Crystal structure of *catena*-(tris(μ -betaine-*O,O'*)manganese(II)) tetrabromomanganate, $[\text{Mn}(\text{C}_5\text{H}_{11}\text{NO}_2)_3][\text{MnBr}_4]$

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Abstract

$\text{C}_{15}\text{H}_{33}\text{Br}_4\text{Mn}_2\text{N}_3\text{O}_6$, triclinic, $P\bar{1}$ (no. 2), $a = 12.7244(4)$ Å, $b = 12.4942(5)$ Å, $c = 9.1120(5)$ Å, $\alpha = 89.443(4)^\circ$, $\beta = 93.963(4)^\circ$, $\gamma = 112.757(3)^\circ$, $V = 1332.5$ Å³, $Z = 2$, $R_g(F) = 0.021$, $wR_{\text{ref}}(F^2) = 0.055$, $T = 100$ K.

Source of material

Yellow crystals of $[\text{Mn}((\text{CH}_3)_3\text{NCH}_2\text{COO})_3][\text{MnBr}_4]$ with up to 2 mm in diameter were crystallized at 293 K by slow evaporation from stoichiometric aqueous solutions of betaine monohydrate, $(\text{CH}_3)_3\text{NCH}_2\text{COO} \cdot \text{H}_2\text{O}$, and MnBr_2 .

Discussion

The pseudo-trigonal structure of triclinic *catena*-(tris(μ -betaine-*O,O'*)manganese(II)) tetrabromomanganate (BMMB) is closely related to those of trigonal $[\text{Mn}(\text{b})_3]\text{MCl}_4$ with $\text{M} = \text{Mn}, \text{Co}, \text{Zn}$ ($\text{b} = (\text{CH}_3)_3\text{NCH}_2\text{COO}$) [1–3]. The structure of BMMB is built up from polymeric chains of slightly distorted MnO_6 octahedra running parallel [001]. The octahedra are connected *via* the carboxylate groups of the betaine molecules. As compared with the corresponding trigonal chlorine compound $[\text{Mn}(\text{b})_3][\text{MnCl}_4]$ (BMMC) [1,2] the site symmetry of the two inequivalent manganese atoms Mn1 and Mn2 of the chains is reduced from $\bar{3}$ to $\bar{1}$. Charge compensation is achieved by isolated tetrahedral $[\text{MnBr}_4]^{2-}$ anions filling the holes between the methylammonium groups of the betaine molecules. The intra- and inter-chain Mn–Mn distances (intra: 4.56 Å; inter: 12.49 Å and 12.69 Å) are similar to those reported for BMMC (4.55 Å and 12.88 Å, respectively). However, in contrast to the situation observed in the corresponding chlorine compound, in BMMB neighbouring chains are shifted against each other by up to 0.9 Å along [001] and the $[\text{MnX}_4]$ ($\text{X} = \text{Cl}, \text{Br}$) tetrahedra are oriented in a different way. The difference in the unit cell volumes of BMMB and BMMC of about 4.1 % at room temperature corresponds to the replacement of chlorine by the larger bromine.

Table 1. Data collection and handling.

Crystal:	yellow prism, size $0.25 \times 0.30 \times 0.33$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	69.78 cm^{-1}
Diffraction, scan mode:	Oxford Diffraction Xcalibur3 & Sapphire3 CCD, ϕ/ω
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	12118, 7448
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6582
$N(\text{param})_{\text{refined}}$:	407
Programs:	SHELXS-97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1A)	2i	0.319(2)	0.456(2)	0.412(3)	0.034(7)
H(2A)	2i	0.372(2)	0.512(2)	0.268(2)	0.015(5)
H(3A)	2i	0.417(3)	0.440(2)	0.362(3)	0.033(7)
H(4A)	2i	0.197(2)	0.426(2)	0.125(3)	0.030(6)
H(5A)	2i	0.140(2)	0.364(2)	0.254(3)	0.027(6)
H(6A)	2i	0.132(2)	0.289(2)	0.132(3)	0.029(7)
H(7A)	2i	0.372(2)	0.398(2)	0.069(3)	0.035(7)
H(8A)	2i	0.418(2)	0.320(2)	0.159(3)	0.028(6)
H(9A)	2i	0.302(2)	0.268(2)	0.068(3)	0.026(6)

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(10A)	2i	0.324(2)	0.238(2)	0.384(2)	0.010(5)
H(11A)	2i	0.219(2)	0.260(2)	0.432(3)	0.023(6)
H(1B)	2i	0.044(2)	−0.283(2)	0.032(2)	0.018(5)
H(2B)	2i	−0.003(2)	−0.412(2)	0.115(2)	0.021(6)
H(3B)	2i	0.121(2)	−0.346(2)	0.055(3)	0.023(6)
H(4B)	2i	0.231(2)	−0.125(2)	0.319(3)	0.023(6)
H(5B)	2i	0.268(2)	−0.171(2)	0.177(2)	0.009(5)
H(6B)	2i	0.175(2)	−0.114(2)	0.166(3)	0.025(6)
H(7B)	2i	0.184(2)	−0.315(2)	0.425(3)	0.019(6)
H(8B)	2i	0.102(2)	−0.421(2)	0.346(3)	0.022(6)
H(9B)	2i	0.216(2)	−0.354(2)	0.278(3)	0.025(6)
H(10B)	2i	−0.044(2)	−0.339(2)	0.333(2)	0.007(5)

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(11B)	2i	0.046(2)	−0.238(2)	0.423(2)	0.018(5)
H(1C)	2i	−0.514(2)	−0.115(2)	0.242(2)	0.015(5)
H(2C)	2i	−0.442(2)	−0.075(2)	0.389(3)	0.030(6)
H(3C)	2i	−0.458(2)	0.026(2)	0.275(3)	0.037(7)
H(4C)	2i	−0.432(2)	−0.074(2)	0.018(2)	0.016(5)
H(5C)	2i	−0.372(2)	0.058(2)	0.055(3)	0.029(6)
H(6C)	2i	−0.297(2)	−0.016(2)	0.018(3)	0.028(6)
H(7C)	2i	−0.259(2)	−0.147(2)	0.184(3)	0.022(6)
H(8C)	2i	−0.392(2)	−0.216(2)	0.182(3)	0.030(7)
H(9C)	2i	−0.321(2)	−0.167(2)	0.336(3)	0.041(7)
H(10C)	2i	−0.247(2)	0.033(2)	0.401(2)	0.013(5)
H(11C)	2i	−0.251(2)	0.126(2)	0.291(2)	0.015(5)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mn(1)	1a	0	0	0	0.0065(2)	0.0084(2)	0.0071(1)	0.0023(1)	0.0012(1)	0.0007(1)
Mn(2)	1b	0	0	½	0.0076(2)	0.0082(2)	0.0071(1)	0.0027(1)	0.0015(1)	0.0006(1)
Mn(3)	2i	0.69460(2)	0.38202(2)	0.23280(3)	0.0107(1)	0.0103(1)	0.0132(1)	0.00308(9)	0.00179(9)	0.00100(9)
Br(1)	2i	0.62508(2)	0.31177(2)	−0.02817(2)	0.01165(8)	0.02156(9)	0.01644(8)	0.00513(7)	−0.00073(6)	−0.00669(6)
Br(2)	2i	0.69494(2)	0.57817(2)	0.26473(2)	0.02157(9)	0.01138(8)	0.01997(9)	0.00668(7)	0.00084(7)	−0.00082(6)
Br(3)	2i	0.88834(1)	0.37569(1)	0.27698(2)	0.01090(8)	0.01652(9)	0.01450(8)	0.00481(6)	0.00197(6)	0.00210(6)
Br(4)	2i	0.56221(2)	0.24587(2)	0.40551(2)	0.01580(9)	0.0245(1)	0.0303(1)	0.00740(7)	0.00976(7)	0.01513(8)
O(1A)	2i	0.1518(1)	0.1029(1)	0.1464(1)	0.0102(6)	0.0152(6)	0.0101(5)	0.0024(4)	0.0003(4)	−0.0013(4)
O(2A)	2i	0.1534(1)	0.0425(1)	0.3796(1)	0.0095(5)	0.0107(5)	0.0129(5)	0.0032(4)	0.0036(4)	0.0023(4)
N(1A)	2i	0.2816(1)	0.3416(1)	0.2423(2)	0.0112(7)	0.0099(6)	0.0123(6)	0.0016(5)	0.0019(5)	0.0024(5)
C(1A)	2i	0.3543(2)	0.4487(2)	0.3304(2)	0.025(1)	0.0088(8)	0.0197(9)	−0.0027(7)	−0.0002(8)	−0.0018(7)
C(2A)	2i	0.1753(2)	0.3541(2)	0.1798(3)	0.018(1)	0.0168(9)	0.041(1)	0.0092(8)	−0.0036(9)	0.0028(9)
C(3A)	2i	0.3496(2)	0.3300(2)	0.1194(2)	0.022(1)	0.0197(9)	0.0161(8)	0.0018(7)	0.0092(7)	0.0022(7)
C(4A)	2i	0.2533(2)	0.2397(1)	0.3441(2)	0.0129(8)	0.0107(7)	0.0087(7)	0.0014(6)	0.0020(6)	0.0016(6)
C(5A)	2i	0.1784(1)	0.1186(1)	0.2817(2)	0.0044(6)	0.0119(7)	0.0114(7)	0.0029(5)	0.0018(5)	−0.0001(6)
O(1B)	2i	−0.0297(1)	−0.1547(1)	0.1274(1)	0.0134(6)	0.0114(5)	0.0095(5)	0.0044(4)	0.0014(4)	0.0024(4)
O(2B)	2i	−0.0855(1)	−0.1431(1)	0.3523(1)	0.0080(5)	0.0109(5)	0.0113(5)	0.0023(4)	0.0015(4)	−0.0020(4)
N(1B)	2i	0.1084(1)	−0.2764(1)	0.2429(2)	0.0098(6)	0.0113(6)	0.0094(6)	0.0050(5)	0.0018(5)	0.0007(5)
C(5B)	2i	−0.0365(1)	−0.1788(1)	0.2611(2)	0.0058(7)	0.0082(7)	0.0120(7)	0.0000(5)	0.0002(5)	−0.0005(5)
C(4B)	2i	0.0155(1)	−0.2628(2)	0.3255(2)	0.0110(7)	0.0144(8)	0.0094(7)	0.0063(6)	0.0039(6)	0.0026(6)
C(3B)	2i	0.1562(2)	−0.3504(2)	0.3325(2)	0.0151(8)	0.0174(9)	0.0143(8)	0.0098(7)	0.0006(6)	0.0028(6)
C(2B)	2i	0.2039(2)	−0.1610(2)	0.2235(2)	0.0116(8)	0.0116(8)	0.0232(9)	0.0024(6)	0.0053(7)	0.0025(7)
C(1B)	2i	0.0643(2)	−0.3342(2)	0.0949(2)	0.0175(9)	0.0195(9)	0.0110(7)	0.0096(7)	0.0005(6)	−0.0028(6)
O(1C)	2i	−0.1155(1)	0.0519(1)	0.1171(1)	0.0102(5)	0.0162(6)	0.0100(5)	0.0066(5)	0.0022(4)	0.0004(4)
O(2C)	2i	−0.0474(1)	0.1109(1)	0.3485(1)	0.0122(6)	0.0101(5)	0.0119(5)	0.0045(4)	−0.0007(4)	0.0012(4)
N(1C)	2i	−0.3449(1)	−0.0427(1)	0.2180(2)	0.0080(6)	0.0112(6)	0.0132(6)	0.0032(5)	0.0020(5)	0.0011(5)
C(5C)	2i	−0.1259(1)	0.0714(1)	0.2488(2)	0.0109(7)	0.0069(7)	0.0107(7)	0.0042(6)	0.0014(6)	0.0023(5)
C(4C)	2i	−0.2441(1)	0.0514(2)	0.2977(2)	0.0102(7)	0.0124(8)	0.0138(7)	0.0009(6)	0.0040(6)	−0.0027(6)
C(3C)	2i	−0.3311(2)	−0.1567(2)	0.2303(2)	0.0154(9)	0.0110(8)	0.0269(9)	0.0039(7)	−0.0033(7)	0.0025(7)
C(2C)	2i	−0.3606(2)	−0.0168(2)	0.0590(2)	0.0107(8)	0.024(1)	0.0165(8)	0.0049(7)	−0.0009(7)	0.0076(7)
C(1C)	2i	−0.4503(2)	−0.0520(2)	0.2910(2)	0.0113(8)	0.022(1)	0.026(1)	0.0018(7)	0.0091(7)	−0.0011(8)

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References

- Chen, X.-M.; Mak, Th. C. W.: A linear polymeric manganese(II) complex bridged by skew-skew bridging carboxylato groups. Crystal structure of *catena*-tris(betaine)manganese(II) tetrachloromanganate(II), [Mn(Me₃NCH₂COO)₃]_n · n MnCl₄. *Inorg. Chim. Acta* **189** (1991) 3–5.
- Schreuer, J.; Haussühl, S.: Crystal structure of *catena*-tri-μ-trimethylammonium-acetatomanganese tetrachloromanganate (((CH₃)₃NCH₂COO)₃Mn)MnCl₄. *Z. Kristallogr.* **205** (1993) 309–310.
- Wiehl, L.; Schreuer, J.; Haussühl, E.: Crystal structures of *catena*-(tris(μ-betaine-*O,O'*)manganese(II)) tetrachlorozincate and *catena*-(tris(μ-betaine-*O,O'*)manganese(II)) tetrachlorocobaltate, [((CH₃)₃NCH₂COO)₃Mn]MCl₄ (M = Zn, Co). *Z. Kristallogr. NCS* **221** (2006) 77–79.
- Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.