Acta Cryst. (1982). B**38**, 952–954

cis-cis-Dicarbonyl(1,10-phenanthroline)bis(trimethyl phosphite)manganese(I) Perchlorate

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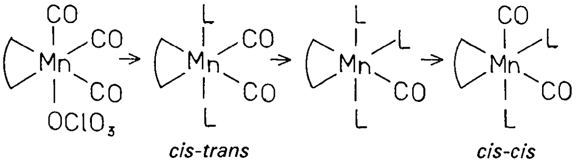
(*Received* 27 *May* 1981; *accepted* 26 *October* 1981)

Abstract. $[Mn(CO)_2\{P(OCH_3)_3\}_2(C_{12}H_8N_2)]ClO_4$, triclinic, $P\bar{1}$, $a = 13{\cdot}320\,(2)$, $b = 8{\cdot}595\,(1)$, $c = 13{\cdot}764\,(2)$ Å, $\alpha = 104{\cdot}11\,(2)$, $\beta = 114{\cdot}68\,(1)$, $\gamma = 96{\cdot}48\,(1)°$, $\rho_c = 1{\cdot}510$ Mg m^{-3}, $Z = 2$; $R = 0{\cdot}05$ for 2110 observed reflexions. The geometry of the first coordination sphere of the Mn atom is only slightly influenced by the relative positions of the ligands and it corresponds to the minimum repulsion expected in molecules of MX_4Y type.

Introduction. The crystal structures found for the title compound and the corresponding *cis-trans* isomer confirm the ligand substitution sequence for the ClO_4^- salts proposed by Uson, Riera, Gimeno & Laguna (1977).



A single crystal of *cis-cis*-$[Mn(CO)_2\{P(OMe)_3\}_2$phen$]ClO_4$ (~0·07 mm in section) was selected for data collection. The intensities of the 2504 independent Friedel pairs up to $\theta = 20°$ were measured on a four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation. No crystal decomposition was observed during the data-collection process. The intensities were corrected for absorption ($\mu = 0{\cdot}80$ mm^{-1}). 2110 of the measured Friedel pairs were considered as observed according to the criterion $I > 2\sigma(I)$. The crystal structure was solved by the heavy-atom method, with the centrosymmetric space group $P\bar{1}$. The Friedel-pair intensities were then averaged, giving a discrepancy of 1·5%. A difference map gave the locations of the H atoms. The last weighted full-matrix least-squares refinement was performed with anisotropic vibration assumed for non-H atoms and fixed isotropic vibration for H atoms. This refinement, with about six data per free parameter, converged to discrepancy indices $R = 0{\cdot}046$ and $R_w = 0{\cdot}052$ (Stewart, Kundell & Baldwin, 1970). Table 1 shows the positional and thermal parameters of the

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 ×10^3) *for non*-H *atoms*

E.s.d.'s in parentheses refer to the last significant digits. $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j\cos(a_i a_j)$.

	x	y	z	U_{eq}
Mn	−926 (1)	1540 (1)	7905 (1)	33 (1)
C(1)	−1394 (5)	3384 (8)	8123 (4)	45 (3)
O(1)	−1665 (4)	4614 (6)	8278 (4)	74 (3)
C(2)	−689 (4)	1579 (6)	9310 (6)	40 (3)
O(2)	−565 (4)	1692 (5)	10200 (4)	63 (3)
N(1)	−169 (3)	−410 (5)	7657 (3)	35 (2)
N(2)	748 (3)	2791 (5)	8592 (3)	36 (2)
C(31)	990 (4)	81 (6)	8107 (4)	38 (3)
C(32)	−639 (5)	−2016 (6)	7154 (4)	44 (3)
C(33)	−3 (7)	−3189 (7)	7084 (5)	53 (4)
C(34)	1150 (7)	−2700 (8)	7547 (5)	56 (4)
C(35)	1681 (5)	−1024 (8)	8081 (5)	47 (4)
C(36)	2897 (6)	−361 (10)	8603 (5)	60 (4)
C(37)	3359 (5)	1265 (11)	9088 (5)	64 (4)
C(38)	2668 (5)	2437 (8)	9118 (4)	48 (3)
C(39)	3101 (5)	4150 (9)	9617 (5)	60 (4)
C(40)	2360 (6)	5127 (8)	9580 (5)	61 (4)
C(41)	1195 (5)	4426 (7)	9067 (5)	49 (4)
C(42)	1491 (5)	1813 (6)	8618 (6)	36 (3)
P(1)	−1202 (1)	1646 (2)	6165 (1)	40 (1)
O(11)	−1817 (4)	2949 (5)	5669 (3)	66 (3)
C(11)	−2964 (7)	3005 (11)	5416 (7)	92 (5)
O(12)	−13 (3)	2291 (6)	6211 (3)	71 (3)
C(12)	146 (6)	2746 (9)	5338 (6)	75 (4)
O(13)	−1801 (4)	−66 (5)	5192 (3)	64 (2)
C(13)	−2264 (7)	−338 (10)	4006 (5)	83 (4)
P(2)	−2679 (1)	71 (2)	7300 (1)	43 (1)
O(21)	−2864 (3)	−1700 (5)	7439 (3)	62 (3)
C(21)	−2572 (7)	−1992 (9)	8475 (6)	77 (5)
O(22)	−3611 (4)	−378 (6)	6028 (3)	77 (3)
C(22)	−4106 (7)	−2000 (11)	5185 (7)	99 (5)
O(23)	−3258 (3)	1090 (5)	7962 (4)	63 (3)
C(23)	−4409 (7)	561 (11)	7758 (8)	95 (6)
Cl	−4032 (1)	4606 (2)	2551 (1)	71 (1)
O(31)	−2902 (5)	4976 (12)	3204 (8)	178 (6)
O(32)	−4391 (7)	3318 (10)	1562 (7)	169 (5)
O(33)	−4370 (8)	5964 (9)	2200 (8)	162 (6)
O(34)	−4625 (8)	4333 (16)	3144 (8)	197 (8)

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0567-7408/82/030952-03$01.00

non-H atoms.* Table 2 shows the bond lengths and angles.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Mn–C(1)	1·771 (8)	N(1)–C(31)	1·370 (7)
–C(2)	1·815 (9)	N(2)–C(42)	1·364 (9)
–P(1)	2·293 (2)	N(1)–C(32)	1·324 (7)
–P(2)	2·222 (2)	N(2)–C(41)	1·340 (7)
–N(1)	2·082 (5)	C(32)–C(33)	1·399 (11)
–N(2)	2·056 (5)	C(41)–C(40)	1·392 (10)
C(1)–O(1)	1·155 (10)	C(33)–C(34)	1·361 (12)
C(2)–O(2)	1·143 (10)	C(40)–C(39)	1·359 (12)
P(1)–O(11)	1·582 (6)		
–O(12)	1·589 (6)	C(34)–C(35)	1·391 (9)
–O(13)	1·575 (4)	C(39)–C(38)	1·399 (10)
O(11)–C(11)	1·429 (11)		
O(12)–C(12)	1·437 (12)	C(35)–C(31)	1·400 (10)
O(13)–C(13)	1·429 (9)	C(38)–C(42)	1·396 (8)
P(2)–O(21)	1·586 (5)	C(35)–C(36)	1·444 (10)
–O(22)	1·582 (5)	C(38)–C(37)	1·444 (12)
–O(23)	1·595 (6)	C(31)–C(42)	1·425 (7)
O(21)–C(21)	1·407 (11)	C(36)–C(37)	1·337 (12)
O(22)–C(22)	1·445 (9)		
O(23)–C(23)	1·434 (11)	Cl–O(31)	1·340 (7)
		–O(32)	1·382 (8)
		–O(33)	1·418 (10)
		–O(34)	1·391 (15)

C(1)–Mn–C(2)	88·3 (3)	C(31)–N(1)–C(32)	116·9 (5)
–P(1)	89·0 (3)	C(41)–N(2)–C(42)	116·9 (5)
–P(2)	89·7 (2)	Mn–N(1)–C(31)	113·4 (3)
–N(1)	171·5 (3)	Mn–N(2)–C(42)	115·1 (4)
–N(2)	93·2 (3)	Mn–N(1)–C(32)	129·7 (4)
C(2)–Mn–P(1)	176·9 (2)	Mn–N(2)–C(41)	127·9 (5)
–P(2)	86·3 (2)	N(1)–C(31)–C(42)	116·8 (6)
–N(1)	94·9 (3)	N(2)–C(42)–C(31)	115·6 (5)
–N(2)	88·8 (2)	N(1)–C(31)–C(35)	123·3 (5)
P(1)–Mn–P(2)	95·28 (7)	N(2)–C(42)–C(38)	123·2 (5)
–N(1)	87·6 (2)	C(42)–C(31)–C(35)	119·9 (6)
–N(2)	89·8 (2)	C(31)–C(42)–C(38)	121·2 (6)
P(2)–Mn–N(1)	98·5 (2)	N(1)–C(32)–C(33)	122·9 (6)
–N(2)	174·2 (2)	N(2)–C(41)–C(40)	122·8 (7)
N(1)–Mn–N(2)	79·0 (2)	C(32)–C(33)–C(34)	120·1 (6)
Mn–C(1)–O(1)	177·9 (6)	C(41)–C(40)–C(39)	120·3 (6)
–C(2)–O(2)	175·7 (6)	C(33)–C(34)–C(35)	119·0 (8)
Mn–P(1)–O(11)	120·5 (2)	C(40)–C(39)–C(38)	118·8 (6)
–O(12)	109·9 (2)	C(34)–C(35)–C(31)	117·8 (7)
–O(13)	114·2 (2)	C(39)–C(38)–C(42)	118·1 (7)
Mn–P(2)–O(21)	119·8 (2)	C(34)–C(35)–C(36)	124·0 (8)
–O(22)	121·0 (2)	C(39)–C(38)–C(37)	124·4 (6)
–O(23)	108·7 (2)	C(31)–C(35)–C(36)	118·3 (6)
P(1)–O(11)–C(11)	124·7 (6)	C(42)–C(38)–C(37)	117·6 (6)
–O(12)–C(12)	126·0 (4)	C(35)–C(36)–C(37)	121·4 (8)
–O(13)–C(13)	126·8 (5)	C(38)–C(37)–C(36)	121·7 (7)
O(11)–P(1)–O(12)	97·3 (3)		
O(11)– –O(13)	105·9 (2)	O(31)–Cl–O(32)	112·5 (6)
O(12)– –O(13)	107·2 (3)	–O(33)	110·6 (6)
P(2)–O(21)–C(21)	124·9 (4)	–O(34)	111·7 (7)
–O(22)–C(22)	127·0 (6)	O(32)–Cl–O(33)	105·0 (6)
–O(23)–C(23)	124·5 (5)	–O(34)	112·3 (7)
O(21)–P(2)–O(22)	98·6 (3)	O(33)–Cl–O(34)	104·3 (8)
O(21)–P(2)–O(23)	104·3 (3)		
O(22)– –O(23)	101·9 (3)		

Discussion. Fig. 1 shows the cation. The ClO_4^- anion presented difficulties during the refinement, as is usual when this group is not hydrogen-bonded. In fact, some trials were performed in order to adjust disordered models but, finally, a non-disordered highly anisotropic model was preferred.

The bond angles around Mn are slightly influenced by the relative locations of the ligands. In fact, these bond angles agree well with those expected (Kepert, 1977) for the lowest repulsion between ligands in general octahedral complexes MX_4Y, Y being a bidentate ligand (phen in our case). For MX_4Y complexes, three parameters define the stereochemistry. The 'normalized bite' b, which is defined as the distance between the donor atoms of the chelate divided by the metal–donor distance, and two angles φ_T and φ_C, which are defined by the midpoint between the two chelate donors, the metal atom and the ligands on this plane (T), or perpendicular to it (C), respectively. Table 3 shows the observed parameters for both isomers, compared with the expected values calculated by Kepert's method. This analysis also predicts more

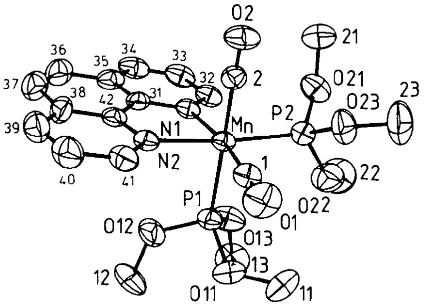

Fig. 1. Computer drawing of a molecule of the *cis-cis* isomer. The C atoms are labelled by their ordinals only.

Table 3. *Observed and calculated Kepert's parameters, for both isomers, using the model* MX_4

Averaged e.s.d.'s are 0·004 for b and 0·03° for φ.

	$\langle b\rangle$	$\langle\varphi_T\rangle_{obs}$ (°)	$\langle\varphi_C\rangle_{obs}$ (°)	$\langle\varphi_T\rangle_{calc}$ (°)	$\langle\varphi_C\rangle_{calc}$ (°)
cis-cis	1·272	135·3	90·3	133	90
cis-trans	1·278	134·3	89·7		

Table 4. *Force constants* K (N m^{-1}), *IR bands* (cm^{-1}) *and X-ray geometry* (Å) *for those carbonyls present in the cis-cis and cis-trans isomers*

Carbonyl	K_{CO}	ν (IR)	C=O	Mn–C
C(2)–O(2)(*cis-cis*)	1621	1984	1·143 (10)	1·815 (9)
C(1)–O(1)(*cis-cis*)	1501	1905	1·155 (10)	1·771 (8)
C(1)–O(1)(*cis-trans*)	1501	1908	1·149 (8)	1·788 (6)
C(2)–O(2)(*cis-trans*)	1501		1·144 (8)	1·792 (6)

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36500 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

repulsion between *M* and *C* ligands than between *M* and *T*, with a repulsion ratio $R_C/R_T \simeq 1\cdot1$, which corresponds to the averaged bond-length ratio $\langle\langle \mathrm{Mn}-L\rangle_C/\langle \mathrm{Mn}-L\rangle_T\rangle_L > 1$ found for both isomers. Nevertheless, these bond lengths are also supposed to be conditioned by the *cis* and *trans* influences. On the other hand, theoretical force constants for both carbonyls have been calculated using the empirical formulae of Timney (1979), and are listed in Table 4 together with the corresponding X-ray bond distances and the observed IR bands for both *cis-cis* and *cis-trans* isomers. These results show that the predicted force constants do not correspond to the X-ray C=O bond distances; nevertheless, the Mn—C bonds seem to be more sensible to the environment, and are in agreement with the calculated force constants.

The authors thank Professor S. García-Blanco for his support, and the Centro de Cálculo of JEN, Madrid, for the facilities provided.

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Acta Cryst. (1982). B**38**, 954–956

cis-[*rac-cis*-1,2-Bis(phenylsulphinyl)ethylene]dichloroplatinum(II)

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(*Received* 10 *July* 1981; *accepted* 27 *October* 1981)

Abstract. $C_{14}H_{12}Cl_2O_2PtS_2$, $M_r = 542\cdot26$, orthorhombic, *Pbca*, $a = 22\cdot087\,(4)$, $b = 12\cdot517\,(2)$, $c = 11\cdot834\,(2)$ Å, $U = 3272\,(1)$ Å^3, $Z = 8$, $D_c = 2\cdot20$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 2\cdot15$ mm^{-1}. The structure was refined by least squares to $R = 0\cdot054$ for 1870 intensities. The Pt atom adopts a square-planar coordination geometry, being bonded to two Cl atoms arranged in a *cis* configuration and two S atoms of the bidentate disulphoxide ligand. This ligand forms a five-membered ring with the Pt atom.

Introduction. Platinum(II) forms cyclic systems with bidentate, chelating ligands such as disulphoxides (Cattalini, Michelon, Marangoni & Pelizzi, 1979). The title complex contains a disulphoxide ligand with an unsaturated centre, and the molecular structure was determined to discover whether any further interaction might arise between the carbon–carbon double bond and any of the Pt atoms.

The title complex was prepared by gently heating and stirring an ethanolic solution of *cis*-$(C_6H_5)SOCH{=}CHSO(C_6H_5)$ with an excess of K_2PtCl_4 for 2 h (Filgueiras, 1981). A beige precipitate was collected and recrystallized from propane. A single crystal with dimensions $0\cdot35 \times 0\cdot21 \times 0\cdot17$ mm was mounted on a Syntex $P2_1$ diffractometer and cell dimensions were determined from the angular measurements of 15 strong reflections in the range $45\cdot0 < 2\theta < 55\cdot0°$. 2036 intensities were recorded in the range $3\cdot0 < 2\theta < 125\cdot0°$ using graphite-monochromated Cu $K\alpha$ radiation and a 96-step ω-2θ scan technique. Lp corrections, and empirical absorption corrections based on a pseudo-ellipsoid model were applied, and equivalent reflections were averaged to give 1870 unique observed intensities $[F > 3\sigma(F)]$.

The Pt atom was located from a Patterson map, and all the remaining non-hydrogen atoms were located by subsequent electron-density difference syntheses. The positions of the H atoms were calculated geometrically and they were constrained to ride 1·08 Å from the relevant C atom; the ethylene H atoms and the H atoms of each phenyl ring were assigned common isotropic temperature factors which refined to 0·05 (4), 0·08 (4), and 0·03 (2) Å^2, respectively. The structure was refined to $R = 0\cdot054$ by blocked full-matrix least squares with all the non-hydrogen atoms assigned anisotropic thermal parameters. Complex neutral-atom scattering factors (*International Tables for X-ray Crystallography*, 1974) and unit weights were employed throughout, since $w\Delta^2$ was fairly independent of

0567-7408/82/030954-03\$01.00