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Structure of *cis-cis*-(*tert*-Butyl isocyanide)dicarbonyl(1,10-phenanthroline)(phenyl isocyanide)manganese(I) Perchlorate, $[\text{Mn}(\text{CO})_2(\text{C}_3\text{H}_9\text{N})(\text{C}_7\text{H}_5\text{N})(\text{C}_{12}\text{H}_8\text{N}_2)]\text{ClO}_4$

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Abstract. $M_r = 576.9$, monoclinic, $P2_1/n$, $a = 15.343(3)$, $b = 12.910(3)$, $c = 14.511(3)$ Å, $\beta = 105.51(2)^\circ$, $V = 2770(2)$ Å³, $Z = 4$, $D_x = 1.383$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 644$ m⁻¹, $F(000) = 1184$, room temperature, $R = 0.054$ for 2698 observed reflections. The Mn ion displays distorted octahedral coordination with the *tert*-butyl isocyanide, the phenanthroline and a carbonyl ligand in the equatorial plane. The Mn–N and Mn–C bond distances alter according to the electronegative or π -acceptor character of the *trans* ligand. The Mn–C (*tert*-butyl isocyanide) bond length is the shortest observed in the literature for similar ligands.

Introduction. Crystal structure determination of the title compound has been undertaken in order to elucidate the ligand arrangement and the distortion of the coordination polyhedron.

The results obtained show that the reaction of *fac*- $\{\text{Mn}(\text{CO})_3(\text{CNR})(\text{NN})\}.\text{ClO}_4$ and CNR' in the presence of ONMe_3 , in chloroform at room temperature, moves the *cis*-CNR ligand to the *trans* position, and does not give the expected *cis-trans* configuration predicted by Howell & Burkinshaw (1983). This result will be related to the formation of *mer*- $\{\text{Mn}(\text{CO})_3(\text{CNR})(\text{NN})\}.\text{ClO}_4$ and *cis-cis*- $\{\text{Mn}(\text{CO})_2(\text{CNR})_2(\text{NN})\}.\text{ClO}_4$ from *fac*- $\{\text{Mn}(\text{CO})_3(\text{CNR})(\text{NN})\}.\text{ClO}_4$ (García-Alonso, Riera, Villafañe & Vivanco, 1985).

Experimental. Red prisms (0.2 × 0.2 × 0.1 mm), Philips PW 1100, Mo $K\alpha$, graphite monochromator, cell parameters from 25 reflections ($4 \leq \theta \leq 8^\circ$), ω -scan technique, scan width 1° , scan speed $0.03^\circ \text{ s}^{-1}$; 2724 independent reflections with $\theta \leq 30^\circ$; 2698 with $I \geq 2.5\sigma(I)$; $hkl = -16$ to 16, 0 to 13, and 0 to 13. Three standard reflections ($2\bar{3}1$, $1\bar{3}2$ and $2\bar{3}2$) measured every two hours, no significant variations; L_p correction, absorption ignored. Mn atom from Patterson map (*SHELX76*; Sheldrick, 1976). Remaining non-hydrogen atoms from weighted Fourier synthesis. Full-matrix least-squares refinement (*SHELX76*), $\sum w|F_o| - |F_c|^2$ minimized, $w = [\sigma^2(F_o) + 0.0015 \times |F_o|^2]^{-1}$; f , f' and f'' from *International Tables for X-ray Crystallography* (1974); number of refined parameters 205. $\Delta\rho$ map at $R = 0.12$ revealed double peaks for oxygen atoms of perchlorate ion; disorder was assumed with occupancy factor 0.5 for each oxygen position; 16 H from $\Delta\rho$ map, remaining H atoms in calculated positions, all H refined with overall isotropic temperature factor; final $R = 0.054$ ($wR = 0.061$) for all observed reflections; max. $\Delta/\sigma = 1.6$ in U_{11} of O(Cl2) (-0.8 in z coordinate of Mn for non-disordered atom); max. and min. peaks in final $\Delta\rho$ map 0.4 and $-0.2 \text{ e } \text{Å}^{-3}$. IBM-4341 computer.

* This paper forms part of the work by this author for a PhD.

Discussion. Final atomic coordinates are listed in Table 1 and selected bond lengths and angles in Table 2.* The atom numbering is shown in Fig. 1.

The Mn ion displays distorted octahedral coordination with 1,10-phenanthroline, *tert*-butyl isocyanide

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42247 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^4$; $\times 10^5$ for Mn) and equivalent isotropic temperature coefficients (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}
Mn	19097 (5)	7797 (6)	81207 (6)	3.97 (4)
N(1)	1856 (3)	2 (3)	9355 (3)	3.9 (2)
C(2)	2490 (4)	-110 (4)	10166 (4)	4.8 (3)
C(3)	2370 (4)	-723 (5)	10919 (4)	5.5 (3)
C(4)	1591 (5)	-1240 (5)	10844 (5)	5.8 (4)
C(5)	898 (4)	-1130 (4)	10010 (5)	5.0 (3)
C(6)	28 (5)	-1595 (5)	9855 (6)	6.3 (4)
C(7)	-620 (4)	-1428 (5)	9048 (6)	6.4 (4)
C(8)	-477 (4)	-770 (5)	8282 (5)	5.3 (3)
C(9)	-1123 (4)	-538 (5)	7436 (6)	6.2 (4)
C(10)	905 (4)	108 (5)	6803 (5)	6.4 (4)
C(11)	47 (4)	536 (4)	6963 (5)	5.3 (3)
N(12)	595 (3)	312 (3)	7758 (3)	4.2 (2)
C(13)	370 (3)	-314 (4)	8410 (4)	4.1 (3)
C(14)	1054 (4)	-499 (4)	9276 (4)	4.1 (3)
C(21)	1611 (3)	2078 (5)	8673 (4)	4.1 (3)
N(21)	1504 (3)	2856 (4)	9017 (4)	4.5 (3)
C(22)	1407 (4)	3799 (4)	9458 (5)	4.3 (3)
C(23)	942 (4)	4589 (5)	8888 (5)	6.0 (4)
C(24)	843 (5)	5526 (5)	9344 (7)	7.9 (5)
C(25)	1181 (5)	5645 (6)	10321 (7)	7.5 (5)
C(26)	1617 (5)	4838 (6)	10853 (6)	6.6 (4)
C(27)	1745 (4)	3916 (5)	10428 (5)	5.3 (3)
C(31)	3113 (4)	1187 (4)	8568 (4)	4.6 (3)
N(31)	3844 (4)	1451 (4)	8819 (4)	5.8 (3)
C(32)	4748 (4)	1969 (6)	9087 (6)	6.6 (4)
C(33)	5375 (5)	1387 (6)	9952 (7)	9.4 (5)
C(34)	4645 (5)	3084 (5)	9397 (6)	7.8 (4)
C(35)	5111 (5)	1887 (7)	8207 (6)	9.7 (6)
O(41)	1865 (4)	1405 (5)	7011 (5)	5.8 (4)
C(41)	1859 (4)	1788 (5)	6281 (4)	9.7 (4)
C(51)	2273 (4)	-405 (5)	7649 (5)	5.3 (3)
O(51)	2513 (4)	-1138 (4)	7355 (4)	8.8 (3)
Cl	3772 (1)	1794 (1)	2013 (1)	5.32 (8)
O(Cl1)	4195 (6)	791 (7)	1847 (7)	5.45 (7)
O(Cl2)	4376 (7)	2300 (9)	2848 (8)	5.84 (9)
O(Cl3)	3786 (9)	2363 (10)	1154 (9)	7.35 (11)
O(Cl4)	3010 (9)	1616 (11)	2278 (10)	8.29 (12)
O(1')	3872 (7)	704 (8)	2109 (8)	6.82 (8)
O(2')	4486 (8)	2370 (10)	2563 (9)	6.12 (11)
O(3')	3476 (9)	2154 (11)	1065 (10)	8.21 (13)
O(4')	2940 (9)	2058 (10)	2290 (9)	7.76 (11)

Table 2. Selected bond lengths (\AA) and angles ($^\circ$)

N(1)—Mn	2.074 (5)	N(21)—C(21)	1.153 (8)
N(12)—Mn	2.036 (4)	C(22)—N(21)	1.401 (8)
C(21)—Mn	1.964 (6)	N(31)—C(31)	1.135 (8)
C(31)—Mn	1.862 (6)	C(32)—N(31)	1.494 (8)
C(41)—Mn	1.787 (8)	C(41)—C(41)	1.167 (10)
C(51)—Mn	1.823 (7)	C(51)—C(51)	1.139 (9)
N(12)—Mn—N(1)	79.3 (2)	C(41)—Mn—C(21)	91.4 (3)
C(21)—Mn—N(1)	89.6 (2)	C(41)—Mn—C(31)	89.0 (3)
C(21)—Mn—N(12)	92.1 (2)	C(51)—Mn—N(1)	90.3 (3)
C(31)—Mn—N(1)	95.8 (2)	C(51)—Mn—N(12)	92.0 (2)
C(31)—Mn—N(12)	174.8 (3)	C(51)—Mn—C(21)	175.8 (2)
C(31)—Mn—C(21)	86.3 (2)	C(51)—Mn—C(31)	89.6 (3)
C(41)—Mn—N(1)	175.2 (2)	C(51)—Mn—C(41)	89.0 (3)
C(41)—Mn—N(12)	96.0 (2)		

and a carbonyl ligand in the equatorial plane (the first ligand is bidentate), while the phenyl isocyanide and the second carbonyl ligand are in apical positions. The Mn, N(1), N(12), C(31) and C(41) atoms are roughly coplanar [the deviations of N(1) and C(41) from the mean plane are 0.021 (7) \AA , while those of N(12) and C(31) are -0.021 (7) \AA]. The Mn—C(21) and Mn—C(51) bonds are orthogonal to this plane. The N(1)—Mn—N(12) bond angle [79.3 (2) $^\circ$] is similar to those observed by Ulibarri & Fayos (1982) in *cis-cis*-dicarbonyl(1,10-phenanthroline)bis(trimethyl phosphite)manganese(I) perchlorate. The metal—N(phenanthroline) bond distances are equivalent when the opposing ligands are the same (Anderson, 1973; Veal, Hatfield & Hodgson, 1973; Stephens & Vagg, 1977). In our structure, as in those determined by Ulibarri & Fayos (1982), these distances alter according to the electronegative character of the *trans* ligand. The Mn—N bond distance is shorter when the *trans* ligand is an isocyanide.

The geometry of the phenyl isocyanide ligand is similar to those observed by Ericsson, Jagner & Ljungström (1980) in $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{I}_3$. The C(41)—O(41) bond [1.167 (10) \AA] is longer than C(51)—O(51) [1.139 (9) \AA], which can be explained by the π bond between the metal and CO groups (Cotton & Wilkinson, 1982). The second bond occupies a *trans* position with respect to a better π acceptor; therefore, Mn—C(41) is shorter than Mn—C(51). A similar argument explains the short Mn—C(31) bond distance [1.862 (6) \AA]. The linearity of the isocyanide group is in agreement with the IR spectrum [$\nu_{\text{CN}} = 2170$ and 2134 $\text{cm}^{-1}(f)$]. These bands are typical for no π interaction between the metal and the isocyanide moieties (Malatesta, 1969), so this short distance can

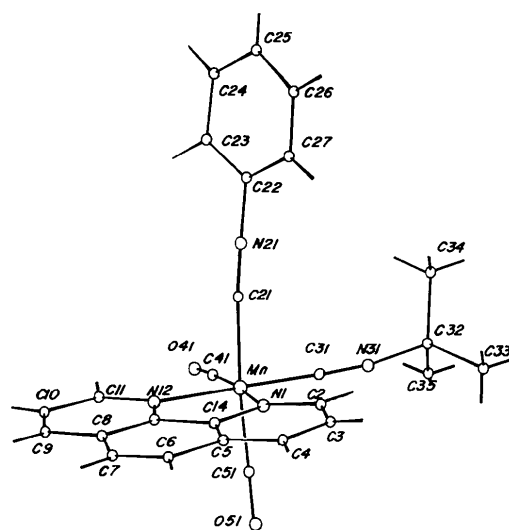


Fig. 1. View of the cation with the numbering of atoms.

only be explained by the π -acceptor character of the *trans* ligand; thus the Mn—C bond distance is equal to 1.97 (1) Å in [Mn(CO)₃(CNCH₃)Br], where the *trans* ligand is CO, 1.924 (3) Å in [Mn(CNC₂H₅)₆]I₃, where it is (CNC₂H₅), and 1.90 (1) Å in [Mn(CNC₆H₅)₆]I₃, where it is (CNC₆H₅) (Sarapu & Fenske, 1972; Ericsson, Jagner & Ljungström, 1979, 1980, respectively).

The phenanthroline ligand differs from the free molecule (Nishigaki, Yoshioka & Nakatsu, 1978) with respect to the dihedral angles between the rings. These are 2.7 (1) and 2.2 (1)° in the ligand, while values of 0.8, 2.5, 1.8 and 1.8° are observed in the free molecule.

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Structure du (Diphényl-2,6 dioxa-1,3 aza-6 phospho-2 cyclooctyl-2)trihydroboron, C₁₆H₂₁BNO₂P

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Abstract. $M_r = 301.13$, monoclinic, $P2_1$, $a = 11.534$ (3), $b = 6.492$ (1), $c = 11.744$ (3) Å, $\beta = 113.21$ (2)°, $V = 808.2$ (3) Å³, $Z = 2$, $D_x = 1.24$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.18$ mm⁻¹,

$F(000) = 320$, $T = 294$ K, $R = 0.039$ for 951 observed diffractometer reflexions. The structure of the title compound shows a distorted crown conformation of the ring due to a strong 1,3 diaxial interaction between the B(4)(H,H',H'') group and the two corresponding hydrogens. This interaction induces an approach between the intracyclic P(1) and N(5) atoms which cannot be attributed to a Lewis acid/base interaction.

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