerequisite to observe an interaction through this bridge between two magnetic centers far apart from each other, and the greater the dihedral angle (β) between the plane of carboxylate group and the plane of benzene ring, the weaker the magnetic coupling should be [15]. In the title complex, the α and β are 12.56° and 29.45° respectively, so the weak antiferromagnetic interaction could be observed despite the large intramolecular metal-metal separation (11.217 Å).

Acknowledgements

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