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The Structure of Chlorotricarbonyl(diphenyl-3,5-dimethylpyrazolylphosphine)-manganese(I)

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$MnCl(CO)_3P[(C_6H_5)_2C_5H_7N_2]$, $M_r = 454{\cdot}7$, monoclinic, space group $P2_1/c$, $a = 14{\cdot}160\,(6)$, $b = 16{\cdot}165\,(8)$, $c = 19{\cdot}002\,(6)$ Å, $\beta = 105{\cdot}67\,(3)°$, $V = 4187{\cdot}7$ Å^3, $Z = 8$, $D_c = 1{\cdot}442$, $D_o = 1{\cdot}42$ g cm^{-3}, μ(Mo $K\alpha$) = 8·88 cm^{-1}. $R = 0{\cdot}070$ for 1615 counter reflexions. There are two independent molecules in the asymmetric unit, each with an irregular octahedral environment around the Mn atom. Coordination of the diphenyl-3,5-dimethylpyrazolylphosphine ligand occurs through P and N atoms. The Cl atoms are *trans* to the carbonyl groups.

Introduction

Photographs taken with Cu $K\alpha$ radiation showed the crystals to be monoclinic. Cell dimensions were obtained by least squares from the setting angles of nine reflexions with $2\theta > 25°$ measured on a Picker FACS-I four-circle diffractometer ($\lambda K\alpha_1 = 0{\cdot}70926$ Å). A single crystal (0·3 × 0·3 × 0·3 mm) was used for the intensity measurements with Nb-filtered Mo $K\alpha$ radiation, a scintillation counter and pulse-height discrimination. 2676 intensities with $2\theta \leq 35°$ were measured and 1615 with $I > 2{\cdot}3\sigma(I)$, where $\sigma(I)$ is the standard deviation derived from counting statistics, were regarded as observed. A θ–2θ scan (2° min^{-1}) was used with a base width of 1·5° which was increased for dispersion. Background measurements of 20 s were taken on either side of the peak. Two standard reflexions were measured at regular intervals to scale the data. Lorentz and polarization corrections were applied but no absorption correction was made.

A Patterson function gave the positions of the Mn, Cl and P atoms. A Fourier map based on these atoms located a further 18 lighter atoms. Least-squares refinement of positional and temperature parameters for these atoms together with the scale factor, followed by a difference synthesis, revealed the remaining atoms. Least-squares refinement with isotropic temperature parameters reduced R to 0·103, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. A difference map revealed 22 of the 34 H atoms. The methyl H atoms of the pyrazolyl groups were not apparent. Inclusion of the 22 H atoms in fixed positions and anisotropic thermal parameters for Mn, Cl and P reduced R to 0·085. A further difference map revealed the remaining H atoms. These H atoms were included and the CO group atoms allowed to refine anisotropically. One of the CO groups refined poorly and the thermal parameters were reset to isotropic. The positional coordinates of the H atoms were refined for one cycle of least squares. The final R was 0·070 for observed reflexions with a maximum shift-to-error ratio of 0·3 for the heavy atoms. In the later stages of refinement, weights derived from counting statistics were used ($w = 1/\sigma F^2$). The scattering factors were those of Cromer & Waber (1965) for the heavy atoms and Stewart, Davidson & Simpson (1965) for H. Anomalous-dispersion corrections were applied for

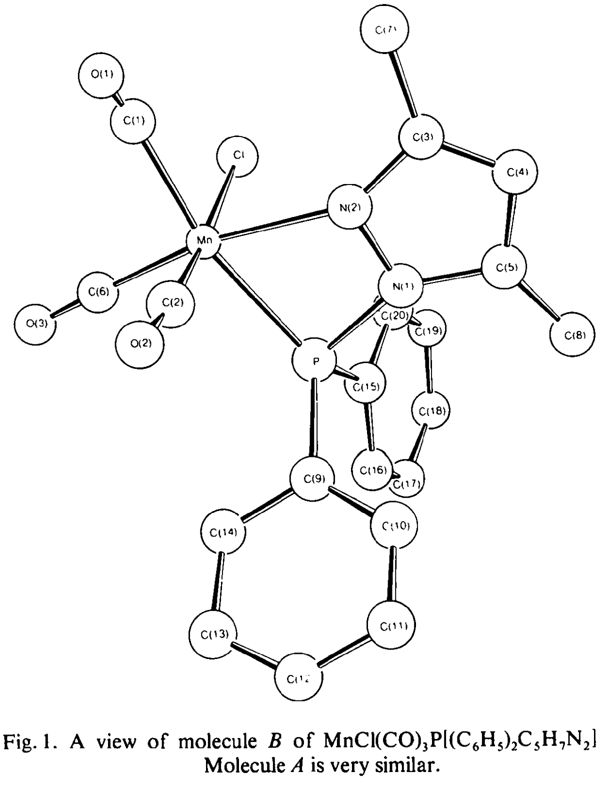

Fig. 1. A view of molecule B of $MnCl(CO)_3P[(C_6H_5)_2C_5H_7N_2]$. Molecule A is very similar.

Table 1. *Final atomic parameters*

The values of the atomic fractional coordinates and their estimated standard deviations (in parentheses) are multiplied by 10^4 for the non-hydrogen atoms and by 10^3 for the H atoms. Isotropic *U* values (Å^2 × 10^3) are given for some of the heavy atoms.

Molecule *A*

	x	*y*	*z*	*U*
Mn	1110 (2)	1092 (2)	3831 (2)	
Cl	275 (3)	129 (3)	2937 (3)	
P	1283 (4)	2024 (3)	2939 (3)	
C(1)	1164 (13)	286 (12)	4502 (11)	
C(2)	1729 (15)	1807 (15)	4493 (12)	
C(6)	−45 (18)	1429 (14)	3970 (11)	
O(1)	1161 (10)	−211 (9)	4926 (8)	
O(2)	2158 (12)	2214 (10)	4954 (9)	
O(3)	−737 (11)	1694 (10)	4024 (8)	
C(3)	3021 (14)	303 (13)	3403 (10)	56 (6)
C(4)	3394 (13)	565 (12)	2827 (10)	49 (6)
C(5)	2919 (13)	1255 (12)	2529 (10)	45 (6)
C(7)	3278 (15)	−429 (14)	3909 (11)	78 (7)
C(8)	3045 (14)	1795 (11)	1953 (11)	67 (7)
C(9)	1683 (14)	3028 (12)	3217 (10)	48 (6)
C(10)	2620 (16)	3329 (15)	3281 (11)	78 (8)
C(11)	2915 (16)	4081 (15)	3561 (12)	80 (7)
C(12)	2334 (19)	4571 (16)	3820 (13)	100 (9)
C(13)	1389 (19)	4306 (18)	3822 (13)	110 (9)
C(14)	1095 (14)	3519 (14)	3521 (11)	63 (7)
C(15)	673 (12)	2111 (12)	1981 (9)	37 (5)
C(16)	325 (13)	2875 (12)	1640 (10)	46 (6)
C(17)	−135 (13)	2909 (12)	912 (10)	49 (6)
C(18)	−328 (14)	2214 (14)	538 (11)	70 (7)
C(19)	−19 (14)	1445 (13)	837 (11)	61 (6)
C(20)	456 (13)	1406 (13)	1580 (11)	51 (6)
N(1)	2299 (10)	1440 (10)	2940 (8)	48 (5)
N(2)	2369 (10)	876 (10)	3462 (8)	43 (5)
H(1)	299 (9)	292 (8)	309 (7)	
H(2)	361 (9)	435 (9)	344 (7)	
H(3)	238 (10)	500 (9)	412 (8)	
H(4)	78 (10)	437 (10)	425 (8)	
H(5)	33 (9)	311 (8)	353 (7)	
H(6)	42 (8)	342 (7)	200 (6)	
H(7)	−48 (8)	346 (8)	73 (6)	
H(8)	−55 (9)	212 (8)	12 (6)	
H(9)	−17 (9)	91 (8)	62 (7)	
H(10)	59 (8)	76 (8)	185 (6)	
H(11)	388 (8)	23 (7)	266 (6)	
H(12)	342 (9)	−32 (9)	435 (7)	
H(13)	385 (10)	−67 (9)	376 (7)	
H(14)	273 (10)	−89 (9)	363 (7)	
H(15)	271 (9)	136 (8)	163 (7)	
H(16)	354 (9)	214 (8)	205 (7)	
H(17)	246 (9)	228 (8)	178 (7)	

Molecule *B*

	x	*y*	*z*	*U*
Mn	6220 (2)	2704 (2)	3811 (2)	
Cl	5226 (5)	3627 (4)	2950 (4)	
P	6340 (3)	1760 (3)	2933 (3)	
C(2)	6977 (14)	2088 (13)	4505 (11)	
C(6)	5148 (18)	2289 (15)	4034 (13)	
O(2)	7423 (11)	1711 (10)	4974 (8)	
O(3)	4519 (13)	2021 (12)	4187 (10)	
C(1)	6447 (14)	3615 (14)	4504 (12)	53 (7)
C(3)	8003 (14)	3523 (13)	3199 (11)	53 (6)
C(4)	8321 (14)	3271 (13)	2638 (11)	59 (7)
C(5)	7881 (13)	2556 (12)	2385 (10)	41 (6)
C(7)	8212 (15)	4300 (15)	3682 (12)	86 (8)
C(8)	7938 (15)	2015 (15)	1812 (12)	83 (8)
C(9)	6790 (13)	756 (11)	3214 (9)	38 (5)
C(10)	7612 (14)	396 (13)	3093 (10)	52 (6)
C(11)	7899 (15)	−381 (14)	3298 (12)	76 (7)
C(12)	7337 (15)	−822 (14)	3636 (11)	69 (7)
C(13)	6562 (15)	−539 (14)	3830 (11)	72 (7)
C(14)	6251 (14)	287 (14)	3594 (11)	66 (7)
C(15)	5624 (12)	1636 (11)	1998 (9)	34 (5)
C(16)	5320 (12)	872 (12)	1709 (10)	43 (6)
C(17)	4758 (14)	815 (13)	996 (11)	59 (6)
C(18)	4489 (14)	1480 (14)	576 (11)	66 (7)
C(19)	4795 (14)	2250 (13)	853 (11)	56 (6)
C(20)	5357 (13)	2350 (12)	1581 (11)	54 (6)
N(1)	7313 (9)	2375 (9)	2862 (7)	37 (4)
N(2)	7371 (10)	2976 (10)	3350 (8)	42 (5)
O(1)	6520 (12)	3936 (11)	4840 (10)	105 (7)
H(1)	766 (8)	68 (8)	273 (6)	
H(2)	868 (9)	−48 (9)	330 (7)	
H(3)	784 (9)	−128 (9)	388 (7)	
H(4)	634 (9)	−63 (8)	413 (7)	
H(5)	584 (8)	57 (8)	369 (6)	
H(6)	556 (8)	41 (7)	192 (6)	
H(7)	444 (8)	21 (8)	85 (6)	
H(8)	406 (9)	144 (8)	3 (6)	
H(9)	458 (8)	274 (8)	56 (6)	
H(10)	559 (8)	290 (9)	184 (6)	
H(11)	869 (9)	365 (8)	247 (6)	
H(12)	875 (10)	415 (9)	421 (8)	
H(13)	786 (10)	472 (9)	387 (7)	
H(14)	852 (10)	452 (9)	339 (8)	
H(15)	828 (10)	147 (10)	194 (8)	
H(16)	802 (11)	218 (10)	137 (8)	
H(17)	725 (11)	168 (9)	141 (8)	

Mn, Cl and P. The programs have been described (Einstein & Jones, 1972).

The final positional and isotropic thermal parameters are shown in Table 1.* Fig. 1 shows the stereochemistry of the molecules and the atom numbering. Bond lengths and angles are given in Table 2.

Discussion

The two independent molecules are very similar and each has distorted octahedral coordination around the Mn atom. The Mn–C(CO) distances range from 1·76 (2) to 1·94 (2) Å, and the Mn–C distance *trans* to the Cl [1·76 (2) Å for molecule *A* and 1·77 (2) Å for molecule *B*] is shorter than the other Mn–C distances, but not significantly so. One CO group of molecule *B* refined poorly giving Mn–C(1) = 1·94 (2) and C(1)–O(1) = 0·81 (2) Å, in spite of shifting the atoms to expected positions at intervals during the refinement. The

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32407 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond distances* (Å), *bond angles* (°) *and their standard deviations*

	Molecule *A*	Molecule *B*
Mn—Cl	2·371 (6)	2·375 (7)
Mn—P	2·330 (6)	2·301 (6)
Mn—C(1)	1·81 (2)	1·94 (2)
Mn—C(2)	1·76 (2)	1·77 (2)
Mn—C(6)	1·81 (2)	1·81 (3)
Mn—N(2)	2·11 (1)	2·09 (1)
C(1)—O(1)	1·14 (2)	0·81 (2)
C(2)—O(2)	1·13 (2)	1·12 (2)
C(6)—O(3)	1·10 (2)	1·10 (2)
P—N(1)	1·72 (1)	1·73 (1)
P—C(9)	1·75 (2)	1·77 (2)
P—C(15)	1·80 (2)	1·80 (2)
N(1)—N(2)	1·33 (2)	1·33 (2)
N(2)—C(3)	1·33 (2)	1·34 (2)
C(3)—C(4)	1·40 (2)	1·33 (2)
C(3)—C(7)	1·51 (3)	1·54 (3)
C(4)—C(5)	1·34 (2)	1·34 (2)
C(5)—N(1)	1·36 (2)	1·40 (2)
C(5)—C(8)	1·45 (2)	1·42 (2)
C(9)—C(10)	1·39 (2)	1·37 (2)
C(10)—C(11)	1·35 (3)	1·34 (2)
C(11)—C(12)	1·33 (3)	1·35 (2)
C(12)—C(13)	1·41 (3)	1·33 (2)
C(13)—C(14)	1·41 (3)	1·44 (3)
C(9)—C(14)	1·39 (2)	1·40 (2)
C(15)—C(16)	1·42 (2)	1·37 (2)
C(16)—C(17)	1·36 (2)	1·38 (2)
C(17)—C(18)	1·32 (2)	1·33 (2)
C(18)—C(19)	1·39 (3)	1·38 (2)
C(19)—C(20)	1·39 (2)	1·41 (2)
C(15)—C(20)	1·36 (2)	1·39 (2)
P—Mn—Cl	91·9 (2)	93·7 (2)
P—Mn—C(1)	170·2 (7)	164·3 (6)
P—Mn—C(2)	88·1 (7)	91·1 (7)
P—Mn—C(6)	100·9 (8)	98·9 (9)
P—Mn—N(2)	66·5 (5)	67·5 (5)
Cl—Mn—C(1)	87·1 (7)	87·1 (6)
Cl—Mn—C(2)	180·0 (7)	175·1 (7)
Cl—Mn—C(6)	90·4 (6)	90·9 (7)
Cl—Mn—N(2)	87·5 (4)	87·9 (4)
C(1)—Mn—C(2)	93 (1)	88·0 (9)
C(1)—Mn—C(6)	89 (1)	97 (1)
C(1)—Mn—N(2)	103·6 (8)	96·9 (7)
C(2)—Mn—C(6)	90 (1)	89·7 (9)
C(2)—Mn—N(2)	92·5 (8)	92·7 (7)
C(6)—Mn—N(2)	167·1 (9)	166·3 (9)
Mn—C(1)—O(1)	177 (2)	170 (3)
Mn—C(2)—O(2)	174 (2)	176 (2)
Mn—C(6)—O(3)	174 (2)	178 (2)
Mn—P—N(1)	84·0 (6)	83·8 (5)
Mn—P—C(9)	117·9 (7)	118·7 (6)
Mn—P—C(15)	132·2 (6)	130·9 (6)
N(1)—P—C(9)	107·8 (9)	108·7 (8)
N(1)—P—C(15)	102·6 (8)	103·6 (7)
C(9)—P—C(15)	105·1 (9)	104·9 (8)
P—N(1)—N(2)	106 (1)	105 (1)
P—N(1)—C(5)	142 (1)	141 (1)
Mn—N(2)—N(1)	103 (1)	103 (1)
Mn—N(2)—C(3)	144 (1)	150 (1)
N(2)—N(1)—C(5)	110 (2)	111 (1)
N(1)—N(2)—C(3)	109 (2)	105 (1)
N(2)—C(3)—C(4)	106 (2)	111 (2)
N(2)—C(3)—C(7)	123 (2)	116 (2)
C(4)—C(3)—C(7)	131 (2)	133 (2)
C(3)—C(4)—C(5)	109 (2)	109 (2)
C(4)—C(5)—N(1)	106 (2)	104 (2)
C(4)—C(5)—C(8)	132 (2)	134 (2)
N(1)—C(5)—C(8)	122 (2)	122 (2)
P—C(9)—C(10)	125 (2)	126 (2)
P—C(9)—C(14)	118 (2)	117 (2)
C(10)—C(9)—C(14)	116 (2)	117 (2)
C(9)—C(10)—C(11)	122 (2)	123 (2)
C(10)—C(11)—C(12)	122 (2)	117 (2)
C(11)—C(12)—C(13)	120 (3)	126 (2)
C(12)—C(13)—C(14)	117 (2)	116 (2)
C(13)—C(14)—C(9)	123 (2)	120 (2)
P—C(15)—C(16)	123 (1)	122 (1)
P—C(15)—C(20)	118 (2)	118 (1)
C(16)—C(15)—C(20)	118 (2)	121 (2)
C(15)—C(16)—C(17)	121 (2)	119 (2)
C(16)—C(17)—C(18)	119 (2)	122 (2)
C(17)—C(18)—C(19)	123 (2)	119 (2)
C(18)—C(19)—C(20)	118·2 (2)	121 (2)
C(19)—C(20)—C(15)	120 (2)	117 (2)

Table 3. *Deviations of atoms* (*Å*) *from the least-squares planes*

The equations of the planes are referred to the orthogonal axes *a*, *b′* and *c**.

(*a*) Plane through N(1), N(2), C(3), C(4) and C(5)

	Molecule *A*	Molecule *B*
N(1)	0·000	−0·011
N(2)	−0·007	0·008
C(3)	0·021	0·002
C(4)	−0·019	−0·016
C(5)	0·012	0·020
Mn	0·502	0·430
P	0·306	0·306
C(7)	0·025	0·027
C(8)	−0·073	0·018

$$-0{\cdot}5667x - 0{\cdot}5401y - 0{\cdot}6222z + 5{\cdot}5934 = 0$$

and $\chi^2 = 2{\cdot}83$ for molecule *A*

$$-0{\cdot}6199x + 0{\cdot}4810y - 0{\cdot}6200z + 6{\cdot}8969 = 0$$

and $\chi^2 = 2{\cdot}83$ for molecule *B*

(*b*) Plane through C(9), C(10), C(11), C(12), C(13) and C(14)

	Molecule *A*	Molecule *B*
C(9)	0·027	0·013
C(10)	−0·026	−0·013
C(11)	−0·002	−0·010
C(12)	0·021	0·032
C(13)	−0·005	−0·025
C(14)	−0·019	0·000
P	−0·155	0·071

$$-0{\cdot}1180x + 0{\cdot}4244y - 0{\cdot}8978z + 3{\cdot}3191 = 0$$

and $\chi^2 = 5{\cdot}24$ for molecule *A*

$$-0{\cdot}3441x - 0{\cdot}3463y - 0{\cdot}8727z + 8{\cdot}3095 = 0$$

and $\chi^2 = 5{\cdot}13$ for molecule *B*

Table 3 (*cont.*)

(*c*) Plane through C(15), C(16), C(17), C(18), C(19) and C(20)

	Molecule *A*	Molecule *B*
C(15)	0·022	0·004
C(16)	−0·022	0·000
C(17)	0·018	0·000
C(18)	−0·014	−0·007
C(19)	0·014	0·011
C(20)	−0·020	−0·010
P	−0·033	−0·030

$0{\cdot}9686x + 0{\cdot}0980y - 0{\cdot}2287z + 0{\cdot}5775 = 0$ and $\chi^2 = 5{\cdot}78$ for molecule *A*

$0{\cdot}9482x - 0{\cdot}0812y - 0{\cdot}3071z - 5{\cdot}2371 = 0$ and $\chi^2 = 0{\cdot}73$ for molecule *B*

Cl atom of the same molecule has higher thermal-vibration parameters than those of the other molecule, and partial disorder of the CO and Cl ligands cannot be ruled out. The Mn—Cl distances in molecules *A* and *B* are 2·371 (6) and 2·375 (7) Å respectively. Each molecule has a bidentate diphenyl-3,5-dimethylpyrazolylphosphine ligand coordinated to the metal *via* the P and N atom lone pairs. The Mn—P distances are 2·330 (6) and 2·301 (6) Å, the Mn—N(2) distances 2·11 (1) and 2·09 (1) Å, and the P—Mn—N (2) angles 66·5 (5) and 67·5 (5)°.

The P—N lengths [1·72 (1) and 1·73 (1) Å] are similar to that of 1·714 (4) Å found in tris(1-pyrazolyl)-phosphine (Cobbledick & Einstein, 1975) and within the limits of the errors the pyrazolyl bond lengths agree. The pyrazolyl and phenyl rings are planar; deviations from the least-squares planes are shown in Table 3. There are no short intermolecular contacts.

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Structures Cristallines de Dérivés des Acides Dipropylacétique et Tripropylacétique. VI. Composés Homologues: Comparaison de la Propyl-3 Hexène-3 Amide et de l'Acide Propyl-2 Pentène-2 Oïque

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3-Propyl-3-hexenamide, C_2H_5—CH=C(—C_3H_7)—CH_2—$CONH_2$, (PHM) and 2-propyl-2-pentenoic acid (PPA) are anticonvulsant compounds. They crystallize with the following space groups and lattice parameters: PHM, space group $P2_1/c$, $a = 13{\cdot}533\,(3)$, $b = 8{\cdot}100\,(3)$, $c = 9{\cdot}498\,(3)$ Å, $\beta = 102{\cdot}95\,(5)°$; PPA, space group $P\bar{1}$, $a = 8{\cdot}023\,(5)$, $b = 11{\cdot}991\,(6)$, $c = 4{\cdot}933\,(3)$ Å, $\alpha = 99{\cdot}70\,(5)$, $\beta = 104{\cdot}40\,(5)$, $\gamma = 103{\cdot}70\,(5)°$. The intensities were collected with an automatic, four-circle diffractometer. The structures were solved by the direct multisolution method. Full-matrix least-squares refinements resulted in weighted reliability indices of 0·11 (PHM) and 0·08 (PPA). The conformation of the C_2H_5—CH=C(—C_3H_7)— group is exactly the same in both compounds. Therefore, this conformation, which is very stable in the crystalline state, is highly probable for the molecules in solution.

Les acides dipropylacétique, $(C_3H_7)_2$—CH—COOH (DPA), et tripropylacétique, $(C_3H_7)_3$—C—COOH (TPA), et leurs dérivés sont des composés d'intérêt pharmacologique par leur activité sur le système ner-