

A pentanuclear bimetallic complex of manganese(II) and aluminium(III) ions: tetra- μ_2 -iodido-iodidobis(μ_3 -2-methoxyethanolato)bis(μ_2 -2-methoxyethanolato)dimethyl(tetrahydrofuran- κO)aluminium(III)tetramanganese(II)

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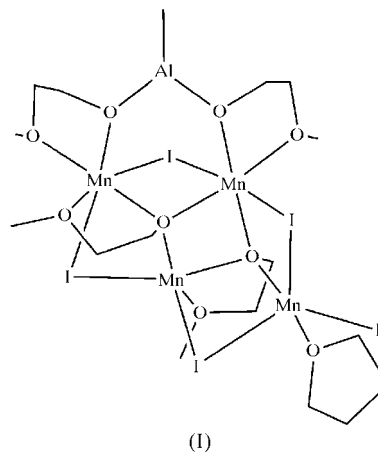
The molecule of the title compound, $[\text{Mn}_4\text{Al}(\text{CH}_3)_2(\text{C}_3\text{H}_7\text{O}_2)_4\text{I}_5(\text{C}_4\text{H}_8\text{O})]$, contains one Al^{III} and four Mn^{II} ions. Two Mn atoms are five-coordinate in the form of a trigonal bipyramid or a square pyramid. The two other Mn atoms are six-coordinate with an octahedral geometry. The four-coordinate Al atom is linked to the manganese core by μ - O_{alkoxo} bridges, forming an almost planar five-membered ring.

Comment

Alkylaluminum alkoxides have been investigated as components of Ziegler–Natta catalyst systems (Lin *et al.*, 1999; Rhine *et al.*, 1999; Sobota, 2004; Lewinski *et al.*, 2005). To date, several heterometallic aluminium complexes have been synthesized and characterized (Evans *et al.*, 1998; Sobota *et al.*, 2000, 2002; Utko *et al.*, 2004; Jerzykiewicz *et al.*, 2006). In a continuation of our systematic study in this field, a new heterometallic aluminium complex with functional alcohols has been prepared. The title compound, (I), crystallizes in the centrosymmetric space group $P2_1/c$. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1.

The crystal structure consists of a tetranuclear manganese(II) unit linked to an $\text{Al}(\text{CH}_3)_2$ group. In the tetramer, there are two types of Mn atoms [five-coordinate (T5) Mn1 and Mn2, and six-coordinate (T6) Mn3 and Mn4], linked by μ_3 - O_{alkoxo} and μ -I bridges. The Al atom is connected to the manganese core by μ - O_{alkoxo} bridges, forming an almost planar Al1/O31/Mn3/Mn4/O41 system [the largest deviation of atoms from the mean plane is 0.014 (2) Å]. This planar arrangement of a five-membered trimetallic ring containing aluminium is comparable to that found in a chloride analogue, *viz.* $[\text{Mn}_3\text{Al}(\mu_3\text{-OCH}_2\text{CH}_2\text{OCH}_3)(\mu\text{-Cl})_3(\mu\text{-OCH}_2\text{CH}_2\text{O}$

$\text{CH}_3)_2(\text{THF})_2(\text{CH}_3)_2\text{Cl}]$ (Jerzykiewicz *et al.*, 2006; THF is tetrahydrofuran), but different from that in another heterometallic aluminium compound with alkoxides, *viz.* $[(\text{CH}_3)_3\text{Al}(\mu\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)\text{Eu}(\mu\text{-}\eta^2\text{-OCH}_2\text{CH}_2\text{OCH}_3)_2\text{Al}(\text{CH}_3)_2]_2$ (Evans *et al.*, 1998).



The five-coordinate Mn atoms have trigonal-bipyramidal (Mn1) and square-pyramidal (Mn2) geometries with the value of the parameter τ equal to 0.73 and 0.02, respectively [$\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles; for square-pyramidal geometry $\tau = 0$, and for trigonal-bipyramidal geometry $\tau = 1$ (Addison *et al.*, 1984)]. To date, only a few examples of complexes containing two Mn^{II} ions with different geometries around the central atoms have been described [*e.g.* $\text{Na}_2(\text{H}_2\text{en})_2(\text{VO})_{10}[\text{B}_{14}\text{O}_{30}(\text{OH})_2]_2\{\text{Mn}_4(\text{C}_2\text{O}_4)[\text{B}_2\text{O}_4(\text{OH})_2]_2\text{Mn}(\text{H}_2\text{O})_2 \cdot (\text{H}_3\text{O})_{12}(\text{H}_2\text{O})_{19}$, where $\tau = 0.25$ and 0.58 (Cao *et al.*, 2005); en is ethylenediamine], in spite of the

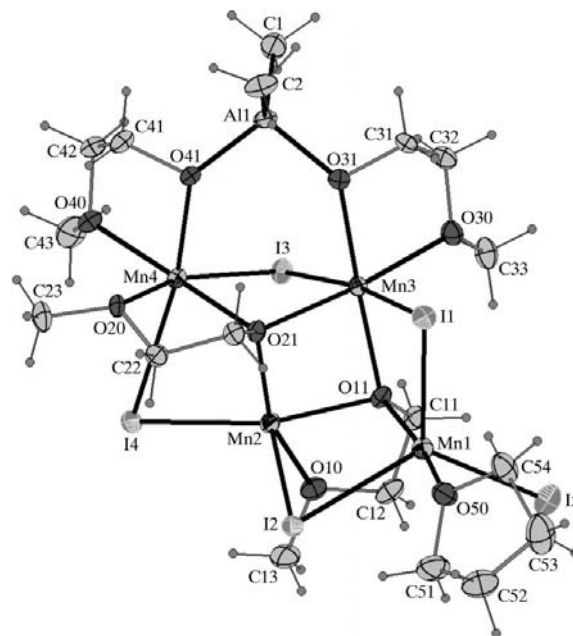


Figure 1

A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

fact that double square-pyramidal geometries are frequently observed (Kitajima *et al.*, 1991; Evans *et al.*, 1998; Pajunen *et al.*, 1998; Crewdson *et al.*, 2003; Bieller *et al.*, 2005).

The surroundings of the six-coordinate Mn3 and Mn4 atoms are both significantly distorted from regular octahedral geometry, as is clearly evident from the deformation of the O—Mn—O, I—Mn—O and I—Mn—I bond angles, which range from 77.88 (15)° for the chelating ligand to 100.76 (11)° for bridging O_{alkoxide} and I ligands.

The Al atom has a distorted tetrahedral geometry. The X—Al1—X angles [X = CH₃ or O_{alkoxo}; 102.5 (2)–117.3 (3)°] are similar to those found in Mn₃Al(CH₃)₂Cl₄(OCH₂CH₂OCH₃)₃·(THF)₂ [102.11 (10)–112.25 (16)°]. The Al—C and Al—O bond distances are in the range observed previously for four-coordinate aluminium compounds (Kumar *et al.*, 1994; Schumann *et al.*, 1996).

The Mn—O bond lengths are similar to those observed for the corresponding manganese compounds (Nihei *et al.*, 2002; Crewdson *et al.*, 2003; Jerzykiewicz *et al.*, 2006) and range from 2.108 (4) to 2.282 (4) Å. These distances can be grouped into six distinct categories (Table 3). The terminal Mn—I distance of 2.688 (2) Å is significantly shorter than the bridging Mn—I distances, which range from 2.773 (2) to 3.033 (2) Å, as expected (Beagley *et al.*, 1984, 1990; Mantel *et al.*, 2004). The closest Mn···Mn distances are in the range 3.152 (2)–3.570 (3) Å.

Only very weak intermolecular hydrogen bonds, formed between the terminal I5 atom and one of the H atoms of a methyl group, have been found (Table 2).

Experimental

All procedures were carried out under a nitrogen atmosphere using a standard Schlenk line. A Schlenk flask was charged with [Mn₄I₄(CH₃OCH₂CH₂O)₄(CH₃OCH₂CH₂OH)₄] (1.63 g, 1.22 mmol), C₆H₅CH₃ (60 ml) and THF (20 ml). The clear solution was stirred vigorously at 253 K and Al(CH₃)₃ (8.5 ml, 2.0 M solution in C₆H₅CH₃, 17.0 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 48 h. The resulting white precipitate was filtered off, and the filtrate was concentrated until a slight turbidity was observed; the solution was then warmed to 333–343 K until it lost its turbidity. The clear solution was layered with hexanes (20 ml). After a few weeks, crystals of (I) (0.62 g, 0.48 mmol, 40%) were obtained directly from the solution.

Crystal data

[Mn ₄ Al(CH ₃) ₂ (C ₃ H ₇ O ₂) ₄ -I ₅ (C ₄ H ₈ O)]	$\beta = 92.26 (4)^\circ$
$M_r = 1283.76$	$V = 3705 (2) \text{ \AA}^3$
Monoclinic, $P2_1/c$	$Z = 4$
$a = 7.896 (4) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 14.899 (4) \text{ \AA}$	$\mu = 5.56 \text{ mm}^{-1}$
$c = 31.516 (8) \text{ \AA}$	$T = 100 (2) \text{ K}$
	$0.12 \times 0.08 \times 0.04 \text{ mm}$

Data collection

Kuma KM-4 CCD κ -axis diffractometer	49961 measured reflections
Absorption correction: analytical (CrysAlis CCD; Oxford Diffraction, 2006)	8496 independent reflections
$T_{\min} = 0.321$, $T_{\max} = 0.666$	6775 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.050$

Table 1

Selected geometric parameters (Å, °).

Mn1—I1	2.773 (2)	Mn2—O21	2.131 (3)
Mn3—I1	2.890 (2)	Mn3—O11	2.214 (4)
Mn1—I2	2.870 (2)	Mn3—O21	2.185 (3)
Mn2—I2	2.802 (2)	Mn3—O30	2.231 (4)
Mn3—I3	2.979 (2)	Mn3—O31	2.109 (4)
Mn4—I3	2.820 (2)	Mn4—O20	2.223 (4)
Mn2—I4	2.780 (2)	Mn4—O21	2.147 (3)
Mn4—I4	3.033 (2)	Mn4—O40	2.192 (3)
Mn1—I5	2.688 (2)	Mn4—O41	2.108 (4)
Mn1—O11	2.232 (3)	Al1—O31	1.817 (4)
Mn1—O50	2.282 (4)	Al1—O41	1.811 (4)
Mn2—O10	2.199 (4)	Al1—C1	1.985 (6)
Mn2—O11	2.171 (3)	Al1—C2	1.979 (6)
Mn1—I1—Mn3	78.13 (5)	O11—Mn3—O31	177.94 (14)
Mn1—I2—Mn2	77.03 (5)	O21—Mn3—O30	169.96 (15)
Mn3—I3—Mn4	73.70 (5)	O21—Mn3—O31	99.93 (13)
Mn2—I4—Mn4	68.19 (5)	O30—Mn3—O31	77.88 (15)
I1—Mn1—I2	117.78 (5)	I3—Mn4—I4	90.26 (5)
I1—Mn1—I5	117.11 (5)	I3—Mn4—O20	163.05 (9)
I1—Mn1—O11	88.45 (10)	I3—Mn4—O21	84.96 (10)
I1—Mn1—O50	86.59 (10)	I3—Mn4—O40	100.76 (11)
I2—Mn1—I5	124.72 (5)	I3—Mn4—O41	98.07 (11)
I2—Mn1—O11	85.50 (10)	I4—Mn4—O20	85.26 (10)
I2—Mn1—O50	87.89 (10)	I4—Mn4—O21	87.07 (10)
I5—Mn1—O11	102.01 (9)	I4—Mn4—O40	94.68 (11)
I5—Mn1—O50	89.23 (12)	I4—Mn4—O41	170.37 (11)
O11—Mn1—O50	168.75 (14)	O20—Mn4—O21	78.50 (12)
I2—Mn2—I4	112.69 (5)	O20—Mn4—O40	95.91 (14)
I2—Mn2—O10	93.70 (12)	O20—Mn4—O41	88.08 (15)
I2—Mn2—O11	88.33 (10)	O21—Mn4—O40	174.00 (14)
I2—Mn2—O21	100.67 (10)	O21—Mn4—O41	98.43 (13)
I4—Mn2—O10	96.34 (12)	O40—Mn4—O41	79.08 (14)
I4—Mn2—O11	158.75 (10)	O31—Al1—O41	102.5 (2)
I4—Mn2—O21	94.20 (9)	O31—Al1—C1	109.2 (2)
O10—Mn2—O11	78.53 (14)	O31—Al1—C2	106.8 (2)
O10—Mn2—O21	157.31 (14)	O41—Al1—C1	109.2 (2)
O11—Mn2—O21	84.39 (13)	O41—Al1—C2	110.8 (2)
I1—Mn3—I3	173.07 (5)	C1—Al1—C2	117.3 (3)
I1—Mn3—O11	85.88 (9)	Mn1—O11—Mn2	106.72 (15)
I1—Mn3—O21	94.14 (9)	Mn1—O11—Mn3	106.83 (14)
I1—Mn3—O30	95.79 (12)	Mn1—O11—C11	116.2 (3)
I1—Mn3—O31	94.06 (11)	Mn2—O11—Mn3	91.91 (12)
I3—Mn3—O11	89.02 (9)	Mn2—O21—Mn3	93.81 (13)
I3—Mn3—O21	80.49 (9)	Mn2—O21—Mn4	99.50 (14)
I3—Mn3—O30	89.73 (12)	Mn3—O21—Mn4	106.90 (14)
I3—Mn3—O31	91.20 (11)	Mn3—O31—Al1	138.4 (2)
O11—Mn3—O21	82.14 (13)	Mn3—O31—C31	108.0 (3)
O11—Mn3—O30	100.07 (14)	Al1—O31—C31	112.5 (3)

Table 2

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C43—H43A···I5 ⁱ	0.98	3.05	4.012 (6)	168

Symmetry code: (i) $x, y - 1, z$.

Table 3

The Mn—O bond lengths (Å) versus coordination number (CN) of the Mn^{II} atom.

	CN	Mn—O	Mn—O _{average}
Mn— μ_2 -O	6	2.108 (4)–2.109 (4)	2.109 (1)
Mn— μ_3 -O	5	2.131 (3)–2.232 (3)	2.178 (5)
Mn— μ_3 -O	6	2.147 (3)–2.214 (4)	2.182 (3)
Mn—O _{ether} (chelating ligands)	5	2.199 (3)	2.199 (3)
Mn—O _{ether} (chelating ligands)	6	2.192 (3)–2.231 (4)	2.215 (1)
Mn—O _{ether} (THF)	5	2.281 (4)	2.281 (4)

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	340 parameters
$wR(F^2) = 0.080$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{\max} = 0.89 \text{ e } \text{\AA}^{-3}$
8496 reflections	$\Delta\rho_{\min} = -2.01 \text{ e } \text{\AA}^{-3}$

All H atoms were located in difference maps and subsequently treated as riding atoms, with C—H distances of 0.98 (CH₃) and 0.99 Å (CH₂), and with $U_{\text{iso}}(\text{H})$ values of 1.5 or 1.2 times $U_{\text{eq}}(\text{C})$ for CH₃ and CH₂ groups, respectively.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXTL*, *PLATON* (Version 1.081; Spek, 2003), *enCIFer* (Version 1.2; Allen *et al.*, 2004) and *publCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3065). Services for accessing these data are described at the back of the journal.

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