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Structure of $Mn(CO)_3[C_5H_4SiMe_2C_5H_4]Mn(CO)_3$

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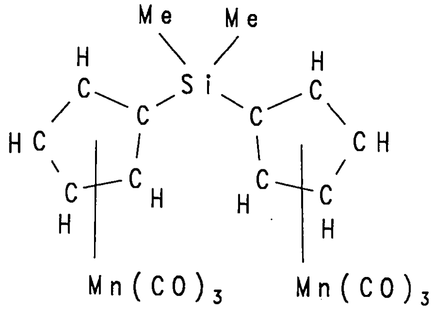
Abstract. Bis(η^5-cyclopentadienyl)dimethylsilanebis(tricarbonylmanganese), $C_{18}H_{14}Mn_2O_6Si$, M_r = 464·3, triclinic, $P\overline{1}$, a = 7·649 (1), b = 11·119 (2), c = 12·203 (3) Å, α = 98·39 (3), β = 104·68 (2), γ = 96·29 (2)°, V = 981·5 (8) Å^3, Z = 2, D_x = 1·57 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 13·7 cm^{-1}, F(000) = 468, T = 293 K, R = 0·039 for 2276 reflections with $F_o^2 > 3\sigma(F_o^2)$. The two (cp) rings form dihedral angles of 89·5 and 144·0° with the central C(cp)–Si–C(cp) plane and one $Mn(CO)_3$ unit is pentahapto bonded to each (cp) ring on the outside of the ligand molecule.



(I)

Experimental. The title complex (I) was obtained by the reaction of $cpMn(CO)_3$ with n-BuLi in THF, followed by the addition of Me_2SiCl_2. Yellow crystals obtained by slow cooling of a 1/20 benzene/pentane solution. Data crystal 0·14 × 0·34 × 0·34 mm mounted with epoxy on a glass fiber. Intensities measured with an Enraf–Nonius CAD-4 diffractometer using ω–2θ scans of 4–16° min^{-1} in θ. Unit cell determined from least-squares analysis of angle data for 25 reflections with $16 < 2\theta < 20°$. Analytical absorption correction varied from 0·72 to 1·00. Data collected to $(\sin\theta)/\lambda$ = 0·59 Å^{-1}, $-7 \le h \le 7$, $-10 \le k \le 0$, $-11 \le l \le 11$. Three standard reflections ($3\overline{2}\overline{2}$; $1\overline{1}4$; $\overline{1}\overline{3}\overline{3}$) indicated crystal decomposition of less than 0·9% over 31·7 h of data collection. 3628 reflections measured, 3435 unique

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($R_{\rm int} = 0{\cdot}014$), 1159 reflections with $I < 3\sigma(I)$ where $\sigma^2(I) = \sigma^2_{\rm cs}(I) + (0{\cdot}05I)^2$; $\sigma_{\rm cs}(I)$ is standard deviation of I based on counting statistics. Solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. Full-matrix least squares minimized $\sum w(F_o - F_c)^2$. Methyl H atom orientation determined from difference maps and all H atoms constrained to idealized positions (C—H = 0·95 Å) with fixed isotropic B values of 1·2 times the B value of the attached atoms. All non-H atoms were refined anisotropically for a total of 244 parameters. $R = 0{\cdot}039$, $wR = 0{\cdot}053$, GOF = 1·4, where non-Poisson $w^{-1} = [\sigma^2(I) + (0{\cdot}05I)^2]/4F^2$. Final $(\Delta/\sigma)_{\rm max} < 0{\cdot}02$; $\Delta\rho_{\rm max} = 0{\cdot}42\ (8)$ and $\Delta\rho_{\rm min} = -0{\cdot}61\ (8)\ {\rm e\ Å^{-3}}$ on final difference map. Atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974) and programs used were those of Enraf–Nonius (1982) *SDP*. Table 1 gives the atomic coordinates and Table 2 gives selected bond distances and angles.* Fig. 1 shows the complex with the numbering scheme.

Related literature. Recent structural studies on the effect of the bridging group between the cp rings in these complexes include the following bridging units: —$C(CH_3)(OH)$— (Cordes, Durham & Askew, 1989*a*), —$C(O)CH{=}C(CH_3)$— (Cordes, Durham & Askew, 1989*a*), —C(Me)(OSiMe₃)— (Cordes, Durham & Askew, 1989*b*) and —CHMe— (Cordes, Durham & Askew, 1989*c*). The structure of a related monomeric manganese complex has been reported by Berndt & Marsh (1963).

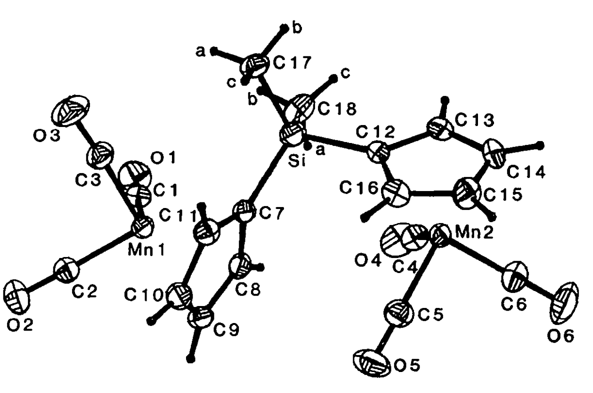

Fig. 1. *ORTEP* (Johnson, 1976) drawing and numbering scheme for (I). The ellipsoids are drawn at the 30% probability surface and H atoms have been given arbitrary radii for figure clarity.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$B_{\rm eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\,\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å²)
Mn(1)	0·23991 (9)	0·36457 (6)	0·56132 (6)	2·84 (1)
Mn(2)	0·19849 (9)	0·23762 (7)	1·01755 (6)	3·04 (2)
Si	0·2494 (2)	0·1314 (1)	0·7367 (1)	3·78 (3)
O(1)	−0·1233 (5)	0·2391 (4)	0·4239 (3)	5·3 (1)
O(2)	0·2363 (5)	0·5461 (4)	0·4090 (3)	4·96 (9)
O(3)	0·4208 (6)	0·2124 (4)	0·4201 (4)	7·1 (1)
O(4)	−0·1732 (5)	0·2228 (4)	0·8714 (4)	6·1 (1)
O(5)	0·2692 (7)	0·5011 (4)	1·0101 (4)	7·0 (1)
O(6)	0·0641 (7)	0·2845 (5)	1·2219 (3)	8·3 (1)
C(1)	0·0181 (7)	0·2878 (4)	0·4778 (4)	3·5 (1)
C(2)	0·2361 (6)	0·4757 (5)	0·4688 (4)	3·5 (1)
C(3)	0·3502 (7)	0·2703 (5)	0·4774 (4)	4·2 (1)
C(4)	−0·0278 (7)	0·2275 (5)	0·9276 (4)	3·9 (1)
C(5)	0·2427 (7)	0·3984 (5)	1·0139 (5)	4·4 (1)
C(6)	0·1193 (8)	0·2670 (6)	1·1414 (5)	4·9 (1)
C(7)	0·2845 (6)	0·2952 (4)	0·7198 (4)	3·0 (1)
C(8)	0·1550 (6)	0·3793 (5)	0·7163 (4)	3·5 (1)
C(9)	0·2354 (7)	0·4956 (5)	0·7082 (4)	4·0 (1)
C(10)	0·4183 (7)	0·4871 (5)	0·7067 (4)	4·1 (1)
C(11)	0·4484 (6)	0·3662 (5)	0·7158 (4)	3·5 (1)
C(12)	0·3100 (6)	0·1324 (4)	0·8953 (4)	2·9 (1)
C(13)	0·2282 (7)	0·0528 (4)	0·9564 (4)	3·7 (1)
C(14)	0·3150 (8)	0·0830 (5)	1·0744 (4)	4·3 (1)
C(15)	0·4554 (7)	0·1816 (5)	1·0902 (4)	4·4 (1)
C(16)	0·4514 (6)	0·2132 (5)	0·9817 (4)	3·6 (1)
C(17)	0·4065 (7)	0·0476 (5)	0·6723 (4)	4·2 (1)
C(18)	0·0085 (7)	0·0557 (6)	0·6712 (5)	4·5 (1)

Table 2. *Selected bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Mn(1)—C(1)	1·788 (4)	Si—C(18)	1·860 (5)
Mn(1)—C(2)	1·789 (6)	O(1)—C(1)	1·141 (5)
Mn(1)—C(3)	1·783 (6)	O(2)—C(2)	1·146 (7)
Mn(2)—C(4)	1·781 (5)	O(3)—C(3)	1·154 (8)
Mn(2)—C(5)	1·792 (6)	O(4)—C(4)	1·141 (6)
Mn(2)—C(6)	1·767 (7)	O(5)—C(5)	1·147 (7)
Si—C(7)	1·861 (5)	O(6)—C(6)	1·163 (8)
Si—C(12)	1·870 (5)	C—C	1·397–1·432 (range)
Si—C(17)	1·855 (6)	C—C	1·414 (mean)

C(1)—Mn(1)—C(2)	91·4 (2)	C(17)—Si—C(18)	110·5 (3)
C(1)—Mn(1)—C(3)	92·1 (2)	Mn(1)—C(1)—O(1)	179·6 (4)
C(2)—Mn(1)—C(3)	90·6 (2)	Mn(1)—C(2)—O(2)	178·8 (5)
C(4)—Mn(2)—C(5)	90·6 (3)	Mn(1)—C(3)—O(3)	177·3 (5)
C(4)—Mn(2)—C(6)	90·4 (3)	Mn(2)—C(4)—O(4)	178·7 (5)
C(5)—Mn(2)—C(6)	92·0 (3)	Mn(2)—C(5)—O(5)	179·0 (5)
C(7)—Si—C(12)	106·2 (2)	Mn(2)—C(6)—O(6)	178·6 (6)
C(7)—Si—C(17)	109·1 (2)	Si—C(7)—C(8)	127·1 (4)
C(7)—Si—C(18)	112·5 (2)	Si—C(7)—C(11)	127·7 (4)
C(12)—Si—C(17)	109·6 (2)	Si—C(12)—C(13)	128·3 (4)
C(12)—Si—C(18)	108·9 (2)	Si—C(12)—C(16)	126·9 (4)
		C—C—C	104·8–110·6 (range)

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* Tables of anisotropic temperature factors, H atom positions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52538 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Bromobis[2,3-di(2-pyridyl)quinoxaline]copper(II) Hydrogensulfate–2,3-Di(2-pyridyl)quinoxaline (1/1)

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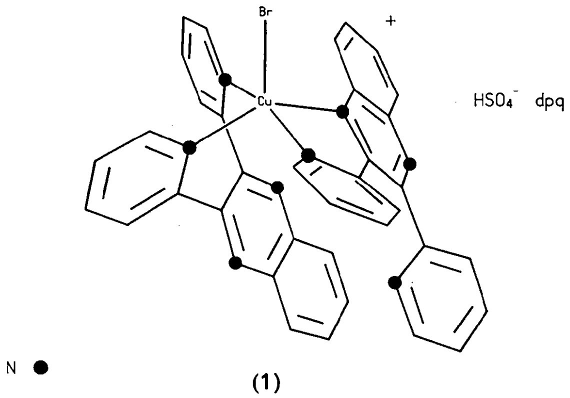
Abstract. $[CuBr(C_{18}H_{12}N_4)_2]HSO_4.C_{18}H_{12}N_4$, $C_{18}H_{12}N_4$ = dpq, M_r = 1093·54, monoclinic, $C2/c$, a = 26·850 (6), b = 13·487 (4), c = 27·295 (6) Å, β = 107·21 (2)°, V = 9441 (4) Å^3, Z = 8, D_x = 1·54 g cm^{-3}, Mo $K\alpha$, λ = 0·71073 Å, μ = 14·04 cm^{-1}, $F(000)$ = 4456, T = 294 K, R = 0·0523 for 3418 observed reflections. The title compound is the product of a side reaction in the bromo-induced oxidation of a copper/dpq system. Two dpq ligands are bonded to copper in a bidentate fashion; one is bonded only through pyridyl N atoms, while the other bonds through one pyridyl and one quinoxaline N atom. A third dpq molecule is not involved in bonding to copper nor in any other intermolecular or ionic interactions. The coordination sphere of the Cu atom has a distorted square pyramidal geometry, with the ligand N atoms forming the basal plane and the Br atom occupying the apical position.



(1)

Experimental. Green parallelepiped crystal of (1) obtained by slow evaporation of an ethanol solution, dimensions 0·20 × 0·25 × 0·38 mm. Data collected at room temperature, graphite-monochromated Mo $K\alpha$ radiation, Nicolet *R3mV* diffractometer, ω scans of 2 – 15° min^{-1}, $2\theta_{max}$ = 45°, h = –29 to 29, k = 0 to 15, l = 0 to 30, 6892 measurements, 6131 unique (R_{int} = 0·076), 3418 observed [$I > 3\sigma(I)$]. Unit-cell dimensions determined by least-squares fit to settings for 29 reflections (16 < 2θ < 30°). Empirical absorption correction (μ = 14·04 cm^{-1}), transmission factors 0·88–1·00; three standards monitored (± 2%), 66·9 h of X-ray exposure. Solved by the Patterson method; full-matrix least-squares refinement on F, R = 0·0523, wR = 0·0568, S = 1·24, $(\Delta/\sigma)_{max}$ = 0·01, 659 variables including positional parameters and anisotropic thermal parameters for all non-H atoms; H atoms located by standard techniques, included in the structure factor calculation in idealized positions (C—H = 0·96 Å) with group isotropic thermal parameter U_H = 0·057 (5) Å^2. Function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o) + 0{\cdot}0005|F_o|^2]$. Final difference map peaks ranged from –0·46 to 0·56 e Å^{-3}. Computer programs *SHELXTL* (Sheldrick, 1986), scattering factors (Cromer & Waber, 1974), real and imaginary anomalous-dispersion corrections (Cromer, 1974). Final atomic coordinates are given in Table 1,† selected distances and angles are reported in Table 2;

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52499 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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