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The crystal structure of $Cs_3Cr_2Cl_9$.

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Introduction

A number of trihalides, in reaction with alkali halides, form complexes in a somewhat unusual 3:2 ratio, the formula then being $A_3B_2X_9$. For some compounds of this type, $K_3W_2Cl_9$ (Brosset, 1935) and $Cs_3Tl_2Cl_9$ (Hoard & Goldstein, 1935; Powell & Wells, 1935), the crystal structure has been investigated. In the case of $K_3W_2Cl_9$, Pauling (1947) showed that there is some evidence that the unexpected magnetic behaviour is due to bond formation between the trivalent ions: the W–W distance is shorter than would be expected for an ionic compound. An indication of covalent character is that $K_3W_2Cl_9$ is diamagnetic.

In view of this unusual behaviour we prepared some related compounds, namely $Cs_3Cr_2Cl_9$, $Cs_3V_2Cl_9$ and $Cs_3Ti_2Cl_9$. The structure determination of the first-named compound is described here.

Preparation

$Cs_3Cr_2Cl_9$ is obtained by fusing a mixture of the two chlorides in the ratio 3:2 in a sealed quartz tube. When the tube was heated at 725° C. for a few days, hexagonal needles appeared in the upper part of the tube. Since the crystals are not formed in the melt it is necessary to check the composition. The chlorine content was determined by chemical analysis (calculated: 38·83%; found: 38·83%, 38·91%).

Crystallographic investigation

Photographs were taken both with Cu $K\alpha$ and Mo $K\alpha$ radiation about the *c* and the *a* axis.

From oscillation and Weissenberg photographs taken with Cu radiation the space group was found to be either $P6_3mc$ or $P6_3/mmc$. The centrosymmetric space group was tried first; since on its basis a satisfactory structure could be found, we will leave the non-centrosymmetric group out of consideration.

The cell constants are

$$a = 7{\cdot}22 \pm 0{\cdot}01,\ c = 17{\cdot}93 \pm 0{\cdot}02\ \text{Å},\ c/a = 2{\cdot}48\,.$$

The density was determined to be 3·36 g.cm.$^{-3}$. From this value the number of molecules per unit cell was found to be 2; this gives a calculated density of 3·37 g.cm.$^{-3}$.

The cell dimensions indicate that Cl and Cs might form a close packing with six layers of four atoms each:

$$a = 7{\cdot}22 = 2d_{Cl};\ c = 17{\cdot}93 \approx 6 \times \tfrac{1}{3} d_{Cl}/6.$$

The fact that many reflexions with $h-k = 3n$ and $l = 2n$ are strong led us to the assumption that four of the Cs ions are placed in position (*f*) of the space group $6_3/mmc$; *z* must be about $\frac{1}{12}$ as reflexions $00l$ with $l = 6n$ are very strong. The other two Cs atoms then lie presumably in (*b*). With the above Cs positions, each layer would contain one Cs atom and three Cl. The only plausible position for the four Cr atoms is then on 4(*f*) (with $z \approx -\frac{1}{6}$), where they are octahedrally surrounded by Cl ions.

The exact co-ordinates were found from a Fourier synthesis of $h0l$ reflexions. Photographs of a very small sublimed crystal, taken with Mo $K\alpha$ radiation, served as a basis for this synthesis. In a first approximation the signs were calculated from the Cs and Cr positions. However, all signs could be calculated without ambiguity after the first Fourier synthesis, which gave also the Cl coordinates.

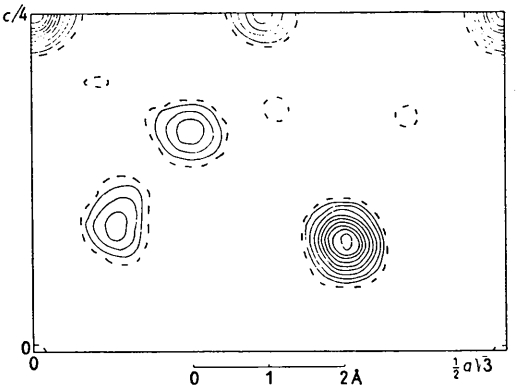

Fig. 1. Projection of the electron density. Contours at intervals of 10 e.Å^{-2}. The lowest contour line is broken and corresponds to a density of 5 e.Å^{-2}.

A second projection (Fig. 1) gave us the following coordinates:

2 Cs_I	in (*b*),	
4 Cs_{II}	in (*f*) with	$z = 0{\cdot}077$;
4 Cr	in (*f*) with	$z = 0{\cdot}837$;
6 Cl_I	in (*h*) with	$x = 0{\cdot}508$,
12 Cl_{II}	in (*k*) with	$x = 0{\cdot}824$ and $z = 0{\cdot}092$.

Taking into account an appropriate temperature factor, these co-ordinates give values for the structure factors as shown in Table 1.

The quantity $R = \sum_{h0l} (|F_c| - |F_o|) \div \sum_{h0l} |F_o|$ was then calculated to have the value 0·151; in the calculation the reflexions 006 and 0,0,12 were omitted because they were suspected to have strong extinction.

Discussion

The structure is shown in Fig. 2, which gives a section in the mirror plane $(11\bar{2}0)$. (Atoms not lying on a threefold axis are repeated by these axes in front of and behind the plane of drawing.) It bears a strong resemblance to the structure of $K_3W_2Cl_9$. There is, however, one striking difference: the distance W–W across the mirror plane at $(x, y, \frac{1}{4})$ is exceptionally short, whereas the Cr atoms are shifted from this plane towards the outer Cl_3 layers of the group Cr_2Cl_9, in accordance with Pauling's rule for

Table 1. *Observed and calculated F(h0l) values of* $Cs_3Cr_2Cl_9$

h l	F_o	F_c	*h l*	F_o	F_c	*h l*	F_o	F_c	*h l*	F_o	F_c
1 0	21	−17	1 18	0	−6	3 12	55	+56	5 8	26	+27
2 0	12	−11	1 19	10	−8	3 13	0	−3	5 9	20	−25
3 0	72	+73	1 20	31	+29	3 14	22	+17	5 10	0	+0
4 0	7	−8	1 21	20	+23	3 15	9	−7	5 11	21	−18
5 0	0	+3				3 16	10	+13	5 12	0	+2
6 0	120	+100	2 1	30	+27	3 17	0	+5	5 13	0	−3
7 0	26	−17	2 2	56	−70	3 18	12	−24	5 14	27	−28
			2 3	62	+82	3 19	0	+3	5 15	0	+15
0 2	18	−14	2 4	61	+80	3 20	31	−22	5 16	0	+4
0 4	24	−18	2 5	52	+54				5 17	38	+38
0 6	77	−115	2 6	12	−11	4 1	21	−20			
0 8	0	−2	2 7	48	−48	4 2	49	−52	6 1	0	+0
0 10	15	−15	2 8	64	+59	4 3	55	−62	6 2	0	−6
0 12	96	+119	2 9	70	−67	4 4	56	+59	6 3	0	+1
0 14	15	−9	2 10	46	−51	4 5	44	−43	6 4	0	−7
0 16	15	−4	2 11	13	−14	4 6	11	−9	6 5	0	+0
0 18	57	−63	2 12	0	−3	4 7	38	+39	6 6	65	−72
0 20	10	+10	2 13	16	+18	4 8	54	+53	6 7	0	−0
0 22	26	−21	2 14	44	−46	4 9	57	+57	6 8	0	−2
0 24	57	+59	2 15	37	+40	4 10	41	−42	6 9	0	−0
			2 16	43	+49	4 11	0	+13	6 10	10	−12
1 1	7	+6	2 17	30	+30	4 12	0	−2	6 11	0	+0
1 2	36	−30	2 18	20	−14	4 13	15	−15	6 12	70	+83
1 3	36	−34	2 19	22	−22	4 14	39	−41			
1 4	34	+35	2 20	39	+37	4 15	34	−36	*l* 1	10	+9
1 5	43	−44	2 21	32	−34	4 16	46	+44	7 2	22	−21
1 6	7	−8				4 17	29	−28	7 3	21	−19
1 7	8	+14	3 1	0	−1	4 18	0	−13	7 4	27	+25
1 8	37	+39	3 2	0	−5	4 19	19	+20	7 5	15	−18
1 9	36	+34	3 3	22	−12	4 20	33	+34	7 6	0	+5
1 10	11	−12	3 4	0	−3				7 7	0	−1
1 11	17	+16	3 5	0	+1	5 1	10	+8	7 8	26	+25
1 12	8	−9	3 6	33	−33	5 2	16	−16			
1 13	24	+16	3 7	0	+3	5 3	23	+24	8 1	0	+13
1 14	33	−32	3 8	22	−19	5 4	15	+16	8 2	27	−34
1 15	16	−19	3 9	16	+10	5 5	44	+37	8 3	35	+39
1 16	18	+16	3 10	22	−28	5 6	17	−16	8 4	35	+39
1 17	44	−41	3 11	0	−3	5 7	25	−20	8 5	20	+28

$F_0 = 0$ too weak to estimate or totally absent.

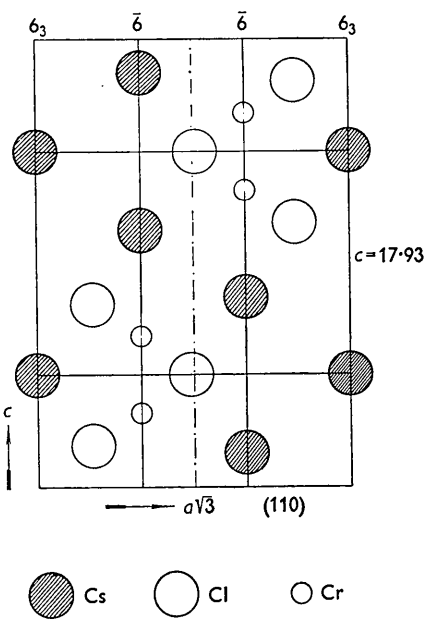

Fig. 2. The mirror plane $11\bar{2}0$.

polyhedra sharing faces. Moreover, $Cs_3Cr_2Cl_9$ is paramagnetic, corresponding to a moment $\mu_{obs.} = 3{\cdot}82\mu_B$; $\mu_{calc.} = 3{\cdot}87\mu_B$ for Cr^{III} having three unpaired *d* electrons. This is the value expected either for ionic Cr^{3+} or for covalently bonded Cr^{III} in octahedral d^2sp^3 configuration.

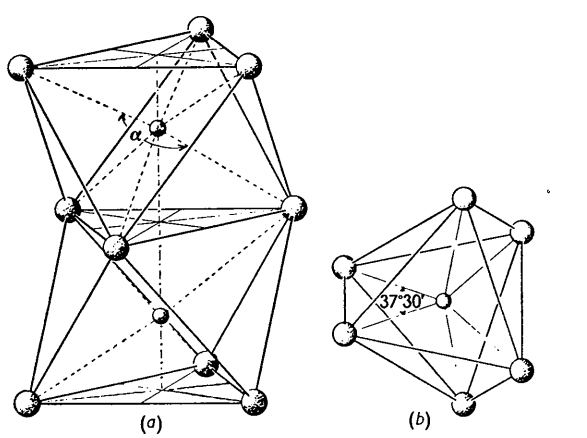

Fig. 3. (*a*) The $Cr_2Cl_9^{3-}$ ion. (*b*) Projection of the $W_2Cl_9^{3-}$ ion on 001.

The shift of the Cr atoms causes a pyramidal distortion of the octahedra in the Cr_2Cl_9 group, the angle α being 176° (Fig. 3(*a*)); in $K_3W_2Cl_9$ a similar distortion is found but in that case α is slightly larger than 180°. A further distortion occurs in the group W_2Cl_9 because the Cl_{II} layers are rotated about the 'axis' W–W until the upper and lower Cl_3 triangles differ 37°30′ in azimuth (Fig. 3(*b*)); in the regular Cl configuration, as found in $Cs_3Cr_2Cl_9$, this difference is 60°.

The following distances are observed in $Cs_3Cr_2Cl_9$:

$Cr–Cl_I = 2{\cdot}52$ Å	$Cl_I–Cl_I = 3{\cdot}43$ Å	$Cs_I–Cl_I = 3{\cdot}61$ Å
$Cr–Cl_{II} = 2{\cdot}34$	$Cl_{II}–Cl_{II} = 3{\cdot}40$	$Cs_I–Cl_{II} = 3{\cdot}59$
$Cr–Cr = 3{\cdot}12$		$Cs_{II}–Cl_I = 3{\cdot}68$
		$Cs_{II}–Cl_{II} = 3{\cdot}62, 3{\cdot}63$

Finally, powder photographs showed that the earlier mentioned compounds $Cs_3V_2Cl_9$ and $Cs_3Ti_2Cl_9$ are isomorphous with the compound described above.

The dimensions of the unit cell are:

$Cs_3V_2Cl_9$: $a = 7{\cdot}24$, $c = 17{\cdot}94$ Å, $c/a = 2{\cdot}48$.
$Cs_3Ti_2Cl_9$: $a = 7{\cdot}32$, $c = 17{\cdot}97$ Å, $c/a = 2{\cdot}45$.

The authors wish to express their thanks to Prof. Dr C. H. MacGillavry and Prof. Dr A. E. van Arkel for their constant help and interest during the investigation. They are also indebted to the F.O.M.R.E. organization for the use of the apparatus.

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Elementarzelle von 1,8-Diaza-*cyclo*-tetradecan.

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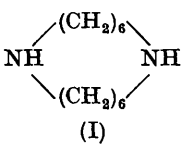
Die von Zahn & Spoor (1956) dargestellte Verbindung (I) kristallisiert in gut ausgebildeten prismatischen Nadeln, monoklin, Nadelachse [101].



(I)

Die Röntgenuntersuchung lieferte die folgenden Abmessungen der Elementarzelle:

$c_0 = 10{,}20 \pm 0{,}03$ Å, $b_0 = 15{,}33 \pm 0{,}02$, $a_0 = 9{,}006 \pm 0{,}01$, $\beta = 112°\,41' \pm 6'$.

Bei Annahme von vier Molekülen in der Elementarzelle berechnet sich daraus die Dichte = $1{,}014 \pm 0{,}004$ g.cm.$^{-3}$, die mit der bei 20° C. gemessenen Dichte 1,002 g.cm.$^{-3}$ hinreichend übereinstimmt.

Beim Versuch eine Kristallnadel quer zur Nadelachse durchzuschneiden, spaltet sich dieselbe sehr leicht in ein faseriges Nadelbündel, das dem Zerschneiden in der Querrichtung grossen Widerstand entgegensetzt. Diese Eigenschaft zeigt, dass die zwischenmolekularen Anziehungskräfte im Gitter in Richtung der Nadelachse offenbar wesentlich grösser sind als senkrecht dazu. Da andererseits die Methylengruppen der Moleküle im Vergleich zu den Aminogruppen nur einen kleinen Beitrag zur zwischenmolekularen Anziehung liefern dürften, kann man annehmen, dass in Richtung [101] Molekülketten im Kristallgitter vorliegen werden, deren Einzelmoleküle über N–H–N-Brücken zusammenhängen.

Eine volle Strukturbestimmung ist z. Zt. nicht beabsichtigt.

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Polymorphism of chloroacetamide.

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In the course of the analysis of the crystal structure of chloroacetamide (Katayama, 1956), the author found a new form of this compound which has strikingly almost the same cell dimensions and belongs to the same space group as the one analysed by Dejace (1955). The former was named tentatively an unstable form and the latter the stable one. In the following, we shall call the former the β-form and the latter the α-form.

The difference between the cell dimensions and space groups of these two forms (Table 1) is found only in the value of β, β being 98° 49′ in the α-form and 102·5° in the β-form. Penfold & Simpson (1956) recently reported