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Structure of *fac*-(*tert*-Butyl isocyanide)tricarbonyl(1,10-phenanthroline)manganese(I) Perchlorate

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Abstract. $C_{20}H_{17}MnN_3O_3.ClO_4$, $M_r = 501{\cdot}8$, triclinic, $P\bar{1}$, $a = 18{\cdot}246\ (3)$, $b = 13{\cdot}554\ (2)$, $c = 9{\cdot}452\ (2)$ Å, $\alpha = 111{\cdot}53\ (2)$, $\beta = 118{\cdot}94\ (2)$, $\gamma = 118{\cdot}63\ (2)°$, $V = 1124{\cdot}5\ (6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}48$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}782$ mm^{-1}, $F(000) = 512$, room temperature, $R = 0{\cdot}051$ for 2246 observed reflections. The Mn ion shows a distorted octahedral coordination with the 1,10-phenanthroline and two carbonyl ligands in the equatorial plane. The Mn—N and Mn—C bond distances differ according to the electron-withdrawing character of the *trans* ligand, as has been noted previously in similar structures.

Introduction. The preparation of the title compound has been described elsewhere (García-Alonso, Riera, Villafañe & Vivanco, 1984). A previous paper (Valín, Moreiras, Solans, Font-Altaba, Solans, García-Alonso, Riera & Vivanco, 1985) reported the crystal structure of *cis-cis*-(*tert*-butyl isocyanide)dicarbonyl-(1,10-phenanthroline)(phenyl isocyanide)manganese(I) perchlorate, which was obtained from reaction of the title compound and phenyl isocyanide in the presence of $ONMe_3$ in chloroform at room temperature. In this reaction the *cis*-CN(*tert*-butyl) ligand of the title compound moves to the *trans* position. Although a number of cationic *fac*-tricarbonyl complexes of manganese(I) have been prepared, to date only one of them, *i.e.* *fac*-$[Mn(CO)_3(NH_3)_3]^+$ has been the subject of an X-ray structure determination (Herberhold, Wehrmann, Neugebauer & Huttner, 1978). In order to confirm the expected ligand arrangement of the title compound and to obtain the geometry values to compare the two structures, a single-crystal X-ray analysis has been carried out.

Experimental. Yellow prismatic crystal (0·1 × 0·2 × 0·2 mm), Philips PW 1100 diffractometer, cell parameters from 25 reflections ($4 \leq \theta \leq 9°$), Mo $K\alpha$ radiation, graphite monochromator, ω-scan technique, scan width 1°, scan speed 0·03° s^{-1}. Three reflections measured every 2 h, no significant intensity variations. 2266 independent reflections ($2 \leq \theta \leq 27°$); 2246 with $I \geq 2{\cdot}5\sigma(I)$; h,k,l range: −18 to 11, −15 to 15 and 0 to 10; Lp correction, absorption ignored. Direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) gave 27 strongest atoms, remaining non-hydrogen atoms from difference synthesis. Isotropic and anisotropic refinements by full-matrix least squares (*SHELX*76; Sheldrick, 1976), $w||F_o| - |F_c||^2$ minimized, $w = [\sigma^2(F_o) + 0{\cdot}0006|F_o|^2]^{-1}$, f, f' and f'' from *International Tables for X-ray Crystallography* (1974); 16 H from ΔF synthesis; all H refined with overall isotropic temperature factor; final $R = 0{\cdot}051$ ($wR = 0{\cdot}055$) for all observed reflections; max. shift/e.s.d. = 0·8 in y coordinate of C(24); max. and min. peaks in final ΔF synthesis 0·6 e Å^{-3} at 1·54 Å from O(4) and −0·3 e Å^{-3}; IBM-3083 computer.

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 a distorted octahedral coordination with 1,10-phenanthroline and two carbonyl ligands in the equatorial plane (the first ligand in a bidentate fashion), while the third carbonyl and the

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[*] This work is a part of this author's PhD thesis.

[†] 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 42534 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature coefficients* (Å^2)

$$B_{eq} = (8\pi^2/3)\sum U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Mn	2273 (1)	−259 (1)	9331 (2)	3·28 (4)
N(1)	478 (5)	−1869 (6)	5589 (8)	3·4 (2)
C(2)	748 (7)	−3622 (8)	3584 (11)	4·2 (3)
C(3)	−1790 (7)	−4567 (9)	1098 (12)	5·0 (3)
C(4)	−1586 (7)	−3683 (10)	639 (12)	4·8 (3)
C(5)	−339 (6)	−1832 (8)	2686 (11)	3·8 (3)
C(6)	22 (8)	−762 (11)	2437 (14)	4·8 (4)
C(7)	1184 (9)	998 (11)	4491 (15)	4·9 (4)
C(8)	2239 (6)	1929 (8)	7047 (12)	3·9 (3)
C(9)	3550 (8)	3782 (9)	9316 (15)	5·0 (4)
C(10)	4481 (8)	4499 (9)	11616 (14)	5·2 (3)
C(11)	4133 (7)	3386 (8)	11728 (12)	4·3 (3)
N(12)	2910 (5)	1636 (6)	9662 (8)	3·4 (2)
C(13)	1958 (6)	896 (7)	7320 (10)	3·3 (3)
C(14)	675 (6)	−967 (7)	5160 (10)	3·2 (3)
C(21)	2877 (6)	−504 (7)	8137 (10)	3·7 (3)
N(22)	3105 (5)	−667 (6)	7200 (9)	4·0 (2)
C(23)	3276 (8)	−859 (9)	5800 (13)	5·0 (4)
C(24)	3369 (14)	231 (16)	5552 (24)	8·7 (9)
C(25)	1964 (13)	−2831 (14)	3204 (19)	9·8 (6)
C(26)	4614 (12)	−145 (16)	7387 (22)	8·3 (7)
C(31)	1615 (7)	−2076 (8)	8702 (11)	4·4 (3)
O(31)	1240 (6)	−3192 (7)	8373 (10)	7·0 (3)
C(32)	1649 (6)	5 (8)	293 (11)	4·2 (3)
O(32)	1323 (6)	215 (7)	10984 (10)	6·7 (3)
C(33)	3939 (7)	1309 (8)	12663 (12)	4·2 (3)
O(33)	4936 (5)	2232 (6)	14752 (8)	5·8 (2)
Cl	2685 (2)	5013 (2)	5389 (4)	5·93 (9)
O(1)	3630 (8)	6380 (10)	6067 (16)	11·6 (5)
O(2)	3267 (10)	5448 (12)	7503 (15)	13·1 (7)
O(3)	2476 (10)	3736 (12)	3964 (15)	14·8 (5)
O(4)	1490 (10)	4332 (18)	3929 (23)	18·3 (10)

Table 2. *Selected bond distances* (Å) *and angles* (°)

N(1)–Mn	2·067 (4)	C(2)–N(1)	1·319 (7)
N(12)–Mn	2·060 (4)	N(22)–C(21)	1·144 (6)
C(21)–Mn	1·969 (6)	C(23)–N(22)	1·463 (6)
C(31)–Mn	1·806 (6)	O(31)–C(31)	1·144 (7)
C(32)–Mn	1·846 (6)	O(32)–C(32)	1·124 (6)
C(33)–Mn	1·819 (7)	O(33)–C(33)	1·141 (7)
N(12)–Mn–N(1)	79·2 (2)	C(33)–Mn–N(1)	174·9 (2)
C(21)–Mn–N(1)	82·9 (2)	C(33)–Mn–N(12)	96·0 (2)
C(21)–Mn–N(12)	83·3 (2)	C(33)–Mn–C(21)	94·9 (2)
C(31)–Mn–N(1)	95·9 (2)	C(33)–Mn–C(31)	88·8 (3)
C(31)–Mn–N(12)	173·8 (2)	C(33)–Mn–C(32)	88·7 (3)
C(31)–Mn–C(21)	92·5 (2)	N(22)–C(21)–Mn	169·6 (5)
C(32)–Mn–N(1)	93·2 (2)	O(31)–C(31)–Mn	177·9 (6)
C(32)–Mn–N(12)	92·4 (2)	O(32)–C(32)–Mn	177·0 (6)
C(32)–Mn–C(21)	174·6 (2)	O(33)–C(33)–Mn	175·6 (5)
C(32)–Mn–C(31)	91·6 (3)		

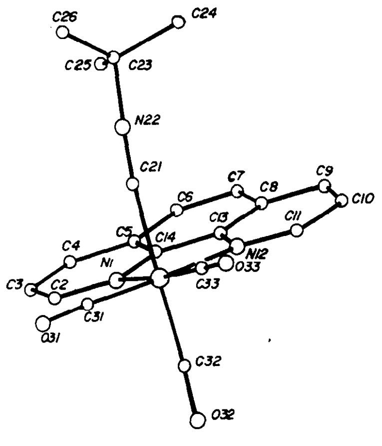

Fig. 1. View of the molecule with atom numbering.

tert-butyl isocyanide ligands are in the apical positions. The Mn, N(1), N(12), C(31) and C(33) atoms are roughly coplanar [largest deviation from mean plane is 0·036 (4) Å for the Mn atom]. The N(1)–Mn–N(12) bond angle [79·2 (2)°] is equal to those observed by Valín, Moreiras, Solans, Font-Altaba, Solans, García-Alonso, Riera & Vivanco (1985) in *cis-cis*-(*tert*-butyl isocyanide)dicarbonyl(1,10-phenanthroline)-(phenyl isocyanide)manganese(I) perchlorate and by Ulibarri & Fayos (1982) in *cis-cis*-dicarbonyl(1,10-phenanthroline)bis(trimethyl phosphite)manganese(I) perchlorate. The Mn–N(phenanthroline) bond distances are equivalent [mean value 2·063 (3) Å] and similar to those observed for other Mn–N bonds with a carbonyl ligand in the *trans* position [mean value 2·060 (5) Å; Valín *et al.* (1985), Fayos & Ulibarri (1982)].

The Mn–C(21)(*tert*-butyl) bond distance [1·969 (6) Å] is larger than the 1·864 (7) Å observed by Valín *et al.* (1985), where the *trans* atom is an N of a phenanthroline ligand, but is similar to 1·961 (7) Å observed in the same structure for Mn–C(phenyl), where the *trans* ligand is a CO. This fact can be explained on the basis of the π character of the *trans* ligands. Also, the Mn–CO bond distances alter according to the π character of the *trans* ligand; the values observed are 1·806 (6) and 1·819 (7) Å for the equatorial bonds (*trans* to phenanthroline) and 1·846 (6) Å for the axial (*trans* to *tert*-butyl isocyanide), while the values observed in the literature for analogous compounds are 1·79 (1) for CO *trans* to phenanthroline (Fayos & Ulibarri, 1982), 1·815 (9) Å *trans* to trimethyl phosphite (Ulibarri & Fayos, 1982) and 1·825 (8) Å *trans* to phenyl isocyanide (Valín *et al.*, 1985).

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