Crystal Structure of [1,3-Bis(dimethylarsino)-2-chloro-1,1,3,3-tetrafluoropropane]tetracarbonylchromium $(Me_2AsCF_2{\cdot}CHCl{\cdot}CF_2AsMe_2)$-$Cr(CO)_4$

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Crystals of [1,3-bis(dimethylarsino)-2-chloro-1,1,3,3-tetrafluoropropane]tetracarbonylchromium, $(Me_2AsCF_2{\cdot}CHCl{\cdot}CF_2AsMe_2)Cr(CO)_4$, are monoclinic, a = 8·55, b = 13·98, c = 16·00 Å, β = 105·61°, Z = 4, space group $P2_1/c$. The structure was determined from diffractometer data by Patterson, electron-density, and full-matrix least-squares methods, the final R being 0·065 for 1475 observed reflexions. The six-membered ring has a chair conformation, with chlorine occupying the less sterically hindered equatorial position. The chromium atom is surrounded by a distorted octahedral arrangement of four carbonyl groups and two arsenic atoms, with Cr–As 2·423(3) and 2·439(3) Å, and As–Cr–As 86·6(1)°. The remaining angles within the ring, mean 116°, are all significantly larger than the regular tetrahedral value. The C–F distances, mean 1·38(2) Å, and the C–Cl bond length of 1·81(2) Å lie close to normal single-bond values.

THE structures of some di(tertiary arsine) complexes of chromium and molybdenum, $(Me_2AsCR^1R^2{\cdot}CF_2AsMe_2)$-$M(CO)_4$, which contain five-membered chelate rings, have been studied,[1] and to obtain information about related six-membered ring systems we have now determined the structure of the complex, $(Me_2AsCF_2{\cdot}CHCl{\cdot}CF_2AsMe_2)$-$Cr(CO)_4$.

EXPERIMENTAL

Crystals of the compound are yellow needles elongated along a with (010) developed. Unit-cell and space-group data were determined by various film and diffractometer measurements.

Crystal Data.—$C_{11}H_{13}As_2ClCrF_4O_4$, M = 522·5, Monoclinic, a = 8·55(1), b = 13·98(2), c = 16·00(2) Å, β = 105·61(3)°, U = 1841·7 Å^3, D_m (by flotation) = 1·87, Z = 4, D_c = 1·88, $F(000)$ = 1016. Mo-K_α radiation, λ = 0·7107 Å, μ = 46·1 cm^{-1}. Space group $P2_1/c$ (C_{2h}^5, No. 14) from systematic absences.

The intensities of the reflexions were measured on a Datex-automated General Electric XRD 6 diffractometer, with Mo-K_α radiation. Of 2364 reflexions with 2θ(Mo-K_α) ⩽45° (minimum interplanar spacing 0·93 Å), 889 were classified as unobserved. The crystal had dimensions 0·48 × 0·28 × 0·31 mm, and was mounted with a^* parallel to the ϕ axis of the goniostat. Lorentz and polarization factors were applied, but no absorption correction was made.

Structure Analysis.—The chromium and arsenic atom positions were determined from the three-dimensional Patterson function, and the chlorine, carbon, oxygen, and fluorine atoms were located on a difference electron-density map. The structure was refined by full-matrix least-squares methods, finally with all atoms given anisotropic thermal parameters. The scattering factors of ref. 2 were

TABLE 1

Final positional parameters (fractional × 10^4) and anisotropic thermal parameters,* with standard deviations in parentheses

	x	y	z	b_{11}	b_{12}	b_{33}	b_{12}	b_{13}	b_{23}
Cr	3207(3)	1150(2)	1499(2)	132(4)	51(1)	67(1)	5(2)	37(2)	−1(1)
As(1)	0840(2)	1967(1)	1706(1)	124(3)	47(1)	54(1)	13(1)	35(1)	2(1)
As(2)	4319(2)	1250(1)	3070(1)	132(3)	54(1)	60(1)	−15(1)	14(1)	9(1)
Cl	0214(7)	1207(5)	4440(4)	348(13)	157(6)	75(3)	−49(7)	91(5)	−1(3)
F(1)	2435(12)	0009(8)	3700(7)	248(19)	77(7)	103(7)	−27(10)	50(10)	22(5)
F(2)	3592(14)	1091(10)	4655(7)	320(25)	170(12)	60(6)	−75(15)	12(9)	18(7)
F(3)	−0402(10)	0550(6)	2558(6)	168(15)	67(6)	90(6)	−37(8)	53(8)	−1(5)
F(4)	−1307(12)	1979(8)	2732(7)	237(20)	97(7)	108(7)	25(10)	101(10)	4(1)
O(1)	1799(18)	1210(10)	−0444(9)	330(32)	111(11)	78(8)	34(16)	34(13)	4(8)
O(2)	1770(16)	−0840(10)	1612(10)	260(27)	59(8)	149(12)	−29(12)	88(15)	−9(8)
O(3)	6027(16)	0014(11)	1279(12)	218(26)	100(11)	184(15)	55(14)	102(16)	−15(10)
O(4)	5096(16)	2944(10)	1339(10)	221(24)	78(9)	143(12)	−21(13)	65(14)	24(9)
C(1)	2330(20)	1150(13)	0304(12)	186(30)	92(13)	63(10)	53(16)	56(15)	8(10)
C(2)	2235(19)	−0066(13)	1587(11)	167(28)	68(12)	67(9)	−1(15)	16(13)	−8(9)
C(3)	4964(23)	0465(12)	1364(13)	214(35)	61(10)	101(12)	15(16)	56(17)	−12(9)
C(4)	4330(18)	2292(12)	1384(10)	153(26)	64(11)	66(9)	23(14)	41(12)	28(8)
C(5)	0775(24)	3329(12)	1939(13)	330(42)	43(10)	102(13)	40(16)	81(19)	1(8)
C(6)	−1234(19)	1799(15)	0799(12)	119(26)	122(16)	74(10)	−1(16)	1(13)	8(10)
C(7)	5224(20)	2462(14)	3602(13)	171(31)	98(14)	92(12)	−80(18)	−8(15)	−19(11)
C(8)	6034(22)	0344(16)	3641(15)	167(32)	115(18)	125(16)	33(19)	17(18)	50(14)
C(9)	0088(19)	1480(11)	2734(12)	177(29)	54(10)	86(12)	−9(14)	71(15)	−3(8)
C(10)	1226(20)	1584(13)	3636(10)	188(31)	84(13)	55(9)	−34(16)	31(13)	−6(8)
C(11)	2762(21)	0983(13)	3804(10)	250(36)	79(13)	52(8)	−51(17)	−1(13)	16(8)

* In the form exp $-10^{-4}(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)$.

[1] I. W. Nowell, S. Rettig, and J. Trotter, following paper.
[2] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

used, those of chromium, arsenic, and chlorine being corrected for real and imaginary components of the anomalous dispersion. 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 final scheme being $\sqrt{w} = 1$ when $|F_o| \leqslant 40$, $\sqrt{w} = 40/|F_o|$ when $|F_o| > 40$, $\sqrt{w} = 0.5$ for the unobserved reflexions. The final R was 0·065 for the 1475 observed reflexions. A final difference-Fourier map showed maximum fluctuations of ± 1.2 eÅ^{-3}, but the hydrogen atoms could not be satisfactorily located. Measured and calculated structure factors are listed in Supplementary Publication No. SUP 20501 (4 pp., 1 microfiche).* Positional and thermal parameters are given in Table 1, and bond lengths and valency angles in Table 2.

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(a) Distances

Cr–As(1)	2·423(3)	Cl–C(10)	1·81(2)
Cr–As(2)	2·439(3)	F(1)–C(11)	1·39(2)
Cr–C(1)	1·86(2)	F(2)–C(11)	1·36(2)
Cr–C(2)	1·91(2)	F(3)–C(9)	1·37(2)
Cr–C(3)	1·84(2)	F(4)–C(9)	1·38(2)
Cr–C(4)	1·90(2)	O(1)–C(1)	1·16(2)
As(1)–C(5)	1·95(2)	O(2)–C(2)	1·16(2)
As(1)–C(6)	1·98(2)	O(3)–C(3)	1·15(2)
As(1)–C(9)	2·04(2)	O(4)–C(4)	1·14(2)
As(2)–C(7)	1·96(2)	C(9)–C(10)	1·52(2)
As(2)–C(8)	1·97(2)	C(10)–C(11)	1·52(3)
As(2)–C(11)	2·03(2)		

(b) Angles

As(1)–Cr–As(2)	86·6(1)	Cr–As(2)–C(11)	116·8(4)
As(1)–Cr–C(1)	91·1(5)	C(7)–As(2)–C(8)	101·3(9)
As(1)–Cr–C(2)	90·8(5)	C(7)–As(2)–C(11)	98·7(8)
As(1)–Cr–C(3)	176·7(6)	C(8)–As(2)–C(11)	97·9(8)
As(1)–Cr–C(4)	94·6(5)	Cr–C(1)–O(1)	176(2)
As(2)–Cr–C(1)	176·6(5)	Cr–C(2)–O(2)	173(2)
As(2)–Cr–C(2)	91·8(5)	Cr–C(3)–O(3)	178(2)
As(2)–Cr–C(3)	92·6(6)	Cr–C(4)–O(4)	175(1)
As(2)–Cr–C(4)	89·1(5)	As(1)–C(9)–F(3)	107(1)
C(1)–Cr–C(2)	90·7(8)	As(1)–C(9)–F(4)	107(1)
C(1)–Cr–C(3)	89·8(8)	As(1)–C(9)–C(10)	118(1)
C(1)–Cr–C(4)	88·6(8)	F(3)–C(9)–F(4)	105(1)
C(2)–Cr–C(3)	86·1(7)	F(3)–C(9)–C(10)	112(1)
C(2)–Cr–C(4)	174·6(7)	F(4)–C(9)–C(10)	107(1)
C(3)–Cr–C(4)	88·6(7)	Cl–C(10)–C(9)	110(1)
Cr–As(1)–C(5)	123·8(6)	Cl–C(10)–C(11)	106(1)
Cr–As(1)–C(6)	117·5(6)	C(9)–C(10)–C(11)	115(1)
Cr–As(1)–C(9)	114·2(5)	As(2)–C(11)–F(1)	105(1)
C(5)–As(1)–C(6)	101·0(9)	As(2)–C(11)–F(2)	108(1)
C(5)–As(1)–C(9)	98·1(7)	As(2)–C(11)–C(10)	118(1)
C(6)–As(1)–C(9)	97·8(7)	F(1)–C(11)–F(2)	105(1)
Cr–As(2)–C(7)	119·7(6)	F(1)–C(11)–C(10)	113(1)
Cr–As(2)–C(8)	118·5(8)	F(2)–C(11)–C(10)	108(2)

DISCUSSION

The six-membered chelate ring is found to have a chair conformation with chromium having a distorted octahedral co-ordination of four carbonyl groups and two arsenic atoms (Figure 1). The As–Cr–As angle [86·6(1)°] is close to those (84—85°) in the five-membered ring compounds.[1] The remaining angles within the ring [114–118(1), mean 116°] are significantly larger than the regular tetrahedral angle. The other angles at chromium lie in the range 86—95° (Table 2).

Substituents at the arsenic and carbon atoms may be considered to be axial or equatorial with respect to the ring: F(1), F(3), methyl carbons C(5) and C(7) occupy axial positions, while F(2), F(4), methyl carbons C(6) and C(8) are equatorial. The hydrogen atom at C(10) is axial while the more bulky chlorine occupies the less sterically hindered equatorial position. As(1), As(2), C(9), and C(11) are coplanar, the equation of the weighted mean plane being $0.0376X + 0.9179Y + 0.3949Z = 3.5605$, with atom displacements 0·0, 0·0, −0·04, and 0·04 Å.

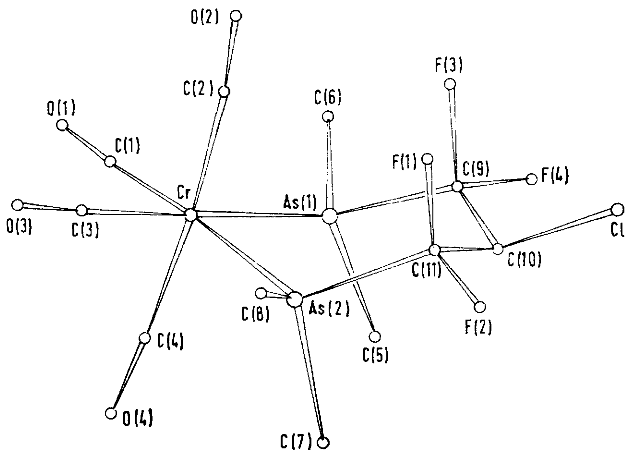

FIGURE 1 The crystal structure showing the atom numbering

The dihedral angles between this plane and those through Cr, As(1), As(2) and C(9), C(10), C(11) are 142 and 126°. The torsion angles (Table 3), 42—73°, differ from the ideal value of 60°, and from those found in more regular chairs, *e.g.* $[(CH_2)_2N{\cdot}GaH_2]_3$ 59—61°,[3] and $[MeHN{\cdot}AlMe_2]_3$ 53°.[4]

TABLE 3

Torsion angles (°) about As–C and C–C bonds within the six-membered chelate ring

(i) Cr–As(1)		(ii) Cr–As(2)	
As(2)......C(5)	−76	As(1)......C(7)	77
As(2)......C(6)	157	As(1)......C(8)	−158
As(2)......C(9)	43	As(1)......C(11)	−42
(iii) As(1)–C(9)		(iv) As(2)–C(11)	
Cr ....F(3)	65	Cr ....F(1)	−70
Cr ....C(10)	−63	Cr ....C(10)	56
C(5) ......F(4)	−50	C(7) ......F(2)	49
C(5) ......C(10)	70	C(7) ......C(10)	−73
C(6) ......F(3)	−60	C(8) ......F(1)	58
C(6) ......F(4)	52	C(8) ......F(2)	−54
(v) C(9)–C(10)		(vi) C(11)–C(10)	
As(1)......C(11)	67	As(2)......C(9)	−62
F(3) Cl	60	F(1) Cl	−62
F(3) ......C(11)	−59	F(1) ......C(9)	60
F(4) Cl	−54	F(2) Cl	54

* 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).

[3] W. Harrison, A. Storr, and J. Trotter, *Chem. Comm.*, 1971, 1101.

[4] K. Gosling, G. M. McLaughlin, G. A. Sim, and J. D. Smith, *Chem. Comm.*, 1970, 1617.

The As–CH_3 bond lengths are 1·95—1·98(2), mean 1·97 Å, and the As–C(fluorocarbon) bond distances are 2·04(2) and 2·03(2), mean 2·04 Å. The mean values of the two types of As–C bond are significantly different;

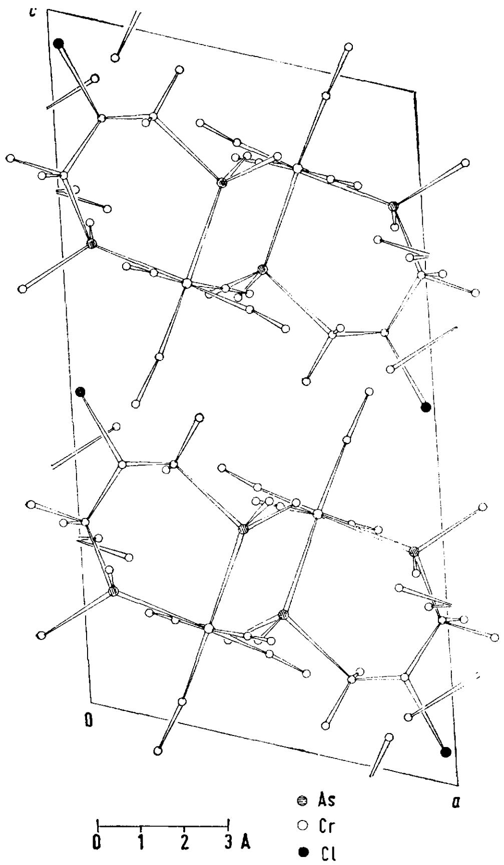

FIGURE 2 Projection of the structure along *b*

possible similar trends in the five-membered ring compounds were not observable because of disorder in the crystals.[1] The Cr–As–CH_3 angles [118—124(1), mean 120°] are significantly larger than regular tetrahedral values, presumably as a result of the steric influence of the $Cr(CO)_4$ group. The CH_3–As–CH_3 and CH_3–As–C-(fluorocarbon) angles [98—101(1), mean 99°] are all significantly less than the regular tetrahedral value. The C–C distances within the ring [1·52(3) Å] represent normal C–C single bonds. The C–F bond lengths (mean 1·38 Å) are close to a normal C–F bond distance (1·33 Å)[5] and to the C–F distances in the five-membered ring compounds (1·37 Å).[1] The C–Cl bond length [1·81(2) Å] corresponds to a normal C–Cl single bond.[5] The valency angles at C(9), C(10), and C(11) involving fluorine or chlorine are in the range 105—113(2), mean 108° (Table 2).

The Cr–As distances [2·423(3) and 2·439(3), mean 2·431 Å] are close to those found in the five-membered ring compounds (2·42—2·45 Å). Taking the chromium(0) single-bond covalent radius and the covalent radius of arsenic as 1·48 and 1·21 Å respectively,[6,7] one would expect a Cr–As single-bond distance of 2·69 Å. The shortening of 0·26 Å is indicative of back-donation from chromium to the arsenic atoms ($d_\pi \rightarrow d_\pi$).

Since carbonyl groups are better π-acceptors than arsenic atoms, back donation to carbonyl groups *trans* to the arsenics is expected[8] to be greater than to those *cis*. The Cr–C distances are in accord with this expectation, the mean Cr–C(*trans*) length being 1·85(2) Å, while the mean Cr–C(*cis*) value is 1·91(2) Å. The C–O distances, 1·14—1·16(2) Å, and the Cr–C bond lengths lie within the range found for other chromium carbonyl complexes.[1,6,9–11] The Cr–C–O groupings are close to linear, with angles 175—177(1)°.

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

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