Acta Cryst. (1964). **17**, 506

A Least-Squares Refinement of the Crystal Structure of Tricaesium Pentachlorocobalt(II), Cs_3CoCl_5

By B. N. Figgis

Department of Chemistry, University of Western Australia, Nedlands, Western Australia

and M. Gerloch and R. Mason

Crystallography Laboratory, Department of Chemistry, Imperial College, London, S.W.7, England

(*Received* 4 *June* 1963)

Bond lengths (e.s.d. 0·013 Å) and bond angles (e.s.d. 0·4°) are reported for the $[CoCl_4]^{2-}$ ion from a least-squares analysis of the three-dimensional X-ray data of Cs_3CoCl_5. Axial distortions in the approximately tetrahedral ligand arrangement are discussed and compared with those in other transition metal complexes.

Introduction and refinement analysis

A recent study of the paramagnetic anisotropies of tetrahedral cobalt(II) complexes and their relation to the coordination geometries (Figgis, Gerloch & Mason, 1964) suggested that a refinement of the crystal structure of Cs_3CoCl_5, beyond that which was possible in the earlier analysis (Powell & Wells, 1935), should be useful. Crystals of this compound are tetragonal, a least-squares analysis of high-angle precession data giving the unit cell

$$a = 9{\cdot}219 \pm 0{\cdot}003,\quad c = 14{\cdot}554 \pm 0{\cdot}005 \text{ Å}$$

compared with

$$a = 9{\cdot}18,\quad c = 14{\cdot}47 \text{ Å (Powell \& Wells, 1935).}$$

The space group is $I4/mcm$ (D_{4h}^{18}; No. 140).

A least-squares refinement of the positional and vibrational atomic parameters was based on 131 $\{h0l\}$ and $\{hhl\}$ reflexions, the relative intensities of which were visually estimated from non-integrated precession photographs (Mo $K\alpha$); no corrections for absorption effects have been made, the maximum difference in path length being some 10% in a crystal of average thickness 0·1 mm. The refinement analysis, with unit weighting of all reflexions, converged to a discrepancy index $R = 0{\cdot}062$ after twelve cycles, the final atomic coordinates, their e.s.d.'s and temperature factors being listed in Table 1. It should be noted that the atomic coordinates are now referred to the origin of the standard setting of $I4/mcm$ rather than that of Powell & Wells (1935).

Final observed and calculated structure factors are listed in Table 2.

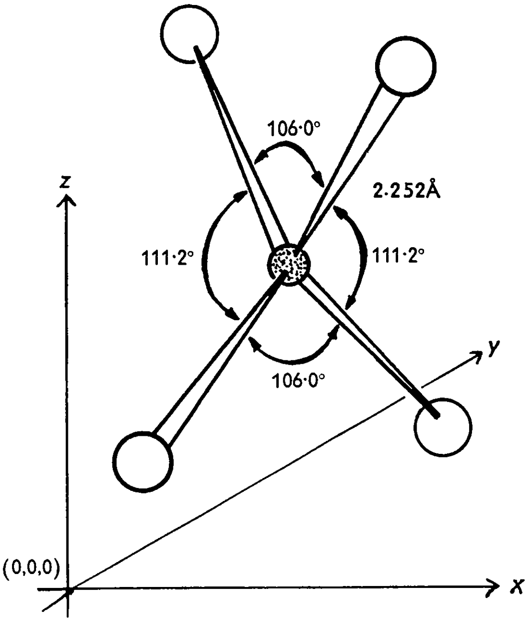

Fig. 1. Cs_3CoCl_5.
Bond length and angles in the $[CoCl_4]^{2-}$ ion.

Discussion

The Co–Cl bond length is 2·252 ± 0·013 Å compared with the Powell & Wells (1935) value of 2·34 Å;

Table 1. *Atomic coordinates and temperature parameters of the Debye factor*

$$B = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}lh + b_{12}hk}$$

Atom	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
Cs(1)	0	0	$\frac{1}{4}$	0·0119	0·0119	0·0038	0	0	0
Cs(2)	0·1655(4)	0·6655(4)	$\frac{1}{4}$	0·0063	0·0073	0·0037	0	0	−0·0013
Co(1)	0	$\frac{1}{2}$	$\frac{1}{4}$	0·0068	0·0068	0·0018	0	0	0
Cl(1)	0	0	0	0·0073	0·0073	0·0060	0	0	0
Cl(2)	0·1380(16)	0·6380(16)	0·1570(6)	0·0105	0·0105	0·0040	0·0031	0·0031	−0·0083

the present result is in good agreement with that of 2·23 Å reported for the Co–Cl distance in Cs_2CoCl_4 (Porai-Koshits, 1954). Bond angles of the distorted tetrahedrally coordinated cobalt are shown in Fig. 1, the values of 106·1° and 111·2° corresponding to angles of 118° and 106° respectively from the earlier analysis.

Other interatomic contacts are collected in Table 3, the results from the earlier analysis being given in parentheses.

The deviation from strict tetrahedral symmetry of the ligand arrangement about the cobalt ion is seen to involve angular distortions rather than bond stretching or contraction. This situation is entirely similar to that of $[CoCl_4]^{2-}$ in Cs_2CoCl_4 (Porai-Koshits, 1954), and of $Co(CNS)_4^{2-}$ in $K_2Co(CNS)_4.4H_2O$ (Zdhanov & Zvonkhova, 1950) and $HgCo(CNS)_4$ (Jeffrey, 1963). The origin of this distortion is of interest, the relative contribution of intramolecular (Jahn–Teller) effects and intermolecular forces being, however, difficult to assess. In the case of tetrahedral Co^{2+} complexes, the lowest lying term of the d^7 configuration is that which is designated by $^4A_2$ and is orbitally non-degenerate. Some distortion from a pure cubic field would come from a 'mixing-in' of the higher-lying T term by spin-orbit coupling but it seems unlikely that this process would explain the observed distortion. For tetrahedral Cu^{2+} (d^9) complexes, on the other hand, Jahn–Teller effects would be operative in removing the degeneracy of the orbitally degenerate ground term and indeed the bond angles of 120° and 104° for $[CuCl_4]^{2-}$ (Helmholz &

Table 2. *Observed and calculated structure factors* (×0·5)

	F_o	F_c		F_o	F_c		F_o	F_c
0 0			2 2			4 4		
2	78.4	69.4	0	385.9	410.4	0	392.0	383.2
4	554.3	561.6	2	167.4	-125.3	2	131.6	-113.6
6	279.9	286.7	4	388.8	357.4	4	196.7	186.7
8	497.3	501.8	6	119.8	-105.9	6	17.2	14.1
10	18.9	-16.5	8	280.2	263.9	8	201.8	204.6
12	378.7	405.0	10	96.2	-81.6	10	116.2	-115.4
14	75.4	70.4	12	183.8	183.5	12	178.5	185.7
16	160.0	163.3	14	59.9	-60.6	14	19.5	-22.5
18	53.1	44.3	16	122.5	119.3	16	63.6	61.3
20	151.8	152.0	18	39.6	-40.1	18	25.8	-19.7
1 1			3 3			5 5		
0	63.8	-45.0	0	305.0	-310.5	0	29.9	25.6
2	124.1	-104.0	2	297.7	-294.9	2	65.5	-61.5
4	127.4	112.1	4	131.8	-115.0	4	25.3	25.9
6	186.9	-184.1	6	367.5	-368.5	6	51.0	-51.0
8	30.2	28.6	8	145.7	-139.0	8	11.8	11.1
10	45.5	-47.5	10	155.3	-155.9	10	39.1	-36.7
12	18.8	-12.1	12	162.3	-150.5	12	12.0	11.0
14	63.6	-67.0	14	157.6	-148.9	14	23.2	-30.3
16	15.7	25.1	16	40.4	-42.4	16	9.9	0.5
18	34.0	-38.2	18	105.7	-100.6			

	F_o	F_c		F_o	F_c		F_o	F_c
6 6			2 0			8 0		
0	299.3	307.3	0	153.1	122.7	0	114.7	117.8
2	95.1	82.8	2	370.9	-401.4	2	203.0	-198.7
4	293.5	283.6	4	180.6	151.3	4	14.8	9.5
6	94.3	79.1	6	334.5	-360.5	6	125.3	-107.7
8	226.6	228.8	8	119.3	97.5	8	53.7	46.7
10	50.9	55.5	10	242.4	-230.5	10	169.6	-165.7
12	184.7	180.5	12	55.9	50.0	12	57.3	56.0
14	33.4	30.0	14	164.8	-165.7	14	71.7	-76.3
7 7			16	51.0	50.2	10 0		
0	57.2	-52.8	18	115.9	-112.3	0	22.5	-19.6
2	20.1	-17.9	20	35.0	25.8	2	119.0	-121.1
4	34.8	34.4	4 0			4	45.0	42.2
6	77.6	-80.0	0	68.5	-54.8	6	148.6	-157.3
8	7.2	2.2	2	273.8	-288.3	8	26.9	21.8
10	7.2	6.4	4	208.1	184.1	10	67.2	-77.5
12	27.5	-31.3	6	390.7	-399.9	12	17.1	-8.9
8 8			8	97.7	68.5	12 0		
0	115.9	112.5	10	162.5	-142.2	0	143.3	140.9
2	34.4	-35.8	12	26.3	-2.5	2	50.6	62.4
4	77.1	68.7	14	169.5	-172.0	4	151.5	166.4
6	13.2	-11.2	16	74.0	77.3	6	34.8	34.3
8	83.2	78.1	18	114.0	-113.3			
9 9			6 0					
0	67.1	-53.2	0	502.0	500.1			
2	86.6	-85.5	2	93.3	87.9			
			4	361.0	382.3			
			6	151.6	135.3			
			8	322.3	320.8			
			10	40.0	39.4			
			12	267.8	265.9			
			14	43.4	41.8			
			16	131.3	141.2			
			18	40.6	34.5			

Table 3. Cs_3CoCl_5. *Interatomic distances less than* 4 Å

Reference atom	Nearest neighbours		
Cs (1)	8 Cl (2) at	3·820 Å	(3·67)
	2 Cl (1)	3·639	(3·62)
Cs (2)	2 Cl (1)	3·440	(3·42)
	2 Cl (2)	3·433	(3·39)
	4 Cl (2)	3·622	(3·85)
Cl (1)	2 Cs(1)	3·639	(3·67)
	4 Cs(2)	3·440	(3·42)
Cl (2)	Co(1)	2·252	(2·34)
	2 Cs(1)	3·820	(3·67)
	1 Cs(2)	3·433	(3·39)
	2 Cs(2)	3·622	(3·85)
	1 Cl (2)	3·982	(3·45)

Kruh, 1952) demonstrate a larger distortion than is found in any tetrahedral cobaltous complex.

It seems more reasonable therefore to associate the distortions in the cobalt complexes with crystal packing effects. In Cs_3CoCl_5, the tetrahedra of $[CoCl_4]^{2-}$ ions arranged about the 001 plane interact more strongly in the *a* (*b*) direction along which the flattening of the tetrahedron is observed (Fig. 2). The chlorine–chlorine distance is 3·892 Å and our magnetic data show that this interaction allows antiferromagnetic interaction between the cobalt ions in the (001) plane via a super-exchange mechanism. Similar close contacts are observed in Cs_2CoCl_4 and $K_2Co(CNS)_4.4H_2O$. While the distortions in the latter molecules are not simple axial ones, it seems generally true that the angular distortions can at least be qualitatively correlated with specific steric effects in the crystal.

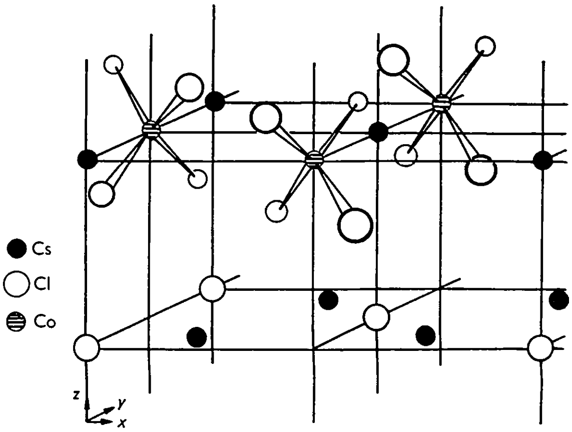

Fig. 2. Cs_3CoCl_5. The crystal structure.

We are grateful to Drs J. S. Rollett and R. Sparks for copies of their programs for the University of London Mercury computer. One of us (M. G.) is in receipt of a D.S.I.R. Research Studentship.

References

Figgis, B. N., Gerloch, M. & Mason, R. (1964). *Proc. Roy. Soc.* A. In the press.

Helmholz, L. & Kruh, R. F. (1952). *J. Amer. Chem. Soc.* **74**, 1176.

Jeffrey, J. W. Personal communication.

Porai-Koshits, M. A. (1954). *Trudy Inst. Krist., Akad. Nauk SSSR.* **10**, 117.

Powell H. M. & Wells, A. F. (1953). *J. Chem. Soc.* p. 359.

Zdhandov, G. S. & Zvonkhova, Z. V. (1950). *Zhur. fiz. Khim.* **24**, 1339.

Acta Cryst. (1964). **17**, 508

The Use of Germanium Dendrites for the Monochromatization of X-rays

By A. Fingerland and L. Červinka

Institute of Solid State Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

(*Received* 16 *May* 1963)

Germanium dendrites have been found to be very suitable as monochromatizing plane or bent crystals owing to their remarkable elasticity and high perfection. Both experimental and theoretical comparison was made with quartz. The intensities of the monochromatized beams in the two crystals were comparable but owing to the fine polishing of the germanium dendrite the reflected intensity was almost doubled. Germanium dendrites are especially suitable as monochromators with variable curvature.

Introduction

Recently more and more attention has been drawn to artificially grown germanium and silicon crystals with a high degree of perfection. Their advantages as plane monochromators in X-ray spectroscopy has been proved in a series of papers (*e.g.* Drahokoupil & Fingerland, 1959; Bubáková, Drahokoupil & Fingerland, 1962). They have, however, one common disadvantage, namely that the preparation of the polished plate is expensive and laborious. When Andrle (1961) published his results on the preparation of perfect germanium dendrites the possibility of using germanium dendrites as monochromatizing bent crys-