Crystal structures of *catena*-(tris(μ -betaine-*O,O'*)manganese(II)) tetrachlorozincate and *catena*-(tris(μ -betaine-*O,O'*)manganese(II)) tetrachlorocobaltate, $[\{(\text{CH}_3)_3\text{NCH}_2\text{COO}\}_3\text{Mn}][\text{MCl}_4]$ ($M = \text{Zn}, \text{Co}$)

L. Wiehl*, J. Schreuer and E. Haussühl

Universität Frankfurt, Institut für Mineralogie/Kristallographie, Senckenberganlage 30, 60054 Frankfurt am Main, Germany

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Abstract

$\text{C}_{15}\text{H}_{33}\text{Cl}_4\text{MnN}_3\text{O}_6\text{Zn}$, trigonal, $P\bar{3}$ (no. 147), $a = 12.7751(5)$ Å, $c = 9.0835(2)$ Å, $V = 1283.9$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.032$, $wR_{\text{ref}}(F^2) = 0.083$, $T = 293$ K.

$\text{C}_{15}\text{H}_{33}\text{Cl}_4\text{CoMnN}_3\text{O}_6$, trigonal, $P\bar{3}$ (no. 147), $a = 12.7832(7)$ Å, $c = 9.0769(4)$ Å, $V = 1284.6$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.076$, $T = 293$ K.

Source of material

$[\{(\text{CH}_3)_3\text{NCH}_2\text{COO}\}_3\text{Mn}][\text{ZnCl}_4]$ (BMZ): 30 mmol (4.05 g) of betaine monohydrate ($\text{C}_5\text{H}_{11}\text{NO}_2 \cdot \text{H}_2\text{O}$) were dissolved in 20 ml distilled water under stirring at about 320 K. Then 10 mmol (1.26 g)

of manganese dichloride (MnCl_2) and 10 mmol (1.36 g) of zinc dichloride (ZnCl_2) were added under continuous stirring until complete dissolution. By evaporation of the solvent (293 K) during several weeks the pink-colored solution yielded nearly colorless crystals with prismatic shape.

$[\{(\text{CH}_3)_3\text{NCH}_2\text{COO}\}_3\text{Mn}][\text{CoCl}_4]$ (BMC): Same preparation as above, but 10 mmol (2.38 g) of cobalt dichloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) was used instead of ZnCl_2 . The solution was deep blue as well as the crystals. All raw materials were commercial products.

Discussion

The title compounds $[\text{3bMn}][\text{MCl}_4]$ ($\text{b} = \text{betaine}$) with $M = \text{Zn(II)}$ (BMZ) and Co(II) (BMC), respectively, are isomorphous with the analogous Mn(II) compound $[\text{3bMn}][\text{MnCl}_4]$ [1,2].

The crystal structure is built up from infinite chains of two inequivalent MnO_6 octahedra, which are connected via the carboxylate groups of the betaine molecules (figure, top). The carboxylate groups are delocalized with similar bond distances $d(\text{O1}—\text{C5}) = 1.248(2)$ Å and $d(\text{O2}—\text{C5}) = 1.252(2)$ Å. All Mn ions lie on the threefold axis through the cell origin and the chains extend along the c axis. The MnO_6 octahedra are rather ideal (Mn site symmetry $\bar{3}$) with six equal bond distances $d(\text{Mn1}—\text{O1}) = 2.182(1)$ Å and $d(\text{Mn2}—\text{O2}) = 2.158(1)$ Å, respectively, and O—Mn—O bond angles of 86.8° and 93.2° for Mn1 and 88.5° and 91.5° for Mn2. For both BMZ and BMC all distances and angles of the Mn coordination have the same values within experimental error. The other metal ion ($M = \text{Zn}, \text{Co}$) occupies only slightly distorted tetrahedral positions. The MCl_4 tetrahedra are located on threefold axes inbetween the chains, filling the holes between the trimethylammonium groups of the betaine molecules (figure, bottom). The bond distances of Zn and Co are similar only along the c axis: $d(\text{Zn3}—\text{Cl1}) = 2.285(1)$ Å and $d(\text{Co3}—\text{Cl1}) = 2.283(1)$ Å, but $d(\text{Zn3}—\text{Cl2}) = 2.2703(7)$ Å and $d(\text{Co3}—\text{Cl2}) = 2.2815(7)$ Å for the other three chlorine ions. This corresponds to the slightly elongated a axis of BMC as compared to BMZ. The angles again are similar for Zn and Co: $\angle \text{Cl1}—\text{M3}—\text{Cl2} = 106.4^\circ$ ($M = \text{Zn}$), 106.5° ($M = \text{Co}$) and $\angle \text{Cl2}—\text{M3}—\text{Cl2} = 112.4^\circ$ ($M = \text{Zn}$), 112.3° ($M = \text{Co}$).

The crystals tend to form twins, where the individuals are rotated by 60° about the c axis. The BMZ specimen of this measurement was a single crystal, but for the BMC crystal a small portion of about 8 % of the twin component had to be considered during refinement. In both compounds as well as in $[\text{3bMn}][\text{MnCl}_4]$, magnetic ordering phenomena within the chains of MnO_6 octahedra are observed at low temperature [3]. For BMC, the structure calculations and the magnetic susceptibility as determined by SQUID measurements [3] suggest a certain amount of cation disorder, which has to be confirmed by alternative methods.

* Correspondence author (e-mail: l.wiehl@kristall.uni-frankfurt.de)

1. catena-(Tris(*μ*-betaine-*O,O'*)manganese(II)) tetrachlorozincate, [(CH₃)₃NCH₂COO]₃Mn][ZnCl₄]
Table 1. Data collection and handling.

Crystal:	colorless cleaved plate, size 0.1 × 0.2 × 0.3 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
<i>μ</i> :	18.75 cm ^{−1}
Diffractometer, scan mode:	Oxford Diffraction Xcalibur3 & Sapphire2 CCD, <i>φ</i> / <i>ω</i>
2 θ _{max} :	55.94°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	21569, 2068
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 1845
<i>N</i> (<i>param</i>) _{refined} :	136
Programs:	SHELXS-97 [4], SHELXL-97 [5], ATOMS [6]

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	6g	0.325(3)	0.466(3)	0.420(4)	0.09(1)
H(1B)	6g	0.371(3)	0.543(3)	0.268(3)	0.062(8)
H(1C)	6g	0.437(3)	0.481(3)	0.341(3)	0.065(9)
H(2A)	6g	0.130(4)	0.350(4)	0.309(5)	0.10(1)
H(2B)	6g	0.119(3)	0.284(3)	0.161(4)	0.08(1)
H(2C)	6g	0.181(3)	0.427(3)	0.159(3)	0.064(8)
H(3A)	6g	0.296(3)	0.307(3)	0.038(4)	0.073(9)
H(3B)	6g	0.420(3)	0.374(3)	0.113(4)	0.08(1)
H(3C)	6g	0.364(3)	0.452(3)	0.046(3)	0.066(8)
H(4A)	6g	0.240(2)	0.265(2)	0.418(3)	0.048(6)
H(4B)	6g	0.347(2)	0.266(2)	0.337(3)	0.049(7)

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

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mn(1)	1a	0	0	0	0.0315(2)	<i>U</i> ₁₁	0.0191(3)	$\frac{1}{2}U_{11}$	0	0
Mn(2)	1b	0	0	$\frac{1}{2}$	0.0308(2)	<i>U</i> ₁₁	0.0188(3)	$\frac{1}{2}U_{11}$	0	0
Zn(3)	2d	$\frac{2}{3}$	$\frac{1}{3}$	0.21046(5)	0.0601(2)	<i>U</i> ₁₁	0.0336(2)	$\frac{1}{2}U_{11}$	0	0
Cl(1)	2d	$\frac{2}{3}$	$\frac{1}{3}$	−0.0411(1)	0.0550(3)	<i>U</i> ₁₁	0.0342(4)	$\frac{1}{2}U_{11}$	0	0
Cl(2)	6g	0.49438(7)	0.16468(7)	0.28096(8)	0.0762(4)	0.0755(4)	0.0643(4)	0.0339(4)	0.0263(3)	0.0214(3)
O(1)	6g	0.1597(1)	0.1174(1)	0.1307(1)	0.0382(7)	0.0396(7)	0.0251(6)	0.0128(5)	−0.0028(5)	−0.0011(5)
O(2)	6g	0.1540(1)	0.0498(1)	0.3592(1)	0.0358(6)	0.0360(6)	0.0297(6)	0.0185(5)	0.0063(5)	0.0058(5)
N	6g	0.2858(2)	0.3636(1)	0.2373(2)	0.0432(8)	0.0333(8)	0.0296(8)	0.0116(7)	0.0000(6)	0.0024(6)
C(1)	6g	0.3641(3)	0.4753(2)	0.3248(3)	0.074(2)	0.038(1)	0.048(1)	0.014(1)	−0.010(1)	−0.006(1)
C(2)	6g	0.1664(2)	0.3555(2)	0.2125(4)	0.054(1)	0.044(1)	0.085(2)	0.024(1)	−0.003(1)	0.011(1)
C(3)	6g	0.3466(3)	0.3746(2)	0.0934(3)	0.070(2)	0.049(1)	0.036(1)	0.016(1)	0.015(1)	0.008(1)
C(4)	6g	0.2702(2)	0.2571(2)	0.3254(2)	0.048(1)	0.0361(9)	0.0259(9)	0.0164(8)	−0.0047(8)	0.0007(7)
C(5)	6g	0.1867(2)	0.1313(2)	0.2641(2)	0.0290(8)	0.0353(8)	0.0262(8)	0.0157(7)	0.0022(6)	0.0009(6)

2. catena-(Tris(*μ*-betaine-*O,O'*)manganese(II)) tetrachlorocobaltate, [(CH₃)₃NCH₂COO]₃Mn][CoCl₄]
Table 4. Data collection and handling.

Crystal:	blue cleaved plate, size 0.10 × 0.15 × 0.35 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
<i>μ</i> :	15.86 cm ^{−1}
Diffractometer, scan mode:	Oxford Diffraction Xcalibur3 & Sapphire2 CCD, <i>φ</i> / <i>ω</i>
2 θ _{max} :	55.94°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	21668, 2053
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 1759
<i>N</i> (<i>param</i>) _{refined} :	138
Programs:	SHELXS-97 [4], SHELXL-97 [5], ATOMS [6]

Table 5. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1A)	6g	0.320(3)	0.469(4)	0.423(5)	0.11(1)
H(1B)	6g	0.369(3)	0.546(3)	0.269(4)	0.069(8)
H(1C)	6g	0.434(3)	0.479(3)	0.345(3)	0.063(8)
H(2A)	6g	0.137(4)	0.355(4)	0.313(5)	0.10(1)
H(2B)	6g	0.118(3)	0.286(3)	0.165(4)	0.063(8)
H(2C)	6g	0.182(2)	0.430(3)	0.162(3)	0.058(7)
H(3A)	6g	0.298(3)	0.311(3)	0.041(4)	0.066(9)
H(3B)	6g	0.420(4)	0.375(3)	0.113(5)	0.10(1)
H(3C)	6g	0.361(2)	0.453(3)	0.047(3)	0.062(8)
H(4A)	6g	0.239(2)	0.263(2)	0.419(4)	0.055(7)
H(4B)	6g	0.348(2)	0.266(2)	0.335(3)	0.049(6)

Table 6. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Mn(1)	1 <i>a</i>		0	0	0	0.0331(2)	<i>U</i> ₁₁	0.0207(3)	½ <i>U</i> ₁₁	0	0
Mn(2)	1 <i>b</i>		0	0	½	0.0327(2)	<i>U</i> ₁₁	0.0206(3)	½ <i>U</i> ₁₁	0	0
Co(3)	2 <i>d</i>		⅔	⅓	0.20918(6)	0.0618(2)	<i>U</i> ₁₁	0.0354(3)	½ <i>U</i> ₁₁	0	0
Cl(1)	2 <i>d</i>		⅔	⅓	−0.0424(1)	0.0575(3)	<i>U</i> ₁₁	0.0363(5)	½ <i>U</i> ₁₁	0	0
Cl(2)	6 <i>g</i>		0.49375(7)	0.16407(7)	0.28059(9)	0.0787(4)	0.0784(4)	0.0667(5)	0.0356(4)	0.0260(4)	0.0214(4)

Table 6. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(1)	6g	0.1595(1)	0.1173(1)	0.1308(1)	0.0396(7)	0.0422(7)	0.0272(7)	0.0136(5)	−0.0020(5)	−0.0005(5)
O(2)	6g	0.1538(1)	0.0497(1)	0.3591(1)	0.0376(6)	0.0389(6)	0.0308(7)	0.0197(5)	0.0059(5)	0.0058(5)
N	6g	0.2856(2)	0.3633(1)	0.2377(2)	0.0449(8)	0.0350(7)	0.0313(9)	0.0126(6)	−0.0005(7)	0.0018(6)
C(1)	6g	0.3641(3)	0.4750(2)	0.3251(3)	0.074(2)	0.040(1)	0.050(2)	0.015(1)	−0.009(1)	−0.007(1)
C(2)	6g	0.1660(2)	0.3551(2)	0.2133(4)	0.057(1)	0.045(1)	0.087(2)	0.026(1)	−0.003(1)	0.009(1)
C(3)	6g	0.3462(3)	0.3746(2)	0.0933(3)	0.073(2)	0.050(1)	0.038(1)	0.017(1)	0.015(1)	0.007(1)
C(4)	6g	0.2702(2)	0.2568(2)	0.3255(2)	0.049(1)	0.0383(9)	0.028(1)	0.0170(8)	−0.0044(8)	0.0016(7)
C(5)	6g	0.1862(1)	0.1311(2)	0.2638(2)	0.0304(7)	0.0365(8)	0.0278(9)	0.0161(6)	0.0023(6)	0.0006(7)

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