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LETTER

A linear polymeric manganese(II) complex bridged by skew–skew bridging carboxylato groups. Crystal structure of *catena*-tris(betaine)manganese(II) tetrachloromanganate(II), $[Mn(Me_3NCH_2COO)_3]_n \cdot nMnCl_4$*

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Introduction

As neutral structural analogues of carboxylato ligands, betaine and its derivatives have been found to exhibit a rich variety of bonding modes in their metal complexes [1–6]. Among them, the carboxylato group of betaine ligands exhibits the common bidentate *syn–syn* bridging mode (Fig. 1(a)) in $[Ag(pyBET)(NO_3)]_n$ [1], the *syn–anti* bridging mode (Fig. 1(b)) in $\{[Mn(pyBET)_2(H_2O)_2]Cl_2\}_n$ [2], the tridentate bridging mode in $[Ag_2(BET)_2(H_2O)_2(NO_3)_2]_n$ and $[Ag_2(pyBET)_2(ClO_4)_2]_n$ [3], the unsymmetrical chelating mode in $[Cu(BET)_4](NO_3)_2$ [4] and the unidentate mode in $[Zn(BET)_2Cl_2]H_2O$ [5] (BET = betaine, $Me_3N^+CH_2COO^-$; pyBET = pyridine betaine, $C_5H_5N^+CH_2COO^-$)†. In the only known example of a discrete trinuclear carboxylato complex, $[Cd_3(pyBET)_4Cl_6]$, pyBET acts as an unusual *syn*–skew bridging ligand [6] (Fig. 1(d)).

The crystal structures of manganese(II) carboxylates have been widely studied, and polymeric structures generally predominate [7]. One-dimensional polymers are however rare, two examples being $[Mn(CH_3CH_2COO)_2(H_2O)_2]_n$ [8] where the Mn(II) atoms are bridged by a *syn–syn* bidentate carboxylato group, a μ-1,1-*O* unidentate carboxylato group and an aqua ligand, and $\{[Mn(pyBET)_2(H_2O)_2]Cl_2\}_n$ [2] where the carboxylato group of pyBET serves as a *syn–anti* bridging ligand. We now report the characterization of a new anhydrous polymeric manganese(II) complex of betaine, $[Mn(BET)_3]_n \cdot nMnCl_4$ (**1**).

Experimental

Preparation

Complex **1** was prepared by dissolving $MnCl_2 \cdot 4H_2O$ (0.495 g, 2.5 mmol) and betaine (0.686 g, 5.0 mmol; Sigma) in water (1.5 ml). After one day, pale yellow prismatic crystals were obtained. The crystals are hygroscopic. Complex **1** shows the following IR absorption bands (cm^{-1}): ν(COO) at 1616vs and 1405s, δ(COO) at 718m. The separation (Δ) of 211 cm^{-1} between ν_{asym}(COO) and ν_{sym}(COO) in complex **1** is similar to that observed for $[Ag_2(BET)_2(H_2O)_2(NO_3)_2]_n$ [3] (with $\Delta = 221$ cm^{-1}) in which the carboxylato group of BET acts as a bridging ligand in the *syn–syn* mode. The Δ values are significantly smaller than that (236 cm^{-1}) of uncomplexed betaine [9] and hence indicative of the bridging mode of the carboxylato group [10].

Crystal data

$C_{15}H_{33}Cl_4N_4O_6Mn_2$, $M_r = 603.13$, trigonal, $a = 12.880(2)$, $c = 9.1173(8)$ Å, $V = 1309.9(3)$ Å^3, $Z = 2$, $T = 295$ K, $D_m = 1.515$ g cm^{-3} ($CCl_4/BrCH_2CH_2Br$), $D_c = 1.529$ g cm^{-3}, $F(000) = 620$, $\lambda = 0.71073$ Å, μ(Mo Kα) = 13.7 cm^{-1}, space group $P\bar{3}$ (No. 147).

X-ray data collection, structure solution and refinement

Intensity data collected on a Nicolet R3m/V diffractometer were processed with the profile-fitting procedure [11] and corrected for absorption using ψ-scan data [12]. The structure was solved by Patterson superposition and all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically (C–H = 0.96 Å) and included in the structure-factor calculations with assigned isotropic thermal parameters. Final R_F and R_{wF^2} are 0.078 and 0.077 for 1830 observed data ($I \geqslant 4\sigma(I)$, $2\theta_{max} = 55°$) using the weight scheme $[\sigma^2(|F_o|) + 0.00001|F_o|^2]^{-1}$. Computations were performed using the SHELTXL-PLUS program package [13]. Analytic expressions of atomic scattering factors were used, and anomalous dispersion corrections were incorporated [14]. The final positional parameters and equivalent isotropic thermal parameters of the non-hydrogen atoms are listed in Table 1, and bond lengths and angles in Table 2.

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*Metal–betaine interactions, Part IX. For Part VIII see ref. 1.

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†The IUPAC names of BET and pyBET are trimethylammonioacetate and pyridinioacetate, respectively.

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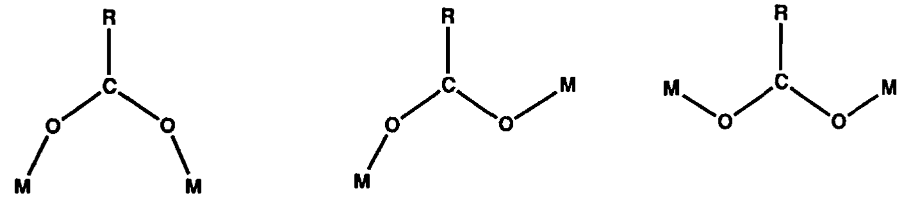
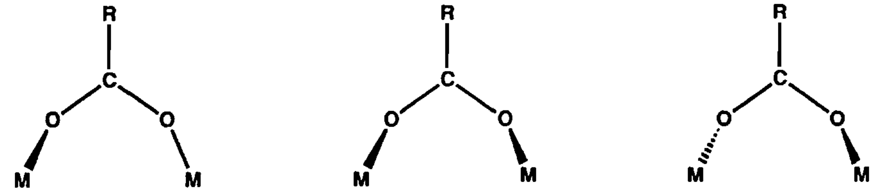


a) *syn-syn* coplanar
(180, 180)

b) *syn-anti* coplanar
(180, 0)

c) *anti-anti* coplanar
(0, 0)



d) *syn*-skew non-planar
(180, -90)

e) skew-skew non-planar
(90, -90)

f) skew-skew non-planar
(90, 90)

Fig. 1. Six idealized bridging modes of carboxylate and betaine ligands in their metal complexes. Enclosed in parentheses are the numerical values of the pair of R–C–O–M torsion angles (°) for each type of geometry.

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^4$ for Mn; 10^3 for others)

	x	*y*	*z*	U_{eq}[a]
Mn(1)	0	0	0	271(5)
Mn(2)	0	0	5000	258(4)
O(1)	1586(3)	412(3)	1307(3)	37(2)
O(2)	1529(3)	1040(3)	3584(3)	35(1)
C(1)	1846(5)	543(5)	2632(5)	31(2)
C(2)	2687(5)	134(5)	3254(5)	39(2)
N(1)	2845(4)	−770(4)	2389(5)	40(2)
C(3)	3429(7)	−289(7)	939(6)	61(4)
C(4)	3625(7)	−1090(7)	3261(7)	61(4)
C(5)	1647(7)	−1885(6)	2158(9)	66(4)
Mn(3)	3333	6667	7906(2)	515(5)
Cl(1)	3333	6667	10500(3)	48(1)
Cl(2)	5115(2)	6701(2)	7189(2)	75(1)

[a] U_{eq} defined as one third of the trace of the orthogonalized *U* tensor.

TABLE 2. Bond lengths (Å) and bond angles (°)

Mn(1)–O(1)	2.189(4)	Mn(2)–O(2)	2.169(3)
Mn(3)–Cl(1)	2.365(3)	Mn(3)–Cl(2)	2.365(3)
O(1)–C(1)	1.243(5)	O(2)–C(1)	1.261(7)
C(1)–C(2)	1.53(1)	C(2)–N(1)	1.502(9)
N(1)–C(3)	1.493(7)	N(1)–C(4)	1.49(1)
N(3)–C(5)	1.507(7)		
O(1)–Mn(1)–O(1a)	93.2(1)	O(1)–Mn(1)–O(1d)	86.8(1)
O(2)–Mn(2)–O(2a)	88.2(1)	O(2)–Mn(2)–O(2g)	91.8(1)
Mn(1)–O(1)–C(1)	135.9(4)	Mn(2)–O(2)–C(1)	121.4(3)
Cl(1)–Mn(3)–Cl(2)	106.0(1)	Cl(2)–Mn(3)–Cl(2i)	112.7(1)
O(1)–C(1)–O(2)	127.1(6)	O(1)–C(1)–C(2)	120.2(6)
O(2)–C(1)–C(2)	112.6(4)	C(1)–C(2)–N(1)	117.7(4)
C(2)–N(1)–C(3)	112.2(5)	C(2)–N(1)–C(4)	107.8(5)
C(3)–N(1)–C(4)	108.5(6)	C(2)–N(1)–C(5)	110.0(5)
C(3)–N(1)–C(5)	109.6(5)	C(4)–N(1)–C(5)	108.7(6)

Symmetry codes: (a) $-y, x-y, z$; (b) $y-x, -x, z$; (c) $-x, -y, -z$; (d) $y, y-x, -z$; (e) $x-y, x, -z$; (f) $-x, -y, 1-z$; (g) $y, y-x, 1-z$; (h) $x-y, x, 1-z$; (i) $y-x, 1-x, z$; (j) $1-y, 1+x-y, z$.

Results and discussion

The crystal structure comprises discrete tetrachloromanganate anions and linear cationic chains. In the anion, the Mn(3) atom, as located on Wyckoff position 2(*d*) of symmetry 3, is coordinated by four chloro ligands in a distorted tetrahedral configuration with Mn–Cl bonds of 2.365(3) Å and Cl–Mn–Cl angles of 106.0(1) and 112.7(1)°. In the cationic polymeric chain, the independent Mn(1) and Mn(2) atoms occupy Wyckoff positions 1(*a*) and 1(*b*) of symmetry $\bar{3}$, respectively; accordingly both adopt axially distorted octahedral (C_{3i}) coordination geometries (Fig. 2). The Mn–O bond lengths are comparable to those found for common manganese(II) carboxylates in six coordination [15]. Each pair of adjacent metal atoms is separated by a non-bonded distance of 4.5587(8) Å, being bridged by the bidentate carboxylato groups of three BET ligands into a linear cationic chain running along the *c* axis.

An interesting structural feature in complex **1** is that the carboxylato group of BET bridges Mn(II) atoms in an abnormal non-planar skew–skew fashion (Fig. 1(e)), which differs from the coplanar *syn–syn*, *syn–anti* and *anti–anti* bridging modes commonly found in metal carboxylates [16], and is also distinct from the unusual non-planar *syn*–skew mode found

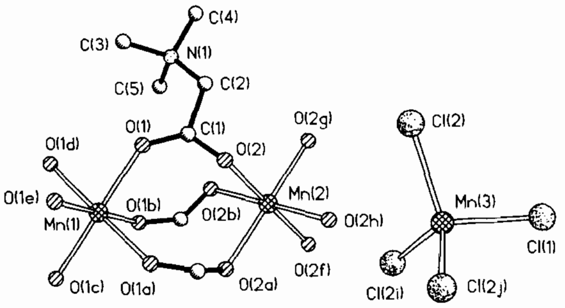


Fig. 2. Perspective view showing the coordination geometry about the Mn(II) atoms in the cationic chain and anion, as well as the numbering scheme. Symmetry codes are given in Table 2.

in $[Cd_3(pyBET)_4Cl_6]$ [6] (Fig. 1(d)). In the present cationic chain, the O(1) atom coordinates Mn(1) in an out-of-plane skew fashion with torsion angle Mn(1)–O(1)–C(1)–C(2) = 145.0(4)°, and the Mn(2)–O(2) bond is rotated out of the plane of the carboxylato group by an even greater extent (torsion angle Mn(2)–O(2)–C(1)–C(2) = −86.2(4)°). The Mn(1) and Mn(2) atoms thus lie on the same side of the plane containing the carboxylato group of the BET ligand. Presumably an alternative skew–skew bridging mode with the two bridged metal atoms on opposite sides of the carboxylato plane (Fig. 1(f)) might also be possible for metal carboxylates and betaine complexes.

Although polymeric structures predominate among manganese(II) carboxylates, most of them are two- or three-dimensional species [2]. Among the rarer one-dimensional polymeric structures, to our knowledge, no tris(carboxylato-*O*,*O*′) bridged Mn(II) complex has hitherto been reported. Indeed, whereas both bis- and tetrakis(carboxylato-*O*,*O*′) bridged metal complexes, e.g. dimeric $[Ag_2(carboxylato\text{-}O,O')_2L_n]$ ($n = 0 \sim 2$) [3] and $[M_2(carboxylato\text{-}O,O')_4L_2]$ (M = Cu(II), Cr(II), Mo(II), etc.; L = H_2O, py, etc.) [17], are now well established, the literature has no record of any tris(carboxylato-*O*,*O*′) bridged complex of divalent and trivalent transition metals. Hence the present cationic polymeric chain constitutes a new structural variety exhibiting not only a unique tris(carboxylato-*O*,*O*′) bridging geometry, but also an unusual skew–skew coordination mode of the carboxylato group.

Supplementary material

Additional material comprising thermal parameters, H atom coordinates, and observed and calculated structure factor amplitudes (10 pages) is available from author T.C.W.M. on request.

References

1 X.-M. Chen and T. C. W. Mak, *Polyhedron,* (1991) in press.
2 X.-M. Chen and T. C. W. Mak, *J. Cryst. Spectrosc. Res., 21* (1991) 21.
3 X.-M. Chen and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.,* (1991) 1219.
4 X.-M. Chen and T. C. W. Mak, *Polyhedron, 10* (1991) 273.
5 X.-M. Chen and T. C. W. Mak, *Inorg. Chim. Acta, 182* (1991) 139.
6 T. C. W. Mak and X.-M. Chen, *J. Aust. Chem., 44* (1991) 639.
7 B. Chiswell, E. D. McKenzie and L. F. Lindoy, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. V, Pergamon, Oxford, 1987, p. 43.
8 T. Lis, *Acta Crystallogr., Sect. A, 24* (1977) 348.
9 K. M. Harmon and G. F. Avci, *J. Mol. Struct., 117* (1984) 295.
10 G. B. Deacon and R. J. Philips, *Coord. Chem. Rev., 33* (1980) 227.
11 R. Diamond, *Acta Crystallogr., Sect. A, 25* (1969) 43.
12 G. Kopfmann and R. Huber, *Acta Crystallogr., Sect. A, 24* (1968) 348.
13 G. M. Sheldrick, in G. M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3: Data Collection, Structure Determination, Protein, and Databases,* Oxford University Press, New York, 1985, p. 175.
14 J. A. Ibers and W. C. Hamilton (eds.), *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, UK, 1974, pp. 55, 99, 149.
15 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Waston and R. Taylor, *J. Chem. Soc., Dalton Trans.,* (1989) S42.
16 C. Mehrotra and R. Bohra, *Metal Carboxylates,* Academic Press, New York, 1983.
17 F. A. Cotton and G. W. Rice, *Inorg. Chem.,. 17* (1978) 2004; Y. B. Koh and G. G. Christoph, *Inorg. Chem., 18* (1979) 1122; V. M. Rao, D. N. Sathyanarayan and H. Manohar, *J. Chem. Soc., Dalton Trans.,* (1983) 2167.