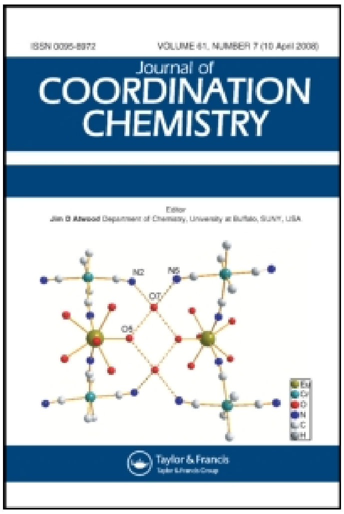

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A New Maleato-Bridged Mn(II) Phen Complex: Structure and Magnetic Properties of Mn(phen)($C_4H_2O_4$)

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A NEW MALEATO-BRIDGED Mn(II) PHEN COMPLEX: STRUCTURE AND MAGNETIC PROPERTIES OF Mn(PHEN)($C_4H_2O_4$)

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Reaction of freshly-precipitated $MnCO_3$, phenanthroline monohydrate and maleic acid in CH_3OH/H_2O (pH = 6.23) at 50°C afforded a new maleato bridged, catenated coordination polymer Mn(phen)($C_4H_2O_4$), where the Mn atoms are each octahedrally coordinated by two N atoms of one phen ligand and four O atoms of three maleato ligands (d(Mn–N) = 2.300, 2.331 Å; d(Mn–O) = 2.112–2.207 Å). The maleato ligand chelates one Mn atom to form a seven membered ring while two carboxylate groups of different maleato ligands bridge two Mn atoms to form an eight-membered ring, 1D $^{1}_{\infty}[\mathrm{Mn(phen)(C_4H_2O_4)_{3/3}}]$ chains being generated in a sequence of seven- and eight-membered rings. Significant interchain π–π stacking interactions are responsible for the supramolecular assembly of the polymeric $^{1}_{\infty}[\mathrm{Mn(phen)(C_4H_2O_4)_{3/3}}]$ chains into 2D layers. At low temperatures, the title complex becomes antiferromagnetic with $T_{\mathrm{N\acute{e}el}} = 7\,\mathrm{K}$ and follows the Curie–Weiss law $\chi_m(T + 9.82) = 4.140\,\mathrm{cm^3\,mol^{-1}\,K}$ between 30–300 K.

Keywords: Mn(II); Maleato complex; Phenanthroline complex; Synthesis; Crystal structure; Magnetism

INTRODUCTION

Rational design and syntheses of one-dimensional coordination polymers are of special interest mainly because one-dimensional magnetic systems are recognized to be ideal examples for developing theoretical models aimed at understanding exchange interaction in extended lattices [1–4]. Supramolecular assembly of metal ions with bridging organic ligands such as carboxylate anions proved to be efficient route to the syntheses of coordination polymers with specific topologies [5,6]. Our recent investigations employing saturated α,ω-dicarboxylate anions yielded a series of 1D, 2D and 3D coordination polymers [7–10] and we found that incorporation of bidentate chelating phen ligand is favorable for formation of 1D coordination polymers. For example, Cu(phen) subunits could be bridged by bis-monodentate succinato and sebacato groups to generate 1D chains, which are further assembled into supramolecular double chains by interdigitation of phen ligands due to π–π stacking interactions

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[11–13]. On the other hand, we are aware that reports of supramolecular assemblies using unsaturated α,ω-dicarboxylate anions as bridging ligands are relatively rare [14–16]. In this article, we report a new maleato-bridged Mn(II) phen polycatenated complex, Mn(phen)($C_4H_2O_4$), which behaves as an antiferromagnet at low temperatures.

EXPERIMENTAL

Physical Measurements

C, H and N microanalyses were performed with a Heraeus Rapid-CHNO instrument. FT-IR spectra were recorded using KBr pellets in the range 4000–400 cm^{-1} on a Protege 460 spectrophotometer. Magnetic susceptibilities were measured on a powdered sample with a SQUID magnetometer (Quantum Design MPMS-7) in the temperature range $5 \leq T(\mathrm{K}) \leq 300$ with an applied field of 10,000 G. The susceptibility was corrected for diamagnetic contributions by using Pascal's constants ($\chi_{\mathrm{dia}} = -157 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$) [17].

Synthesis

All chemicals of p.a. grade were purchased from the Shanghai Chemicals Company and used without further purification. For successful synthesis, fresh $MnCO_3$ was necessary. Dropwise addition of 4.0 cm^3 of 1M aqueous Na_2CO_3 to a stirred aqueous solution of $MnSO_4 \cdot H_2O$ (0.43 g, 2.50 mmol) in 5.0 cm^3 of H_2O produced a white precipitate, which was then separated and washed by double-distilled water until no SO_4^{2-} anions were detectable. The precipitate was then added to a stirred aqueous solution of maleic acid (0.29 g, 2.5 mmol) in 20 cm^3 of H_2O, followed by addition of a methanolic solution (20 cm^3) of phenanthroline monohydrate (0.50 g, 2.5 mmol). The mixture was further stirred for 30 min and insoluble solids filtered off. The yellow filtrate ($pH = 6.23$) was kept at 50°C and yellow, plate-like crystals grew overnight. Yield: *ca.* 75%. *Anal.* Calc. for $C_{16}H_{10}MnN_2O_4$ (%): C, 55.03; H, 2.89; N, 9.16. Found: C, 55.14; H, 2.96; N, 9.07. IR (cm^{-1}): 3054m, 1953w, 1824w, 1560vs, 1512s, 1435vs, 1390s, 1345m, 1305vs, 1223m, 1198m, 1144m, 1102m, 1092m, 1052w, 990m, 977w, 891m, 865s, 849vs, 779m, 728s, 665m, 637m, 630s, 549m, 483m, 419m.

X-ray Crystallography

A crystal of approximate dimensions 0.60 × 0.11 × 0.09 mm was selected under a polarizing microscope and glued to a glass fiber with epoxy cement. Unit cell parameters and the orientation matrix were determined by least-squares refinement using the setting angles of 25 centred reflections ($10 \leq 2\vartheta \leq 25°$) measured on a Bruker P4 diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were collected at 293 K using a $\vartheta - 2\vartheta$ scan technique up to a maximum 2ϑ value of 55°. Three standard reflections were monitored for crystal and instrument stability after every 97 data measurements. No significant variation was observed. Of 3730 measured reflections ($h - 10$ to 1, $k - 10$ to 10, $l - 13$ to 13), 3080 reflections were independent ($R_{\mathrm{int}} = 0.0223$) and 2651 reflections with $I \geq 2\sigma(I)$ were considered as observed and used for the structure determination. The intensity data were corrected for Lorentz and polarization effects and (empirical) absorption. SHELXS-97 and SHELXL-97 programs were used for the structure determination and refinement [18,19]. The structure was solved using direct methods. Subsequent difference Fourier syntheses enabled all heavier atoms to be located. After several cycles of refinement, all hydrogen atoms were located from successive difference Fourier syntheses. The hydrogen and nonhydrogen atoms were refined with isotropic and anisotropic displacement parameters, respectively. Final refinement based on full-matrix least-squares techniques converged smoothly to agreement factors $R1 = 0.0296$ and $wR2 = 0.0726$. Atomic scattering factors were supplied by the SHELX programs [18,19]. Crystal data, intensity collection and structure refinement details are summarized in Table I and final atomic positional parameters, selected interatomic distances and bond angles are given in Tables II and III, respectively. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 172032 (Mn(phen)$C_4H_2O_4$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033: E-mail: deposit@ccdc.cam.ac.uk).

TABLE I Crystal data and structure refinement details for the complex

Compound	Mn(phen)($C_4H_2O_4$)
Empirical formula	$C_{16}H_{10}MnN_2O_4$
Color/shape	Yellow/needle-like
Size (mm)	$0.60 \times 0.11 \times 0.09$
Formula weight	349.20
Temperature	293 K
Crystal system, Space group	triclinic, $P\bar{1}$(no. 2)
a(Å)	8.208(1)
b(Å)	8.413(1)
c(Å)	10.578(1)
α(°)	74.58(1)
β(°)	84.60(1)
γ(°)	73.45(1)
Volume(Å^3), Z	674.9(4), 2
$D_{\text{calcd.}}$(g cm^{-3})	1.718
μ(Mo$K\alpha$) (cm^{-1})	10.02
F(000)	354
Diffractometer	Bruker P4
Radiation	Graphite monochromated Mo$K\alpha$ ($\lambda = 0.71073$ Å)
Scan type	$\vartheta - 2\vartheta$
No. of measured reflections	Total: 3730; unique: 3080 ($R_{\text{int}} = 0.0335$)
Correction	Semi-empirical based on psi-scan
Structure solution	Direct methods (SHELXS-97) [18]
Refinement	Full-matrix least-squares (SHELXL-97) [19]
Refinement method	Full-matrix least-squares on F^2
Treatment of H atoms	Diff. Map and refined isotropically
No. of observed reflections [$I \geq 2\sigma(I)$]	2651
No. of variables	249
Goodness-of-fit on F^2	1.016
Final R indices [$I \geq 2\sigma(I)$][a]	$R1 = 0.0296$, $wR2 = 0.0726$
R indices (all data)[a]	$R1 = 0.0381$, $wR2 = 0.0764$
A, B values in weighting scheme[b]	0.0338, 0.2489
Extinction coefficient	0.009 (1)
Max. and min. peak in final diff. Map	0.244 and -0.238 e$^-$/Å^3

[a] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$; [b] $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for nonhydrogen atoms. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Mn	0.74207(3)	0.54075(3)	0.87621(2)	0.0211(1)
N(1)	0.6671(2)	0.3586(2)	0.7742(2)	0.0265(3)
N(2)	0.7974(2)	0.6247(2)	0.6549(1)	0.0247(3)
C(1)	0.6039(3)	0.2278(3)	0.8311(2)	0.0340(4)
C(2)	0.5706(3)	0.1180(3)	0.7643(3)	0.0397(5)
C(3)	0.5984(3)	0.1502(3)	0.6320(2)	0.0390(5)
C(4)	0.6612(2)	0.2889(3)	0.5665(2)	0.0325(4)
C(5)	0.6905(3)	0.3331(3)	0.4269(2)	0.0418(5)
C(6)	0.7517(3)	0.4663(3)	0.3677(2)	0.0397(5)
C(7)	0.7894(2)	0.5708(3)	0.4417(2)	0.0312(4)
C(8)	0.8535(3)	0.7119(3)	0.3840(2)	0.0378(5)
C(9)	0.8847(3)	0.8068(3)	0.4608(2)	0.0371(5)
C(10)	0.8560(3)	0.7579(3)	0.5965(2)	0.0312(4)
C(11)	0.7627(2)	0.5320(2)	0.5788(2)	0.0251(4)
C(12)	0.6962(2)	0.3891(2)	0.6427(2)	0.0254(4)
C(13)	0.3550(2)	0.7074(2)	0.8762(2)	0.0216(3)
C(14)	0.2106(3)	0.8660(2)	0.8561(2)	0.0304(4)
C(15)	0.0492(3)	0.8790(2)	0.8936(2)	0.0279(4)
C(16)	− 0.0329(2)	0.7396(2)	0.9640(2)	0.0234(4)
O(1)	0.4977(2)	0.7308(2)	0.8372(1)	0.0285(3)
O(2)	0.3281(2)	0.5644(2)	0.9289(1)	0.0257(3)
O(3)	0.0116(2)	0.6528(2)	1.0765(1)	0.0316(3)
O(4)	− 0.1508(2)	0.7318(2)	0.9007(2)	0.0356(3)

TABLE III Selected interatomic distances (Å) and bond angles (°) for the complex

Mn–O(1)	2.174(1)	C(4)–C(5)	1.438(3)	C(11)–C(12)	1.439(3)
Mn–O(2)$^{\#2}$	2.112(1)	C(4)–C(12)	1.410(3)	C(12)–N(1)	1.356(2)
Mn–O(3)$^{\#2}$	2.207(1)	C(5)–C(6)	1.337(4)	C(13)–O(1)	1.257(2)
Mn–O(4)$^{\#3}$	2.120(1)	C(6)–C(7)	1.431(3)	C(13)–O(2)	1.257(2)
Mn–N(1)	2.331(2)	C(7)–C(8)	1.403(3)	C(13)–C(14)	1.492(3)
Mn–N(2)	2.300(2)	C(7)–C(11)	1.410(3)	C(14)–C(15)	1.329(3)
C(1)–N(1)	1.326(3)	C(8)–C(9)	1.365(3)	C(15)–C(16)	1.509(3)
C(1)–C(2)	1.398(3)	C(9)–C(10)	1.401(3)	C(16)–O(3)	1.245(2)
C(2)–C(3)	1.363(3)	C(10)–N(2)	1.324(3)	C(16)–O(4)	1.253(2)
C(3)–C(4)	1.398(3)	C(11)–N(2)	1.357(2)	Mn ··· Mn$^{\#2}$	4.665(1)
O(1)–Mn–O(2)$^{\#2}$	93.26(5)	O(2)$^{\#2}$–Mn–O(4)$^{\#3}$	101.63(5)	O(4)$^{\#3}$–Mn–N(1)	159.24(6)
O(1)–Mn–O(3)$^{\#2}$	177.92(5)	O(2)$^{\#2}$–Mn–N(1)	98.83(5)	O(4)$^{\#3}$–Mn–N(2)	87.89(6)
O(1)–Mn–O(4)$^{\#3}$	89.61(5)	O(2)$^{\#2}$–Mn–N(2)	170.45(5)	N(1)–Mn–N(2)	71.70(6)
O(1)–Mn–N(1)	92.68(5)	O(3)$^{\#2}$–Mn–O(4)$^{\#3}$	89.99(6)	O(1)–C(13)–O(2)	125.1(2)
O(1)–Mn–N(2)	86.09(5)	O(3)$^{\#2}$–Mn–N(1)	88.42(5)	O(3)–C(16)–O(4)	126.6(2)
O(2)$^{\#2}$–Mn–O(3)$^{\#2}$	84.83(5)	O(3)$^{\#2}$–Mn–N(2)	95.93(5)		

Symmetry codes: #1: $-1+x, y, z$; #2: $1-x, 1-y, 2-z$; #3: $1+x, y, z$.

RESULTS AND DISCUSSION

Repeated synthetic experiments showed that reaction of freshly-precipitated $MnCO_3$, maleic acid and phenanthroline in CH_3OH/H_2O at 50°C afforded the title complex. However, reaction at room temperature favored formation of $\{[Mn(\mu\text{-maleate})(phen)(H_2O)_2]\cdot 2H_2O\}_n$ [14].

The crystal structure determination reveals that the title complex consists of 1D $^1_\infty[Mn(phen)(C_4H_2O_4)_{3/3}]$ chains. As illustrated in Fig. 1, Mn atoms are each

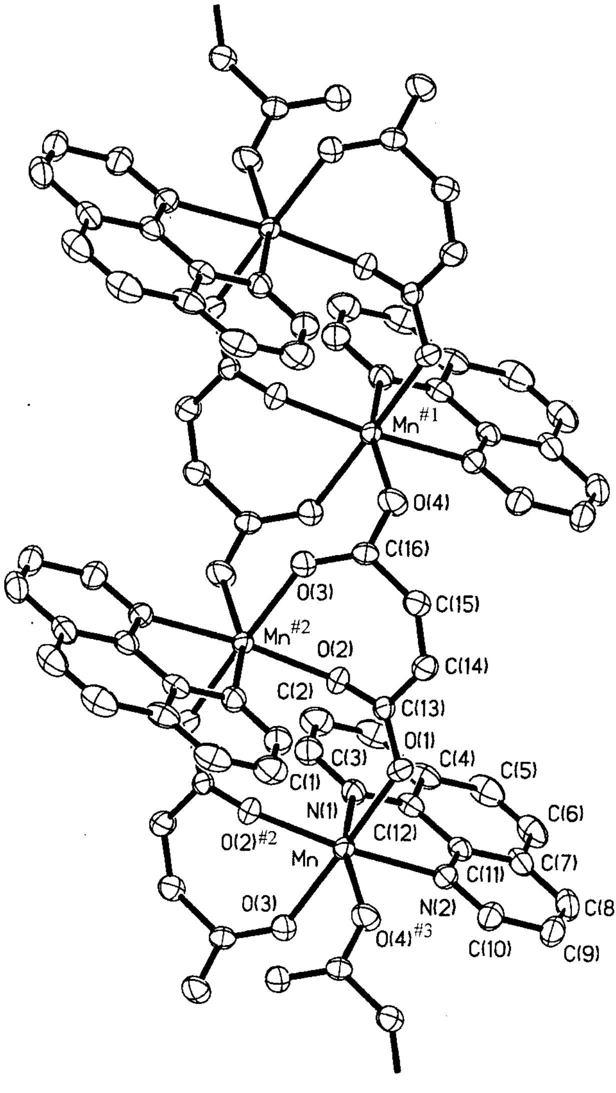

FIGURE 1 ORTEP view of a selected fragment of the 1D ${}^{1}_{\infty}[\mathrm{Mn(phen)}(C_4H_2O_4)_{3/3}]$ chain with the atom numbering scheme. Thermal ellipsoids are drawn at the 45% probability level.

octahedrally coordinated by two N atoms of one phen ligand and four O atoms of three maleato ligands. The maleate chelates one Mn atom to form a seven membered ring while two carboxylate groups of different maleato ligands bridge two Mn atoms to form an eight-membered ring. As a result, a 1D ${}^{1}_{\infty}[\mathrm{Mn(phen)}(C_4H_2O_4)_{3/3}]$ chains extending along the [1 0 0] direction are generated in a sequence of seven- and eight-membered rings. The chelating phen ligands on both sides of the chains extend outwards. As usual, Mn–N distances of 2.300 and 2.331 Å are considerably longer than Mn–O bond distances ranging from 2.112 to 2.207 Å (Table II). Two *trans* N–Mn–O angles exhibit more significant deviation from linearity than the axial O(1)–Mn–O(3)$^{\#2}$ angle of 177.9(1)°, and the *cis* bond angles about the central Mn atom

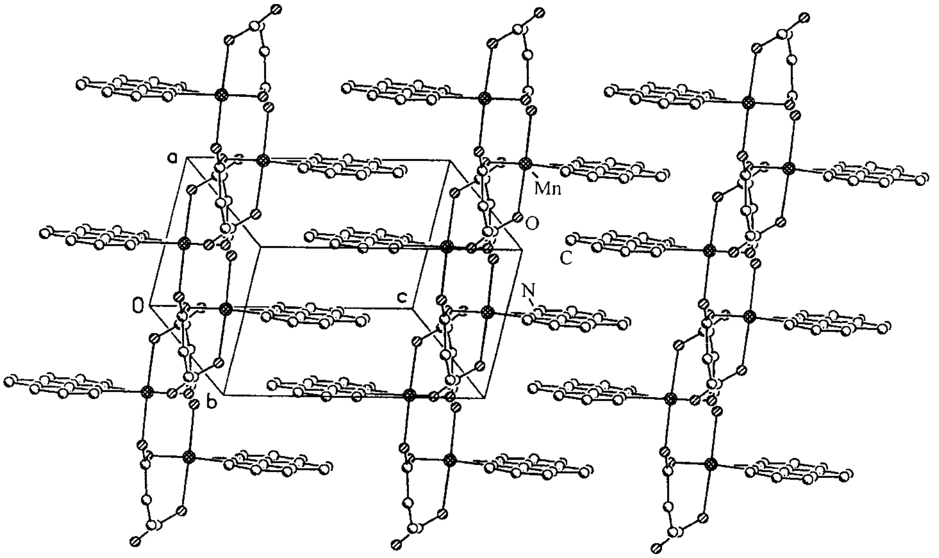

FIGURE 2 Supramolecular assembly of the 1D $^{1}_{\infty}[Mn(phen)(C_4H_2O_4)_{3/3}]$ chains into 2D layers via π–π stacking interactions.

substantially deviate from 90°, showing strongly distorted octahedral coordination. All C atoms of the maleato ligand lie in a common plane, from which both terminal carboxylate groups are twisted about the terminal C–C bonds by 3.0° and 60.1°, respectively. Obviously, the coordination mode of the maleato ligands is somewhat similar to those reported for $\{[Mn(maleate)(4,4'\text{-bipy})]\cdot 0.5H_2O$ [15], but significantly different from those observed in $\{[M(\mu\text{-maleate})(phen)(H_2O)_2]\cdot 2H_2O\}_n$ with M = Mn [14], Co [16], where the maleate groups serve as bis-monodentate ligands to link metal atoms into polymeric chains. The phen ligands show nearly perfect coplanarity, and the neighboring 1D chains approach each other so that each phen of one chain protrudes into the void space between two phen planes of the adjacent chains. Interplanar spacings are alternatively 3.23 and 3.36 Å, indicating strong π–π stacking interactions [20]. Such interdigitation of the phen ligands assembles neigboring chains into 2D layers parallel to (010) (Fig. 2). Within the resulting 2D layer, the closest intra- and inter-chain Mn···Mn distances are 4.665(1), and 8.755(1) Å, respectively.

Magnetic Properties

The magnetic behavior of the title complex is shown in Fig. 3 in the form of χ_m, χ_m^{-1} *vs* T plots, χ_m and χ_m^{-1} being the molar susceptibility and reciprocal molar susceptibility per Mn(II) ion, respectively, and T the temperature. The complex becomes antiferromagnetic at low temperatures with a Néel temperature of 7 K (Fig. 3). Between 30 and 300 K its magnetic behavior obeys the Curie–Weiss law $\chi_m(T+9.82) = 4.140\,\text{cm}^3\,\text{mol}^{-1}\,\text{K}$ with the effective magnetic moment $\mu_{\text{eff}} = 5.65$ BM at room temperature. The observed magnetic moment is close to the spin-only value (5.92 BM) for an octahedrally coordinated, high-spin Mn(II) compound [21]. Obviously, the antiferromagnetic property results from superexchange between the Mn atoms through the bridging carboxylate groups of the maleato ligands.

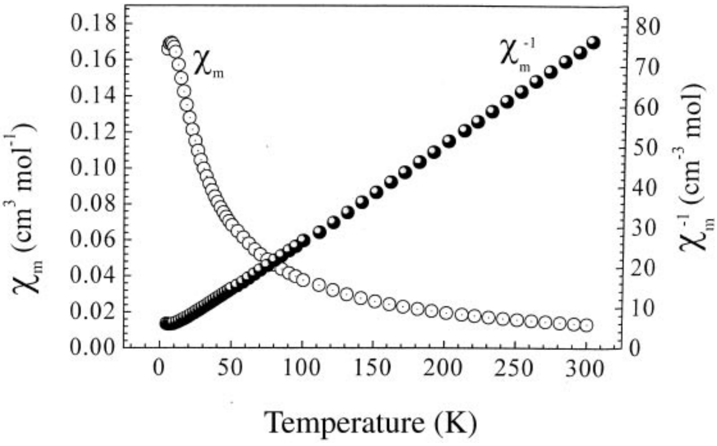

FIGURE 3 Temperature dependence of molar susceptibilities χ_m (cm^3 mol^{-1}) and inverse molar susceptibilities χ_m^{-1}(cm^{-3} mol) for Mn(phen)($C_4H_2O_4$).

Acknowledgments

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