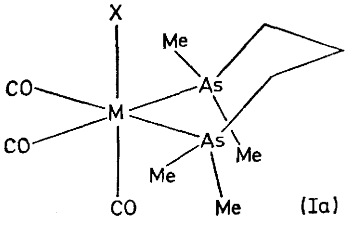
Crystal Structure of *fac*-Chloro-[1,3-bis(dimethylarsino)propane]tricarbonylmanganese

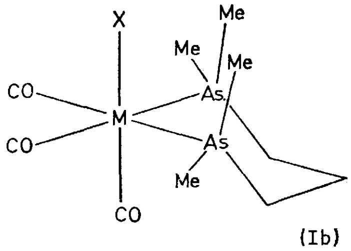
By **C. A. Bear** and **J. Trotter,*** Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

Crystals of the title compound are orthorhombic, a = 15·279, b = 15·445, c = 13·982 Å, Z = 8, space group *Pbca*. The structure was determined from diffractometer data by Patterson and Fourier methods, and refined by full-matrix least-squares techniques to R 0·116 for 783 observed reflections. The conformation found is that which shows the least interaction between the axial methyl group of the arsenic atoms and the substituents of the metal atom.

In compounds of the type (I), there are two conformers resulting from the orientation of the six-membered ring with respect to the substituents of the metal atom. In [1,3-bis(dimethylarsino)propane]tetracarbonylchromium ($M = Cr^0$, $X = CO$), the two conformers are obviously equivalent and n.m.r. spectral evidence[1] also indicates that the two conformers interchange in solution. However, when $M = Mn^I$ and X = halogen the two conformers are not equivalent and n.m.r. evidence[1] shows that in solution only one of these conformers is present. The X-ray crystal analysis of *fac*-chloro-[1,3-bis(dimethylarsino)propane]tricarbonylmanganese has been undertaken to determine which of the two conformers is favoured and to obtain information on the factors influencing the choice of conformation.



(Ia)



(Ib)

EXPERIMENTAL

Crystals of the compound are yellow plates with (010) developed. Unit-cell and space-group data were determined from film and diffractometer measurements.

Crystal Data.—$C_{10}H_{18}As_2ClMnO_3$, M = 426·5, Orthorhombic, a = 15·279(8), b = 15·445(8), c = 13·982(8) Å, U = 3229 Å^3, Z = 8, D_c = 1·72. μ(Mo-K_α) = 52·0 cm^{-1}. Space group *Pbca* (No. 61).

The intensities of the reflections were measured on a Datex-automated General Electric XRD 6 diffractometer with Mo-K_α radiation (λ = 0·7107 Å). However, during data collection the crystal decomposed, with the check reflections showing a decrease of *ca.* 50%. 783 observed reflections were measured with $2\theta \leqslant 35°$. Lorentz and polarization factors were applied but no absorption corrections were made.

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[1] W. R. Cullen, L. D. Hall, J. T. Price, and G. Spendjian, unpublished work.

Structure Analysis.—The positions of the arsenic atoms were determined from a three-dimensional Patterson function and the manganese, chlorine, oxygen, and carbon atoms were located from an electron-density map. The structure was refined by full-matrix least-squares methods. The function minimised was $\Sigma w(F_o - F_c)^2$; w was adjusted to give best constancy of average values of $w(F_o - F_c)^2$, the weighting scheme being $w = (A + BF_o + CF_o^2 + DF_o^3)^{-1}$. The final values of these parameters were $A = 78{\cdot}62$, $B = -2{\cdot}07$, $C = 0{\cdot}02$, and $D = 0{\cdot}00$. After refinement, in which the four heaviest atoms had been given anisotropic temperature factors, a difference-Fourier synthesis was calculated. From this, however, the hydrogen atoms could not be satisfactorily located, a result not too surprising in view of the inaccuracy of the data resulting from the decomposition of the crystal during the collection. Because of this inaccuracy the carbon and oxygen atoms were refined with isotropic thermal parameters only and the final R was 0·116 for the 783 observed reflections. Measured and calculated structure factors are listed in Supplementary Publications No. SUP 20601 (8 pp., 1 microfiche).* Positional and thermal parameters are given in Table 1, and bond lengths and angles are listed in Table 2.

TABLE 1

(*a*) Final positional parameters and isotropic thermal parameters

	x/a	y/b	z/c	$B_{iso}/\text{Å}^2$
Mn	0·1866(3)	0·1764(3)	0·0929(3)	
As(1)	0·0466(2)	0·1988(2)	0·1717(2)	
As(2)	0·1943(2)	0·0384(2)	0·1764(2)	
Cl	0·2507(6)	0·2368(5)	0·2360(6)	
O(8)	0·102(1)	0·094(2)	−0·079(2)	6·2(5)
O(9)	0·176(2)	0·351(2)	0·003(2)	6·5(3)
O(10)	0·358(2)	0·143(2)	0·008(2)	8·0(5)
C(1)	0·032(2)	0·151(2)	0·300(2)	2·6(6)
C(2)	0·053(2)	0·056(2)	0·315(2)	5·0(8)
C(3)	0·147(2)	0·030(2)	0·311(2)	4·1(7)
C(4)	0·008(2)	0·323(2)	0·192(3)	4·6(9)
C(5)	−0·059(2)	0·146(2)	0·108(3)	4·8(8)
C(6)	0·316(3)	−0·002(3)	0·204(3)	7·3(11)
C(7)	0·140(2)	−0·058(2)	0·114(2)	3·8(7)
C(8)	0·134(2)	0·131(2)	−0·009(3)	4·3(8)
C(9)	0·181(2)	0·279(3)	0·043(3)	5·0(8)
C(10)	0·287(3)	0·159(2)	0·042(3)	5·7(9)

(*b*) Final anisotropic thermal parameters ($\times 10^4$)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Mn	46(3)	23(2)	23(3)	−7(2)	1(2)	1(2)
As(1)	46(2)	21(2)	26(2)	1(1)	−3(1)	−5(1)
As(2)	41(2)	19(2)	25(2)	0(1)	−3(2)	−4(1)
Cl	70(6)	26(5)	41(6)	−9(4)	−20(5)	−1(4)

The scattering factor for an atom is expressed as:

$$f_0 \exp-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl).$$

DISCUSSION

The manganese atom is found to have a slightly distorted octahedral co-ordination of the three carbonyl groups, two arsenic atoms, and the chlorine atom (Figure 1). The angles subtended at the manganese atom range from 85—94° and from 175—178°. In spite of the high standard deviations of the bond lengths and angles, some reliability can be placed on the determined values as these agree reasonably well with appropriate ones of the similar compound, [1,3-bis(dimethylarsino)-2-chloro-1,1,3,3-tetrafluoropropane]tetracarbonylchromium.[2] The As–Mn–As angle of 87·1° and the mean value of 117° for the remaining ring angles agree with the values of 86·6 and 116° of the chromium complex. Also, the mean value of 1·99 Å for the As–C distances is the same as the mean of those in the chromium com-

TABLE 2

Bond lengths and angles

(*a*) Distances (Å)

Mn–As(1)	2·432(6)	As(2)–C(3)	2·02(3)
Mn–As(2)	2·432(5)	As(2)–C(6)	2·01(4)
Mn–Cl	2·415(9)	As(2)–C(7)	1·92(3)
Mn–C(8)	1·78(4)	O(8)–C(8)	1·23(4)
Mn–C(9)	1·73(4)	O(9)–C(9)	1·24(4)
Mn–C(10)	1·72(5)	O(10)–C(10)	1·19(4)
As(1)–C(1)	1·95(3)	C(1)–C(2)	1·53(4)
As(1)–C(4)	2·02(4)	C(2)–C(3)	1·49(4)
As(1)–C(5)	2·01(4)		

(*b*) Angles (°)

As(1)–Mn–As(2)	87·1(2)	Mn–As(2)–C(3)	119·1(9)
As(1)–Mn–Cl	85·8(3)	Mn–As(2)–C(6)	114(1)
As(1)–Mn–C(8)	91(1)	Mn–As(2)–C(7)	116(1)
As(1)–Mn–C(9)	90(1)	C(3)–As(2)–C(6)	98(1)
As(1)–Mn–C(10)	178(1)	C(3)–As(2)–C(7)	103(1)
As(2)–Mn–Cl	85·5(2)	C(6)–As(2)–C(7)	104(1)
As(2)–Mn–C(8)	94(1)	As(1)–C(1)–C(2)	118(2)
As(2)–Mn–C(9)	175(1)	C(1)–C(2)–C(3)	117(3)
As(2)–Mn–C(10)	91(1)	As(2)–C(3)–C(2)	111(2)
Cl–Mn–C(8)	177(1)	Mn–C(8)–O(8)	175(3)
Cl–Mn–C(9)	90(1)	Mn–C(9)–O(9)	177(3)
Cl–Mn–C(10)	93(1)	Mn–C(10)–O(10)	177(3)
C(8)–Mn–C(9)	91(2)		
C(8)–Mn–C(10)	90(2)		
C(9)–Mn–C(10)	91(2)		
Mn–As(1)–C(1)	117·6(8)		
Mn–As(1)–C(4)	117(1)		
Mn–As(1)–C(5)	116(1)		
C(1)–As(1)–C(4)	101(1)		
C(1)–As(1)–C(5)	100(1)		
C(4)–As(1)–C(5)	102(1)		

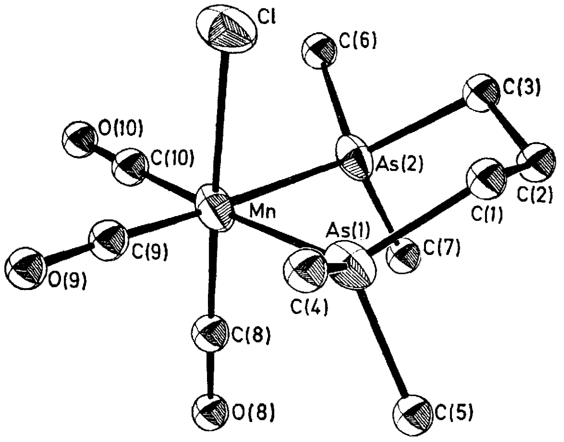

FIGURE 1 The structure of *fac*-chloro-[1,3-bis(dimethylarsino)propane]tricarbonylmanganese

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[2] I. W. Nowell and J. Trotter, *J.C.S. Dalton*, 1972, 2378.

pound. Further, the value of the Mn–C–O angles (175—177°) and the C–C distances of 1·53 and 1·49 Å are fairly close to the expected values.

The six-membered ring is found to have a chair conformation, though this is distorted, as would be expected. As(1), As(2), C(1), and C(3) are coplanar (Table 3). The angles between this plane and the planes through Mn, As(1), and As(2), and C(1), C(2), and C(3) are 31 and 61°. The angles of torsion about the bonds of the ring (Table 3) range from 33—71°, differing from the ideal value of 60°. The orientation of the six-membered ring is such that C(1) and C(3) make their closest approach to the chlorine atom rather than to the carbonyl group *trans* to the chlorine atom, *i.e.* the conformation is (Ia).

TABLE 3

(*a*) Equations of mean planes and deviations (Å) of relevant atoms from the planes

Plane (1): As(1), As(2), C(1), C(3)
$-0\cdot693x - 0\cdot641y - 0\cdot391z + 3\cdot251 = 0$
As(1) 0·00, As(2) 0·00, C(1) 0·03, C(3) −0·04, Mn −0·90, C(2) 0·69, C(4) −0·91, C(5) 1·92, C(6) −1·01, C(7) 1·82

Plane (2): Mn, As(1), As(2)
$-0\cdot466x - 0\cdot445y - 0\cdot765z + 3\cdot533 = 0$

Plane (3): C(1), C(2), C(3)
$-0\cdot078x - 0\cdot155y - 0\cdot985z + 4\cdot531 = 0$

(*b*) Angles (°) between planes

(1)–(2)	31	(1)–(3)	61

(*c*) Angles (°) of torsion

Mn–As(1)–C(1)–C(2)	−52
As(1)–C(1)–C(2)–C(3)	+71
C(1)–C(2)–C(3)–As(2)	−71
C(2)–C(3)–As(2)–Mn	+58
C(3)–As(2)–Mn–As(1)	−37
As(2)–Mn–As(1)–C(1)	+33

The most probable reason for the choice of this conformation is a result of the steric repulsion of the axial methyl groups and the 'axial' groups of the metal.[3] The Mn–As(1)–C(5) and Mn–As(2)–C(7) angles of 116° are somewhat greater than the normal tetrahedral angle and suggest the relief of steric strain resulting from the interaction between the axial methyl groups and the carbonyl group *trans* to the chlorine atom. With this increased angle the C(8) to C(5) and C(7) distances of 3·38 and 3·40 Å are equal to the sum of the van der Waals radii.[4] A similar situation also occurs with equatorial methyl groups and the carbonyl groups *trans* to the arsenic atoms. If, however, the carbonyl group were replaced by the chlorine atom this interaction would probably be even greater, the calculated Cl to CH_3 distance being 3·45 Å. Thus, it would seem that the conformation found is energetically more favourable than the alternative. All other contacts between the six-membered ring, the chlorine atom, and the carbonyl group are >3·6 Å and are unlikely to have an influence on the conformation.

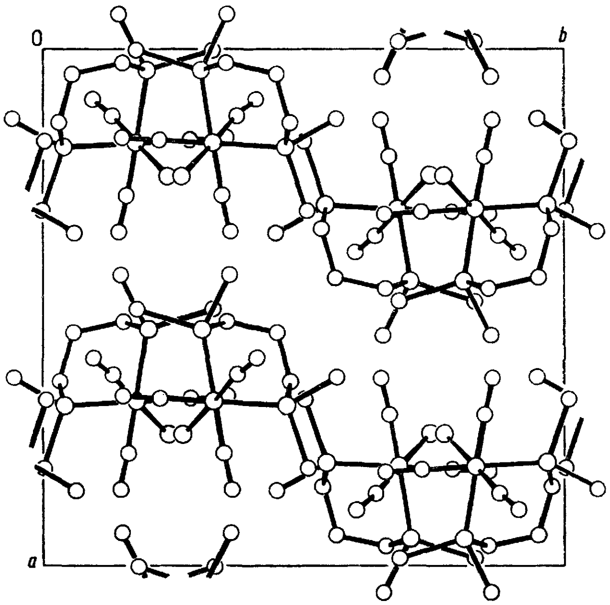

FIGURE 2 Projection of the unit cell along *c*

The packing of the molecules in the unit cell, as projected down the *c* axis, is shown in Figure 2, the molecules being held together by van der Waals forces.

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[3] D. A. Buckingham and A. M. Sargeson, *Topics Stereochem.*, 1971, **6**, 219.

[4] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.