Disordered Crystal Structures of Six Complexes of the Type, $Me_2XCR^1R^2{\cdot}CF_2XMe_2{\cdot}M(CO)_4$ (M = Mo or Cr; X = As or P; R^1 = F or H; and R^2 = H, CF_3, or Cl)

By **Ian W. Nowell, Steve Rettig,** and **James Trotter,*** Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada

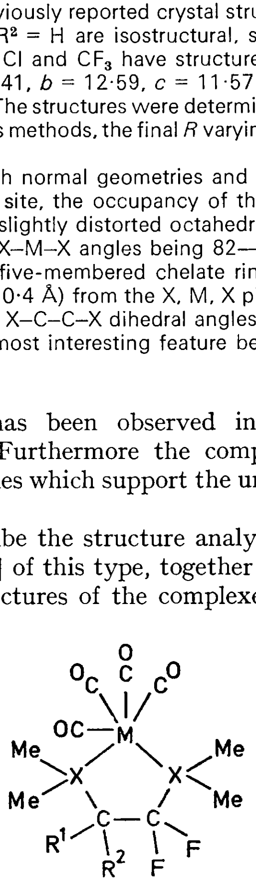
Crystal structures of four compounds of the type $Me_2XCR^1R^2{\cdot}CF_2XMe_2{\cdot}M(CO)_4$ (M = Mo or Cr; X = As or P; R^1 = F or H; and R^2 = H or Cl) have been determined, and two previously reported crystal structures of this type (R^2 = H or CF_3) have been reinterpreted. Four compounds with R^2 = H are isostructural, space group *Pbca*, *a ca.* 18, *b ca.* 15, *c ca.* 13 Å, *Z* = 8. Two compounds with R^2 = Cl and CF_3 have structures which are quite similar to each other, the former having space group *Pbca*, *a* = 23·41, *b* = 12·59, *c* = 11·57 Å, *Z* = 8, and the latter *C*2/*c*, *a* = 25·06, *b* = 13·27, *c* = 11·56 Å, β = 102·8°, *Z* = 8. The structures were determined from diffractometer data by Patterson, electron-density, and full-matrix least-squares methods, the final *R* varying from 0·05—0·08 for 1200—1800 observed reflexions.

The crystals all contain disordered arrangements of molecules with normal geometries and dimensions; each crystal has two molecular configurations distributed at each lattice site, the occupancy of the two orientations varying from 1 : 1 to *ca.* 6 : 1. The metal atoms are co-ordinated in slightly distorted octahedral arrangements to two arsenic or phosphorus atoms and to four carbonyl groups, the X–M–X angles being 82—85°. The Mo–As, Mo–P, and Cr–As bond lengths are 2·58, 2·48, and 2·43 Å. The five-membered chelate rings have the usual puckered conformation, with one carbon atom displaced further (*ca.* 0·4 Å) from the X, M, X plane than the other (*ca.* −0·25 Å); the ligands thus have staggered conformations with X–C–C–X dihedral angles of *ca.* 50°. Intermolecular packing is governed by van der Waals interactions, the most interesting feature being the disordered arrangements.

CRYSTAL-STRUCTURE analyses of the di(tertiary arsine) complexes, $Me_2XCR^1R^2{\cdot}CF_2XMe_2{\cdot}M(CO)_4$ (M = Mo; X = As; R^1 = F; R^2 = CF_3 [1] or H [2]) have revealed some apparently very unusual features in the molecular structures. The C–C bond in the five-membered chelate rings seemed to be shorter, and the C–F (axial) distances longer than normal single bonds. The compound with R^2 = H was refined with anisotropic thermal parameters;[2] the parameters for the carbon atoms of the chelate ring corresponded to root-mean-square displacements of *ca.* 0·5 Å normal to the mean ring plane, and those for the axial fluorine atoms to *ca.* 0·4 Å parallel to the ring plane. These large apparent vibrations, while physically not completely unrealistic, did suggest the possibility that the structure was disordered, with normal molecular dimensions. However it was not possible to improve the structure factor agreement (R = 0·052) by the introduction of disorder,[3] and the structure with the abnormal geometry was taken as the best fit to the *X*-ray data.

Extension of these studies to the compounds with M, X, R^1, R^2 = Cr, As, F, H and Mo, P, F, H has revealed apparent extreme molecular geometries, with a planar five-membered ring, C–C bond of 1·3 Å, and C–F(axial) bonds of 1·8 Å, the fluorines being situated above and below the centre of the C–C bond.[4] Although some rationalization of these unusual features can be given,[4a] the observance of the apparently extreme structures suggested that, in spite of the good fit of the *X*-ray data, the unusual features might be the result of disordered arrangements of molecules with normal geometries, and that the possibility of disorder should be reinvestigated.[4b] Such disorder has been observed in five-membered chelate rings.[5] Furthermore the compounds have no chemical properties which support the unusual molecular structures.

We now describe the structure analyses of four complexes [(II)—(V)] of this type, together with a re-evaluation of the structures of the complexes [(I) and (VI)] reported in refs. 1 and 2, which indicate that all the crystals contain molecules with normal geometries and dimensions, and exhibit various amounts of disorder in the crystal to produce the apparently unusual features.



	M	X	R^1	R^2
(I)	Mo	As	F	H
(II)	Mo	P	F	H
(III)	Cr	As	F	H
(IV)	Cr	As	H	H
(V)	Cr	As	F	Cl
(VI)	Mo	As	F	CF_3

EXPERIMENTAL

The six complexes were prepared from the metal hexacarbonyls and the ligands.[6] Crystals are colourless or yellow prisms, elongated along *a* or *c*, with (100), (010), and

---

[1] P. J. Roberts and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 1501.

[2] I. W. Nowell and J. Trotter, *J. Chem. Soc.* (*A*), 1971, 2922.

[3] I. W. Nowell and J. Trotter, unpublished.

[4] (*a*) W. R. Cullen, I. W. Nowell, P. J. Roberts, J. Trotter, and J. E. H. Ward, *Chem. Comm.*, 1971, 560; (*b*) *ibid.*, 1972, 36.

[5] See, *e.g.*, U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc.* (*A*), 1971, 1118.

[6] W. R. Cullen, L. D. Hall, and J. E. H. Ward, *Chem. Comm.*, 1970, 625.

(001) variously developed. Unit-cell and space-group data were obtained from film and diffractometer measurements, the lattice parameters for each compound being determined by least-squares treatment of $\sin^2\theta$ for 30 reflexions measured on a diffractometer (Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å). The data are summarized in Table 1. Complexes (I)—(IV), all with $R^2 = H$, are isostructural; compounds (V), $R^2 = Cl$, and (VI), $R^2 = CF_3$, have unit-cells which are quite similar to each other, although the former is orthohombic, the latter monoclinic.

TABLE 1

Crystal data, and summaries of intensity data and structure refinements for six compounds of the type $Me_2XCR^1R^2{\cdot}CF_2XMe_2{\cdot}M(CO)_4$

	(II)	(III)	(IV)	(V)
Formula	$C_{10}H_{13}F_3MoO_4P_2$	$C_{10}H_{13}As_2CrF_3O_4$	$C_{10}H_{14}As_2CrF_2O_4$	$C_{10}H_{12}As_2ClCrF_3O_4$
M	412·1	456·1	448·0	490·5
(*a*) Crystal data				
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
a/Å	17·85(2)	17·51(2)	17·52(3)	23·71(2)
b	14·70(2)	14·77(2)	14·97(1)	12·59(2)
c	12·58(2)	12·63(2)	12·37(1)	11·57(2)
U/Å^3	3302	3266	3244	3455
D_m	1·68	1·84	1·82	1·87
Z	8	8	8	8
D_c	1·66	1·86	1·83	1·89
F(000)	1632	1776	1712	1904
μ(Mo-K_α)/cm^{-1}	10	50	50	49
Space group	*Pbca*	*Pbca*	*Pbca*	*Pbca*
(*b*) Intensity data				
Crystal dimensions/mm †	0·50 × 0·28 × 0·33	0·50 × 0·17 × 0·18	0·48 × 0·33 × 0·25	0·18 × 0·20 × 0·48
Crystal mounting	*a*	*a*	*a*	*c*
Total reflexions	2215	2189	2197	2132
Obs. reflexions	1670	1232	1500	1604
Criterion for obs.	$\geqslant 1\sigma$	$\geqslant 2\sigma$	$\geqslant 2\sigma$	$\geqslant 1\sigma$
(*c*) Structure refinements				
Weighting schemes, $\sqrt{w}$				
Unobs. reflexions	0·5	0·33	$\left\{[29{\cdot}2 - 0{\cdot}15\lvert F_o\rvert + 0{\cdot}0046\lvert F_o\rvert^2 + 0{\cdot}000011\lvert F_o\rvert^3]^{-\frac{1}{2}}\right\}$	0·5
$\lvert F_o\rvert \leqslant F^*$	1·0	$\lvert F_o\rvert/F^*$		1·0
$\lvert F_o\rvert > F^*$	$F^*/\lvert F_o\rvert$	$F^*/\lvert F_o\rvert$		$F^*/\lvert F_o\rvert$
F^*	70	70		50
(*d*) R (i) Anisotropic model				
R (obs. reflexions)	0·080	0·064	0·073	0·076
R (all reflexions)	0·113	0·131	0·114	
(ii) Disordered model				
Ratio of molecules	1 : 1	1 : 1	15 : 85 ‡	3 : 1
R (obs. reflexions)	0·088	0·067	0·074	
R (all reflexions)	0·119	0·134	0·110	

Data for (I) and (VI) are given in refs. 2 and 1 respectively. The ratio of disordered molecules, and the four R values quoted for the other compounds are: (I) 2 : 1, 0·052, 0·078, 0·058, 0·084; (II) 1 : 4,‡ 0·073, 0·085, —, —.

† Parallel to *a*, *b*, *c*. ‡ See footnote to Table 2.

Intensities were measured on a Datex-automated General Electric XRD 6 diffractometer, with a scintillation counter, Mo-K_α radiation (zirconium filter and pulse-height analyser), and a θ—2θ scan, at a scan speed of 2° min^{-1} over a range of $(1{\cdot}80 + 0{\cdot}86\tan\theta)$ degrees in 2θ, with 20 s background counts being measured at each end of the scan. Data were measured to $2\theta = 45°$ (minimum interplanar spacing, 0·93 Å) for compounds (I)—(V), and 40° (1·04 Å) for (VI). Reflexions were classified as unobserved if $I < k\sigma(I)$, $\sigma(I)$ being calculated from the counting statistics, and k being taken as 1 or 2, depending on the quality of the crystal specimen. Details of the data collection are in Table 1 Lorentz and polarization factors were applied, but no absorption corrections were made.

Structure Analyses.—Heavy-atom positions were determined from the three-dimensional Patterson functions, and carbon, oxygen, and fluorine atoms were then located from electron-density maps. The structures were refined by full-matrix least-squares methods, with minimization of $\Sigma w(F_o - F_c)^2$, with the scattering factors of ref. 7, corrections for anomalous dispersion being introduced for the heavy atoms, and initially with isotropic, finally with anisotropic thermal parameters for all atoms, except C and O in (VI). The weighting schemes (Table 1) were adjusted to give constant average values of $w(F_o - F_c)^2$ over ranges of $\lvert F_o\rvert$. The final values of R for these anisotropic refinements varied from 0·052 to 0·080 for the observed reflexions (Table 1). Difference-Fourier maps showed random fluctuations, maximum $\pm 1{\cdot}5$ eÅ^{-3}, and hydrogen atoms could not be located.

The molecular dimensions calculated from the atomic parameters at this stage corresponded to the unusual struc-

---

[7] ' International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

TABLE 2

Final positional (fractional × 10^4) and thermal parameters (U_{ij} are the components of the thermal vibration tensors, Å^2 × 10^2)

(*a*) Compound (I)

(i) Anisotropic model

x, *y*, *z* are as in ref. 2

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	4·85(5)	5·05(6)	5·22(6)	−0·00(4)	−0·41(5)	−0·05(4)
As(1)	4·70(7)	5·90(8)	7·19(9)	−0·41(5)	0·23(6)	−0·63(5)
As(2)	6·60(8)	4·68(7)	7·73(9)	0·59(5)	0·01(7)	0·15(6)
O(1)	10·3(8)	6·1(6)	14·5(10)	2·0(5)	−0·3(7)	2·0(6)
O(2)	14·6(11)	11·9(9)	7·0(6)	−1·0(7)	−4·0(7)	−2·4(6)
O(3)	6·5(6)	13·6(9)	9·9(8)	0·2(6)	1·9(6)	−1·3(6)
O(4)	12·6(10)	16·1(11)	8·2(7)	1·5(8)	−3·9(7)	−3·6(7)
C(1)	5·5(7)	6·6(9)	8·1(9)	0·2(6)	−0·4(6)	0·5(6)
C(2)	8·5(10)	7·4(8)	5·3(8)	−0·7(7)	−1·1(7)	−0·5(6)
C(3)	5·3(7)	7·5(8)	4·7(6)	0·1(6)	−0·4(6)	0·2(6)
C(4)	7·4(9)	8·8(10)	7·0(9)	−0·1(8)	−1·4(7)	−1·0(7)
Mean F(3)	13·9(9)	7·4(6)	21·3(12)	−0·7(6)	3·1(9)	4·4(6)
Mean F(1)	19·7(12)	13·3(9)	7·2(6)	−3·3(8)	0·7(7)	1·0(5)
Mean F(2)	17·0(11)	13·4(9)	15·7(10)	−7·4(8)	−7·6(9)	−1·5(7)
Mean C(5)	4·8(8)	15·1(16)	13·5(15)	1·0(9)	−2·8(9)	−3·8(12)
Mean C(6)	7·9(10)	10·8(11)	7·6(9)	−0·8(8)	2·0(8)	−2·8(8)
Mean C(7)	14·2(16)	11·6(13)	10·3(12)	4·4(12)	−2·2(12)	3·0(1)
Mean C(8)	16·9(19)	8·7(12)	14·0(17)	3·9(12)	0·1(14)	−5·7(11)
Mean C(9)	9·2(12)	6·7(10)	17·7(20)	0·5(9)	2·8(12)	1·3(10)
Mean C(10)	12·8(16)	7·3(11)	24·7(28)	1·2(11)	6·4(18)	7·9(14)

(ii) Disordered model

Molecule (1) Multiplicity 0·67					Molecule (2) Multiplicity 0·33					Separation/Å
	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*	
F(11)	0703(10)	0179(11)	4401(11)	8·6(5)	F(22)	1022(16)	0006(18)	4401(21)	6·1(6)	0·64
F(21)	0253(9)	−0710(10)	1943(12)	8·1(4)	F(12)	−0056(17)	−0475(20)	2152(22)	7·0(6)	0·71
C(51)	−0591(25)	1187(28)	1890(37)	8·8(14)	C(62)	−0684(34)	1381(43)	1917(49)	5·0(13)	0·34
C(61)	−0069(17)	2037(20)	3977(24)	6·5(8)	C(52)	0033(27)	1829(34)	4144(41)	4·6(12)	0·42
C(71)	2353(22)	−0477(27)	3549(30)	8·1(10)	C(82)	2443(48)	−0622(57)	3279(66)	8·7(23)	0·43
C(81)	1814(17)	−1064(21)	1280(25)	7·5(7)	C(72)	1524(38)	−1108(50)	1156(61)	9·1(19)	0·56
C(91)	0266(15)	0056(17)	3517(24)	6·8(6)	C(92)	0145(23)	0012(28)	3033(38)	4·8(9)	0·65
C(101)	0708(13)	−0557(15)	2854(19)	6·2(5)	C(102)	0837(22)	−0365(27)	3494(37)	5·2(8)	0·88

(*b*) Compound (II)

(i) Anisotropic model

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	1555(1)	1466(1)	1887(1)	5·21(6)	5·15(7)	5·35(6)	−0·08(5)	−0·68(6)	0·08(5)
P(1)	0307(2)	1297(2)	2751(3)	5·50(21)	6·47(21)	7·78(23)	−0·60(16)	0·06(17)	−0·83(17)
P(2)	1672(2)	−0143(2)	2417(3)	7·18(24)	5·55(19)	8·67(24)	0·96(17)	−0·68(21)	0·37(18)
O(1)	1268(7)	3532(8)	1359(12)	11·6(9)	5·8(7)	16·4(11)	0·2(6)	−2·3(8)	3·2(7)
O(2)	2321(7)	2048(9)	4070(8)	13·2(10)	12·4(9)	7·1(6)	−2·6(8)	−3·9(7)	−2·0(6)
O(3)	3146(7)	1482(10)	0826(10)	5·7(6)	17·2(13)	11·4(9)	0·5(8)	0·9(7)	−1·9(8)
O(4)	0882(8)	0860(10)	−0330(9)	15·6(12)	14·7(12)	8·1(7)	−0·1(9)	−5·1(8)	−2·4(8)
C(1)	1375(8)	2786(11)	1532(13)	6·9(10)	6·2(9)	10·5(11)	0·8(7)	−2·1(8)	1·4(8)
C(2)	2025(8)	1835(10)	3307(11)	7·2(9)	6·1(8)	6·7(8)	−0·9(7)	−1·0(7)	−0·5(7)
C(3)	2575(9)	1476(10)	1218(10)	6·5(9)	7·8(9)	5·8(7)	0·2(8)	−0·2(7)	−0·4(7)
C(4)	1124(8)	1078(10)	0463(11)	6·5(9)	9·0(10)	6·5(8)	0·2(8)	−1·8(7)	−1·0(7)
Mean F(3)	0775(8)	−1293(7)	3552(11)	16·3(11)	7·9(7)	17·8(11)	−1·0(6)	1·6(9)	4·1(7)
Mean F(1)	0886(10)	0139(9)	4391(10)	26·2(17)	15·6(12)	11·0(8)	−4·2(12)	−0·3(10)	3·4(8)
Mean F(2)	0141(8)	−0589(9)	2087(9)	18·5(12)	15·6(11)	13·9(9)	−10·1(10)	−6·9(9)	1·5(8)
Mean C(5)	−0535(8)	1301(13)	1919(16)	5·8(9)	10·1(13)	15·4(16)	1·1(8)	−2·2(9)	−5·8(12)
Mean C(6)	0061(9)	1997(13)	3936(12)	7·8(11)	12·6(14)	9·6(11)	−0·6(10)	2·1(9)	−3·8(10)
Mean C(7)	2382(12)	−0476(13)	3432(14)	15·5(18)	9·4(12)	10·4(12)	4·6(12)	−3·8(12)	2·8(10)
Mean C(8)	1736(13)	−1036(13)	1405(17)	18·6(22)	7·2(11)	14·7(16)	3·7(13)	−4·4(16)	−4·0(12)
Mean C(9)	0151(15)	0101(11)	3395(20)	24·2(29)	6·1(10)	20·1(24)	5·6(15)	−9·9(22)	−1·0(13)
Mean C(10)	0783(16)	−0437(15)	3132(22)	16·4(22)	10·0(16)	23·8(31)	−3·1(16)	4·1(22)	8·1(19)

(ii) Disordered model

Molecule (1) Multiplicity 0·5					Molecule (2) Multiplicity 0·5					Separation/Å
	x	*y*	*z*	*B*		*x*	*y*	*z*	*B*	
F(11)	0705(11)	0235(12)	4420(14)	9·0(4)	F(22)	1050(11)	0056(12)	4377(14)	8·3(4)	0·67
F(21)	0303(10)	−0705(11)	1999(12)	6·6(3)	F(12)	−0114(10)	−0440(11)	2214(12)	10·2(3)	0·88
C(51)	−0530(34)	1288(39)	1943(49)	8·6(15)	C(62)	−0521(33)	1321(38)	1904(49)	7·4(15)	0·07
C(61)	0045(26)	2137(30)	3834(35)	5·9(12)	C(52)	0097(26)	1856(31)	4035(34)	5·9(12)	0·49
C(71)	2260(22)	−0501(27)	3593(30)	9·4(10)	C(82)	2449(23)	−0454(27)	3343(30)	4·8(9)	0·47
C(81)	1847(22)	−0996(24)	1322(27)	5·9(8)	C(72)	1547(22)	−1086(24)	1473(28)	9·2(8)	0·58
C(91)	0216(21)	0115(23)	3608(29)	9·9(8)	C(92)	0178(20)	0079(24)	3201(30)	6·3(8)	0·52
C(101)	0723(18)	−0526(22)	2832(25)	6·6(7)	C(102)	0875(18)	−0368(22)	3438(26)	6·3(7)	0·84

TABLE 2 (*Continued*)

(*c*) Compound (III)

(i) Anisotropic model

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	1529(2)	1469(2)	1876(2)	5·62(14)	4·65(13)	4·50(14)	−0·43(13)	−0·37(11)	0·12(11)
As(1)	0280(1)	1306(1)	2706(1)	5·03(9)	4·80(10)	5·26(10)	−0·18(8)	0·21(9)	−0·76(9)
As(2)	1699(1)	−0106(1)	2381(2)	6·19(9)	3·99(9)	5·91(11)	0·31(8)	−0·40(9)	0·35(9)
O(1)	1234(9)	3427(10)	1336(13)	8·8(9)	5·5(8)	11·3(10)	−1·0(8)	−0·3(8)	1·0(8)
O(2)	2234(11)	2081(11)	3948(12)	13·2(13)	10·5(11)	6·7(9)	−2·4(9)	−3·6(9)	−2·5(8)
O(3)	3076(9)	1547(14)	0834(13)	5·7(8)	13·8(13)	10·5(11)	−0·5(9)	2·1(8)	0·1(10)
O(4)	0862(10)	0871(12)	−0249(12)	13·1(13)	11·8(12)	5·2(8)	0·5(10)	−4·0(9)	−1·9(8)
C(1)	1344(9)	2669(13)	1542(13)	4·1(9)	5·7(10)	5·0(9)	−0·1(8)	0·4(8)	0·4(8)
C(2)	1954(10)	1823(12)	3190(15)	4·6(9)	5·4(10)	6·3(11)	−0·5(8)	−1·3(9)	−0·1(9)
C(3)	2487(14)	1523(14)	1248(14)	9·7(14)	6·1(11)	4·2(10)	0·7(12)	−1·6(11)	0·4(9)
C(4)	1108(11)	1110(14)	0554(16)	4·9(9)	7·9(13)	6·9(12)	0·6(10)	−1·3(10)	0·1(10)
Mean F(3)	0780(10)	−1336(9)	3535(14)	13·4(10)	6·6(8)	16·4(12)	−0·9(7)	0·6(9)	5·2(8)
Mean F(1)	0871(11)	0148(11)	4434(9)	21·8(16)	11·6(10)	4·8(6)	−4·7(10)	−0·5(8)	−0·1(7)
Mean F(2)	0066(12)	−0591(11)	2097(12)	20·0(14)	11·9(11)	11·1(10)	−9·2(10)	−6·9(10)	1·5(8)
Mean C(5)	−0663(13)	1336(17)	1883(19)	6·7(12)	10·9(17)	8·0(13)	0·3(12)	−2·2(10)	−2·5(12)
Mean C(6)	0007(13)	2021(17)	3962(17)	7·4(12)	9·7(15)	7·7(13)	0·2(11)	1·2(11)	−3·8(12)
Mean C(7)	2501(17)	−0457(16)	3390(20)	13·6(18)	7·8(14)	10·3(16)	3·5(14)	−4·5(16)	2·7(13)
Mean C(8)	1724(20)	−1072(17)	1331(22)	20·7(31)	6·9(13)	10·8(18)	2·2(16)	−3·8(18)	−4·2(14)
Mean C(9)	0180(13)	0076(16)	3306(24)	8·1(16)	5·7(12)	15·5(20)	−0·2(13)	2·4(15)	−1·4(13)
Mean C(10)	0766(21)	−0457(20)	3204(39)	14·0(22)	7·4(17)	30·0(46)	2·3(17)	8·6(28)	10·7(24)

(ii) Disordered model

	Molecule (1) Multiplicity 0·5					Molecule (2) Multiplicity 0·5				
	x	y	z	B		x	y	z	B	Separation/ Å
F(11)	0691(13)	0233(14)	4439(16)	5·8(5)	F(22)	1062(12)	0049(14)	4408(16)	5·7(5)	0·71
F(21)	0235(14)	−0716(15)	2002(16)	6·2(5)	F(12)	−0113(13)	−0466(15)	2190(16)	6·4(5)	0·75
C(51)	−0643(64)	1308(67)	1820(80)	6·9(32)	C(62)	−0661(58)	1418(64)	1912(74)	5·8(27)	0·20
C(61)	−0007(24)	2092(29)	3866(33)	3·7(10)	C(52)	0016(32)	1928(36)	4103(41)	5·9(15)	0·39
C(71)	2308(29)	−0476(34)	3524(40)	7·8(13)	C(82)	2644(21)	−0433(25)	3324(31)	4·8(9)	0·64
C(81)	1888(26)	−1058(30)	1263(35)	6·6(10)	C(72)	1518(26)	−1097(29)	1400(34)	6·6(11)	0·67
C(91)	0212(22)	0029(26)	3535(31)	4·6(8)	C(92)	0154(21)	0123(26)	3114(31)	4·5(9)	0·56
C(101)	0677(21)	−0576(25)	2914(32)	5·5(8)	C(102)	0857(26)	−0376(31)	3498(40)	7·4(11)	0·86

(*d*) Compound (IV)

(i) Anisotropic model

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	1503(2)	1476(2)	1745(2)	5·33(17)	4·28(15)	5·55(16)	−0·24(13)	−0·23(15)	0·02(14)
As(1)	0233(1)	1331(1)	2588(2)	4·68(11)	4·00(10)	6·04(13)	−0·15(8)	0·44(11)	−0·28(10)
As(2)	1661(1)	−0066(1)	2332(2)	5·85(12)	3·35(10)	6·20(13)	0·47(8)	−0·56(11)	0·20(10)
O(1)	1219(10)	3407(10)	1176(14)	11·2(14)	3·2(8)	11·7(14)	1·0(9)	−0·7(11)	1·8(8)
O(2)	2224(11)	2094(13)	3859(13)	10·9(15)	11·8(15)	6·4(10)	−1·9(11)	−2·6(10)	−2·9(10)
O(3)	3064(11)	1549(13)	0738(15)	6·7(11)	11·8(14)	11·0(15)	−0·5(11)	1·6(11)	−1·6(12)
O(4)	0809(12)	0866(12)	−0391(15)	12·5(16)	9·3(13)	8·0(12)	2·1(11)	−2·7(12)	−2·6(10)
C(1)	1313(12)	2677(14)	1378(18)	6·7(14)	5·1(15)	7·5(15)	0·0(11)	−1·0(12)	0·3(11)
C(2)	1950(14)	1857(14)	3100(19)	8·1(15)	5·5(13)	5·8(14)	−0·7(11)	−0·4(12)	1·2(11)
C(3)	2448(13)	1510(15)	1124(18)	5·1(13)	6·3(14)	7·5(13)	−0·1(11)	−0·5(12)	−1·1(12)
C(4)	1059(12)	1080(13)	0428(17)	5·7(12)	5·0(12)	5·3(12)	1·1(10)	−0·6(10)	0·2(10)
Mean F(3)	0720(9)	−1244(9)	3539(14)	10·3(11)	6·6(9)	15·8(15)	−0·2(7)	1·6(11)	4·2(9)
Mean F(2)	0961(11)	−0007(13)	4327(14)	15·1(17)	14·1(17)	10·2(12)	2·7(12)	−0·1(12)	2·4(12)
Mean C(5)	−0684(13)	1503(17)	1688(20)	6·7(15)	9·0(17)	8·1(16)	−0·5(13)	−2·4(14)	−1·2(15)
Mean C(6)	−0012(14)	2048(20)	3855(21)	6·7(16)	11·9(21)	8·6(18)	−0·9(15)	0·6(14)	−5·0(17)
Mean C(7)	2509(15)	−0443(18)	3297(21)	8·6(17)	8·7(18)	10·1(19)	1·8(14)	−3·9(17)	3·6(16)
Mean C(8)	1599(19)	−1048(17)	1296(24)	18·5(32)	5·0(4)	8·5(20)	1·7(18)	0·8(21)	−2·3(14)
Mean C(9)	0042(18)	0096(19)	3084(29)	8·7(20)	9·3(18)	17·2(31)	3·3(15)	6·1(22)	7·4(20)
Mean C(10)	0736(14)	−0352(16)	3288(20)	10·1(18)	6·5(15)	6·8(16)	−0·4(13)	−0·6(14)	3·1(13)

(ii) Disordered model

	Molecule (1) Multiplicity 0·15 *					Molecule (2) Multiplicity 0·85			
	x	y	z	B		x	y	z	Separation/ Å
					H(eq)	−0393	−0007	3938	
H(11)		Not located			F(22)	0965(9)	−0007(11)	4339(11)	
F(21)	0180(42)	−0711(48)	2036(56)	7·8(16)	H(12)	−0299	−0449	2400	1·03
C(51)	−0627(80)	1366(91)	1612(108)	6·0(29)	C(62)	−0705(14)	1513(17)	1697(21)	0·28
C(61)	0010(71)	2325(83)	3660(100)	2·8(25)	C(52)	−0013(15)	2001(18)	3894(19)	0·57
C(71)	2319(76)	−0502(90)	3534(101)	5·6(28)	C(82)	2534(14)	−0446(16)	3249(19)	0·52
C(81)	1768(73)	−1018(89)	1310(103)	4·9(27)	C(72)	1576(19)	−1045(17)	1290(22)	0·34
C(91)	−0002(63)	−0014(70)	3366(86)	11·9(21)	C(92)	0066(15)	0115(16)	3067(22)	0·23
C(101)	0653(73)	−0503(83)	3042(104)	4·5(26)	C(102)	0755(13)	−0326(14)	3330(18)	0·48

TABLE 2 (*Continued*)

Temperature factors for molecule (2) [for H(12) and H(eq), B fixed at 6·0 Å^2]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(22)	11·6(12)	12·5(13)	7·7(9)	2·7(9)	−0·2(8)	2·2(9)
C(62)	6·7(15)	8·4(17)	9·0(17)	0·2(13)	−2·4(14)	−2·3(15)
C(52)	8·2(17)	9·9(18)	7·1(14)	−1·5(14)	0·4(12)	−3·7(14)
C(82)	8·1(15)	7·7(16)	8·0(15)	1·2(12)	−2·6(13)	3·1(13)
C(72)	17·6(30)	5·2(14)	8·8(18)	1·0(17)	−0·3(18)	−2·5(14)
C(92)	8·6(16)	6·6(15)	13·7(20)	2·0(13)	7·0(15)	5·5(15)
C(102)	9·6(17)	5·1(12)	6·3(13)	−0·2(11)	−0·3(11)	2·5(10)

(*e*) Compound (V)

Anisotropic model

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	1065(1)	1289(1)	2437(2)	6·72(11)	4·53(10)	5·58(14)	0·09(9)	−0·08(11)	0·09(10)
As(1)	0896(1)	−0473(1)	3201(1)	6·19(9)	4·36(6)	5·89(10)	−0·36(8)	0·31(7)	0·44(7)
As(2)	1652(1)	0384(1)	1034(1)	7·58(9)	4·97(8)	6·95(12)	−0·26(8)	2·10(8)	−0·18(7)
O(1)	0311(6)	2213(10)	4268(11)	13·6(11)	13·2(11)	8·7(9)	5·9(9)	2·4(8)	−2·6(8)
O(2)	2064(6)	1621(11)	3977(11)	10·4(9)	14·4(11)	10·8(10)	−2·6(8)	−4·2(8)	−0·2(8)
O(3)	1295(5)	3464(8)	1447(10)	14·8(11)	4·7(6)	11·1(10)	−2·3(7)	1·1(7)	1·4(6)
O(4)	0016(5)	0983(9)	0956(11)	8·8(8)	11·4(9)	10·9(10)	−2·0(7)	−5·8(8)	1·1(7)
C(1)	0601(7)	1854(10)	3600(14)	7·9(10)	5·3(8)	7·8(12)	0·7(8)	−1·5(9)	1·1(7)
C(2)	1694(6)	1476(11)	3402(15)	6·4(9)	5·9(9)	10·6(13)	−1·5(8)	−1·9(10)	1·2(8)
C(3)	1220(6)	2632(11)	1786(13)	9·6(10)	5·8(9)	5·4(10)	−0·4(8)	0·4(8)	−1·6(8)
C(4)	0412(7)	1111(10)	1465(12)	8·4(11)	4·9(8)	5·7(11)	0·9(7)	0·2(8)	0·0(6)
Mean F(3)	1956(5)	−1776(7)	0755(9)	16·3(10)	7·6(6)	12·1(8)	3·6(6)	5·9(7)	−1·1(5)
Mean F(1)	2036(5)	−1221(9)	2915(10)	10·1(8)	13·3(9)	15·8(10)	3·0(7)	−4·7(8)	−0·9(8)
Mean F(2)	0994(5)	−1502(8)	0824(10)	17·5(11)	8·1(6)	15·1(10)	0·5(7)	−6·7(9)	−4·4(6)
Mean C(5)	0513(7)	−1166(13)	2988(18)	9·1(13)	10·1(13)	14·1(17)	−5·6(11)	−1·4(12)	2·1(12)
Mean C(6)	1039(9)	−0802(13)	4845(14)	16·0(18)	9·1(11)	6·5(12)	−1·7(11)	−4·9(12)	3·8(9)
Mean C(7)	2473(8)	0523(15)	0994(21)	9·7(13)	12·8(16)	17·8(20)	−2·3(13)	4·1(14)	−2·4(15)
Mean C(8)	1490(9)	0346(16)	−0658(13)	17·9(19)	13·9(16)	2·8(9)	−0·7(15)	−1·3(10)	−1·7(10)
Mean C(9)	1419(9)	−1449(12)	2409(20)	15·9(18)	6·4(10)	14·6(17)	4·0(11)	10·2(15)	4·4(11)
Mean C(10)	1592(8)	−1183(13)	1372(19)	12·7(16)	6·0(10)	13·6(17)	1·9(10)	5·4(14)	−0·3(11)
Mean Cl	1307(3)	−2809(4)	2690(5)	22·2(7)	6·8(3)	12·0(4)	1·6(3)	3·8(4)	1·1(3)

(*f*) Compound (VI)

Anisotropic model

Parameters as in ref. 1 (which uses a different atom numbering system). For direct comparison with compound (V), the positional parameters may be transformed to $\frac{1}{4} - x$, $\frac{1}{4} - y$, $0{\cdot}06 + z$.

(*g*) Disordered model for (V) and (VI)

Approximate positional parameters ($\times 10^2$)

	Molecule (1)				Molecule (2)		
(V) Multiplicity 0·75				Multiplicity 0·25			
	x	y	z		x	y	z
(VI) Multiplicity 0·20 *				Multiplicity 0·80			
	$\frac{1}{4} - x$	$\frac{1}{4} - y$	$0{\cdot}06 + z$		$\frac{1}{4} - x$	$\frac{1}{4} - y$	$0{\cdot}06 + z$
F(11)	20	−12	29	F(22)	22	−07	21
F(21)	10	−15	08	F(12)	10	−15	11
C(51)	02	−12	30	C(62)	03	−12	35
C(61)	10	−08	48	C(52)	12	−07	47
C(71)	25	05	10	C(82)	24	09	02
C(81)	15	03	−07	C(72)	14	02	−08
C(91)	14	−14	24	C(92)	14	−14	20
C(101)	16	−12	14	C(102)	18	−08	13

* Multiplicities of <0·5 for molecule (1) correspond to a preponderance of the second orientation for (IV), in comparison with (I), and for (VI), in comparison with (V).

tures previously described.[4] The extreme geometries, (II) and (III), involve apparently planar five-membered chelate rings, with short C–C bonds, and axial fluorine atoms above and below the centres of the C–C bonds, with C–F *ca.* 1·8 Å. The rings become apparently more non-planar, and the geometries and dimensions more normal successively in the complexes (I), (V), (VI), (IV), the one C–F (axial) bond in (IV) being 1·44 Å. Although it seemed possible to give some rationalization of these variations of the unusual features in terms of electronegativities of equatorial substituents, it appeared equally likely that their observance is a result of the presence of disorder, with at each lattice site two molecules with normal geometries and dimensions (non-planar ring, C–C 1·54, C–F 1·33 Å, tetrahedral angles), but with different configurations [not conformations: the two molecules have the same conformation, but are optical enantiomorphs, except in (IV), which has no asymmetric carbon atom]. The possible presence of disorder is supported by an examination of the anisotropic thermal parameters (Table 2). These are very large for the carbon and fluorine atoms involved in the unusual features. The root-mean-square vibrations are as large as 0·6 Å for C(10) in (III), and the longest axes of the thermal vibration ellipsoids are approximately normal to the mean ring plane for the carbon atoms, and approximately parallel to the plane for the axial fluorine atoms.

The two orientations in the disordered arrangements would be distributed randomly at each site in a crystal, with equal occupancy for (II) and (III) giving rise to the apparently symmetrical structures. To extend the disorder interpretation to the complexes with apparently unsymmetrical geometries *e.g.* (I), it is necessary to postulate that, at any one site, molecules of one configuration occur more frequently than those of the other configuration. This is a reasonable postulate, since the amount of disorder required to explain the details of the apparently unusual geometries does vary systematically with the packing requirements of the various complexes. Disorder is least in (IV), which has only one axial fluorine atom, so that the mirror image of a molecule at one lattice site is less able to pack at that site. The amount of disorder is increased for the other compounds, which all have two axial fluorine atoms, but is least for (V) and (VI), which have bulky equatorial substituents, Cl and CF_3, are therefore less able to pack two different orientations than are (I), (II), and (III), which have smaller H equatorial substituents.

TABLE 3

Bond lengths (Å) and valency angles (°) in the complexes

	(I)	(II)	(III)	(IV)	(V)	(VI)
Mo–As	2·58					2·57
Mo–P		2·48				
Cr–As			2·43	2·45	2·42	
Mo–C	2·00	2·03				1·94
Cr–C			1·88	1·89	1·90	
C–O	1·15	1·13	1·16	1·14	1·13	1·19
As–C	1·99		1·99	1·98	1·99	1·96
P–C		1·89				
X–M–X	82	82	84	84	85	82
Other ∠ at M	88—94	89—93	89—92	88—93	88—94	87—95
M–C–O	178	179	178	178	177	177
M–X–Me	121	120	121	120	122	121
Other ∠ at X	94—109	95—110	97—108	99—112	99—107	95—108
C–C	1·50					
C–F	1·37					
∠ at C	108					

The presence of disorder was further supported by a detailed examination of the electron-density distributions, which revealed elongated or egg-shaped peaks in the F(ax.)–C–C–F(ax.) regions, and in the case of (IV) a small additional peak in the axial position not occupied by fluorine. The chemically more reasonable disordered arrangements of molecules with normal dimensions fit the density distributions slightly better, although for a crystal of *e.g.* (III) a disordered model, with the required atom separations of *ca.* 0·08 Å is equivalent to an ordered model with the observed anisotropic thermal parameters [8] (particularly as the minimum *d*-spacing of the *X*-ray data is 0·93 Å).

Disordered models were derived for compounds (I)—(IV) from previous atomic positions (Table 2) and from the thermal vibration ellipsoids by use of the formula for fractional atom representation of ref. 8. Two positions were used for each of the chelate ring carbon atoms, the axial fluorine atoms, and the methyl groups, mean positions being used for the other atoms, including the equatorial fluorine atom F(3). The proportion of each configuration was estimated from the deviation from normal values of the molecular dimensions corresponding to the mean positions. General views of the structures of two typical compounds are shown in Figure 1 and in Figure 4 of ref. 2, and the disordered arrangement is illustrated in Figure 2.

Further refinement of the disordered structures proceeded by full-matrix least-squares methods. For (I), (II), and (III) only the positional and isotropic thermal parameters of the split atoms and an overall scale factor were allowed to vary, the parameters for all the other atoms being fixed at their values from the anisotropic refinement, and the occupancy factors of the two disordered molecules being fixed at their initial values. The disordered structure for (IV) was fully refined, with inclusion of anisotropic thermal parameters, occupancy factors for the C(10) atoms (which were then applied to the remainder of the split atoms), and hydrogen atoms (not refined), which appeared on difference-Fourier maps. In these refinements most of the positional and thermal parameters behaved reasonably well, in spite of the close proximity of some of the split atoms. Since it appeared that the disorder would prevent the attainment of accurate molecular dimensions, molecules (1) and (2) of the disordered structures for (V) and (VI) were approximated as the anisotropic structures for (V) and (VI) respectively, and these were not further refined.

The *R* values (Table 1) are slightly lower for the anisotropic, unusual geometry models than for the disordered, normal geometry structures, except *R* (all reflexions) for (IV). Hamilton's test [9] indicates that the anisotropic models fit the data significantly better; *e.g.* for (I), with 181—174 (*i.e.* with inclusion of one occupancy parameter) equivalent to 7 degrees of freedom, the *R* ratio is 1·12 for the observed reflexions (1·08 for all reflexions; the corresponding weighted

---

[8] G. Kartha and F. R. Ahmed, *Acta Cryst.*, 1960, **13**, 532.

[9] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

R ratios are 1·08 and 1·06), so that the anisotropic model fits the data better at a very high significance level. For (IV), *R* (all reflexions) and the corresponding weighted *R* indicate significantly better fit for the disordered structure. Since the treatment of the disorder was more thorough for complex (IV), it is possible that some improvement could be achieved for the other structures by the introduction of anisotropic thermal parameters, but little increase in the accuracy of the structure determinations could be expected.

The final conclusion about these structures is that the anisotropic models fit the data marginally better than the approximate disordered models, but that the abnormal thermal parameters of the anisotropic models, the detailed appearance of the electron-density maps, and the structurally more reasonable parameters of the split-atom models indicate that the crystals do in fact contain disordered arrangements of molecules with normal geometries and dimensions. Finally no chemical properties have been observed which correspond to the unusual molecular geometries of the anisotropic model.

The final positional and thermal parameters for the anisotropic and disordered models for all the structures are given in Table 2; for (IV) the refined mean atom parameters in the disordered model do not differ significantly from those in the original anisotropic refinement. The standard deviations are those calculated from the least-squares inverse matrices; the standard deviations of bond distances and angles will be generally greater than indicated by these least-squares values, since the disorder makes it uncertain how each refined position is related to the exact atomic positions in the disordered model.

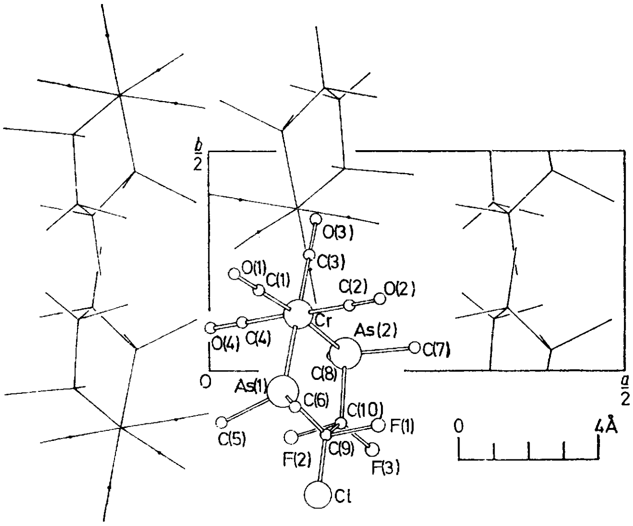


FIGURE 1 Structure of compound (V). The most abundant orientation is shown; the second orientation is obtained by reflection of each molecule in its As, Cr, As plane

The bond distances and valency angles for all the complexes are summarized in Table 3, the values being those of the appropriate final refinement for each structure. Because of the uncertainty in the exact meaning of an atomic parameter as a result of the disorder, it seems useful to list only mean values. The least-squares standard deviations are *ca.* 0·002—0·004 for M–X bond lengths, 0·01—0·03 for M–C and C–O, and 0·03—0·04 Å for most of the bonds involving the disordered atoms, with values as high as 0·18 Å for one of the bonds in the least abundant configuration in (IV); corresponding bond-angle standard deviations vary from 0·1° for X–M–X to as high as 10° for angles involving the disordered atoms. These standard deviations give a general measure of the accuracy, but they should be applied with caution in individual comparisons, because of the uncertainties resulting from the disorder. The C–C bond lengths in the disordered refinement vary from 1·44 to 1·63 Å, and it seems useful to list only the mean value of 1·50 Å in Table 3 for all the compounds; the angles at the carbon atoms are in the range 98—120, mean 108°. The C–F bond lengths vary from 1·31 to 1·54 Å. The best values are probably those of the C(10)–F(3) equatorial bond in the anisotropic refinements, since these atoms have similar thermal parameters; these range from 1·35 to 1·38 Å, and the mean 1·37 Å, is given as the C–F distance for all the complexes in Table 3.

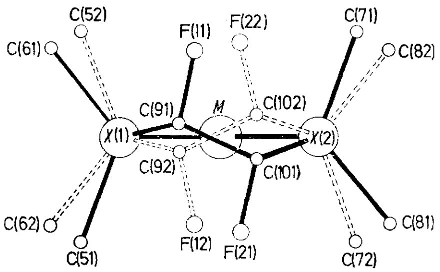


FIGURE 2 View showing the conformation of the chelate ring, and the disordered arrangement of molecules

Measured and calculated structure factors are listed in Supplementary Publications No. SUP 20113 (2 pp., 1 microfiche) for (VI), No. SUP 20198 (4 pp., 1 microfiche) for (I), and No. SUP 20502 (13 pp., 1 microfiche) for (II)—(V).* The calculated values for the anisotropic and split-atom models are very similar.

DISCUSSION

All six complexes are derived, both chemically and structurally, from the metal hexacarbonyls, by replacement of two carbonyl groups by the arsenic or phosphorus atoms of the chelating ligands (Figure 1). The co-ordination around each metal atom is approximately octahedral; the X–M–X angles are 82—85° (Table 3), and the other angles at the metal atoms are 87—95°.

The five-membered chelate rings are non-planar, with the C–C bonds rotated about 25° out of the X, M, X planes (Figure 2), resulting in X–C–C–X torsion angles of *ca.* 50°, typical of the situation usually found in such rings.[10] The carbon atoms are displaced unequally from the X, M, X planes, with the CF_2 atom, C(10), having the

---

* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[10] See, *e.g.*, M. R. Churchill and T. A. O'Brien, *J. Chem. Soc.* (*A*), 1970, 206; J. H. Cross and R. H. Fenn, *ibid.*, 1970, 3019.

larger displacement (Figure 2), *ca.* 0·4 Å, and the deviation of C(9) being *ca.* —0·25 Å. The substituent fluorine atoms and groups R^1 and R^2 may be classified as axial or equatorial with respect to the chelate ring. The R^2 group, whether it be the bulky CF_3 and Cl or the smaller hydrogen atom, occupies an equatorial position in all compounds [in (IV) there is no other possibility, of course, since $R^1 = R^2 = H$]. There is thus an unusual tendency for these complexes to adopt a conformation with fluorine atoms occupying axial positions of the puckered chelate ring, as suggested by n.m.r. data.[6]

The Mo–As (mean 2·58 Å), Mo–P (2·48 Å), and Cr–As (mean 2·43 Å) bond lengths are all shorter than the values (2·83, 2·72, and 2·69 Å), predicted for single bonds from the covalent radii of Mo^0,[2] Cr^0,[11] and arsenic and phosphorus.[12] The shortenings of *ca.* 0·25 Å are probably a result of some back-donation from the central-metal atom to arsenic or phosphorus ($d_\pi \rightarrow d_\pi$). The values of the Mo–C (1·94—2·03 Å), Cr–C (1·88—1·90 Å), and C–O (1·13—1·19 Å) bond lengths are similar to those previously reported for these bonds.[13] All the M–C–O groupings are almost exactly linear. The values of the As–C (1·96—1·99 Å) and P–C (1·89 Å) bond distances are close to normal;[14] the loss in accuracy resulting from the disorder prevents comment on any possible differences between X–C(methyl) and X–C(fluorocarbon) bond lengths. The M–X–Me bond angles (mean 120—122°) are all significantly larger than the tetrahedral angle, presumably as a result of the steric influence of the $M(CO)_4$ groups. The other angles at the X atom are in the range 94—112° (Table 3). The C–C (1·50 Å), C–F (1·37 Å), and C–Cl [1·76 Å in (V)] bond lengths, and the valency angles (mean 108°) in the fluorocarbon groups are all close to normal values.[14]

Complexes (I)—(IV) are isostructural, and a typical crystal structure is shown in Figure 4 of ref. 2.

The most interesting feature of the crystal packing is the presence of disorder, each lattice site being occupied randomly by two molecules which are optical enantiomorphs (Figure 2), and the proportion of each configuration varying according to packing requirements. Intermolecular packing is governed by van der Waals interactions; for complexes (II) and (III) both orientations appear to be able to fit into the structure equally well, while for (IV), which has only one axial fluorine substituent, one of the orientations is greatly preferred in a particular lattice site.

Complexes (V) and (VI), which have bulky equatorial substituents, have different structures from (I)—(IV), and although (V) and (VI) crystallize in different crystal systems they have in fact rather similar structures (Figure 1, and Figure 3 of ref. 1). Both contain similar layers of molecules in the *bc* plane. The only difference within these layers is that opposite configurations predominate in the two structures (indicated by the multiplicity factors in Tables 1 and 2). The layers are stacked together differently, to give an orthorhombic structure for (V), and a monoclinic arrangement for (VI).

We thank Dr. W. R. Cullen for crystals and discussion, the University of British Columbia Computing Centre for assistance, and the National Research Council of Canada for financial support.

[2/911 *Received, 24th April,* 1972]

---

[11] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 1966, **5**, 1851.

[12] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 224.

[13] See, *e.g.*, M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1967, **6**, 1213; F. A. Cotton and M. D. La Prade, *J. Amer. Chem. Soc.*, 1969, **91**, 7000; A. D. Redhouse and O. S. Mills, *J. Chem. Soc. (A)*, 1969, 1274.

[14] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.