Synthesis, Structure and Magnetic Properties of a Singly Carboxylate-bridged Dinuclear Manganese(II) Complex†

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A novel dinuclear manganese(II) complex bridged by a single carboxylate ligand $[\{Mn(bipy)_2(H_2O)\}_2(Me_3NCH_2CO_2)][ClO_4]_4\cdot2H_2O$ (bipy = 2,2′-bipyridine) has been prepared and structurally characterized by X-ray crystallography. It crystallizes in the monoclinic space group $C2$, with a = 16.321(5), b = 13.354(5), c = 13.298(2) Å, β = 96.55(2)°. Refinement converged to R = 0.066 for 1975 observed reflections with $I \geqslant 2\sigma(I)$. The crystal structure comprises a dinuclear cation, perchlorate anions and lattice water molecules. The pair of metal ions separated at 5.67 Å in the cation is bridged by a single *syn-anti* carboxylate ligand. Each metal ion is co-ordinated in a distorted octahedral N_4O_2 geometry by two chelate bipy ligands [Mn–N 2.238(8)–2.257(7) Å], one aqua ligand [2.173(7) Å] and one μ-carboxylate oxygen atom [Mn–O = 2.081(10), 2.193(10) Å]. The powder EPR spectrum at 77 K shows a broad absorption at g = 1.970. The temperature-dependent magnetic susceptibility data (4.4–95.0 K) were fitted based on $H = -2JS_1\cdot S_2$, yielding the intramolecular coupling constant J value of -0.193 cm^{-1}.

There has been considerable interest in co-ordination chemistry of manganese complexes with carboxylate ligands, due to the fact that polynuclear metal carboxylates are good candidates for the investigation of exchange-coupling interactions between adjacent metal ions,[1,2] as well as that there is an increased recognition of the metal's role in biological systems.[3–6] Dinuclear manganese(II) complexes are of special interest, since such systems are known to exist at the active centres of some manganese-containing enzymes. Recently dinuclear units with one to three carboxylate bridges were suggested to be plausible structures of the dinuclear sites in manganese-containing enzymes.[7,8] Some dinuclear manganese(II) complexes containing double and triple carboxylate bridges have been structurally established.[1,9–16] In contrast, dinuclear manganese complexes bridged by a single carboxylate bridge are rare, although a dinuclear manganese(II) complex consolidated by a macrocyclic Schiff base and a *syn-anti* acetate bridge as well as a manganese(III) complex bridged only by a single *syn-anti* carboxylate group have recently been reported.[17,18]

Betaine ($Me_3N^+CH_2CO_2^-$) and its derivatives are structural analogues of monocarboxylate anions. The charge neutrality of betaines can be utilized to prepare metal carboxylate complexes of different metal–carboxylate molar ratios.[19–23] Among them, two polymeric manganese(II) complexes with double and triple carboxylate bridges of betaine and its derivatives have been reported.[22,23] Previously we have reported an unusual monomeric manganese(II) complex with the metal ion simultaneously co-ordinated by *o*-phenanthroline, nitrate and carboxylate ligands of betaine[21] In this paper we wish to report the synthesis, single-crystal structure and magnetic properties of a novel dinuclear manganese(II) complex with betaine and 2,2′-bipyridine (bipy) ligands, namely $[\{Mn(bipy)_2(H_2O)\}_2(Me_3NCH_2CO_2)][ClO_4]_4\cdot2H_2O$, where the two metal ions are bridged by a single μ-carboxylate group.

Experimental

Materials.—Betaine, 2,2′-bipyridine and $Mn(ClO_4)_2\cdot6H_2O$ were purchased from Aldrich and used without further purification. The C, H and N microanalyses were carried out with a Perkin-Elmer 250Q elemental analyser.

Preparation of $[\{Mn(bipy)_2(H_2O)\}_2(Me_3NCH_2CO_2)][ClO_4]_4\cdot2H_2O$ **1**.—To a warm aqueous solution (10 cm^3) containing $Me_3NCH_2CO_2$ (0.234 g, 2.0 mmol) was added $Mn(ClO_4)_2\cdot6H_2O$ (0.362 g, 1.0 mmol), and the mixture was stirred at 50–60 °C for 10 min. A 1 : 1 aqueous ethanol solution (5 cm^3) of bipy (0.156 g, 1.0 mmol) was then added with stirring. The resulting solution was allowed to stand in a desiccator charged with silica gel. After about a week, pale yellow block crystals were deposited, which are stable in air. The yield was *ca.* 40% (based on Mn) (Found: C, 40.8; H, 3.8; N, 9.3. Calc. for $C_{45}H_{51}Cl_4Mn_2N_9O_{22}$: C, 40.9; H, 3.9; N, 9.5%); IR data (cm^{-1}): 3437m, 3107m, 3078m, 2966w, 2924w, 1630s, 1595s, 1567m, 1475m, 1440vs, 1405w, 1342w, 1314w, 1243w, 1215w, 1096vs (br), 1011s, 927w, 906w, 814w, 765vs, 737m, 653m, 625s and 414w.

CAUTION. Metal perchlorate salts containing organic ligands are potentially explosive, and should be handled with great care.

Physical Measurements.—FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer at room temperature. Temperature-dependent magnetic susceptibility measurements were carried out on a microcrystalline sample in the temperature range 4.4–95 K and in an applied field of 200 G with a Hoxan SQUID magnetometer. The magnetic data were corrected for diamagnetism using Pascal's constants.[24] The X-band EPR spectra were recorded from a powdered sample on a Bruker ER-420 spectrometer operating at 77 K.

Crystallography.—The intensity data ($3 \leqslant 2\theta \leqslant 50°$) were collected at 21 °C on a Siemens R3m/V diffractometer using the ω-scan (2.9–14.6 ° min^{-1}) mode. The lattice parameters were derived from 22 reflections in the range $15 \leqslant 2\theta \leqslant 25°$. The reflection data were corrected for Lorentz–polarization effects and absorption based on ψ-scan data.[25] Structure solution and

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, issue 1, pp. xxv–xxx.

Non-SI units employed: G = 10^{-4} T, $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

full-matrix least-squares refinement were performed with the SHELXTL-PC program package.[26] The non-hydrogen atoms were refined anisotropically, except the two-fold orientationally disordered alkyl carbon atoms and oxygen atoms of the betaine ligand, and oxygen atoms of two perchlorate anions. The interatomic distance restraints are Cl–O 1.41 ± 0.01 Å and O ··· O 2.35 ± 0.01 Å for perchlorate anions, and C–N 1.51 ± 0.01 Å and C ··· C 2.43 ± 0.01 Å for the ammonium group of betaine; the disordered atoms were assigned site occupancy factors of 0.5 and refined isotropically.

All the hydrogen atoms of the organic ligands were generated geometrically (C–H 0.96 Å), assigned isotropic temperature factors and included in the structure-factor calculations. Hydrogen atoms of the water molecules have not been located from the difference maps. The absolute configuration was determined using Rogers' η test;[27] the η value was 1.16(10). Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[28] The important crystal parameters and final discrepancy indices at the conclusion of refinements are summarized in Table 1, the atomic coordinates for the non-hydrogen atoms and selected interatomic distances and bond angles in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises non-hydrogen and hydrogen atomic coordinates, thermal parameters and the remaining bond lengths and angles.

Table 1 Crystallographic data for **1**

Formula	$C_{45}H_{51}Cl_4Mn_2N_9O_{22}$
M	1321.64
Crystal system	Monoclinic
Space group	*C*2
a/Å	16.321(5)
b/Å	13.354(5)
c/Å	13.298(2)
β/°	96.55(2)
Z	2
D_c/g cm^{-3}	1.515
Crystal size/mm	0.40 × 0.40 × 0.42
μ(Mo-Kα)/cm^{-1}	0.71073
No. of collected data	2888
No. of unique data	2763
No. of observed data[a] (*n*)	1975
No. of refined parameters (*p*)	360
$R\ [=\Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\Sigma\lvert F_o\rvert]$	0.0657
$R'\ \{=[\Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.0837
S[b]	1.82

[a] $I \geqslant 2.0\sigma(I)$. [b] $S = [\Sigma(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)^2/(n - p)]^{\frac{1}{2}}$.

Results and Discussion

Crystal Structure of Complex 1.—The crystal structure of complex **1** comprises dinuclear cations, perchlorate anions and lattice water molecules. As illustrated in Fig. 1, a pair of manganese(II) atoms separated at a distance of 5.67 Å are bridged by a *single* carboxylate group into a dinuclear structure. The carboxylate group acts in the common coplanar *syn-anti* mode, in contrast to the non-planar *syn*-skew and skew-skew modes found in the two polymeric manganese(II) complexes containing betaine and its derivative.[22,23] It is noteworthy that a two-fold axis bisects the dinuclear cation through the N(1) and C(1) atoms, hence the remaining atoms of $Me_3NCH_2CO_2$ are disordered over two positions. Each manganese(II) atom in the cation is co-ordinated by four nitrogen atoms from a pair of chelate bipy ligands, one aqua ligand, and one carboxy oxygen atom of $Me_3NCH_2CO_2$ in a distorted octahedral geometry; the most distorted angles of the octahedron are from the chelate bipy ligands [72.3(3)–73.2(2)°]. The Mn–N bond lengths range from 2.238(8) to 2.266(8) Å, and the Mn–O(aqua) length is 2.173(7) Å. The Mn–O(carboxy) bonds are 2.081(10) and 2.193(10) Å, the shorter one being associated with longer carboxy C–O bond. Considering the different Mn–O(carboxy) bonds for each metal ion in the dinuclear cation, the remaining metal–ligand bond lengths should accordingly be different. That differences have not been observed is due to fact that the undisordered part is an average structure. Moreover, the different Mn–O(carboxy) bond lengths may be attributed to different basicities of *syn* and *anti* carboxy oxygen atoms, which result in different electron donating abilities.[29–31]

The intramolecular metal–metal separation is very similar to that [5.598(3) Å] found for the singly *syn-anti* carboxylate-bridged manganese(III) complex.[18] In contrast, the metal–metal

Table 2 Atomic coordinates (× 10^{-4})

Mn(1)	444(1)	0	3000(1)
O(1w)	1619(4)	−427(6)	3822(5)
N(11)	689(5)	−1150(6)	1847(5)
N(12)	−256(5)	−1382(6)	3345(5)
C(11)	1116(7)	−1001(9)	1062(7)
C(12)	1291(6)	−1723(9)	405(8)
C(13)	1010(7)	−2700(9)	613(8)
C(14)	587(6)	−2867(8)	1390(8)
C(15)	424(5)	−2104(8)	2007(7)
C(16)	−88(5)	−2206(7)	2859(6)
C(17)	−389(6)	−3136(8)	3133(8)
C(18)	−886(8)	−3137(9)	3919(9)
C(19)	−1066(7)	−2294(9)	4386(8)
C(20)	−754(6)	−1428(8)	4100(7)
N(21)	1007(5)	1347(6)	2303(5)
N(22)	−559(4)	745(7)	1952(5)
C(21)	1784(6)	1665(8)	2551(8)
C(22)	2028(7)	2615(10)	2315(9)
C(23)	1479(7)	3274(8)	1853(9)
C(24)	685(7)	2970(8)	1587(8)
C(25)	454(6)	2000(7)	1813(6)
C(26)	−375(5)	1619(7)	1520(6)
C(27)	−918(7)	2046(9)	804(7)
C(28)	−1693(7)	1664(10)	592(8)
C(29)	−1905(7)	762(10)	997(9)
C(30)	−1302(6)	322(8)	1731(7)
O(1)	172(7)	542(8)	4392(7)
O(2)	−182(7)	1100(9)	5854(6)
C(1)	0	1210(7)	5000
C(2)	−62(11)	2196(7)	4417(9)
N(1)	0	3155(6)	5000
C(3)	−39(10)	4062(10)	4339(10)
C(4)	611(8)	3321(12)	5903(9)
C(5)	−843(6)	3045(13)	5376(11)
O(2w)	2623(6)	−1770(8)	3107(7)
Cl(1)	−3607(2)	−138(2)	−1204(2)
O(01)	−3378(8)	880(6)	−1313(10)
O(02)	−3930(7)	−234(9)	−259(6)
O(03)	−4245(6)	−365(9)	−1968(7)
O(04)	−2929(6)	−754(9)	−1219(10)
O(01′)	−4417(5)	42(10)	−987(10)
O(02′)	−3634(9)	−580(10)	−2170(7)
O(03′)	−3172(7)	775(7)	−1204(10)
O(04′)	−3202(8)	−774(9)	−472(8)
Cl(2)	2201(2)	5605(3)	3911(2)
O(05)	2310(9)	4816(8)	3227(9)
O(06)	1681(8)	6332(9)	3437(10)
O(07)	1892(9)	5221(11)	4767(8)
O(08)	2990(6)	6035(10)	4200(11)
O(05′)	2583(7)	6088(9)	4766(7)
O(06′)	2223(9)	6192(9)	3037(7)
O(07′)	1357(5)	5435(10)	4035(10)
O(08′)	2580(8)	4674(7)	3780(10)

Table 3 Selected bond lengths (Å) and bond angles (°)

Mn(1)–O(1w)	2.173(7)	Mn(1)–N(11)	2.238(8)
Mn(1)–N(12)	2.245(8)	Mn(1)–N(21)	2.266(8)
Mn(1)–N(22)	2.257(7)	Mn(1)–O(1)	2.081(10)
O(2)–Mn(1a)	2.193(10)	O(1)–C(1)	1.257(12)
O(2)–C(1)	1.215(9)		
O(1w)–Mn(1)–N(11)	87.0(3)	O(1w)–Mn(1)–N(12)	97.0(3)
N(11)–Mn(1)–N(12)	73.2(3)	O(1w)–Mn(1)–N(21)	92.2(3)
N(11)–Mn(1)–N(21)	98.7(3)	N(12)–Mn(1)–N(21)	167.3(3)
O(1w)–Mn(1)–N(22)	164.4(3)	N(11)–Mn(1)–N(22)	93.0(3)
N(12)–Mn(1)–N(22)	97.9(3)	N(21)–Mn(1)–N(22)	72.3(3)
O(1w)–Mn(1)–O(1)	84.8(4)	N(11)–Mn(1)–O(1)	157.0(4)
N(12)–Mn(1)–O(1)	86.5(4)	N(21)–Mn(1)–O(1)	103.0(4)
N(22)–Mn(1)–O(1)	100.5(4)	O(1a)–Mn(1a)–O(2)	93.3(3)
N(11a)–Mn(1a)–O(2)	178.5(4)	N(12a)–Mn(1a)–O(2)	105.3(4)
N(21a)–Mn(1a)–O(2)	82.7(3)	N(22a)–Mn(1a)–O(2)	87.1(3)
Mn(1)–N(11)–C(11)	125.7(7)	Mn(1)–N(11)–C(15)	116.5(6)
Mn(1)–N(12)–C(16)	116.5(6)	Mn(1)–N(12)–C(20)	123.2(7)
Mn(1)–N(21)–C(21)	124.5(6)	Mn(1)–N(21)–C(25)	115.2(6)
Mn(1)–N(22)–C(26)	117.6(5)	Mn(1)–N(22)–C(30)	121.6(6)
Mn(1)–O(1)–C(1)	154.8(8)	C(1)–O(2)–Mn(1*a*)	144.9(9)
O(1)–C(1)–O(2)	127.7(10)		
Hydrogen bonding			
O(1w) ··· O(2w)	2.68	O(1w) ··· O(05′b)	2.96
O(2w) ··· O(02′c)	2.70	O(2w) ··· O(06′d)	2.80
Mn(1)–O(1w)–O(2w)	124	Mn(1)–O(1w) ··· O(05′b)	116
O(05′b) ··· O(1w) ··· O(2w)	116	O(1w) ··· O(2w) ··· O(02′c)	102
O(1w) ··· O(2w) ··· O(06′d)	116		

Symmetry codes: a $-x, y, 1-z$; b $0.5-x, -0.5+y, 1-z$; c $-x, y, -z$; d $x, -1+y, z$.

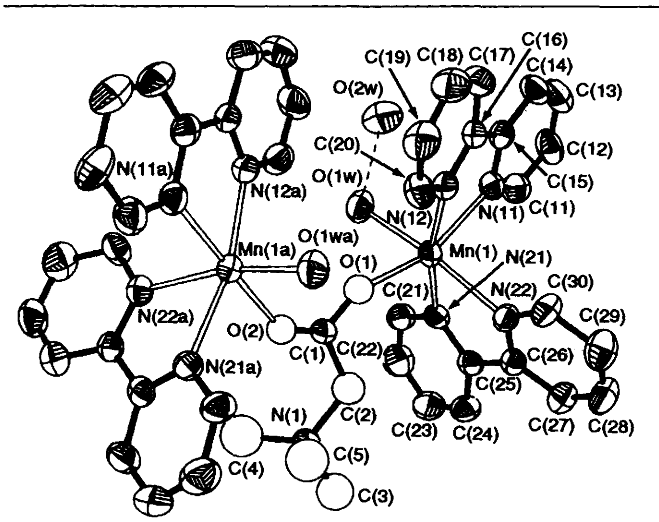

Fig. 1 ORTEP[32] drawing (30% probability) of the dinuclear $[\{Mn(bipy)_2(H_2O)\}_2(Me_3NCH_2CO_2)]^{4+}$ cation in complex **1**. For clarity, only one orientational position of the two-fold disordered atoms of betaine has been shown. Symmetry code: a $-x, y, 1-z$

distance is much longer than that (4.83 Å) found for a dinuclear manganese(II) complex comprising a macrocyclic Schiff-base ligand and a *syn-anti* acetate bridge,[17] indicating that the macrocyclic ligand plays an important role in shortening the metal–metal distance. In context of manganese(II) complexes composed of carboxylate groups as the only bridges, the intramolecular metal–metal distance is much longer than those of 4.03–4.44 Å and 4.15–4.79 Å, respectively, found for triply[13,16,33] and doubly[3,9–12] μ-carboxylate-bridged manganese(II) complexes. In the doubly bridged manganese(II) complexes, the μ-carboxylate groups act in a similar *syn-anti* co-ordination mode. This fact implies that the metal–metal separation in the (μ-carboxylate)$_n$ bridged systems may be controlled by the number of the carboxylate bridges.

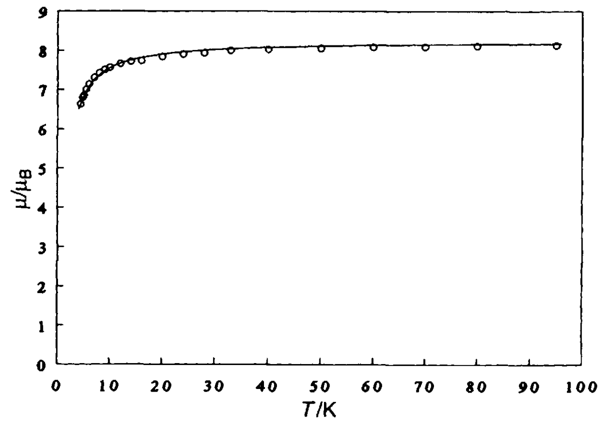

Fig. 2 Temperature-dependence of molar effective magnetic moment μ_{eff}. The solid line corresponds to the best theoretical fit using $J = -0.193$ cm^{-1} and $g = 1.970$ (see text)

Hydrogen bonding plays an important role in consolidating the solid-state structure. The aqua ligand forms two hydrogen bonds with the lattice water molecule (2.68 Å) and one perchlorate oxygen atom (2.96 Å), while the lattice water molecule forms two more hydrogen bonds with the perchlorate oxygen atoms (2.70–2.80 Å). Detailed parameters for the hydrogen bonding are presented in Table 3.

Physical Properties.—The EPR spectrum of complex **1** at 77 K exhibits a featureless broad absorption at $g = 1.970$ with a half-height width of *ca*. 500 G. The broadness of this EPR signal is characteristic of polynuclear manganese(II) complexes.[34]

Temperature-dependent magnetic susceptibility data for complex **1** have been measured from 95 K down to 4.4 K. The μ_{eff} values are plotted *versus* temperature in Fig. 2. At 95 K, the μ_{eff} value is 8.13 μ_B per molecule, which is slightly smaller than that (8.33 μ_B) expected for two uncoupled high-spin manganese(II) ions. The μ_{eff} values decrease slowly with decrease of temperature down to 7.83 μ_B at 20 K and then decrease more significantly and reach 6.62 μ_B at 4.4 K. This magnetic behaviour is typical of a very weak antiferromagnetic interaction, similar to that found for the singly *syn-anti* carboxylate-bridged manganese(III) complex.[18]

Since the shortest intermolecular metal–metal distance is 7.95 Å in complex **1**, much longer than the intramolecular metal–metal distance of 5.67 Å, it is reasonable to analyse the magnetic susceptibility data for the dinuclear cation precluding contribution of the intermolecular interaction.[10] Assuming isotropic exchange, the exchange Hamiltonian is $H = -2JS_1 \cdot S_2$ with $S_1 = S_2 = \frac{5}{2}$, and the magnetic susceptibility per cation is given by equation (1)[35] where N, g, β, k are

$$\chi_m T = \frac{2Ng^2\beta^2}{k} \times \left[\frac{55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28}}{11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}}\right] \quad (1)$$

Avogadro's constant, g factor, Bohr magneton, and Boltzman constant, respectively, $x = \exp(-J/kT)$ and J is the exchange coupling constant for the dinuclear cation. The least-squares fitting with a fixed g value of 1.970 obtained from the EPR spectrum gives $J = -0.193$ cm^{-1}. The discrepancy factor defined as $R = \{\Sigma[\chi_m T)_{obs} - (\chi_m T)_{calc}]^2/\Sigma(\chi_m T)_{obs}{}^2\}$ was 2.3×10^{-4}; the very good match is indicative of the fact that intermolecular magnetic interaction is negligible. The antiferromagnetic interaction in complex **1** is smaller than those found for the doubly[9,10] and triply[13,16] carboxylate-bridged dimeric manganese(II) complexes reported previously, where the J values are in range of -0.972 to -1.7 cm^{-1} and -3.5 to -4.4 cm^{-1}, respectively. Hence it may be concluded that the decrease of the number of the carboxylate bridges is at least in part responsible for the decrease of the extent of antiferromagnetic interaction between the pair of manganese(II) ions in dinuclear structures.

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