A Two-Dimensional Manganese(II) Carboxylato Polymer. Structure, Magnetism, and EPR Study

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The synthesis, crystal structure, and properties of $[Mn^{II}(MCPA)_2(H_2O)_2]_n$ (MCPA = 2-methyl-4-chlorophenoxyacetic acid), **1**, a 2-D manganese carboxylato polymer is reported. The synthesis of **1** has been achieved via the reaction of MCPA with $MnCl_2{\cdot}2H_2O$ and $NaHCO_3$ in methanol. Crystal structure data: $[C_{18}H_{20}Cl_2O_8Mn]$; orthorhombic; space group *Pbca*; $a = 7.811(6)$ Å; $b = 34.67(3)$ Å; $c = 7.481(6)$ Å; $Z = 4$. The compound has a two-dimensional structure with Mn^{2+} atoms in an octahedral environment and mixed water/carboxylate coordination. The metal atoms are segregated in planes which are perpendicular to the *b* axis and are spaced 17.73 Å apart. Variable-temperature magnetic susceptibility measurements indicate the presence of antiferromagnetic behavior. The EPR spectra of polycrystalline samples at 4 K show that the intensity of the signal decreases significantly with decreasing temperature and below ∼4 K becomes EPR silent.

Introduction

The chemistry of manganese has received considerable attention in recent years because manganese is catalytically active in a variety of metalloenzymes.[1−3] Whereas considerable information is now available about the higher oxidation states of the polymanganese oxo centers through the study of model compounds, much less is known about the reduced 2+ state.

We have reported extensively on the preparation and characterization of a variety of mononuclear, binuclear, and trinuclear complexes with carboxylato−donor ligands in oxidation states Mn^{III} and mixed-valence $Mn^{II}Mn^{III}$ in order to understand the fundamental coordination, structural, and magnetochemistry of complexes potentially relevant to the active site of metalloenzymes.[4−6] In addition, a number of workers have also prepared binuclear, trinuclear, and multinuclear complexes in oxidation state 2+[7−27] or higher[28−45] containing carboxylato ligands. Manganese(II) carboxylate polymers are very rare,[12a,18a,20,22−25] and when it comes to 2-D polymers, only two examples have been reported in the literature.[26,27] Herbicidal compounds with carboxylato active groups interact with metal ions giving a variety of structural arrangements.[46,47]

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In this paper we report the crystal structure and magnetic properties of the two-dimensional (2-D) polymer $[\mathrm{Mn^{II}(MCPA)_2(H_2O)_2}]_n$ which represents only the third example of a layered polymeric $\mathrm{Mn^{2+}}$/carboxylate compound.

Experimental Section

The following abbreviations are used throughout the text: MCPA = 2-methyl-4-chlorophenoxyacetic acid, dpph = diphenylpicrylhydrazyl, dmf = dimethylformamide.

Materials. The chemicals for the synthesis of the compounds were used as purchased. $\mathrm{CH_3OH}$ was distilled from magnesium and was stored over 3 Å molecular sieves. MCPA and $\mathrm{MnCl_2{\cdot}4H_2O}$ were purchased from Aldrich Co. All chemicals and solvents were reagent grade.

Physical Measurements. Infrared spectra (400−4000 $\mathrm{cm^{-1}}$) were recorded on a Perkin-Elmer FT-IR 1650 spectrometer with samples prepared as KBr pellets. UV−vis spectra were recorded on a Shimadzu-160A dual-beam spectrophotometer. EPR spectra were recorded on a Bruker EPR 300 spectrometer equipped with a Varian variable-temperature controller. dpph was used as an external standard. Room-temperature magnetic measurements were carried out by Faraday's method using mercury tetrathiocyanatocobaltate(II) as a calibrant. C, H, and N elemental analysis were performed on a Perkin-Elmer 240B elemental analyzer; Mn was determined by atomic absorption spectroscopy on a Perkin-Elmer 1100B spectrophotometer. The variable-temperature magnetic measurements were carried out on a polycrystalline sample (30.0 mg) using a Quantum Design Squid susceptometer, and 60 points were collected in the range temperature 4.00−300 K. The applied magnetic field was 1000 G. The correction for the diamagnetism of the complex was estimated from Pascal constants; a value of $56 \times 10^{-6}\ \mathrm{cm^3\ mol^{-1}}$ was used for the temperature-independent paramagnetism (TIP) of the Mn ion. The magnetism of the sample was found to be field independent. Electric conductance measurements were carried out with a WTW Model LF 530 conductivity outfit and a type C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 °C with potassium chloride. All temperatures were controlled with an accuracy of 0.1 °C using a Haake thermoelectric circulating system.

Preparation of the Compound. Synthesis of Bis(aqua)bis[(2-methyl-4-chlorophenoxy)acetato]manganese(II) (1). MCPA (10.0 mmol, 2.00 g) was dissolved in $\mathrm{CH_3OH}$ (50 $\mathrm{cm^3}$), and 5.0 mmol of $\mathrm{MnCl_2{\cdot}2H_2O}$ (0.99 g) and 5.0 mmol (0.42 g) of $\mathrm{NaHCO_3}$ were added. The reaction mixture was stirred for 1 h and reduced in volume under vacuum. Crystals of $[\mathrm{Mn[C_6H_3(CH_3)Cl\text{-}OCH_2COO]_2(H_2O)_2}]_n$ (**1**) suitable for X-ray structure determination were deposited by slow evaporation in 1 week. Yield 60% (F_w = 490.20). Anal. Calcd for $\mathrm{C_{18}H_{20}Cl_2O_8Mn}$: C, 44.10; H, 4.10; Mn, 11.20. Found: C, 44.60; H, 4.20; Mn, 10.90. IR (KBr pellet, $\mathrm{cm^{-1}}$) ν(O−H) 3510 (vs); $\nu_\mathrm{as}(\mathrm{CO_2})$ 1580 (vs); $\nu_\mathrm{sym}(\mathrm{CO_2})$ 1415 (vs). UV−vis [$\lambda(\epsilon)$, dmf] 280 (2300). **1** is not an electrolyte in dmf solution.

X-ray Crystal Structure Determination. A pale-yellow prismatic crystal of **1** with approximate dimensions 0.08 × 0.12 × 0.50 mm was mounted in air. Diffraction measurements were made on a Crystal Logic[48] dual goniometer diffractometer using graphite-monochromated Mo radiation. Crystal data and parameters for data collection are reported in Table 1. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$. Intensity data were recorded using $\theta-2\theta$ scan to $2\theta(\max) = 48°$ with scan speed 1.5 deg/min and scan range 2.5 2θ deg plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections, showed <3.0% intensity fluctuation and no decay. Lorentz, polarization and ψ-scan absorption corrections were applied using Crystal Logic software.

Symmetry equivalent data of **1** were averaged with $R(\mathrm{int}) = 0.0533$, respectively to give 1594 independent reflections from a total of 3187 collected. The structure was solved by direct methods using the programs SHELXS-86[49] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93[50] using 1593 reflections and refining 173 parameters. All hydrogen atoms were located by difference maps

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Table 1. Crystallographic Data for $[Mn[C_6H_3(CH_3)Cl{-}OCH_2COO]_2(H_2O)_2]_n$ (**1**)

	1
F	$C_{18}H_{20}Cl_2O_8Mn$
a	7.811(6) Å
b	34.67(3) Å
c	7.481(6) Å
V	2026(3) $Å^3$
T	298 K
space group	*Pbca*
Z	4
Fw	490.20
λ	0.710 73
ρ_{obsd}	1.59 g cm^{-3}
ρ_{calcd}	1.607 g cm^{-3}
μ	0.927 mm^{-1}
R^a indices [1092 refs $I > 2\sigma(I)$]	$R_1 = 0.0409$, $wR_2 = 0.0910$

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P_2 = (\max(F_o^2, 0) + 2F_c^2)/3$, where $a = 0.0365$, $b = 1.1508$. $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

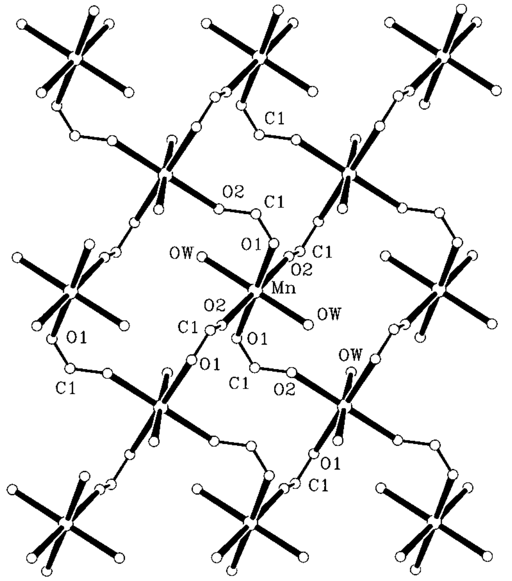


Figure 1. 2-D polymeric structure. For clarity, only the carboxylate groups of the MCPA ligands are drawn.

and their positions were refined isotropically. All non-hydrogen atoms were refined anisotropically. The final values for R_1, wR_2, and GOF, for observed data with $I > 2\sigma(I)$, are given in Table 1, for all data these are 0.0729, 0.1114, and 1.111, respectively. The maximum and minimum residual peaks in the final difference map were 0.349 and −0.324 e/$Å^3$. The largest shift/esd in the final cycle was 0.022.

Results and Discussion

Description of the Structure. The compound possesses a lamellar structure similar to that of $[Mn[C_6H_3OCH_2COO]_2(H_2O)_2]_n$,[27] which is infinitely extended along the *a*- and *c*-crystallographic directions. The Mn^{2+} centers are octahedral, and they are bridged by carboxylate groups forming the infinite sheets. The coordination sphere around Mn is centrosymmetric, consisting of two oxygens from water molecules and four oxygens from MCPA ligands. The coordination of MCPA ligands involves carboxylate oxygen atoms only, where each carboxylate group bridges two Mn atoms. This bridging arrangements generates the 2-D polymeric structure (Figure 1) in which the closest Mn···Mn separation is 5.40 Å. The layers stack along the *b* axis and are separated by van der Waals contacts. The Mn atoms within a layer are found in the (010) and in the (020) planes, which gives an interlayer separation of 17.73 Å (Figure 2).

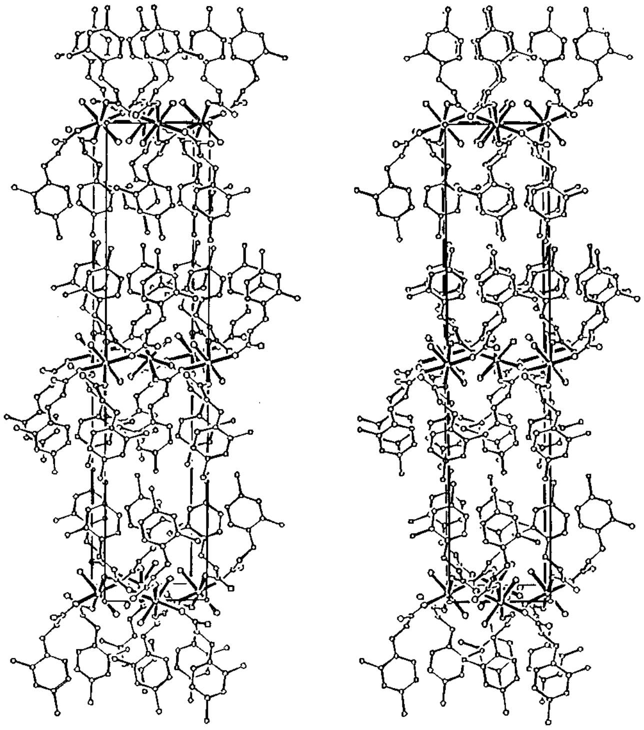


Figure 2. Stereoview packing diagram.

Table 2. Selected Bond Distances (Å) and Angles (deg) of **1**[a]

Bond Distances (Å)

Mn−O(1)	2.179(3)	Mn(1)−O_w	2.172(3)	C(1)-O(2)	1.260(4)
Mn−O(2)	2.183(3)	C(1)-O(1)	1.242(4)	Mn···Mn(1)′	5.40

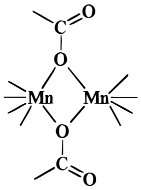
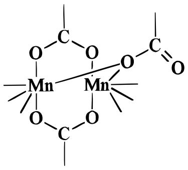
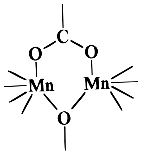
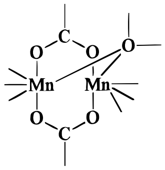
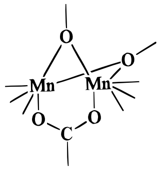
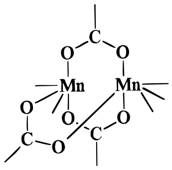
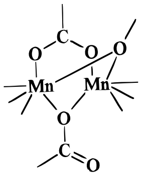
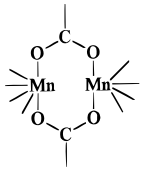
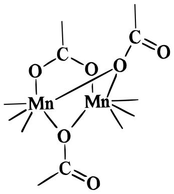
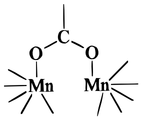
Angles (deg)

O_w−Mn−$(O_w)_1$	180.0	$O(1)_1$−Mn−$O(2)_2$	96.37(10)
$O(1)_1$−Mn−$(O_w)_1$	88.80(13)	O(1)−Mn−$O(2)_2$	83.63(10)
$O(1)_1$−Mn−O_w	91.20(13)	$O(2)_3$−Mn−$(O_w)_1$	90.22(12)
O(1)−Mn−O_w	88.80(13)	$O(2)_3$−Mn−O_w	89.78(12)
O(1)−Mn−$(O_w)_1$	91.20(13)	$O(1)_1$−Mn−$O(2)_3$	83.63(10)
$O(1)_1$−Mn−O(1)	180.0	O(1)−Mn−$O(2)_3$	96.37(10)
$O(2)_2$−Mn−$(O_w)_1$	89.78(12)	$O(2)_2$−Mn−$O(2)_3$	180.0
$O(2)_2$−Mn−O_w	90.22(12)		

[a] Symmetry code: $O(1)_1$, $-x + 2$, $-y + 1$, $-z$; $O(2)_2$, $-x + {}^3/_2$, $-y + 1$, $z - {}^1/_2$; $O(2)_3$, $x + {}^1/_2$, y, $-z + {}^1/_2$.

The intralayer Mn···Mn separation is ~0.2 Å longer than that found for the 2-D analog (Mn···Mn = 5.21 Å) but significantly longer than that found for Mn^{II} carboxylato-bridged compounds (Table 3). We may distinguish three distance areas for Mn^{II}···Mn^{II} separations: an area between 3.10 and 3.70 Å in which the coordination modes 1−7 may be included, the range between 4.00 and 4.30 Å with examples of the coordination modes 8 and 9, and this between 5.30 and 5.70 Å with unibridged mode 10. The coordination polyhedron is slightly removed from idealized octahedral symmetry, as is obvious from the bond distances and angles about the coordination sphere (Table 2). A view of the 6-fold coordination octahedron and the atom numbering scheme is presented in Figure 3. The Mn−O_w = 2.172(3) Å distance shows a slight difference to an analogous 2-D polymer[27] [Mn−O_w = 2.216(2) Å] but lies in the range found for a number of manganese(II) polymeric complexes involving coordinated water.[8,27] The presence of water coordinated to the Mn^{2+} atoms provides the opportunity for controlled selectivity dehydration of the compound to give rise to activated Mn atoms in the layers through coordination unsaturation. The Mn−O(carboxylato) [Mn−O(1) = 2.179(3) Å, Mn(1)−O(2) = 2.183(3) Å] distances are very similar while the C−O(carbonyl) [C(1)−O(1) = 1.242(4) Å] and C−O(hydroxyl) [C(1)−O(2) = 1.260(4) Å] distances of the herbicide

Table 3. $\mathrm{Mn^{II}\cdots Mn^{II}}$ Separation with Various Coordination Modes of Carboxylato Bridges

	coordination mode	$\mathrm{Mn^{II}\cdots Mn^{II}}$ sep (Å)		coordination mode	$\mathrm{Mn^{II}\cdots Mn^{II}}$ sep (Å)
1		3.53[a]	6		3.387,[d] 3.614,[e] 3.635,[f] 3.700,[f] 3.658,[f] 3.560,[f] 3.716,[f] 3.691,[f] 3.370,[f] 3.600,[g] 3.753[h]
2		3.760[w]	7		3.29,[i] 3.50,[j] 3.351,[k] 3.595,[v] 3.621,[v] 3.589[u]
3		3.150,[w] 3.163[w]	8		4.034,[l] 4.558,[m] 4.444[n]
4		3.35[b]	9		4.145,[o] 4.643,[p] 4.849,[t] 4.557[t]
5		3.289[c]	10		5.40,[q] 5.45,[s] 5.598,[r] 5.7,[g] 6.4[g]

[a] $\mathrm{Mn[C_6H_2Cl_3\text{-}OCH_2COO]_2(H_2O)_4]}$.[8a] [b] $\mathrm{Mn(C_2H_5COO)_2(H_2O)_2}$.[23] [c] $\mathrm{Mn_3(CH_3COO)_2(bpc)_2(py)_4(H_2O)_2}$, ($\mathrm{H_2bpc}$ = 2,2′-bipyridyl-3,3′-dicarboxylic acid).[13] [d] $\mathrm{Mn_3(CH_3COO)_6(phen)_2}$, (phen = 1,10-phenanthroline).[19] [e] $\mathrm{Mn_3(CH_3COO)_6(bipy)_2}$, (bipy = 2,2′-bipyridine).[17] [f] $\mathrm{Mn_3(CH_3COO)_6(BIPhMe)_2}$, (BIPhMe = 2,2′-bis(1-methylimidazolyl)phenylmethoxymethane).[19] [g] $\mathrm{Mn(CH_3COO)_2\cdot 4H_2O}$.[26] [h] $\mathrm{Mn\{HB(3,5\text{-}Pr^i_2pz)_3\}(\mu\text{-}OBz)_3Mn(3,5\text{-}Pr^i_2pzH)_2}$, ($\mathrm{HB(3,5\text{-}Pr^i_2pz)_3}$ = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate, 3,5-$\mathrm{Pr^i_2pzH}$ = 3,5-diisopropylpyrazole, Obz = benzoate.[16] [i] $\mathrm{K_2\{Mn(H_2O)_2\text{-}[Mn_3O(HCOO)_9]_2\}}$[7b] [j] $\mathrm{[L_2Mn_2(\mu\text{-}OH)(\mu\text{-}CH_3COO)_2]ClO_4}$ (L = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane).[15] [k] $\mathrm{[L_2Mn_2(\mu\text{-}OH)(\mu\text{-}MeCOO)_2]\ PF_6}$ (L = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane).[15b] [l] $\mathrm{[L_2Mn(\mu\text{-}CH_3COO)_3]\ [BPh_4]}$ (L = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane).[15a] [m] $\mathrm{[Mn\{(CH_3)_3NCH_2COO\}_3]_n\cdot nMnCl_4}$.[18a] [n] $\mathrm{Mn_3(CF_3COO)_6(benz)_6}$ (benz = benzonitrile)[13a] [o] $\mathrm{[Mn(tpa)(\mu\text{-}MeCOO)]_2\ (TCNQ)_2}$ (tpa = tris(2-pyridylmethyl)amine, TCNQ = tetracyanoquinodimethane).[21] [p] $\mathrm{[Mn_2(bipy)_4(ta)](ClO_4)_2}$ (ta = terephthalate, bipy = 2,2′-bipyridine).[20] [q] $\mathrm{[Mn[C_6H_3(CH_3)Cl\text{-}OCH_2COO]_2(H_2O)_2]_n}$, present work. [r] $\mathrm{[\{Mn(bipy)_2(H_2O)\}_2\ \{(CH_3)_3NCH_2COO\}](ClO_4)_4\cdot 2H_2O}$.[18b] [s] $\mathrm{[Mn(C_4H_4O_5)(H_2O)]_n\cdot H_2O}$.[25] [t] $\mathrm{Mn_2(XDK)(NO_3)\text{-}(CH_3OH)_4(H_2O)}$ and $\mathrm{Mn_2(XDK)(bpy)_2(NO_3)(H_2O)}$, $\mathrm{H_2XDK}$ = *m*-xylenediaminebis(Kemp's triacid imide).[19b] [u] $\mathrm{Mn_2(LO)(\mu\text{-}OAc)_2(ClO_4)}$, LOH = 2,6-bis[[[2-(2-pyridyl)ethyl]amino]methyl]phenol.[14] [v] $\mathrm{\{Mn_2(H_2O)(piv)_4(Mepy)_2]}$ and $\mathrm{Mn_2(H_2O)(OAc)_4(tmeda)_2}$.[19c] [w] $\mathrm{Mn_3(py)_5(OAc)_3(\mu_3\text{-}OH)(cat)}$.[10]

ligand show an unsymmetrical coordination mode, in contrast to the analogous 2-D polymer in which the two distances are identical 1.250 Å.[27]

The herbicide ligands have a *syn*−*anti* arrangement around the manganese(II) atom with a dihedral angle of 73.04° for the *cis*-carboxylato planes. The phenyl plane is almost perpendicular to the carboxylato plane [C(1)−O(1)−O(2)] resulting in a dihedral angle of 89° while to the plane [C(2)−C(1)−O(1)−O(2)], which includes the carboxylato group the dihedral angle, is 86.8°. The interlayer Mn···Mn separation is 17.73 Å without any H-bond interaction.

EPR Study. The EPR behavior of **1** is consistent with long-range order in a two-dimensional Heisenberg antiferromagnet. The temperature dependence of the spectra at three selected temperatures is shown in Figure 4. More specifically, the three spectra at 4, 18, and 58 K represent three important extremes in the behavior of **1**. The intensity of the signal decreases significantly at 4 K, a temperature very close to the temperature where the magnetic ordering occurs and where the sample becomes EPR silent. The temperature dependence of the intensity of the signal is shown in Figure 5. The intensity of the signal is very close to zero at the lowest temperature, increases to a maximum at ∼18 K, and then decreases with increasing temperature. The intensity of the signal was calculated by integration over the magnetic field range 2400−4200 G. The importance of the temperature dependence of the line width in the study of one-, two-, and three-dimensional systems as well as 0-D complexes has been[51] confirmed. In the case of 2-D antiferromagnets, the line width increases dramatically when the temperature reaches the T_{Neel} point.[52−54] An explicit study of the temperature dependence of the line width at the temperature range 4−60 K is shown in Figure 6. At 4 K the line width is 560 G, which is lower than the value found for other 2-D antiferromagnets,[52,53] almost 3500 G for $\mathrm{K_2MnF_4}$ and $\mathrm{Rb_2MnF_4}$, but in accordance with the small

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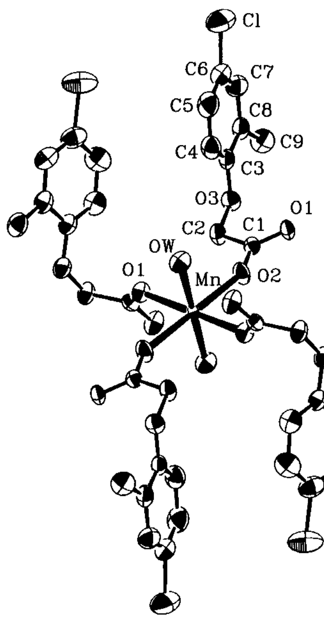

Figure 3. ORTEP view of **1** with 50% thermal ellipsoids showing the atom labeling scheme.

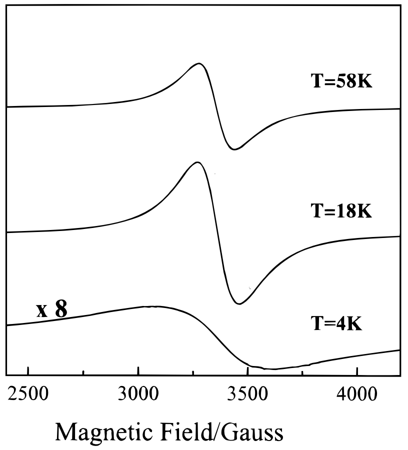

Figure 4. Powder ESR spectra of **1** at various temperatures.

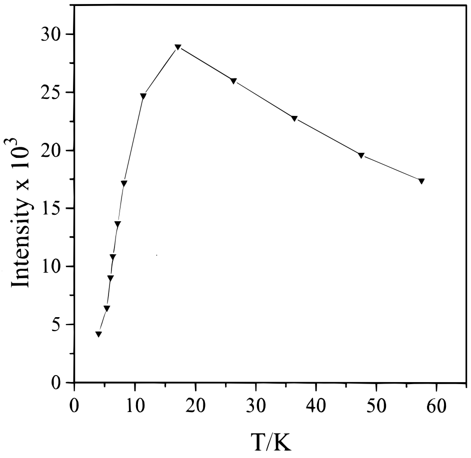

Figure 5. Temperature dependence of the intensity of the signal $g = 2$ over the field range 2000−4500 G for **1**.

antiferromagnetic interaction due to the large Mn···Mn separation and the low T_{Neel} value. A quantitative view of the increase of the line width is represented also in Figure 4 where the spectrum at 4 K becomes considerably broader than the other two. The isotropic signal is centered around $g = 2$ with small temperature variations.

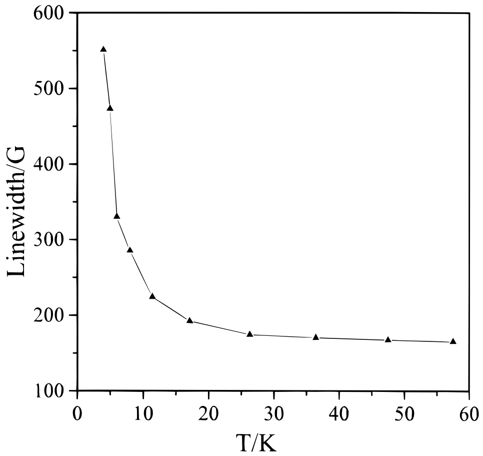

Figure 6. Temperature dependence of the line width ΔH for the **1**.

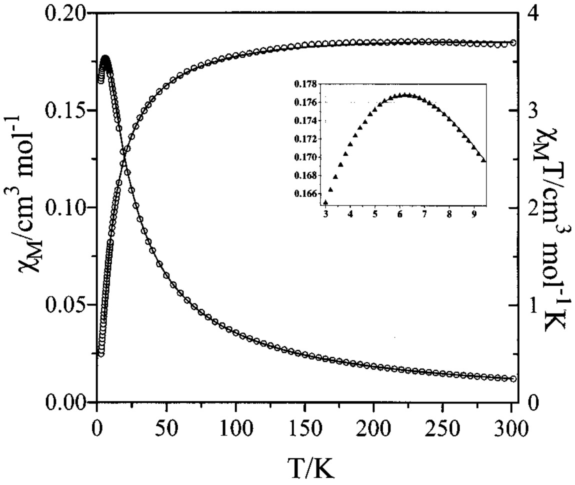

Figure 7. Magnetic susceptibility of **1** plotted as χ_M versus T (left axis) and $\chi_M T$ versus T (right axis) with the fit to eq 1.1(solid line).

Magnetic Studies. Variable-temperature solid-state magnetic measurements were performed on powdered samples in the range 3−300 K at various magnetic fields. The susceptibility increases as the temperature decreases, reaching a maximum at $T_{max} = 6.2$ K with $\chi_M = 0.177$ cm^3 mol^{-1}, and then slowly decreases to a value of $\chi_M = 0.165$ cm^3 mol^{-1} at 3 K (Figure 7). The value of $\chi_M T$ at room temperature is 3.7 cm^3 mol^{-1} K ($\mu_{eff} = 5.43\ \mu_B$), close to the spin-only value for the Mn^{II} ion ($\mu_{eff} = 5.91\ \mu_B$), and decreases to the value of 0.49 cm^3 mol^{-1} K at 3 K ($\mu_{eff} = 1.99\ \mu_B$). The decrease of the $\chi_M T$ is indicative of a small antiferromagnetic interaction, and the behavior at the low-temperature region is consistent with that of a two-dimensional Heisenberg antiferromagnet. The isotropic behavior of the system is maintained to 3 K, below the maximum of susceptibility, and the T_{Neel} is close to that temperature. We anticipate the anisotropy of the system—the parallel susceptibility tends to zero whereas the perpendicular susceptibility increases slightly—to appear below 3 K according to the EPR findings. According to Lines[55] the high-temperature susceptibility data have been fit to the expansion series,

$$\frac{Ng^2\mu^2_B}{2\chi_M|J|} = 3\theta + \sum_{n=1}^{6}\frac{C_n}{\theta^{n-1}} \qquad (1)$$

where $\theta = kT/2|J|S(S + 1)$; C_n are the coefficients given in ref

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(55) Lines, M. E. *J. Phys. Chem. Solids* **1970,** *31,* 101.

55.[56] All the other symbols have the usual meaning, for a $S = {}^5/_2$ antiferromagnetic layer. The validity of this expansion ceases[55] to be of much quantitative value below $kT \approx 1.8|J|S(S + 1)$. The correlation between the maximum T_{max} in the susceptibility data and the intraplanar exchange $|J|$ is

$$\frac{kT_{max}}{2|J|} = 1.12S(S + 1) + 0.10 \qquad (2)$$

and the value for J, obtained from this formula, is -0.24 cm^{-1}. So the limitation that the theory of Lines[55] enters is that the lower limit of the temperature must be ~5 K. The fitting procedure of the χ_M data as well as the $\chi_M T$ data to the temperature range 5−300 K gave the following set of parameters: $J = -0.30(1)$ cm^{-1}, $g = 1.90$ with a reliability factor $R = 4.9 \times 10^{-4}$, where the definition of the R is

$$\sum_n [(\chi_M T)_{calc} - (\chi_M T)_{exp}]^2$$

The agreement between the experimentally expected value of J and the value obtained from the fitting procedure is in line with our characterization of **1** as a 2-D Heisenberg antiferromagnet.

The structural and magnetic studies of polynuclear Mn^{II} complexes containing double and triple carboxylato bridges[7−28] show a weak antiferromagnetic interaction in the range of -0.9 to -1.7 cm^{-1} for double-bridged complexes[20,21] and -3.5 to -4.4 cm^{-1} for the triple-bridged compounds.[15,17,19] The case of a single carboxylato bridge is rare, and only for a dinuclear Mn^{II} complex of the formula $[\{Mn(bipy)_2(H_2O)\}_2\{(CH_3)_3NCH_2CO_2\}][ClO_4]_4$ has the magnetic behavior been reported.[18b] The magnetic behavior of the latter is weakly antiferromagnetic with $J = -0.193$ cm^{-1}, very close to the value of 1($J = -0.30(1)$ cm^{-1}). The Mn···Mn separation in $[\{Mn(bipy)_2(H_2O)\}_2\{(CH_3)_3NCH_2CO_2\}][ClO_4]_4$ is 5.598 Å similar to the intralayer separation of the manganese ions in **1** (Mn···Mn = 5.4 Å). The decrease of the antiferromagnetic interaction is probably related to the decrease of the number of the carboxylato bridges between the two paramagnetic centers. The large interlayer Mn···Mn separation of 17.73 Å for **1** makes the interaction through layers negligible at high temperatures, giving a good example of a local $S = {}^5/_2$ two-dimensional magnetic system. A recent report[54] of a 2-D Heisenberg antiferromagnetic Mn^{II} polymer with azide bridges and a coordination sphere consisting only of nitrogen atoms also shows an antiferromagnetic behavior with $J = -3.83$ cm^{-1} and $T_{max} = 51$ K. This system has a characteristic plot with T_c around 35 K, at which temperature it becomes anisotropic and EPR silent (28 K). The relatively strong coupling of this compound has been attributed to the important role of the t_{2g} orbitals of the manganese in the magnetic interaction.[54]

Conclusion

While Mn^{II} polymers have been reported previously, some very interesting features are presented in this report. **1** is the third example of a structurally characterized 2-D Mn^{II}−carboxylato compound. For the first time an EPR study is reported of a 2-D Mn^{II}−carboxylato polymer at various temperatures in which the intensity of the signal decreases significantly at 4 K, a temperature very close to the temperature where magnetic ordering occurs and where the sample becomes EPR silent. Finally, the magnetic study has shown that the agreement between the experimentally expected value of J and the value obtained from the fitting procedure is in line with the characterization of **1** as a 2-D Heisenberg antiferromagnet.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available. Access and/or ordering information is given on any current masthead page.

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(56) The general Hamiltonian that describes such systems is $H = -2J\sum S_i S_j$, so following Lines, various magnetic studies of 2-D systems modified the C_n coefficients of high-temperature series expansion in order to take care of this change (2J instead of J).[57−59]

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