

High-temperature phase of *trans*-tetraaqua-bis(trifluoroacetato-O)-manganese(II)

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Received 20 March 2000

Accepted 9 August 2000

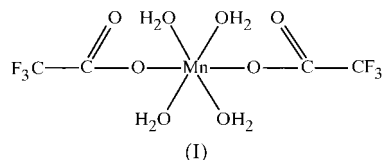
The title compound, $[\text{Mn}(\text{CF}_3\text{COO})_2(\text{H}_2\text{O})_4]$, crystallizes in the monoclinic space group $C2/c$. At about 215 K, it undergoes a reversible phase transition, which leads to crystal twinning. The crystal structure of the high-temperature phase was determined at 220 K. The Mn^{2+} ion lies on a twofold axis and is octahedrally coordinated by two monodentate trifluoroacetate ligands in apical positions and by four equatorial aqua ligands, two of which lie on the twofold axis. Hydrogen-bonding interactions connect the complex molecules, generating a three-dimensional network.

Comment

The crystal structure study of the title compound, (I), was undertaken as a continuation of our previous work on the structural characterization of manganese(II) carboxylates (Lis, 1979). The room-temperature data for the present compound revealed a monoclinic unit cell with $a = 13.300$ (3), $b = 12.700$ (3), $c = 8.440$ (2) Å and $\beta = 118.70$ (3)°. Due to disorder of the CF_3 group, low-temperature investigations were undertaken with the expectation that the disorder would be reduced. However, on cooling, we observed splitting of reflections, which started at about 215 K. The effect was reversible, and several cycles of warming and cooling gave no apparent deterioration of the crystal quality. This could be interpreted as an indication of the crystal twinning induced by a structural phase transition. The phase transition was then confirmed by differential scanning calorimetry (DSC) measurements which showed an exotherm ($T = 216$ K) on cooling and an endotherm ($T = 218$ K) on warming. Investigations of the low-temperature phase are in progress and will be reported later. We present here the crystal structure of the high-temperature phase determined at 220 K.

In contrast to most manganese(II) carboxylate salts, which have bridged polymeric structures, the present compound has a monomeric structure. The Mn^{2+} ion is coordinated by two monodentate anionic trifluoroacetate ligands in a *trans* geometry and by four aqua ligands. The complex lies on a twofold rotation axis, which passes through O4, Mn and O5.

The metal ion has only a slightly distorted octahedral geometry; the largest angular distortions occur for the carboxylate O1 atom. In the case of aqua ligands, the Mn—O distances appear to correlate with the strength of the hydrogen bonding of the associated proton (Tables 1 and 2).



The stability of the present structure derives from intra- and intermolecular hydrogen-bonding interactions, which involve all aqua ligands and both O atoms of the carboxylate ligands (Table 2). Each complex is connected to four others by donating six and accepting six O—H...O hydrogen bonds, forming a continuous three-dimensional network. The crystal packing can be described as being composed of zigzag chains parallel to the [001] direction. Adjacent complexes in the chains, which are related by centres of symmetry, are joined by two pairs of intermolecular hydrogen bonds, *i.e.* O4—H4...O3 and O3—H3...O1. In turn, the [001] chains are linked by the strongest hydrogen bond, formed between the uncoordinated carboxylate O2 atom as an acceptor and the O3 atom of an aqua ligand as a donor. It is important that the uncoordinated O2 atom of the carboxylate ligand is involved simultaneously in intramolecular hydrogen bonding with the O5 atom of the aqua ligand. It seems that a change in the balance of these inter- and intramolecular hydrogen-bond interactions of the pendant carboxylate O2 atom may be responsible for the structural phase transition found.

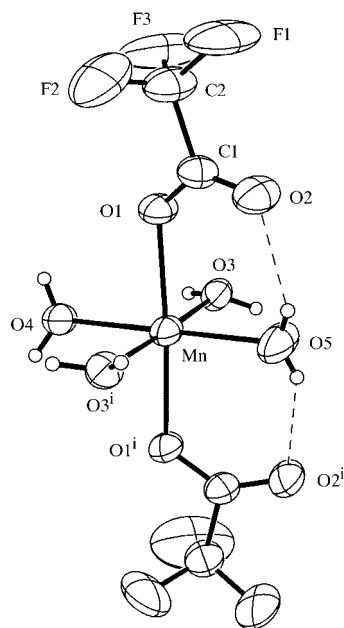


Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Intramolecular hydrogen bonding is shown with dashed lines. Only the major rotamer of the CF_3 group is shown.

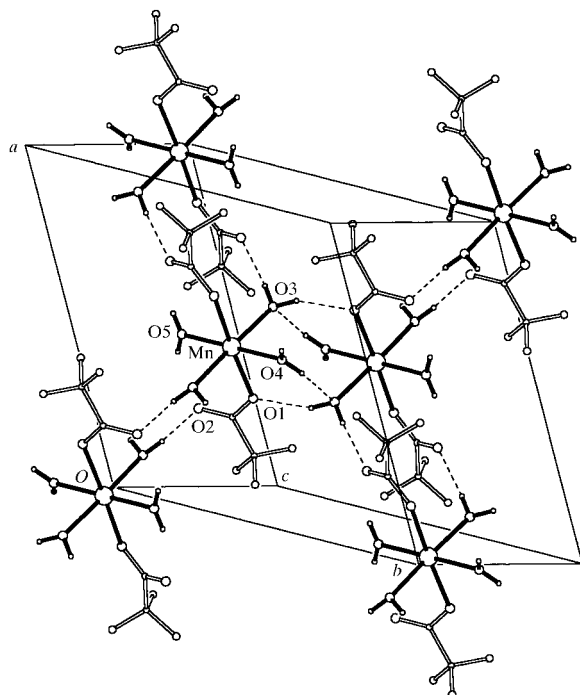


Figure 2
The packing diagram with dashed lines indicating the hydrogen-bond network.

Experimental

To a suspension of manganese(II) carbonate in water was added a small portion of trifluoroacetic acid. After CO_2 had evolved, the excess carbonate was filtered off. The filtrate, on standing at room temperature for several days, gave chunky pink crystals. The crystal used for X-ray study was cut from a larger crystal and was ground into a sphere by water polishing.

Crystal data

$[\text{Mn}(\text{C}_2\text{F}_3\text{O}_2)_2(\text{H}_2\text{O})_4]$
 $M_r = 353.04$
 Monoclinic, $C2/c$
 $a = 13.383$ (5) Å
 $b = 13.038$ (4) Å
 $c = 8.372$ (3) Å
 $\beta = 121.76$ (4)°
 $V = 1242.1$ (7) Å³
 $Z = 4$
 $D_x = 1.888$ Mg m⁻³
 $D_m = 1.875$ Mg m⁻³

D_m measured by flotation in
 dibromoethane/cyclohexane
 Mo $K\alpha$ radiation
 Cell parameters from 1518
 reflections
 $\theta = 4\text{--}27^\circ$
 $\mu = 1.17$ mm⁻¹
 $T = 220$ (2) K
 Sphere, pale pink
 0.1 mm (radius)

Table 1

Selected geometric parameters (Å, °).

Mn—O5	2.136 (4)	O1—C1	1.255 (3)
Mn—O4	2.157 (3)	O2—C1	1.224 (3)
Mn—O1	2.193 (2)	C1—C2	1.541 (4)
Mn—O3	2.198 (2)		
O5—Mn—O4	180	O1—Mn—O3	87.97 (9)
O5—Mn—O1	92.20 (5)	O3—Mn—O3 ⁱ	177.08 (12)
O4—Mn—O1	87.80 (5)	C1—O1—Mn	126.04 (18)
O1 ⁱ —Mn—O1	175.60 (10)	O2—C1—O1	128.8 (3)
O5—Mn—O3	91.46 (6)	O2—C1—C2	117.8 (3)
O4—Mn—O3	88.54 (6)	O1—C1—C2	113.4 (3)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O3—H3 ⁱ ···O1 ⁱ	0.86 (4)	1.97 (4)	2.772 (3)	155 (3)
O3—H3 ⁱ ···O2 ⁱⁱ	0.83 (4)	1.87 (4)	2.693 (3)	170 (4)
O4—H4 ⁱ ···O3 ⁱ	0.82 (3)	2.07 (3)	2.807 (2)	150 (3)
O5—H5 ⁱ ···O2	0.74 (5)	2.11 (5)	2.757 (2)	146 (5)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Data collection

Kuma KM4CCD κ -geometry diffractometer
 ω scans
 Absorption correction: spherical
 (*International Tables for Crystallography*, Vol. C, 1992)
 $T_{\min} = 0.840, T_{\max} = 0.841$
 3808 measured reflections

1331 independent reflections
 1144 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 27^\circ$
 $h = -16 \rightarrow 16$
 $k = -16 \rightarrow 16$
 $l = -10 \rightarrow 8$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.109$
 $S = 1.108$
 1331 reflections
 117 parameters
 All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 1.7678P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.40 \text{ e \AA}^{-3}$

The CF_3 group was found to be disordered over two alternative orientations, which could not be fully occupied simultaneously because of the close contact found between the two equivalent positions. Thus, the disorder was modelled in the form of a major (F1, F2 and F3) and minor (F4, F5 and F6) component, the occupancy factor refining to 0.88 (2) for the major component. Anisotropic displacement parameters were applied only for the F atoms of the major orientation. The magnitude of these factors indicates that the disorder is more extensive than in the assumed model. The H atoms of the water molecules were located from a difference Fourier map and were refined isotropically; the O—H distances are in the range 0.74 (5)–0.86 (4) Å. The DSC studies were carried out on a Perkin-Elmer DSC-7 calorimeter with cooling/heating rates of 20 K min⁻¹. The measurements were performed between 120 and 310 K.

Data collection: *KM4CCD Software* (Kuma Diffraction, 1995–1999); cell refinement: *KM4CCD Software*; data reduction: *KM4CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1539). Services for accessing these data are described at the back of the journal.

References

- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Kuma Diffraction (1995–1999). *KM4CCD Software*. Version 1.161. Kuma Diffraction Instruments GmbH, Wroclaw, Poland.
 Lis, T. (1979). *Acta Cryst.* **B35**, 1699–1701, 2212–2214.
 Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.