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cis-Tetracarbonyl(methoxycarbonyl)(triphenylphosphine)manganese, $Mn(CO)_4(PPh_3)(COOCH_3)$

BY DONALD E. WILLIAMS, SANTOSH K. MANDAL AND DOROTHY H. GIBSON

Department of Chemistry, University of Louisville, Louisville, KY 40292, *USA*

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Abstract. $[Mn(C_2H_3O_2)(C_{18}H_{15}P)(CO)_4]$, $M_r = 488{\cdot}32$, monoclinic, $P2_1/n$, $a = 20{\cdot}497\,(10)$, $b = 10{\cdot}099\,(10)$, $c = 22{\cdot}157\,(10)$ Å, $\beta = 93{\cdot}69\,(4)°$, $V = 4576{\cdot}8$ Å^3, $Z = 8$, $D_x = 1{\cdot}42$ g cm^{-3}, $\lambda = 0{\cdot}7107$ Å, $\mu = 6{\cdot}6$ cm^{-1}, $F(000) = 2000$, room temperature, 4251 reflections measured, $R = 0{\cdot}058$, $wR = 0{\cdot}063$ for 2826 observed reflections with $I > 3\sigma(I)$. The manganese has octahedral coordination, with the triphenylphosphine group *cis* to the methoxycarbonyl group. There are two molecules in the asymmetric unit which have only minor differences in structure.

Introduction. Metallocarboxylates are an important class of organometallic compounds which are implicated as intermediates in the water gas shift (WGS) reaction; little structural information is available for these compounds, however (Ford & Rokicki, 1988). During the course of another investigation, a sample of the ester, $Mn(CO)_4(PPh_3)(COOCH_3)$, became available; the determination of its structure is reported herein.

Experimental. To a saturated methanolic solution containing 1·00g of $[Mn(CO)_5(PPh_3)]BF_4$ and maintained at 273 K was added 1·1 ml of a 25% solution of Et_4NOH in methanol. Reaction was complete after about 1 min; solvent was removed and the residue was extracted with hexane. The hexane extracts were concentrated and then chilled to 263 K; pale yellow crystals, m.p. 359–360 K, were collected by filtration.

X-ray diffraction data were obtained with an Enraf–Nonius CAD-4H diffractometer, Mo $K\alpha$ radiation, incident-beam graphite monochromator, from a yellow needle crystal $0{\cdot}1 \times 0{\cdot}3 \times 0{\cdot}5$ mm glued on a glass fiber. The cell dimensions were taken from a least-squares fit to 25 reflections whose θ angles ranged from 8 to 14°. The space group was uniquely determined from the observed extinctions ($h0l$): $h+l = 2n+1$; ($0k0$): $k = 2n+1$. Intensity data were taken by $\omega/2\theta$ scan with ω scan width $(0{\cdot}8 + 0{\cdot}34\tan\omega)°$; the maximum θ was 22·5°. Three reference reflections were remeasured every 2 h of exposure; no significant change in intensity occurred. Intensities were corrected for Lp and equivalent reflections averaged to give 4251 unique reflections, of which 2826 had $I > 3\sigma(I)$. The structure was solved by direct methods using *MULTAN*82 (Main *et al.*, 1982); the manganese and phosphorus atoms of both molecules were visible on the E map, as well as sets of three carbons on P and several carbons around the manganese atoms. The remaining nonhydrogen atoms were located by successive difference Fourier syntheses. Refinement was by full-matrix least squares with hydrogens placed in calculated positions, with

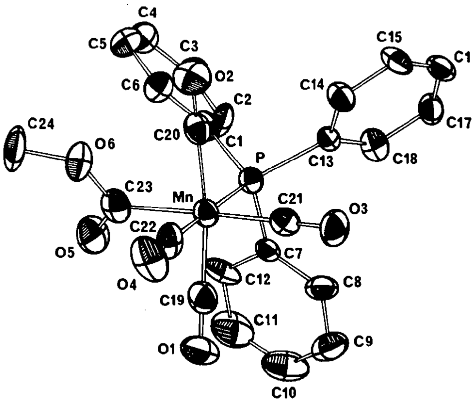

Fig. 1. *ORTEP* plot of molecule 1 showing the atomic numbering system. The thermal ellipsoids are plotted at the 30% probability level. Molecule 2 is similar but with small differences in bond lengths and bond angles as shown in Table 2.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}(Å^2)
Mn(1)	0·60456 (7)	0·1513 (2)	0·56952 (6)	3·88 (3)
P(1)	0·5766 (1)	0·2608 (3)	0·6579 (1)	3·42 (6)
O(1)	0·7086 (4)	−0·0035 (9)	0·6387 (4)	8·1 (2)
O(2)	0·5159 (4)	0·3226 (8)	0·4918 (3)	6·8 (2)
O(3)	0·5033 (4)	−0·0524 (7)	0·5840 (4)	6·4 (2)
O(4)	0·6431 (4)	0·0090 (9)	0·4614 (4)	8·3 (2)
O(5)	0·7242 (4)	0·3102 (8)	0·5905 (4)	7·0 (2)
O(6)	0·6674 (3)	0·3547 (8)	0·5049 (3)	6·3 (2)
C(1)	0·5885 (4)	0·439 (1)	0·6635 (4)	3·8 (2)
C(2)	0·5898 (5)	0·499 (1)	0·7198 (4)	5·1 (3)
C(3)	0·5943 (6)	0·635 (1)	0·7246 (5)	5·9 (3)
C(4)	0·5994 (5)	0·712 (1)	0·6747 (5)	5·0 (3)
C(5)	0·5982 (5)	0·655 (1)	0·6189 (4)	5·1 (3)
C(6)	0·5924 (5)	0·517 (1)	0·6140 (4)	4·6 (3)
C(7)	0·6222 (4)	0·1921 (9)	0·7237 (4)	3·6 (2)
C(8)	0·6034 (5)	0·074 (1)	0·7490 (5)	5·2 (3)
C(9)	0·6438 (6)	0·012 (1)	0·7942 (5)	6·8 (3)
C(10)	0·7007 (6)	0·070 (1)	0·8141 (6)	8·5 (4)
C(11)	0·7194 (6)	0·186 (1)	0·7899 (6)	8·4 (4)
C(12)	0·6809 (5)	0·248 (1)	0·7436 (5)	6·5 (3)
C(13)	0·4909 (4)	0·2459 (9)	0·6773 (4)	3·0 (2)
C(14)	0·4410 (5)	0·245 (1)	0·6307 (4)	4·7 (3)
C(15)	0·3759 (5)	0·244 (1)	0·6438 (5)	5·2 (3)
C(16)	0·3609 (4)	0·243 (1)	0·7034 (5)	4·8 (3)
C(17)	0·4077 (5)	0·241 (1)	0·7490 (5)	4·9 (3)
C(18)	0·4735 (5)	0·243 (1)	0·7364 (4)	4·8 (3)
C(19)	0·6686 (5)	0·058 (1)	0·6137 (5)	5·7 (3)
C(20)	0·5498 (5)	0·260 (1)	0·5225 (4)	4·6 (3)
C(21)	0·5428 (5)	0·029 (1)	0·5803 (4)	4·3 (3)
C(22)	0·6292 (5)	0·066 (1)	0·5027 (5)	5·4 (3)
C(23)	0·6771 (5)	0·287 (1)	0·5585 (5)	5·3 (3)
C(24)	0·7132 (6)	0·460 (1)	0·4929 (6)	8·7 (4)
Mn(1′)	0·40464 (7)	0·8533 (2)	0·93716 (6)	3·90 (3)
P(1′)	0·4224 (1)	0·6801 (3)	0·8696 (1)	3·48 (6)
O(1′)	0·3001 (4)	0·7089 (9)	0·9979 (4)	8·0 (2)
O(2′)	0·4905 (4)	1·0388 (8)	0·8745 (3)	6·4 (2)
O(3′)	0·5103 (4)	0·7550 (8)	1·0227 (3)	5·9 (2)
O(4′)	0·3792 (4)	1·0686 (8)	1·0228 (3)	6·7 (2)
O(5′)	0·2831 (4)	0·8320 (9)	0·8615 (4)	8·5 (2)
O(6′)	0·3237 (4)	1·0311 (7)	0·8624 (3)	5·9 (2)
C(1′)	0·4160 (4)	0·7089 (9)	0·7878 (4)	3·2 (2)
C(2′)	0·4121 (5)	0·835 (1)	0·7633 (4)	4·2 (2)
C(3′)	0·4101 (5)	0·852 (1)	0·7004 (4)	5·1 (3)
C(4′)	0·4134 (5)	0·746 (1)	0·6629 (4)	4·5 (3)
C(5′)	0·4190 (5)	0·623 (1)	0·6878 (4)	5·1 (3)
C(6′)	0·4209 (5)	0·603 (1)	0·7494 (4)	4·3 (3)
C(7′)	0·3655 (4)	0·5477 (9)	0·8812 (4)	3·4 (2)
C(8′)	0·3107 (5)	0·531 (1)	0·8412 (4)	4·4 (3)
C(9′)	0·2642 (5)	0·437 (1)	0·8551 (6)	6·6 (3)
C(10′)	0·2731 (5)	0·360 (1)	0·9056 (5)	6·2 (3)
C(11′)	0·3267 (5)	0·374 (1)	0·9435 (5)	5·5 (3)
C(12′)	0·3723 (5)	0·470 (1)	0·9323 (4)	4·3 (2)
C(13′)	0·5033 (4)	0·603 (1)	0·8793 (4)	3·4 (2)
C(14′)	0·5128 (4)	0·467 (1)	0·8751 (4)	4·1 (2)
C(15′)	0·5746 (5)	0·414 (1)	0·8798 (5)	5·1 (3)
C(16′)	0·6277 (5)	0·494 (1)	0·8876 (5)	5·5 (3)
C(17′)	0·6212 (5)	0·629 (1)	0·8898 (5)	5·4 (3)
C(18′)	0·5583 (5)	0·684 (1)	0·8868 (4)	4·7 (3)
C(19′)	0·3409 (5)	0·762 (1)	0·9745 (5)	5·3 (3)
C(20′)	0·4584 (5)	0·965 (1)	0·8983 (4)	4·6 (3)
C(21′)	0·4700 (5)	0·792 (1)	0·9888 (4)	4·3 (2)
C(22′)	0·3881 (4)	0·988 (1)	0·9880 (4)	4·3 (2)
C(23′)	0·3269 (5)	0·906 (1)	0·8793 (5)	4·9 (3)
C(24′)	0·2692 (6)	1·063 (1)	0·8205 (5)	7·0 (3)

Table 2. *Molecular structure*

(*a*) Selected bond distances (Å)

Mn(1)–P(1)	2·353 (3)	Mn(1′)–P(1′)	2·346 (4)
Mn(1)–C(19)	1·85 (2)	Mn(1′)–C(19′)	1·84 (2)
Mn(1)–C(20)	1·84 (2)	Mn(1′)–C(20′)	1·83 (2)
Mn(1)–C(21)	1·79 (1)	Mn(1′)–C(21′)	1·81 (1)
Mn(1)–C(22)	1·81 (2)	Mn(1′)–C(22′)	1·81 (2)
Mn(1)–C(23)	2·05 (2)	Mn(1′)–C(23′)	2·06 (1)
C(19)–O(1)	1·14 (1)	C(19′)–O(1′)	1·14 (1)
C(20)–O(2)	1·13 (1)	C(20′)–O(2′)	1·15 (1)
C(21)–O(3)	1·16 (1)	C(21′)–O(3′)	1·14 (1)
C(22)–O(4)	1·13 (1)	C(22′)–O(4′)	1·15 (1)
C(23)–O(5)	1·18 (1)	C(23′)–O(5′)	1·21 (1)
C(23)–O(6)	1·38 (1)	C(23′)–O(6′)	1·32 (1)
O(6)–C(24)	1·45 (2)	O(6′)–C(24′)	1·44 (1)
P(1)–C(1)	1·82 (2)	P(1′)–C(1′)	1·832 (9)
P(1)–C(7)	1·817 (9)	P(1′)–C(7′)	1·80 (1)
P(1)–C(13)	1·842 (9)	P(1′)–C(13′)	1·834 (9)
Phenyl C–C (mean)	1·378 (15)	Phenyl C′–C′ (mean)	1·378 (14)

(*b*) Bond angles (°) at the metal atom

P(1)–Mn(1)–C(19)	90·1 (4)	P(1′)–Mn(1′)–C(19′)	93·2 (4)
P(1)–Mn(1)–C(20)	91·1 (3)	P(1′)–Mn(1′)–C(20′)	92·1 (3)
P(1)–Mn(1)–C(21)	90·1 (3)	P(1′)–Mn(1′)–C(21′)	90·7 (3)
P(1)–Mn(1)–C(23)	90·3 (4)	P(1′)–Mn(1′)–C(23′)	86·6 (4)
C(19)–Mn(1)–C(21)	93·5 (5)	C(19′)–Mn(1′)–C(21′)	93·6 (4)
C(19)–Mn(1)–C(22)	88·0 (5)	C(19′)–Mn(1′)–C(22′)	93·6 (4)
C(19)–Mn(1)–C(23)	84·7 (5)	C(19′)–Mn(1′)–C(23′)	82·3 (4)
C(20)–Mn(1)–C(21)	94·3 (4)	C(20′)–Mn(1′)–C(21′)	93·6 (4)
C(20)–Mn(1)–C(22)	90·7 (5)	C(20′)–Mn(1′)–C(22′)	88·6 (4)
C(20)–Mn(1)–C(23)	87·5 (4)	C(20′)–Mn(1′)–C(23′)	90·8 (4)
C(21)–Mn(1)–C(22)	91·1 (5)	C(21′)–Mn(1′)–C(22′)	91·3 (4)
C(22)–Mn(1)–C(23)	88·6 (5)	C(22′)–Mn(1′)–C(23′)	91·5 (4)

anisotropic temperature factors for the heavy atoms and estimated isotropic temperature factors for the hydrogens. Weights were taken inversely proportional to the estimated variance of the observed structure factor; the quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*; they were corrected for anomalous dispersion (Cromer & Waber, 1974). No absorption or extinction correction was made. The final R was 0·058 and wR was 0·063 for 577 variable parameters. In the final cycle the largest parameter shift was 0·01 times its e.s.d. The standard deviation of an observation of unit weight was 1·51. The final difference Fourier map had highest and lowest peaks of 0·50 (7) and −0·38 (7) e Å^{-3}. Final values of the parameters are given in Table 1.*

Discussion. Fig. 1 gives a view with the atomic numbering of the first molecule in the asymmetric unit. The corresponding atoms of the second molecule are indicated with primes in Table 1. Bond distances and bond angles are given in Table 2, which shows that nearly all of the equivalent bond distances in the two molecules are identical within experimental error. The only difference of possible borderline significance (0·06 Å) is in C(23)–O(6). The C=O bond length in the methoxycarbonyl group (1·19 Å) falls in the range 1·13–1·30 Å reported for other metallocarboxylates (Ford & Rokicki, 1988); also, the C–O bond length in this group (1·38 Å) is within the usual range of 1·27–1·39 Å which has been observed in these complexes.

There are small differences in the bond angles of the two molecules such as would be expected to result from

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, and a complete list of bond distances, bond angles, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51130 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecular packing stress. The largest effect is shown by the methoxycarbonyl group. The Mn(1)–C(23)–O(6) angles are 111·8 (7) and 116·6 (7)° so that the difference of 4·8° is experimentally significant. This tilt of the methoxycarbonyl group is accompanied by a rotation of the group about the metal atom which is shown by the C(21)–Mn(1)–C(23) angles of 178·3 and 174·9°. The torsion angle of the methoxycarbonyl group to the metal atom changes by 9·9° between the two molecules. The phenyl to phosphorus torsion angles change by 10·7, 9·3, and 8·6° between the two molecules.

The shortest intermolecular nonbonded distances relative to expected van der Waals values are several C···H contacts, the shortest being 2·77 Å, and several O···H contacts, the shortest being 2·53 Å. The molecular packing thus appears to be of normal van der Waals type, but influenced by Coulombic attraction favoring short distances between hydrogen (which is expected to carry a positive net charge) and carbon and oxygen (expected to carry negative net charges).

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Structure of the Barium Salt of a Cu^{2+} Complex with a Tetraaza Macrocyclic Tetraacetate

BY ANDREAS RIESEN, MARGARETA ZEHNDER AND THOMAS A. KADEN

Institute of Inorganic Chemistry, University of Basel, CH-4056 Basel, Switzerland

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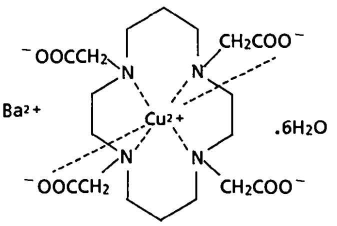
Abstract. Barium (1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetraacetato)cuprate hexahydrate, $Ba[Cu(C_{18}H_{28}N_4O_8)].6H_2O$, $M_r = 737·40$, triclinic, $P\bar{1}$, $a = 8·928$ (3), $b = 10·893$ (4), $c = 15·889$ (2) Å, $\alpha = 91·98$ (2), $\beta = 101·96$ (1), $\gamma = 117·28$ (3)°, $V = 1328·5$ Å^3, $D_m = 1·83$, $D_x = 1·843$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2·21$ mm^{-1}, $F(000) = 738$, $T = 298$ K, $R = 0·055$ for 3755 reflections with $I \geq 2\sigma(I)$. In the unit cell two crystallographically different complex anions are situated with their Cu^{2+} atoms on two different inversion centres of the triclinic cell. The geometry for both units is a distorted octahedron with four amino nitrogens in a plane and two apical acetate oxygen donors. The Cu atom is situated exactly in the N_4 plane of the macrocycle, which takes the *trans*-III configuration.

Introduction. The coordination behaviour of tetrafunctionalized macrocyclic ligands with transition-metal ions has been described previously (Riesen, Zehnder & Kaden, 1985, 1986). So the structures of the binuclear Cu^{2+} complexes with dota (dota = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid) and teta (teta = 1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid) as well as that of the mononuclear Cu^{2+} complex with dota have been described. The mononuclear complex of teta was crystallized as a complex anion, $Ba[Cu(teta)].6H_2O$, and its structure was determined.



Experimental. Blue crystals of $Ba[Cu(teta)].6H_2O$ were prepared according to the literature procedure (Riesen *et al.*, 1986). An Enraf–Nonius CAD-4 diffractometer controlled by a Digital MicroVAX computer was used for measurements. The Mo $K\alpha$ radiation was monochromated by graphite. Cell parameters were taken on a crystal of size 0·1 × 0·1 × 0·2 mm from least-squares

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