A dodecanuclear manganese(II,III) complex of pentaerythritol

Arindam Mukherjee, Colette Boskovic* and Robert W. Gable

School of Chemistry, University of Melbourne, Victoria 3010, Australia
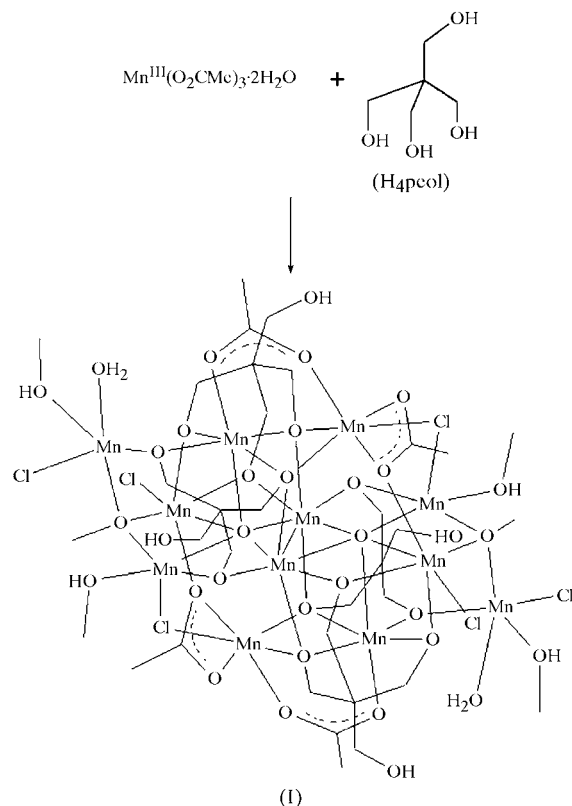Correspondence e-mail: c.boskovic@unimelb.edu.au

The molecule of the title compound, tetra-μ_2-acetato-diaquadi-μ_2-chloro-tetrachlorotetrakis[μ_4-3-hydroxy-2,2-bis-(oxidomethyl)propanolato]tetramethanoldi-μ_3-methanolato-di-μ_5-oxo-octamanganese(II)tetramanganese(III), [$Mn_4^{III}Mn_8^{II}$-$(CH_3O)_2(C_2H_3O_2)_4(C_5H_9O_4)_4Cl_6O_2(CH_4O)_4(H_2O)_2$], displays a centre of symmetry. The structure of the {$Mn_4^{III}Mn_8^{II}$-$O_{18}Cl_2$}$^{10-}$ core is composed of three layers and features two oxo ligands binding in a rare μ_5-mode.

Comment

Studying the structural aspects of new polynuclear transition metal complexes is of considerable interest because of their potential to act as single-molecule magnets (Gatteschi & Sessoli, 2003; Christou *et al.*, 2000; Sessoli *et al.*, 1993). We are presently exploring the solvothermal reactions of simple transition metal salts with polyalcohol-containing proligands in an effort to synthesize new polynuclear complexes with interesting magnetic properties (Labat *et al.*, 2005; Alley *et al.*, 2006). The complex [$Mn_4^{III}Mn_8^{II}(OMe)_2(O_2CMe)_4(HPeol)_4$-$Cl_6O_2(MeOH)_4(H_2O)_2$] (H$_4$peol is pentaerythritol), (I), is a neutral mixed-valent species that was synthesized by solvo-thermal methods (Laye & McInnes, 2004) at 393 K and obtained in high yield (see scheme). The presence of chloro ligands in (I) is due to the decomposition of dichloroethane (Park *et al.*, 2000; Walter *et al.*, 1994; Petrosius *et al.*, 1993) as a result of the high temperature and autogenous pressure. The methanol employed in the reaction as a solvent acts as the source of the methanolate ligand in the complex. Crystals could not be obtained upon changing the composition of the solvent mixture.

Complex (I) crystallizes in the centrosymmetric triclinic space group $P\bar{1}$; an *ORTEP* (Farrugia, 1997) diagram is provided in Fig. 1, and selected bond lengths and angles are given in Table 1. Hydrogen-bond parameters are given in Table 2. The structure of the {$Mn_4^{III}Mn_8^{II}O_{18}Cl_2$}$^{10-}$ core can be considered to consist of three layers. The central layer has two

Mn^{III} (Mn2 and Mn3) and four Mn^{II} centres (Mn1 and Mn4–Mn6; Fig. 2) bridged by eight O atoms, while the peripheral layers each contain one Mn^{III} and two Mn^{II} centres bridged by five O atoms and one Cl atom. All the Mn atoms (Mn^{II}/Mn^{III}) are six-coordinate. The three layers are linked through the bridging O and Cl atoms. While the atoms within the central layer are essentially coplanar, the atoms in the two peripheral layers deviate more substantially from planarity.

(I)

The two oxo ligands (O9) bind in a rare μ_5-mode, displaying a square-pyramidal geometry (Fig. 2) (Khan *et al.*, 1992; Murugesu *et al.*, 2006) with one long bond (Mn5—O9) of 2.625 (3) Å. Of the four O atoms of the Hpeol^{3-} ligands, one remains as a pendant alcohol group (*i.e.* O8), two coordinate in a μ_3-manner (*i.e.* O5 and O6) and the remaining O atom (*i.e.* O7) binds two Mn^{II} ions in a μ_2-fashion (Fig. 1). Two MeO$^-$ and two Cl$^-$ ligands bridge Mn centres in μ_3- and μ_2-modes, respectively. Two of the acetate ligands contribute O atoms to the core of complex (I), binding in a η^1,η^2,μ_2-fashion, while the other two bind in the common *syn,syn*,μ_2-manner. The peripheral ligation is completed by terminally bound MeOH, H$_2$O and chloro ligands. The average Mn$^{II}\cdots$Mn^{II}, Mn$^{II}\cdots$Mn^{III} and Mn$^{III}\cdots$Mn^{III} distances are 3.535, 3.365 and 3.035 Å, respectively. Each of the Mn^{II} ions is coordinated to five O atoms and one Cl atom, in contrast to the Mn^{III} centres that possess six O atoms in their coordination environment. The Mn^{II} ions display an average Mn—O distance of 2.22 (2) Å, with little difference between intra-layer and inter-layer connectivities. The intra- and inter-layer Mn—O distances for the Mn^{III} ions are in the ranges 1.91 (2)–1.94 (2) and 2.16 (2)–2.29 (2) Å, respectively. Thus, the Jahn–Teller elongated axes of the Mn^{III} centres are essentially parallel and

metal-organic compounds

aligned along the inter-layer vector. The average bridging and terminal Mn^{II}—Cl distances are 2.48 (1) and 2.44 (1) Å, respectively.

There has recently been a report of a structure of similar formulation and architecture (Murugesu *et al.*, 2006). However, this compound is obtained from an entirely different synthetic route and has no chloro ligands. The Mn centres bridged by Cl atoms in complex (I) are bridged by the O atoms of carboxylate ligands in the literature compound. In addition, while all of the Mn centres in complex (I) are six-coordinate, two of the Mn^{II} centres in the literature compound are seven-coordinate. Differences in the magnetic behaviour will likely result from these different magnetic exchange pathways. The literature compound displays the slow magnetic relaxation characteristic of a single-molecule magnet and thus it is of interest to probe the magnetic properties of complex (I) in the future.
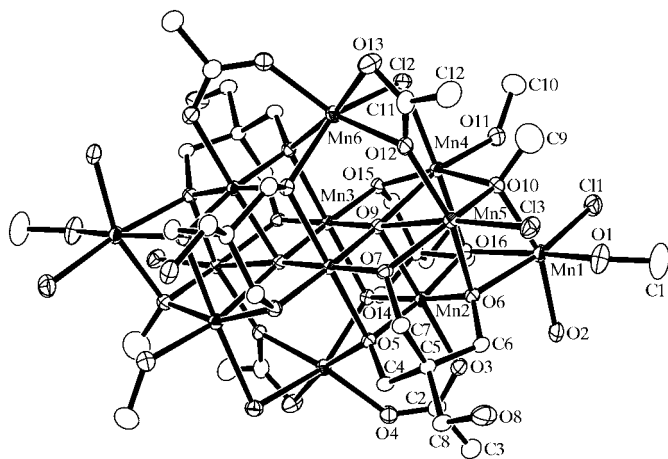

Figure 1
An *ORTEP-3* (Farrugia, 1997) diagram of complex (I), with the atoms in the asymmetric unit labelled (except for atoms C14, C15, C16 and C17, and pendant atom O17 of the second Hpeol unit lying at the back in the figure). Displacement ellipsoids are shown at the 50% probability level.
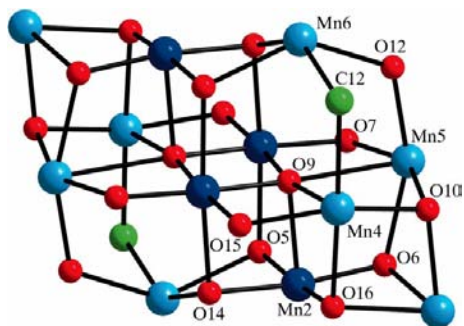

Figure 2
A labelled ball-and-stick diagram of the core of complex (I) (colour code for the electronic version: Mn^{III} dark blue, Mn^{II} light blue, O red and Cl green).

Experimental

Mn^{III}(O$_2$CMe)$_3$·2H$_2$O (0.248 g, 0.90 mmol), pentaerythritol (0.061 g, 0.45 mmol) and 10 ml of an 8:2 *v/v* dichloroethane–methanol solution were combined in a Teflon-lined solvothermal reaction vessel. The mixture was heated at 393 K for 48 h and then cooled at a rate of 2 K h^{-1}. Brown crystalline blocks coated the walls and bottom of the Teflon vessel (yield 0.090 g, 0.047 mmol, 60%). Elemental analysis calculated for C$_{34}$H$_{74}$Cl$_6$Mn$_{12}$O$_{34}$: C 21.51, H 3.93%; found C 21.47, H 3.87%. IR (KBr): 3384 (*br, s*), 2914 (*br*), 2868 (*m*), 1630 (*m*), 1601 (*s*), 1552 (*s*), 1448 (*s*), 1429 (*s*), 1356 (*m*), 1113 (*s*), 1064 (*m*), 1012 (*s*), 989 (*m*), 686 (*m*), 649 (*s*), 580 (*vs*), 547 (*m*), 508 (*m*), 474 (*m*), 451 (*w*) cm^{-1}.

Crystal data

[Mn$_{12}$(CH$_3$O)$_2$(C$_2$H$_3$O$_2$)$_4$-(C$_5$H$_9$O$_4$)$_4$Cl$_6$O$_2$(CH$_4$O)$_4$-(H$_2$O)$_2$]	$\gamma = 108.916\ (1)°$
	$V = 1564.76\ (16)$ Å^3
$M_r = 1898.91$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 2.015$ Mg m^{-3}
$a = 11.3575\ (7)$ Å	Mo $K\alpha$ radiation
$b = 11.6949\ (7)$ Å	$\mu = 2.68$ mm^{-1}
$c = 13.8332\ (8)$ Å	$T = 130\ (2)$ K
$\alpha = 101.753\ (1)°$	Cubic, brown
$\beta = 107.337\ (1)°$	$0.37 \times 0.25 \times 0.21$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	9180 measured reflections
	6251 independent reflections
φ and ω scans	5762 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick 1997)	$R_{int} = 0.013$
	$\theta_{max} = 26.4°$
$T_{min} = 0.544$, $T_{max} = 0.774$ (expected range = 0.401–0.570)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.044P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$+ 1.886P]$
$wR(F^2) = 0.081$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.009$
6251 reflections	$\Delta\rho_{max} = 0.83$ e Å^{-3}
415 parameters	$\Delta\rho_{min} = -0.83$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

H atoms on the hetero atoms were located in difference Fourier maps and were refined with individual isotropic displacement parameters. All other H atoms were constrained at geometrical estimates with isotropic displacement parameters of 1.2–1.5 times those of the parent C atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3024). Services for accessing these data are described at the back of the journal.

Table 1
Selected geometric parameters (Å, °).

Mn1—O2	2.131 (2)	Mn3—Mn4	3.1201 (5)
Mn1—O1	2.158 (2)	Mn3—Mn5^i	3.2226 (5)
Mn1—O10	2.2054 (18)	Mn4—O15^i	2.0787 (17)
Mn1—O16^i	2.2462 (18)	Mn4—O10	2.1147 (18)
Mn1—O6	2.3049 (17)	Mn4—O11	2.219 (2)
Mn1—Cl1	2.4275 (8)	Mn4—O16^i	2.3089 (17)
Mn1—Mn2	3.1953 (5)	Mn4—O9	2.3491 (17)
Mn2—O16^i	1.9275 (17)	Mn4—Cl2	2.4834 (7)
Mn2—O5	1.9282 (17)	Mn5—O7	2.0763 (17)
Mn2—O6	1.9293 (17)	Mn5—O10	2.1143 (18)
Mn2—O14^i	1.9431 (17)	Mn5—O12	2.1344 (19)
Mn2—O3	2.1580 (18)	Mn5—O6	2.2869 (17)
Mn2—O9	2.2735 (16)	Mn5—Cl3	2.4531 (7)
Mn2—Mn3^i	3.1123 (5)	Mn5—Mn3^i	3.2226 (5)
Mn2—Mn3	3.1384 (5)	Mn6—O4^i	2.1256 (19)
Mn2—Mn6^i	3.1419 (5)	Mn6—O14	2.1948 (17)
Mn3—O15^i	1.9060 (17)	Mn6—O5^i	2.2470 (17)
Mn3—O7^i	1.9085 (17)	Mn6—O13	2.262 (2)
Mn3—O9^i	1.9358 (17)	Mn6—O12	2.2845 (18)
Mn3—O9	1.9442 (17)	Mn6—Cl2	2.4788 (7)
Mn3—O5^i	2.2793 (17)	Mn6—C11	2.635 (3)
Mn3—O14^i	2.2855 (17)	Mn6—Mn2^i	3.1419 (5)
Mn3—Mn3^i	2.8558 (7)	O9—Mn3^i	1.9358 (17)
Mn3—Mn2^i	3.1123 (5)		
O2—Mn1—O1	92.89 (9)	O9—Mn3—O14^i	84.01 (6)
O2—Mn1—O10	159.70 (8)	O5^i—Mn3—O14^i	173.06 (6)
O1—Mn1—O10	92.58 (8)	O15^i—Mn4—O10	157.54 (7)
O2—Mn1—O16^i	91.04 (8)	O15^i—Mn4—O11	101.40 (7)
O1—Mn1—O16^i	163.94 (8)	O10—Mn4—O11	91.22 (7)
O10—Mn1—O16^i	78.71 (6)	O15^i—Mn4—O16^i	82.70 (6)
O2—Mn1—O6	83.91 (8)	O10—Mn4—O16^i	79.18 (7)
O1—Mn1—O6	92.78 (8)	O11—Mn4—O16^i	88.23 (7)
O10—Mn1—O6	76.31 (6)	O15^i—Mn4—O9	74.57 (6)
O16^i—Mn1—O6	72.15 (6)	O10—Mn4—O9	88.61 (6)
O2—Mn1—Cl1	99.49 (7)	O11—Mn4—O9	165.64 (7)
O1—Mn1—Cl1	98.13 (7)	O16^i—Mn4—O9	77.63 (6)
O10—Mn1—Cl1	99.07 (5)	O15^i—Mn4—Cl2	96.09 (5)
O16^i—Mn1—Cl1	96.57 (5)	O10—Mn4—Cl2	101.46 (5)
O6—Mn1—Cl1	168.36 (5)	O11—Mn4—Cl2	94.23 (6)
O16^i—Mn2—O5	172.17 (7)	O16^i—Mn4—Cl2	177.43 (5)
O16^i—Mn2—O6	88.05 (7)	O9—Mn4—Cl2	99.87 (4)
O5—Mn2—O6	93.85 (7)	O7—Mn5—O10	150.12 (7)
O16^i—Mn2—O14^i	93.43 (7)	O7—Mn5—O12	91.04 (7)
O5—Mn2—O14^i	83.78 (7)	O10—Mn5—O12	97.71 (7)
O6—Mn2—O14^i	172.85 (7)	O7—Mn5—O6	82.55 (6)
O16^i—Mn2—O3	93.11 (7)	O10—Mn5—O6	78.49 (6)
O5—Mn2—O3	94.38 (7)	O12—Mn5—O6	157.49 (7)
O6—Mn2—O3	92.99 (7)	O7—Mn5—Cl3	107.96 (5)
O14^i—Mn2—O3	93.92 (7)	O10—Mn5—Cl3	97.51 (5)
O16^i—Mn2—O9	87.66 (7)	O12—Mn5—Cl3	104.27 (5)
O5—Mn2—O9	84.79 (7)	O6—Mn5—Cl3	98.24 (5)
O6—Mn2—O9	88.70 (7)	O4^i—Mn6—O14	91.20 (7)
O14^i—Mn2—O9	84.37 (7)	O4^i—Mn6—O5^i	87.23 (7)
O3—Mn2—O9	178.16 (7)	O14—Mn6—O5^i	71.16 (6)
O15^i—Mn3—O7^i	94.23 (7)	O4^i—Mn6—O13	82.58 (7)
O15^i—Mn3—O9^i	173.88 (7)	O14—Mn6—O13	111.03 (7)
O7^i—Mn3—O9^i	91.88 (7)	O5^i—Mn6—O13	169.59 (7)
O15^i—Mn3—O9	88.67 (7)	O4^i—Mn6—O12	134.00 (7)
O7^i—Mn3—O9	176.80 (7)	O14—Mn6—O12	85.85 (6)
O9^i—Mn3—O9	85.21 (7)	O5^i—Mn6—O12	133.81 (7)
O15^i—Mn3—O5^i	95.52 (7)	O13—Mn6—O12	56.41 (7)
O7^i—Mn3—O5^i	88.29 (7)	O4^i—Mn6—Cl2	116.35 (6)
O9^i—Mn3—O5^i	84.46 (7)	O14—Mn6—Cl2	145.68 (5)
O9—Mn3—O5^i	90.10 (7)	O5^i—Mn6—Cl2	89.19 (5)
O15^i—Mn3—O14^i	88.03 (7)	O13—Mn6—Cl2	93.43 (6)
O7^i—Mn3—O14^i	97.41 (7)	O12—Mn6—Cl2	88.42 (5)
O9^i—Mn3—O14^i	91.38 (6)	O4^i—Mn6—C11	109.11 (8)

Table 1 *Continued*

O14—Mn6—C11	99.32 (8)	Mn3^i—O9—Mn4	169.31 (9)
O5^i—Mn6—C11	161.61 (8)	Mn3—O9—Mn4	92.74 (6)
O13—Mn6—C11	28.57 (8)	Mn2—O9—Mn4	91.74 (6)
O12—Mn6—C11	27.85 (8)	Mn5—O10—Mn4	103.13 (8)
Cl2—Mn6—C11	90.86 (6)	Mn5—O10—Mn1	104.14 (7)
Mn6—Cl2—Mn4	96.50 (2)	Mn4—O10—Mn1	102.86 (7)
Mn2—O5—Mn6^i	97.32 (7)	Mn4—O11—H11	109 (3)
Mn2—O5—Mn3^i	95.05 (7)	Mn5—O12—Mn6	122.72 (9)
Mn6^i—O5—Mn3^i	113.14 (7)	Mn2^i—O14—Mn6	98.62 (7)
Mn2—O6—Mn5	109.00 (7)	Mn2^i—O14—Mn3^i	95.50 (7)
Mn2—O6—Mn1	97.59 (7)	Mn6—O14—Mn3^i	111.90 (7)
Mn5—O6—Mn1	95.82 (6)	Mn3^i—O15—Mn4^i	102.99 (8)
Mn3^i—O7—Mn5	107.87 (8)	Mn2^i—O16—Mn1^i	99.63 (7)
Mn3^i—O9—Mn3	94.79 (7)	Mn2^i—O16—Mn4^i	102.76 (7)
Mn3^i—O9—Mn2	95.02 (7)	Mn1^i—O16—Mn4^i	95.73 (7)
Mn3—O9—Mn2	95.85 (7)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$Cl3	0.78 (4)	2.35 (4)	3.097 (2)	159 (3)
O2—H21$\cdots$O17^{ii}	0.87 (4)	1.77 (4)	2.630 (3)	169 (4)
O2—H22$\cdots$O3	0.74 (4)	1.96 (4)	2.658 (3)	158 (4)
O8—H8$\cdots$O13^{iii}	0.81 (5)	2.27 (5)	2.952 (3)	142 (5)
O11—H11$\cdots$Cl1	0.76 (4)	2.32 (4)	3.069 (2)	172 (4)
O17—H17$\cdots$Cl3^{iv}	0.82 (4)	2.32 (4)	3.132 (2)	173 (4)

Symmetry codes: (ii) $x, y, z + 1$; (iii) $x - 1, y, z$; (iv) $-x, -y + 1, -z$.

References

Alley, K. G., Bircher, R., Waldmann, O., Ochsenbein, S. T., Güdel, H. U., Moubaraki, B., Murray, K. S., Fernandez-Alonso, F., Abrahams, B. F. & Boskovic, C. (2006). *Inorg. Chem.* **45**, 8950–8957.

Brandenburg, K. (1997). *DIAMOND*. Version 3.0. Crystal Impact GbR, Bonn, Germany.

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Christou, G., Gatteschi, D., Hendrickson, D. N. & Sessoli, R. (2000). *Mater. Res. Soc. Bull.* **25**, 66–71.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gatteschi, D. & Sessoli, R. (2003). *Angew. Chem. Int. Ed.* **42**, 268–297.

Khan, M. I., Chen, Q., Goshorn, D. P., Hope, H., Parkin, S. & Zubieta, J. (1992). *J. Am. Chem. Soc.* **114**, 3341–3346.

Labat, G., Boskovic, C. & Güdel, H. U. (2005). *Acta Cryst.* E**61**, m611–m613.

Laye, R. H. & McInnes, J. L. (2004). *Eur. J. Inorg. Chem.* pp. 2811–2818.

Murugesu, M., Wernsdorfer, W., Abboud, K. A., Brechin, E. K. & Christou, G. (2006). *Dalton Trans.* pp. 2285–2287.

Park, M., Komarneni, S. & Roy, R. (2000). *Mater. Lett.* **43**, 259–263.

Petrosius, S. C., Drago, R. S., Young, V. & Grunewald, G. C. (1993). *J. Am. Chem. Soc.* **115**, 6131–6137.

Sessoli, R., Tsai, H. L., Schake, A. R., Wang, S., Vincent, J. B., Folting, K., Gatteschi, D., Christou, G. & Hendrickson, D. N. (1993). *J. Am. Chem. Soc.* **115**, 1804–1816.

Sheldrick, G. M. (1997). *SHELXS97, SHELXL97* and *SADABS*. University of Göttingen, Germany.

Walter, W. K., Jones, R. G., Waugh, K. C. & Bailey, S. (1994). *Catal. Lett.* **24**, 333–342.

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Mukherjee *et al.* · [Mn$_{12}$(CH$_3$O)$_2$(C$_2$H$_3$O$_2$)$_4$(C$_5$H$_9$O$_4$)$_4$Cl$_6$O$_2$(CH$_4$O)$_4$(H$_2$O)$_2$] **m73**