Table 1. *Selected geometric parameters (Å, °)*

N1—C1	1.498 (1)	N2—C9	1.474 (1)
N1—C5^{i}	1.502 (1)	C8—O1	1.254 (1)
N1—C6	1.508 (1)	C8—O2	1.2653 (9)
N2—C2	1.4653 (9)	C11—O3	1.2570 (9)
N2—C3	1.470 (1)	C11—O4	1.270 (1)
N1—C1—C2—N2	−39.3 (1)	N1—C6—C7—C8	−172.01 (9)
C1—C2—N2—C3	169.17 (8)	C6—C7—C8—O1	6.9 (1)
C2—N2—C3—C4	−79.2 (1)	C6—C7—C8—O2	−174.69 (9)
N2—C3—C4—C5	−68.17 (8)	C1—C2—N2—C9	−69.2 (1)
C3—C4—C5—N1^{i}	−179.53 (6)	C2—N2—C9—C10	161.47 (7)
C4—C5—N1^{i}—C1^{i}	−168.91 (6)	C4—C3—N2—C9	157.98 (7)
C5—N1^{i}—C1^{i}—C2^{i}	63.34 (8)	C3—N2—C9—C10	−77.05 (9)
C2—C1—N1—C6	167.46 (7)	N2—C9—C10—C11	−72.1 (1)
C1—N1—C6—C7	71.5 (1)	C9—C10—C11—O3	0.1 (1)
C4^{i}—C5^{i}—N1—C6	−63.70 (8)	C9—C10—C11—O4	−179.42 (9)
C5^{i}—N1—C6—C7	−57.0 (1)		
Na···OW1^{ii}	2.3778 (9)	Na···OW2^{iii}	2.4094 (8)
Na···OW8	2.3891 (9)	Na···OW6	2.4341 (9)
Na···OW2^{ii}	2.3899 (7)	Na···OW4^{iii}	2.4706 (9)

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

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—HN1···O3	0.93 (1)	1.84 (1)	2.7222 (8)	157 (1)
N1—HN1···N2	0.93 (1)	2.38 (1)	2.806 (1)	108 (1)
OW2—H1W2···O1	0.81 (2)	2.00 (2)	2.804 (1)	175 (1)
OW5—H2W5···O1	0.80 (2)	2.07 (2)	2.845 (1)	161 (2)
OW4—H1W4···O1	0.91 (2)	2.11 (2)	3.001 (1)	165 (2)
OW3—H1W3···O2	0.85 (2)	1.98 (2)	2.8028 (9)	163 (1)
OW8—H1W8···O2	0.84 (2)	1.97 (2)	2.811 (1)	173 (2)
OW1—H1W1···O2	0.83 (2)	2.02 (2)	2.846 (1)	176 (1)
OW5^{i}—H1W5^{i}···O3	0.83 (2)	1.98 (2)	2.795 (1)	167 (1)
OW2^{ii}—H2W2^{ii}···O4	0.84 (2)	1.92 (2)	2.7634 (9)	175 (2)
OW7^{iii}—H1W7^{iii}···O4	0.91 (2)	1.90 (2)	2.765 (1)	159 (1)
OW3^{i}—H2W3^{i}···O4	0.78 (2)	2.14 (2)	2.886 (1)	158 (2)
OW1—H2W1···OW7	0.87 (2)	1.92 (2)	2.778 (1)	168 (2)
OW8^{iv}—H2W8^{iv}···OW3	0.83 (2)	1.92 (2)	2.7468 (9)	169 (2)
OW7^{v}—H2W7^{v}···OW4	0.83 (2)	2.04 (2)	2.837 (1)	160 (2)
OW4—H2W4···OW7	0.91 (1)	2.06 (1)	2.9703 (9)	179 (2)
OW6^{vi}—H1W6^{vi}···OW5	0.84 (2)	1.98 (2)	2.803 (1)	170 (2)
OW6—H2W6···OW8	0.82 (2)	2.14 (2)	2.832 (1)	142 (2)

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

All H atoms were located from difference Fourier maps and were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DREAM* (Blessing, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP* (Johnson, 1970).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1178). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
Dahaoui-Gindrey, V. (1995). PhD thesis, Henri Poincaré, Nancy I University, France.
Dahaoui-Gindrey, V., Lecomte, C., Chollet, H., Mishra, A. K., Mehadji, C. & Guilard, R. (1995). *New J. Chem.* **19**, 839–850.
Dale, J. (1980). *Isr. J. Chem.* **20**, 3–11.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1970). *ORTEP*. Report ORNL-3794, 2nd revision. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1976). *SHELX76*. *Program for Crystal Structure Determination*. University of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86*. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

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Octacarbonyl-μ-chloro-μ-dicyclohexylphosphido-dimanganese

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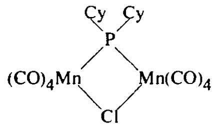
Abstract

The title compound, $[Mn_2(\mu\text{-}Cl)\{\mu\text{-}P(C_6H_{11})_2\}(CO)_8]$, has as central molecular fragment, a planar Mn_2ClP ring, with Mn—Cl and Mn—P bond lengths of 2.4010 (12) and 2.4134 (11) Å, respectively.

Comment

The title compound, (I), is the first example of a structurally characterized μ-Cl- and μ-P-bridged dimanganese–carbonyl complex. The centre of the molecule lies on a crystallographic twofold axis that runs through the Cl and P atoms.



(I)

Both the Mn atoms attain slightly distorted octahedral coordination *via* the bridging Cl and P atoms, and the four carbonyl groups. The latter show an almost eclipsed arrangement at the manganese centres, with torsion angles C3—Mn1—Mn1*A*–C2*A* −0.2 (2), C1—Mn1—Mn1*A*—C1*A* −0.8 (3) and C4—Mn1—Mn1*A*—C4*A* −2.0 (2)°. According to the twofold axis, the central Mn_2ClP ring is planar, with a non-bonding Mn···Mn distance of 3.648 (1) Å. The short Mn—Cl bond length of 2.4010 (12) Å may be compared with values of 2.395 (1) Å for $[Mn_2(\mu\text{-}Cl)_2(CO)_8]$ (Clegg & Morton, 1978) and 2.397 (2) Å for $[Mn_2(\mu\text{-}Cl)_2(CO)_6(thf)_2]$ (Van Derveer & Burlitch, 1980). The Mn—P bond length of 2.4134 (11) Å is equal to that of the twofold phosphido-bridged cyclohexyl complex $[Mn_2(\mu\text{-}PCy_2)_2(CO)_8]$ [2.408 (1) Å; Flörke & Haupt, 1993]. This supports the general observation that Mn—P distances of phosphido-bridged Mn_2–carbonyl complexes depend strongly on the nature of the ligands *R* attached to the P atoms (Flörke & Haupt, 1993). The typical shortening of *M*—C bonds involving carbonyl groups *trans* to bridging-halogeno ligands (*e.g.* Lal De, 1983; Geoffroy, Rosenberg, Herlinger & Rheingold, 1986) is observed for the Mn—C4 distance of 1.794 (4) Å compared with the bond lengths Mn—C1 1.852 (4) and Mn—C2 1.868 (4) Å. The ring angles enclosed at the bridging atoms [Mn—P—Mn 98.18 (6) and Mn—Cl—Mn 98.86 (6)°] are nearly the same. The above-mentioned twofold chloro-bridged manganese–carbonyl complexes exhibit somewhat more acute Mn—Cl—Mn angles of 96.3 (1) and 95.9 (1)°, respectively. There are no intermolecular interactions shorter than van der Waals distances.

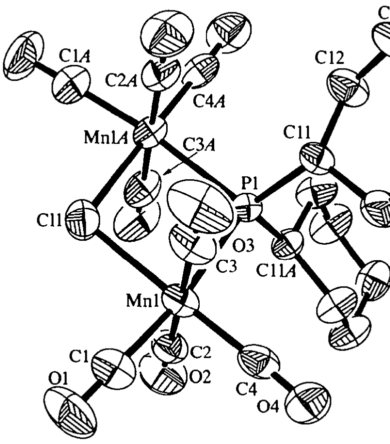


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The synthesis of (I) was carried out by adding a solution of chlorine in CCl_4 to a solution of $[NEt_4][Mn_2(CO)_8(\mu\text{-}PCy_2)]$ in THF at 273 K. After a TLC separation, the title compound was recrystallized from $CHCl_3$–pentane.

Crystal data

$[Mn_2Cl(C_{12}H_{22}P)(CO)_8]$
$M_r = 566.68$
Monoclinic
$C2/c$
$a = 17.659 (3)$ Å
$b = 8.477 (2)$ Å
$c = 17.763 (3)$ Å
$\beta = 114.100 (10)°$
$V = 2427.3 (8)$ Å^3
$Z = 4$
$D_x = 1.551$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 8.0$–$17.5°$
$\mu = 1.258$ mm^{-1}
$T = 293 (2)$ K
Prism
0.40 × 0.30 × 0.18 mm
Red

Data collection

Siemens *R*3*m* diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL*; Siemens, 1995)
$T_{min} = 0.674$, $T_{max} = 0.797$
2886 measured reflections
2794 independent reflections
1834 reflections with $I > 2\sigma(I)$

$R_{int} = 0.042$
$\theta_{max} = 27.56°$
$h = -22 \rightarrow 20$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 23$
3 standard reflections every 400 reflections intensity decay: insignificant

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.104$
$S = 1.103$
2794 reflections
146 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 1.6821P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.538$ e Å^{-3}
$\Delta\rho_{min} = -0.354$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn1	−0.07727 (3)	−0.04693 (7)	0.29364 (3)	0.0395 (2)
P1	0	−0.2334 (2)	1/4	0.0315 (3)
Cl1	0	0.1373 (2)	1/4	0.0525 (4)
C1	−0.1281 (3)	0.1183 (6)	0.3232 (3)	0.0586 (11)
O1	−0.1584 (2)	0.2192 (4)	0.3424 (2)	0.0888 (11)
C2	−0.1596 (2)	−0.0481 (5)	0.1863 (2)	0.0484 (9)
O2	−0.2098 (2)	−0.0468 (4)	0.1219 (2)	0.0749 (9)
C3	0.0094 (2)	−0.0487 (6)	0.3981 (2)	0.0526 (9)
O3	0.0606 (2)	−0.0468 (5)	0.4619 (2)	0.0805 (10)
C4	−0.1343 (2)	−0.1898 (5)	0.3241 (2)	0.0496 (10)
O4	−0.1726 (2)	−0.2773 (4)	0.3430 (2)	0.0730 (9)
C11	0.0678 (2)	−0.3623 (4)	0.3379 (2)	0.0381 (8)
C12	0.1353 (2)	−0.4585 (6)	0.3254 (2)	0.0550 (10)
C13	0.1946 (2)	−0.5273 (6)	0.4067 (3)	0.0634 (12)
C14	0.1512 (3)	−0.6284 (5)	0.4469 (3)	0.0603 (11)
C15	0.0826 (3)	−0.5401 (6)	0.4564 (2)	0.0660 (12)
C16	0.0218 (2)	−0.4681 (5)	0.3751 (2)	0.0547 (10)

Table 2. *Selected geometric parameters (Å, °)*

Mn1—C4	1.794 (4)	Mn1—C2	1.868 (4)
Mn1—C1	1.852 (4)	Mn1—Cl1	2.4010 (12)
Mn1—C3	1.861 (4)	Mn1—P1	2.4134 (11)
Cl1—Mn1—P1	81.48 (4)	Mn1^i—Cl1—Mn1	98.86 (6)
Mn1—P1—Mn1^i	98.18 (6)		

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

Program(s) used to solve structure: *SHELXTL* (Siemens, 1995). Program(s) used to refine structure: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1124). Services for accessing these data are described at the back of the journal.

References

Clegg, W. & Morton, S. (1978). *Acta Cryst.* **B34**, 1707–1709.
Flörke, U. & Haupt, H.-J. (1993). *Acta Cryst.* **C49**, 374–376.
Geoffroy, G. L., Rosenberg, S., Herlinger, A. W. & Rheingold, A. L. (1986). *Inorg. Chem.* **25**, 2916–2919.
Lal De, R. (1983). *J. Organomet. Chem.* **243**, 331–337.
Siemens (1995). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Van Derveer, M. C. & Burlitch, J. M. (1980). *J. Organomet. Chem.* **197**, 357–368.

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Polymeric Aquatri-μ-chloro-(tetrahydrofuran-*O*)lanthanum(III)

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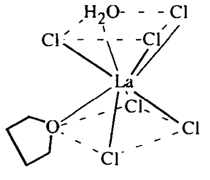
Abstract

The structure of the title compound, $[La(\mu\text{-}Cl)_3(C_4H_8O)(H_2O)]_n$, is based on a bidimensional mesh-like polymer. The metal is eight-coordinate with distorted square antiprismatic geometry; each $[LaCl_3(thf)(H_2O)]$ unit is linked to three others *via* pairs of chloride bridges.

Comment

The title compound, (I), was isolated as a partial dehydration product from the reaction system $LaCl_3(H_2O)_6/SOCl_2/THF$ (Taylor, 1962). The La atom is eight-coordinate, with the ligands providing a distorted square antiprismatic environment (Fig. 1). The atoms in the square faces of the antiprism have r.m.s. deviations of 0.083 (Cl3, Cl1, O2, Cl3*A*; see Fig. 1) and 0.100 Å (Cl2, O1, Cl1*A*, Cl2*A*; see Fig. 1), while the dihedral angle between these faces is 2.8 (1)°. Each La atom is linked to three others *via* $(\mu_2\text{-}Cl)_2$ halogen bridging to produce polymeric layers. A single layer as viewed down the *c* axis (Fig. 2) shows that the tetrahydrofuran molecules coordinated to adjacent La atoms lie on opposite sides of the polymeric layer. The water molecules are located within the La–Cl layers. The shortest water O to Cl distance is 3.295 (10) Å; this is about the same as the sum of the respective van der Waals radii and thus there is no strong evidence for hydrogen bonding.



(I)

The title compound is isostructural with the Ce and Nd analogues, *i.e.* $[Ce(\mu\text{-}Cl)_3(thf)(H_2O)]_n$ (Hubert-Pfalzgraf, Machado & Vaissermann, 1996; Evans, Feldman & Ziller, 1996) and $[Nd(\mu\text{-}Cl)_3(thf)(H_2O)]_n$ (Willey, Woodman & Drew, 1997).

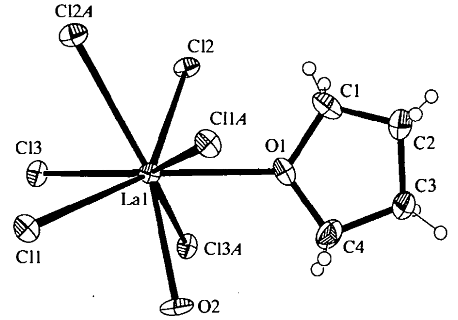


Fig. 1. View of the environment of one metal centre showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii; water H atoms are not shown. Atoms Cl1*A*, Cl2*A* and Cl3*A* have been generated by the symmetry operations $(-x, 1-y, 2-z)$, $(-x, -y, 2-z)$ and $(1-x, -y, 2-z)$, respectively.

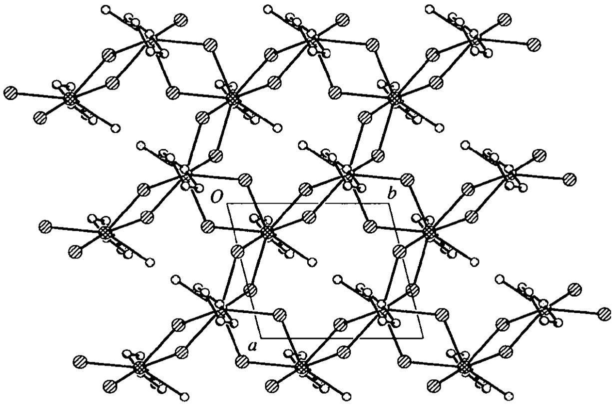


Fig. 2. Packing diagram viewed down the *c* axis.

Two other polymeric lanthanum(III) chloride (solvate) species are known, namely $[La(\mu\text{-}Cl)_3(2,6\text{-dimethyl-4-pyrone})_2]_n$ (Castellani & Coda, 1985) and $[LaCl(\mu\text{-}Cl)_2(2,6\text{-dimethyl-4-pyrone})(H_2O)]_n$ (Castellani & Tazzoli, 1984). In the present structure, there are six La—Cl(bridging) bond distances in the range 2.854 (2)–2.952 (2) Å. Eight-coordinate $[La(\mu\text{-}Cl)_3(2,6\text{-dimethyl-4-pyrone})_2]_n$ has La—Cl(bridging) bond distances in the range 2.845 (2)–3.018 (3) Å, whereas seven-

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