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## Key indicators

Single-crystal X-ray study

T = 100 K

Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$ 

R factor = 0.054

wR factor = 0.097

Data-to-parameter ratio = 18.6

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.A trinuclear mixed-valence manganese carboxylate:  
tris(acetic acid- $\kappa\text{O}$ )- $\mu_3$ -oxo-hexakis( $\mu_2$ -trichloro-  
acetato- $\kappa^2\text{O}:\text{O}'$ )trimanganese(II,III,III)

The title mixed-valence manganese carboxylate,  $[\text{Mn}_3(\text{C}_2\text{Cl}_3\text{O}_2)_6\text{O}(\text{C}_2\text{H}_4\text{O}_2)_3]$ , was synthesized starting from an acetic acid solution of  $\text{Mn}(\text{CCl}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{CCl}_3\text{COOH}$  and  $\text{KMnO}_4$ . The molecule features a planar trinuclear  $\mu_3$ -oxo-centered manganese(II,III,III) complex. Differences in the geometric parameters of the Mn atoms due to strong Jahn–Teller effects in the  $\text{Mn}^{3+}$  ions allow the metal atoms with oxidation states +2 and +3 to be distinguished.

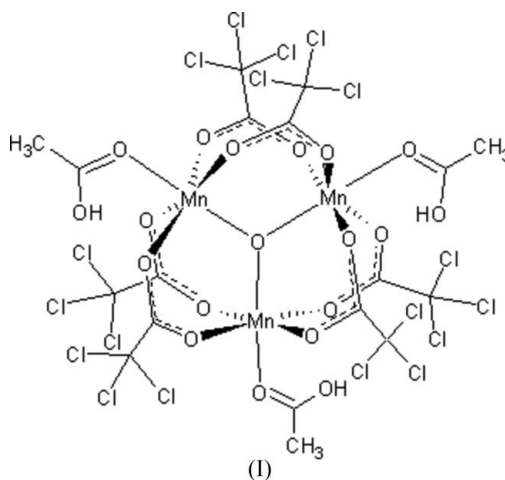
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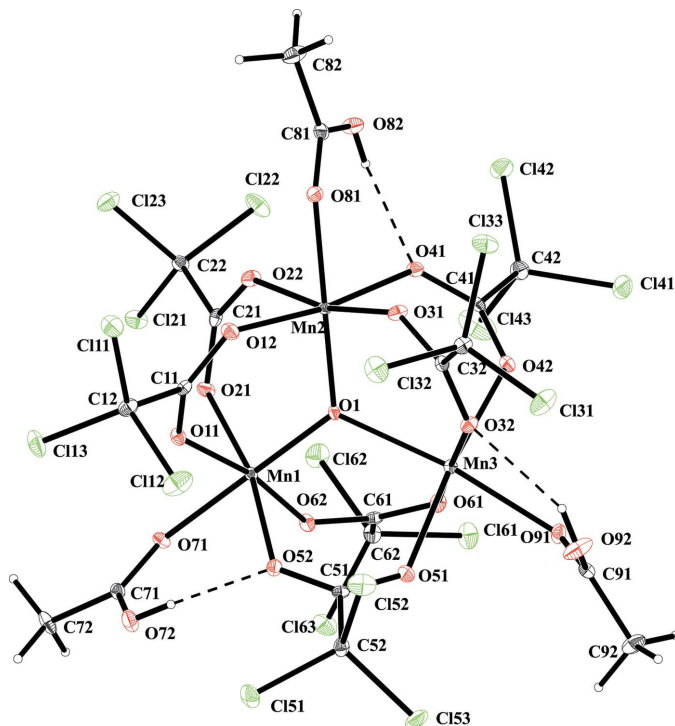
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## Comment

A number of trinuclear oxo-centered mixed-valence manganese carboxylates are known (Baikie *et al.*, 1980; Cañada-Vilalta *et al.*, 2004; Li *et al.*, 2002; Zhao *et al.*, 2003, and references therein). These compounds might have interesting magnetic properties or biological activity. Recent studies on trinuclear manganese trichloroacetate (Kim & Cho, 2004; Tsai *et al.*, 2003) revealed the  $D_{3h}$  symmetry of  $[\text{Mn}_3\text{O}(\text{CCl}_3\text{COO})_6(\text{H}_2\text{O})_3]$ , which results in chemical equivalence of all three manganese cations. Thus, the metal centers are subject either to electronic delocalization or to rapid intramolecular electron transfer (Vincent *et al.*, 1987). Simple substitution of the water molecules by other residues which break the  $D_{3h}$  symmetry of the  $\text{Mn}_3$  triangle enables accurate recognition of each metal oxidation state. In this work, we report the synthesis and the structure determination of a trinuclear oxo-centered mixed-valence manganese trichloroacetate with ordered  $\text{Mn}^{3+}$  and  $\text{Mn}^{2+}$  sites, *viz.*  $[\text{Mn}_3\text{O}(\text{CCl}_3\text{COO})_6(\text{CH}_3\text{COOH})_3]$ , (I).





**Figure 1**  
View of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown with dashed lines.

acetate anions bridge adjacent Mn atoms. The central O atom deviates by 0.017 (2) Å from the plane of the three Mn atoms. The coordination environment of each Mn atom is completed by terminal acetic acid molecules. The oxidation state of each Mn cation can clearly be recognized because of strong Jahn–Teller effects in the Mn<sup>3+</sup> environment and longer distances in the Mn<sup>2+</sup> coordination sphere. Atoms Mn1 and Mn2 can easily be recognized as Mn<sup>3+</sup> cations, and Mn3 as Mn<sup>2+</sup>. The coordination environment of the Mn<sup>2+</sup> cation is much less distorted and is characterized by longer Mn–O distances ranging from 2.139 (3) to 2.188 (3) Å (Table 1). The Mn–Mn distances are comparable to those observed in other  $\mu_3$ -oxo manganese(II,III,III) complexes. The two Mn<sup>2+</sup>···Mn<sup>3+</sup> distances are somewhat longer than the Mn<sup>3+</sup>···Mn<sup>3+</sup> distance. The hydroxy groups form strong intramolecular contacts with O atoms of the trichloroacetate anions. In turn, methyl H atoms take part in weak intermolecular hydrogen bonds (Table 2).

## Experimental

Mn(CCl<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O (2.12 g; Shova *et al.*, 1996) and CCl<sub>3</sub>COOH (20.60 g) were dissolved in 99.5% CH<sub>3</sub>COOH (210 ml). The solution was stirred and heated to 323 K for 2.5 h. After half an hour, a portion of KMnO<sub>4</sub> was added (0.25 g total). The reaction mixture was then heated to 373 K for 30 min. The red–brown mixture was allowed to stand at room temperature. After a week, dark-brown crystals appeared.

## Crystal data

[Mn<sub>3</sub>(C<sub>2</sub>Cl<sub>3</sub>O<sub>2</sub>)<sub>6</sub>O(C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>)<sub>3</sub>]  
*M<sub>r</sub>* = 1335.20  
 Triclinic, *P* $\bar{1}$   
*a* = 10.121 (3) Å  
*b* = 10.424 (3) Å  
*c* = 22.891 (5) Å  
 $\alpha$  = 88.01 (3)°  
 $\beta$  = 79.45 (3)°  
 $\gamma$  = 65.94 (3)°  
*V* = 2165.8 (12) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 2.047 Mg m<sup>-3</sup>

*D<sub>m</sub>* = 1.943 Mg m<sup>-3</sup>  
*D<sub>m</sub>* measured by flotation in  
 CHCl<sub>3</sub>/CHBr<sub>3</sub>  
 Mo *K*α radiation  
 Cell parameters from 18242  
 reflections  
 $\theta$  = 0–27.6°  
 $\mu$  = 2.04 mm<sup>-1</sup>  
*T* = 100 (2) K  
 Parallelepiped, dark brown  
 0.2 × 0.2 × 0.05 mm

## Data collection

Kuma KM-4 CCD  $\kappa$ -geometry  
 diffractometer  
 $\omega$  scans  
 Absorption correction: analytical  
 (CrysAlis RED; Oxford  
 Diffraction, 2003)  
*T<sub>min</sub>* = 0.691, *T<sub>max</sub>* = 0.899  
 30649 measured reflections

9906 independent reflections  
 8642 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.039  
 $\theta_{\max}$  = 27.6°  
*h* = −13 → 12  
*k* = −13 → 13  
*l* = −29 → 29

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.054  
*wR*(*F*<sup>2</sup>) = 0.097  
*S* = 1.16  
 9906 reflections  
 532 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0043P)^2 + 12.065P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.64 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{Å}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Mn1–O1	1.826 (3)	Mn2–O12	2.182 (3)
Mn1–O11	1.952 (3)	Mn3–O42	2.139 (3)
Mn1–O62	1.965 (3)	Mn3–O61	2.149 (3)
Mn1–O71	1.983 (3)	Mn3–O51	2.153 (3)
Mn1–O21	2.153 (3)	Mn3–O91	2.160 (3)
Mn1–O52	2.201 (3)	Mn3–O1	2.167 (3)
Mn2–O1	1.830 (3)	Mn3–O32	2.188 (3)
Mn2–O22	1.956 (3)	Mn1···Mn2	3.2223 (12)
Mn2–O31	1.981 (3)	Mn1···Mn3	3.4126 (13)
Mn2–O81	1.989 (3)	Mn2···Mn3	3.4521 (16)
Mn2–O41	2.178 (3)		
Mn1–O1–Mn2	123.61 (15)	Mn2–O1–Mn3	119.18 (14)
Mn1–O1–Mn3	117.18 (14)		

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O72–H72···O52	0.78 (6)	1.85 (6)	2.621 (4)	168 (6)
O82–H82···O41	0.75 (6)	1.98 (6)	2.641 (4)	149 (6)
O92–H92···O32	0.72 (7)	2.16 (7)	2.815 (5)	151 (7)
C72–H72B···O91 <sup>i</sup>	0.98	2.37	3.142 (5)	135
C72–H72C···O81 <sup>ii</sup>	0.98	2.46	3.367 (5)	155
C92–H92C···O72 <sup>iii</sup>	0.98	2.52	3.243 (6)	130

Symmetry codes: (i) *x*, *y* − 1, *z*; (ii) *x* − 1, *y*, *z*; (iii) *x*, *y* + 1, *z*.

All H atoms were found in difference Fourier maps. The coordinates of the hydroxy H atoms were refined. The C-bound H atoms were refined using a riding model, with C–H = 0.98 Å, and *U*<sub>iso</sub>(H) =

$1.2U_{\text{eq}}(\text{O})$  or  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The torsion angles of the methyl groups were refined.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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