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Di-μ-chloro-bis(tetracarbonylmanganese)

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Abstract. $\{Mn(CO)_4\}_2Cl_2$, monoclinic, $P2_1/c$, $a = 9\cdot421$ (2), $b = 11\cdot589$ (2), $c = 12\cdot767$ (1) Å, $\beta = 109\cdot68$ (2)°, $Z = 4$, $D_o = 2\cdot02$, $D_c = 2\cdot05$ g cm^{-3}. The complex has long Mn—C bonds [average: $1\cdot888$ (2) Å, axial; $1\cdot816$ (2) Å, equatorial] and shows a pronounced *trans* influence.

Introduction. Initial cell dimensions were determined by precession photography (Mo $K\alpha$ radiation). Systematic absences ($h0l$ for l odd, $0k0$ for k odd) indicated space group $P2_1/c$.

A thin plate (ca 0·01 mm thick, dominant faces {100}) was sealed in a Lindemann-glass tube and mounted on a Hilger & Watts Y290 four-circle diffractometer, with **b** several degrees from the φ axis. Cell parameters and the orientation matrix were refined by least squares (12 reflexions, $34 < 2\theta < 48°$). Intensities were collected for all unique reflexions with $2\theta \leq 55°$ (Mo $K\alpha$ radiation, Zr filter, $\lambda = 0\cdot71069$ Å, θ–2θ scan mode). No reflexions were intense enough to require attenuation. Three standard reflexions showed a steady decay of about 10% during data collection; linear decay functions were calculated and applied to the data together with absorption corrections (Sheldrick & Sheldrick, 1970), adapted for four-circle geometry [$\mu = 24\cdot53$ cm^{-1}; a minimum in the value of $R_w = (\sum \Delta^2/\sum wF_o^2)^{1/2}$ was obtained for $\mu t = 0\cdot0235$, corresponding to a thickness of 0·0095 mm]. Of the

2057 measured reflexions with net positive recorded intensity, 57 were rejected because of plate edge effects on absorption.

Atoms were located by automatic direct methods and Fourier techniques and refined by full-matrix least squares to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| - |F_c|$, $w = 1/\sigma^2(F_o)$]. Scattering factors were those of Cromer

Table 1. *Atomic coordinates* $(\times 10^4)$

	x	y	z
Mn(1)	5932 (1)	3791 (1)	3245 (1)
Mn(2)	1910 (1)	3734 (1)	2234 (1)
Cl(1)	3887 (2)	4895 (1)	3445 (1)
Cl(2)	3952 (2)	2619 (1)	2048 (1)
C(11)	5867 (7)	4697 (5)	1999 (4)
O(11)	5854 (6)	5211 (4)	1253 (3)
C(12)	7338 (7)	4749 (5)	4161 (4)
O(12)	8236 (5)	5333 (4)	4728 (3)
C(13)	7396 (7)	2910 (5)	3038 (4)
O(13)	8325 (5)	2378 (4)	2913 (4)
C(14)	5945 (6)	2884 (5)	4478 (4)
O(14)	6001 (6)	2340 (4)	5220 (3)
C(21)	1932 (7)	4676 (5)	1037 (5)
O(21)	1931 (6)	5244 (4)	328 (3)
C(22)	435 (8)	4628 (5)	2439 (4)
O(22)	−477 (6)	5168 (4)	2575 (4)
C(23)	495 (7)	2814 (5)	1282 (5)
O(23)	−400 (6)	2262 (4)	686 (4)
C(24)	1947 (7)	2789 (5)	3448 (4)
O(24)	1962 (6)	2224 (4)	4166 (4)

& Waber (1974), with corrections for anomalous dispersion (Cromer & Ibers, 1974). The final value of R was 6·91%, with R_w 5·06%. 181 parameters were refined, including anisotropic thermal parameters for all atoms. All shift/e.s.d. ratios in the final cycle were <0·07, and a subsequent difference map showed no
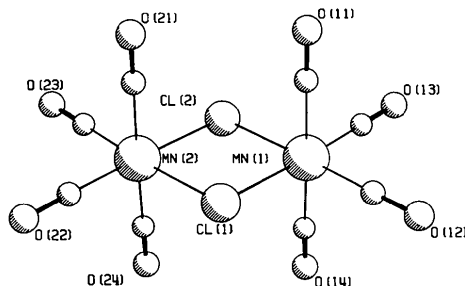

Fig. 1. Perspective view of the molecule.

Table 2. Bond lengths (Å) and angles (°)

Mn(1)—Cl(1)	2·396 (1)	Mn(2)—C(23)	1·817 (3)
Mn(1)—Cl(2)	2·396 (1)	Mn(2)—C(24)	1·888 (3)
Mn(2)—Cl(1)	2·394 (1)	C(11)—O(11)	1·119 (3)
Mn(2)—Cl(2)	2·395 (1)	C(12)—O(12)	1·134 (3)
Mn(1)—C(11)	1·890 (3)	C(13)—O(13)	1·125 (3)
Mn(1)—C(12)	1·819 (3)	C(14)—O(14)	1·124 (3)
Mn(1)—C(13)	1·806 (3)	C(21)—O(21)	1·120 (3)
Mn(1)—C(14)	1·889 (3)	C(22)—O(22)	1·122 (3)
Mn(2)—C(21)	1·884 (3)	C(23)—O(23)	1·125 (3)
Mn(2)—C(22)	1·822 (3)	C(24)—O(24)	1·122 (3)

Cl(1)—Mn(1)—Cl(2)	83·6 (1)	Cl(1)—Mn(2)—C(21)	88·8 (1)
Cl(1)—Mn(2)—Cl(2)	83·7 (1)	Cl(1)—Mn(2)—C(22)	93·1 (1)
Mn(1)—Cl(1)—Mn(2)	96·3 (1)	Cl(1)—Mn(2)—C(24)	90·0 (1)
Mn(1)—Cl(2)—Mn(2)	96·3 (1)	Cl(2)—Mn(2)—C(21)	90·2 (1)
Cl(1)—Mn(1)—C(13)	176·8 (1)	Cl(2)—Mn(2)—C(23)	92·9 (1)
Cl(2)—Mn(1)—C(12)	176·1 (1)	Cl(2)—Mn(2)—C(24)	88·6 (1)
Cl(1)—Mn(1)—C(11)	89·6 (1)	C(21)—Mn(2)—C(24)	178·4 (1)
Cl(1)—Mn(1)—C(12)	92·5 (1)	C(21)—Mn(2)—C(22)	90·2 (1)
Cl(1)—Mn(1)—C(14)	89·3 (1)	C(21)—Mn(2)—C(23)	90·2 (1)
Cl(2)—Mn(1)—C(11)	88·9 (1)	C(22)—Mn(2)—C(23)	90·4 (1)
Cl(2)—Mn(1)—C(13)	93·2 (1)	C(22)—Mn(2)—C(24)	91·0 (1)
Cl(2)—Mn(1)—C(14)	90·1 (1)	C(23)—Mn(2)—C(24)	90·9 (1)
C(11)—Mn(1)—C(14)	178·6 (1)	Mn(1)—C(11)—O(11)	178·0 (3)
C(11)—Mn(1)—C(12)	90·7 (1)	Mn(1)—C(12)—O(12)	178·6 (3)
C(11)—Mn(1)—C(13)	90·0 (1)	Mn(1)—C(13)—O(13)	178·8 (3)
C(12)—Mn(1)—C(13)	90·7 (1)	Mn(1)—C(14)—O(14)	177·8 (3)
C(12)—Mn(1)—C(14)	90·3 (1)	Mn(2)—C(21)—O(21)	179·1 (3)
C(13)—Mn(1)—C(14)	91·0 (1)	Mn(2)—C(22)—O(22)	179·0 (3)
Cl(1)—Mn(2)—C(23)	176·4 (1)	Mn(2)—C(23)—O(23)	178·7 (3)
Cl(2)—Mn(2)—C(22)	176·7 (1)	Mn(2)—C(24)—O(24)	179·6 (3)

significant peaks except near the heavy atoms. Refined atomic coordinates are given in Table 1.*

Discussion. The compound (Fig. 1), prepared by the reaction of $[HMn(CO)_4\{P(CF_3)_2(OCH_2CH_2Cl)\}]$ with CCl_4 (Clegg & Morton, 1978), was originally believed to be $[ClMn(CO)_4\{P(CF_3)_2(OCH_2CH_2Cl)\}]$, which is the major product. Attempts at a structure solution by Patterson techniques were, however, not successful, and the use of automatic sign-expansion methods followed by E maps and Fourier syntheses yielded the correct solution. Structure refinement was completed in order to make comparisons with $\{Mn(CO)_4\}_2Br_2$ (Dahl & Wei, 1963) and $Mn(CO)_5Cl$ (Greene & Bryan, 1971), and to test the recently programmed absorption-correction method.

Bond lengths and angles are listed in Table 2. The coordination of Mn is close to regular octahedral, except for the reduced ClMnCl angle of 83·7 (1)°. Structural comparisons with related compounds are made in Table 3.

The difference between the average axial and equatorial Mn—C lengths is 0·073 Å, and is statistically very significant. (The Mn_2Cl_2 group defines the equatorial plane.) A similar *trans* influence was noted for $\{Mn(CO)_4\}_2Br_2$ (Dahl & Wei, 1963), but was not significant, since e.s.d.'s derived from the photographic data were larger. A *trans* influence of this magnitude might be expected to result also in a difference in C—O lengths. Such a difference is here observed, but is not significant. It has been argued, however, that the C—O length in metal carbonyls is rather insensitive to bond order (Cotton & Wing, 1965).

The axial Mn—C bonds are quite long [average 1·888 (2) Å]: the Mn—C lengths *cis* to non-carbonyl substituents in a range of XMn(CO)$_5$ compounds (see references in Clegg & Wheatley, 1974) average 1·81 Å, the shortest being 1·78 (1) Å in (phen)Cd[Mn(CO)$_5$]$_2$

Table 3. Crystallographic data for some manganese complexes

	$\{Mn(CO)_4\}_2Cl_2$	$\{Mn(CO)_4\}_2Br_2$[a]	$Mn(CO)_5Cl$[b]
Mn—C *trans* to halogen (Å)	1·816 (2)	1·76 (4)	1·807 (9)
Mn—C *cis* to halogen (Å)	1·888 (2)	1·87 (4)	1·893 (4)
Mn—X (Å)	2·395 (1)	2·526 (5)	2·347 (4)
Mn···Mn (Å)	3·569 (1)	3·743 (8)	–
X—Mn—X (°)	83·7 (1)	84·4 (2)	–

(a) Dahl & Wei (1963). (b) Greene & Bryan (1971).

(Clegg & Wheatley, 1974), and the longest, 1·893 (4) Å, in Mn(CO)$_5$Cl (Greene & Bryan, 1971), not significantly longer than in {Mn(CO)$_4$}$_2$Cl$_2$. This effect can be attributed to the electron-withdrawing Cl ligands, which, by removing electron density from Mn, reduce overall Mn—CO π bonding.

The Mn—Cl lengths are slightly longer than those in Mn(CO)$_5$Cl, as expected for bridging ligands. Greene & Bryan (1971) also report an approximate value for Mn—Br in Mn(CO)$_5$Br of 2·50 (1) Å, which is slightly shorter than in {Mn(CO)$_4$}$_2$Br$_2$ (Dahl & Wei, 1963).

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Dichlorobis(thiomorpholine)palladium(II)

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Abstract. C$_8$H$_{18}$N$_2$S$_2$Cl$_2$Pd, M_r = 383·69, triclinic, $P\bar{1}$, a = 11·31 (1), b = 5·697 (6), c = 6·731 (8) Å, α = 116·54 (5), β = 109·14 (6), γ = 97·3 (1)°, V = 363·58 Å^3, Z = 1, D_o = 1·834 (2), D_c = 1·837 (1) g cm^{-3}. The structure was refined to R = 0·068 for 1997 unique non-zero reflexions. The coordination of the Pd atom is *trans* square-planar.

Introduction. Crystals were provided by Dr N. Johnson of the Chemistry Department, Portsmouth Polytechnic. 2016 unique reflexions (1997 non-zero) were measured with Mo $K\alpha$ radiation on a Stoe STADI-4, four-circle computer-controlled diffractometer. An $\omega/2\theta$ step scan was adopted and balanced filters were used for monochromatization. The intensities were corrected for Lorentz and polarization effects and those reflexions for which $I < 2\sigma(I)$ were given zero weight. The cell parameters were refined by least squares from 2θ values measured on the diffractometer for 10 reflexions. A Delauney reduction established that this was the reduced cell.

The structure was solved by Patterson and Fourier techniques. Refinement was by block-diagonal least squares minimizing $\sum (w\Delta^2) = \sum [w(K|F_o| - |F_c|)^2]$. Scattering factors were obtained from $f = A \exp(-ax^2) + B \exp(-bx^2) + C$ (Forsyth & Wells, 1959). Reflexions were rejected if $|F_o| \geq 3|F_c|$ and the weighting scheme was $w = 1$ for $|F_o| < F^*$ and $w = F^*/|F_o|$ if $|F_o| \geq F^*$. The value of F^* for the final cycles was 5·0. The H atoms were included at fixed calculated positions. The final R for 1997 non-zero reflexions was 0·068, when the shifts to the parameters were all <10% of their respective e.s.d.'s. The final parameters are listed in Table 1.‡

Discussion. The structure determination was carried out to support an IR spectroscopic study of the stereochemistry of transition-metal complexes, and, in par-

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