79. The Structure of Cæsium Cobalt Chloride (Cs_3CoCl_5).

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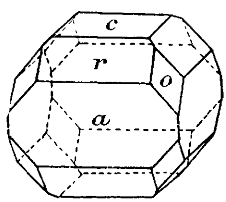
ALTHOUGH a co-ordination number of 5 seems certainly to exist in some molecules, *e.g.*, those of phosphorus pentafluoride and iron pentacarbonyl, in general it is not to be expected. The avoidance of odd co-ordination numbers by heavy-metal atoms, even if this requires otherwise unusual effective atomic numbers in the molecule, has been demonstrated by Menzies (J., 1934, 1755). Stable complex ions AX_3 and AX_4 are well known, but if the co-ordination number exceeds 4, the next stable group is AX_6. There are, however, compounds of the type M_nRCl_5 which might appear to contain an RCl_5 group. Most of these are monohydrated, *e.g.*, K_2FeCl_5,H_2O, and it may be reasonably supposed that they contain the group $[RCl_5,H_2O]$, R having co-ordination number 6. A few, however, are anhydrous, and it appeared to be of interest to investigate the structure of such a compound.

Cæsium cobalt chloride, Cs_3CoCl_5, was selected for this purpose; its composition was established by Campbell (*Amer. J. Sci.*, 1894, **48**, 419), and according to microscopic examination by Vermande (*Pharm. Weekblad*, 1918, **55**, 1117), it crystallises in the tetragonal system.

EXPERIMENTAL.

Our material was prepared by crystallisation of an aqueous solution of cobalt chloride and excess of cæsium chloride. Deep blue tetragonal crystals Cs_3CoCl_5 were obtained, which on recrystallisation from water gave similarly coloured orthorhombic Cs_2CoCl_4. Analysis of the former substance was made on material which was shown microscopically to be free from included Cs_2CoCl_4 (Found: Co, as pyrophosphate, 9·51; Cl, as AgCl, 27·87. Calc. for Cs_3CoCl_5: Co, 9·28; Cl, 27·93%. Calc. for Cs_3CoCl_5,H_2O: Co, 9·03; Cl, 27·16%). There was no appreciable loss of weight on heating the substance to 140°, and the X-ray and density measurements support the anhydrous formula.

FIG. 1.



Crystallographic Examination.—The crystals (Fig. 1) were found by measurement on a two-circle goniometer to be tetragonal. The lettering of the figure corresponds to indices according to the Barker system. For X-ray purposes, different axes and indices given by the transformation below are required:

Barker	a(100)	c(001)	r(101)	o(111)	cr = 48° 15′
X-Ray	110	001	112	101	

Optically the crystals were uniaxial with weak positive double refraction. They showed no pyroelectric effect by the liquid-air method. The density was found by pyknometer to be 3·39 g./c.c. at 20°.

A complete series of 15° oscillation photographs about the a and c axes was made with copper radiation, and comparison spacing photographs with gypsum gave the cell dimensions a = 9·18, c = 14·47 Å.; $c : a$ = 1·576 (calc., goniometric, 1·584). The number of molecules per unit cell is thus 3·95 ≈ 4. The oscillation photographs, indexed by the chart method, show that the space group is $I\,4cm$ or $I\,4/mcm$ (C_{4v}^{10} or D_{4h}^{18}), and from the absence of any evidence of polarity, the correct group is taken to be the latter. A preliminary determination of the distribution of the atoms in the cell was made from consideration of the space group symmetry and some intensity comparisons. The possible equivalent positions are, in Wyckoff's notation (" Analytical Expression," 2nd. Edn.), four 4-fold *a, b, c, d,* and one 8-fold *e* without freedom, three 8-fold *f, g, h,* and two 16-fold *i, j,* with one degree of freedom, two 16-fold *k, l,* with two degrees of freedom, and one 32-fold with three degrees of freedom. In order to place 12Cs, 4Co, and 20Cl in the unit cell one 4-fold position must be assigned to each type of atom, and the possible distributions are 12Cs (8 + 4), 4Co (4), 20Cl (16 + 4), or (8 + 8 + 4). With three of the positions *a, b, c, d,* occupied, *e* and *f* become impossible for 8Cs or 8Cl, since there is now insufficient space to contain these atoms. The intensity calculated for the reflexion (400) is independent of the distribution of atoms among *a, b, c, d,* and, the observed intensity being nil, shows that 8Cs cannot be in either of the positions *e* and *f* or in *g* whatever the position of the remaining 16Cl. 8Cs must therefore be in *h* with fixed *c* axis co-ordinates, and it now becomes possible to determine the position occupied by 16Cl. The intensities for reflexions (00*l*) are such that there must be atoms in planes parallel to (001) other than those at heights 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ along the *c* axis. Since all the atoms placed so far have fixed *c* co-ordinates 0, $\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$, positions *e, h, i, j,* and *k* for chlorine are excluded. We therefore obtain the distribution 8Cs (*h*), u, $u + \frac{1}{2}, \frac{1}{4}$, etc., 16Cl (*l*), u', $u' + \frac{1}{2}, v$, etc., with 4Co, 4Cs, and 4Cl in some arrangement of *a, b, c, d*; $a = 000, 00\frac{1}{2}, \frac{1}{2}\frac{1}{2}\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$, $b = 0\frac{1}{2}0, \frac{1}{2}00, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}$, $c = 00\frac{1}{4}, 00\frac{3}{4}, \frac{1}{2}\frac{1}{2}\frac{3}{4}, \frac{1}{2}\frac{1}{2}\frac{1}{4}$, $d = 0\frac{1}{2}\frac{1}{4}, \frac{1}{2}0\frac{1}{4}, 0\frac{1}{2}\frac{3}{4}, \frac{1}{2}0\frac{3}{4}$. The possible distributions among *a, b, c, d,* fall into six groups as far as their effect on the intensities of reflexions (00*l*) is concerned, and of these six, five are incompatible with observation for any value of the parameter v. Agreement is obtained with 4Cs in *a* or *b*, 4Co in *a* or *b*, 4Cl in *c* or *d*, and a chlorine parameter $v = \frac{1}{12}$ or $\frac{11}{12}$. The intensities calculated for (*h*00), which are the same for all combinations of *a, b, c, d,* allow a preliminary limitation of u and u' to the regions u or $(\frac{1}{2} - u) = 0{\cdot}13 - 0{\cdot}19$, u' or $(\frac{1}{2} - u') = 0{\cdot}11 - 0{\cdot}22$. There are only two essentially different ways of combining the alternative values for u, u', and v, and one of these,

TABLE I.

(Visually estimated intensities are in decreasing order vs, s, ms, m, w, vw.)

Indices.	Calc. $\sqrt{I}$.	Obs. *I*.	Indices.	Calc. $\sqrt{I}$.	Obs. *I*.	Indices.	Calc. $\sqrt{I}$.	Obs. *I*.	Indices.	Calc. $\sqrt{I}$.	Obs. *I*.
200	110	w	206	451	s	554	35	nil	181	81	vw
400	30	nil	208	110	w	556	80	nil	183	201	m
600	580	vs	20*10*	210	m	572	64	vw	185	93	w
800	67	nil	20*12*	30	nil	352	70	w	581	82	w
*10*00	35	nil	20*14*	146	m	354	196	m	583	213	m
002	120	w	402	309	ms	356	93	nil	585	79	w
004	870	vs	404	166	m	372	20	nil	347	21	nil
006	350	s−	406	398	s	374	134	w	222	193	m
008	440	vs	408	113	w	376	146	w+	224	627	vs
00*10*	20	nil	40*10*	152	m−	392	154	m	226	94	vw
00*12*	430	s−	40*12*	8	nil	394	64	w+	228	283	ms
00*14*	10	nil	602	40	nil	396	268	m+	22*10*	79	vw
00*16*	262	m	604	352	ms	121	300	ms	22*12*	210	m−
110	40	nil	606	186	w	123	590	vs	242	138	vw
220	600	vs	608	290	ms	125	227	m+	244	339	ms+
330	390	vs	60*10*	30	nil	127	162	w+	246	55	nil
440	370	vs	60*12*	371	vs	129	270	ms	248	222	ms
550	29	nil	802	190	w	321	16	nil	442	156	m−
660	370	s	804	55	nil	323	45	vw	444	236	m+
770	38	nil	806	166	w	521	136	w	446	16	nil
310	540	vs	808	52	nil	523	305	ms	448	206	ms
350	230	m	80*10*	183	m	525	134	w+	622	238	m
370	245	m	112	184	m−	527	116	w	624	93	w
390	150	w	114	166	w+	721	118	w	626	280	ms−
190	172	w+	116	197	m	723	192	m	628	72	nil
570	14	nil	132	110	w	725	118	w	642	182	m
590	170	w+	134	356	s−	141	200	m	644	96	vw
240	430	vs	136	150	w+	143	366	s	646	288	ms
260	40	nil	138	222	m	145	190	m	648	97	w
280	180	m−	332	270	s	147	148	m	662	34	w
2*10*0	222	m−	334	114	w	149	208	m	664	272	ms
460	0	nil	336	512	vs	541	124	m	666	138	w
480	165	w	338	77	w	543	251	m+	824	183	w+
4*10*0	230	m	33*10*	172	w	545	123	w	844	182	m
202	566	s	33*12*	187	w	547	127	w	846	70	vw
204	215	m	552	78	vw	563	41	vw			

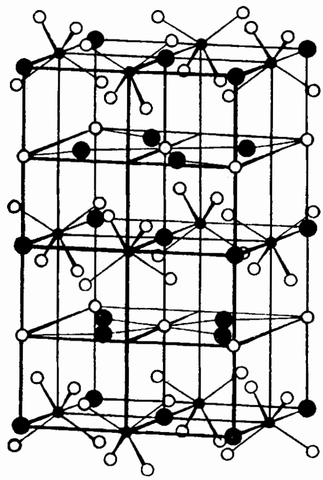
which would bring cæsium and chlorine atoms to within 2·7 Å. or less, is clearly impossible. The arrangement selected to represent the structure has $v = \frac{11}{12}$, $u = 0{\cdot}13 - 0{\cdot}19$, $u' = 0{\cdot}11 - 0{\cdot}22$. It then follows that 4Cl must be in c $00\frac{1}{4}$, etc., 4Cs in a 000, etc., and 4Co in b $0\frac{1}{2}0$, etc. This distribution may be obtained by consideration of ionic radii alone, and is supported by the probable atomic environments.

On the assumption of these co-ordinates, the parameters u and u' were determined simultaneously from the intensities of the reflexions $h00$, $hk0$, $hh0$, which are independent of v. The values could be easily limited to $u = 0{\cdot}15 - 0{\cdot}18$, $u' = 0{\cdot}13 - 0{\cdot}20$. With the aid of contour diagrams constructed to show the effect on intensities of simultaneous variation of u and u' in these limited regions, the values $u = 0{\cdot}167$, $u' = 0{\cdot}155$ were chosen to give the best agreement with observation. Intensities were compared by the formula

$$\sqrt{I} \propto \left(\frac{1 + \cos^2 2\theta}{2 \sin 2\theta}\right)^{\frac{1}{2}} \sum_n f_n e^{2\pi i(hx_n + ky_n + lz_n)}$$

In Table I are the values of $\sqrt{I}$ calculated as above. The f values of Pauling and Sherman (*Z. Krist.*, 1932, **81**, 1) were used, and where necessary the correction according to Cox and Shaw (*Proc. Roy. Soc.*, 1930, *A*, **127**, 71) for spots not on the zero layer line has been applied to the calculated $\sqrt{I}$.

FIG. 2.



● = Cs, ○ = Cl, • = Co.

DISCUSSION.

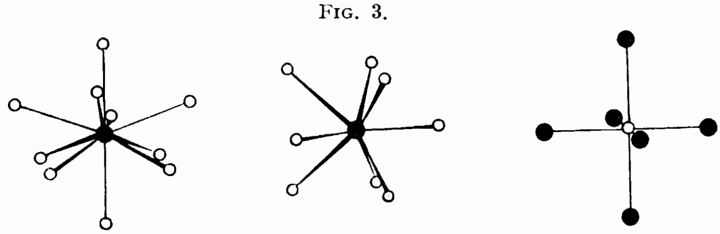
A unit cell of the structure and the immediate environment of the atoms are illustrated by Figs. 2 and 3. The principal interatomic distances are given in Table II, in which structurally different cæsium and chlorine atoms are distinguished by Roman numerals.

TABLE II.

Atom.	Co-ordinates.	Neighbours.	Distance, Å.
Cs^{I}	000	$8Cl^{II}$	3·67
		$2Cl^{I}$	3·62
Cs^{II}	$u, u+\frac{1}{2}, \frac{1}{4}$	$2Cl^{I}$	3·42
		$2Cl^{II}$	3·39
		$4Cl^{II}$	3·85
Cl^{I}	$00\frac{1}{4}$	$2Cs^{I}$	3·67
		$4Cs^{II}$	3·42
Cl^{II}	$u', u'+\frac{1}{2}, v$	1Co	2·34
		$2Cs^{I}$	3·67
		$1Cs^{II}$	3·39
		$2Cs^{II}$	3·85
Co	$0\frac{1}{2}0$	$4Cl^{II}$	2·34

The distances are in accordance with accepted values. For Cs–Cl in 10 co-ordination, the distance calculated from Zachariasen's tables (*Z. Krist.*, 1931, **80**, 137) is 3·64 Å., in good agreement with the Cs^{I}–Cl values. For eight neighbours Cs^{II}–Cl would be 3·58,

FIG. 3.



10Cl around Cs^{I} 8Cl around Cs^{II} 6Cs around Cl^{I}

but the arrangement of chlorine around Cs^{II} is such that some variation in the distances is to be expected. In particular, it may be seen from the figures that four chlorine atoms which belong to $CoCl_4$ groups are pulled away on one side to 3·85 Å. On the same side also there is a cæsium ion at 4·32 Å., closer than the other cæsium neighbours at 4·84 Å., and these two influences account for the compression to *ca.* 3·4 Å. of the four Cs–Cl distances on the other side. The distance 2·34 for Co–Cl is what would be expected. From the co-valent radii (Sidgwick, " The Covalent Link ") the value is 2·22, or, from the crystal structure of cobalt chloride (Ferrari, *Atti R. Accad. Lincei*, 1927, **6**, 56; Grimes and Santos, *Z. Krist.*, 1934, **88**, 136) after allowance for co-ordination number, 2·42 Å.

Space-group considerations alone show that one of the four chlorine atoms per chemical molecule is different from the other four in relation to the cobalt. The detailed investigation reveals the presence of $CoCl_4$ groups in approximately regular tetrahedral configuration. The fifth chlorine stands apart as a Cl^{1-} ion far removed from the cobalt atom, and the compound should therefore be formulated $Cs_3{}^{1+}[CoCl_4]^{2-}Cl^{1-}$. It is analogous to $(NH_4)_3{}^{1+}[ZrF_6]^{2-}F^{1-}$ (Hassel and Mark, *Z. Physik*, 1924, **27**, 89).

Our results show how it is possible for a compound to simulate in chemical formula an RX_5 complex without necessarily containing a group of this unusual co-ordination number. It is difficult to predict when compounds of this type should be formed, but some light is thrown on this by the analogous *rubidium* compound. It was found possible to obtain blue tetragonal crystals of this compound (Found: Cl, 36·45. Rb_3CoCl_5 requires Cl, 36·0%) from a hot solution of the mixed chlorides, but it is very unstable, rapidly decomposing at the ordinary temperature either in or out of its solution. A fragment, which proved to be not altogether a single crystal, was treated to remove solution as completely as possible, and a 5° oscillation photograph taken about the [110] axis with a very short exposure. The results indicate a tetragonal cell, $a = 8{\cdot}7$, $c = 14{\cdot}0$ Å., and the substance is presumably isomorphous with the cæsium compound. The tendency for $M_3[CoCl_4]Cl$ to decompose into MCl and other products will be greater the higher the lattice energy of MCl. The stability of the compound therefore decreases with decreasing atomic number of the alkali metal M, in agreement with these observations, and corresponding potassium and sodium compounds will probably not exist.

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