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The Cooperative Jahn–Teller Distorted Structures of Rubidium Chromium(II) Trichloride and Caesium Chromium(II) Trichloride

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Abstract. β-$RbCrCl_3$ (at 295 K), monoclinic, $C2/m$ (C^3_{2h}), $a = 12\cdot224$ (4), $b = 7\cdot040$ (3), $c = 6\cdot250$ (3) Å, $\beta = 93\cdot34$ (5)°, $V = 537\cdot68$ Å^3, $Z = 4$, $D_x = 3\cdot008$, $D_m = 3\cdot01$ g cm^{-3} [Seifert & Klatyk (1964). *Z. Anorg. Allg. Chem.* **334**, 113–124]. This phase has a slightly distorted hexagonal perovskite structure and consists of chains of alternating elongated and compressed face-sharing octahedra. Below 170 K $CsCrCl_3$ is isomorphous with β-$RbCrCl_3$.

Introduction. $RbCrCl_3$ and $CsCrCl_3$ were prepared by melting equimolar amounts of RbCl (CsCl) and $CrCl_2$ in an evacuated quartz tube and crystallized by the Bridgman method.

Single-crystal measurements were performed on a three-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. 1512 reflections from a crystal of $RbCrCl_3$ (0·07 × 0·16 × 0·36 mm) were measured. All data were corrected for absorption.

Powder neutron diffraction experiments on $CsCrCl_3$ at 5 and 60 K were carried out at the HFR reactor at Petten. A Ge double monochromator ($\lambda = 2\cdot403$ Å) was used to avoid second-order contamination. Collimators of 15′ were applied in front of the monochromator and the detector.

From systematic absences (hkl, $h + k = 2n + 1$) the space group appeared to be $C2/m$, Cm or $C2$. The cell constants are given in Table 1, together with the results of X-ray powder diffraction for $RbCrBr_3$.

Starting with small deviations from the $CsNiCl_3$ structure (Tishenko, 1955) the positional and thermal parameters of $RbCrCl_3$ were refined for all three possible space groups. The final discrepancy indices are given in Table 2.* The final difference Fourier synthesis in space group $C2/m$ gives some negative and positive peaks in the neighbourhood of the heaviest ions (Rb^+ and Cr^{2+}). The positional parameters of this refinement are given in Table 3 together with the results of the powder neutron diffraction refinement of $CsCrCl_3$ ($R = 0\cdot075$ for both 5 and 60 K).†‡

Discussion. Cr^{2+} compounds are difficult to prepare because of their fast oxidation. In octahedral coordination Cr^{2+} exhibits an $E \otimes \varepsilon$ Jahn–Teller effect.§ For these reasons good structure determinations are relatively scarce. Therefore it seemed of interest to study the structures of $RbCrCl_3$ and $CsCrCl_3$.

By means of temperature-dependent powder X-ray diffraction, we found that above 470 K $RbCrCl_3$ has a hexagonal structure (α phase) and that below 470 K it is monoclinic (β phase). With DTA another transition at 201 K was detected, which implies the existence of a third phase (γ). $CsCrCl_3$ is hexagonal (McPherson, Kistenmacher, Folkers & Stucky, 1972) above 170 K (detected by DTA) and below 170 K it is isomorphous with β-$RbCrCl_3$.

Table 1. *Cell constants of* $RbCrCl_3$, $CsCrCl_3$ *and* $RbCrBr_3$

	$RbCrCl_3$ (295 K)	$CsCrCl_3$ (60 K)	$CsCrCl_3$ (5 K)	$RbCrBr_3$ (295 K)
a (Å)	12·224 (4)	12·523 (2)	12·508 (3)	12·885 (4)
b (Å)	7·040 (3)	7·152 (1)	7·145 (1)	7·428 (3)
c (Å)	6·250 (3)	6·171 (1)	6·164 (1)	6·591 (2)
β (°)	93·34 (5)	91·38 (1)	91·41 (1)	93·94 (3)

Table 2. *Final discrepancy indices of* $RbCrCl_3$

	R_w	R	Number of reflections	Number of parameters
$C2/m$	0·0991	0·0784	641	30
	0·1263	0·0963	1127	30
Cm	0·0802	0·0671	647	53
$C2$	0·1233	0·0939	1127	45

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* The calculations were carried out on the Leiden University IBM 370/158 computer using programs written or modified by Mrs Rutten-Keulemans and Dr de Graaff.

† These calculations were performed on the CDC 6600 computer of the ECN, Petten, using a powder intensity profile refinement program of Rietveld (1969).

‡ Lists of structure factors for both compounds and anisotropic thermal parameters for $RbCrCl_3$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33380 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

§ $\otimes$ is a symbol linking two representations in a direct-product representation.

Table 3. *The positional parameters of* $RbCrCl_3$ *and* $CsCrCl_3$(60 K)

	$CsCrCl_3$			$RbCrCl_3$		
	x	*y*	*z*	*x*	*y*	*z*
Cs/Rb 4(*i*)	0·339 (4)	0	0·739 (9)	0·334 (2)	0	0·754 (2)
Cr(1) 2(*a*)	0	0	0	0	0	0
Cr(2) 2(*e*)	0	0	0·500	0	0	0·500
Cl(1) 4(*i*)	0·158 (2)	0	0·282 (3)	0·164 (3)	0	0·307 (4)
Cl(2) 8(*j*)	0·076 (1)	0·238 (2)	0·762 (2)	0·081 (3)	0·241 (2)	0·780 (3)

Table 4. Cr—Cl *distances* (Å) *in* $RbCrCl_3$ *and* $CsCrCl_3$

	$RbCrCl_3$(295 K)	$CsCrCl_3$(60 K)	
Cr(1)—Cl(1)	2·69 (3)	2·67 (2)	(2×)
Cr(1)—Cl(2)	2·43 (2)	2·43 (5)	(4×)
Average	2·52 (3)	2·51 (3)	
Cr(2)—Cl(1)	2·40 (3)	2·36 (2)	(2×)
Cr(2)—Cl(2)	2·59 (2)	2·55 (5)	(4×)
Average	2·53 (3)	2·49 (3)	

Single crystals were grown above the transition point. At the transition temperature the hexagonal crystals have three possibilities of changing to the monoclinic phase and therefore a single crystal of $RbCrCl_3$ in the β phase could only be obtained by carefully crushing a twinned crystal. For this reason a single crystal of $CsCrCl_3$ below 170 K could not be obtained. However, powder neutron diffraction data were available.

For statistical reasons space group *Cm* should be preferred (Hamilton, 1965). However, because of the non-ideal absorption correction and the possibility of stacking faults due to the transition we fear that the errors in the structure factors are not random. Moreover, because of the high correlations between the positional parameters of the Cl ions and the improbable results for the thermal ellipsoids in *Cm*, we prefer the description in the space group *C*2/*m*.

Oscillation photographs of $RbCrCl_3$ at 150 K show a doubling of the *c* axis. Perhaps the anisotropic motion of the Cl(2) ions along the *c* axis in the β phase is related to the γ phase. Further investigations of the γ phase are planned.

The most striking difference when compared with the $CsNiCl_3$ structure is the change of the *z* parameters of the Cl ions. The result is a distortion of the $CrCl_6$ octahedra. We found around Cr(1) two long and four short Cr—Cl distances and around Cr(2) two short and four long Cr—Cl distances (Table 4). For comparison the average Cr—Cl distances in $CrCl_2$ (Tracey, 1961), Rb_2CrCl_4 (Fair, Gregson, Day & Hutchings, 1977) and Cs_2CrCl_4 (Hutchings, Gregson, Day & Leech, 1974) are 2·57, 2·54 and 2·53 Å respectively.

This implies that the structure consists of chains of face-sharing alternating elongated and compressed 'D_{4h}' octahedra. The unique axes of the octahedra lie in planes parallel to the mirror plane.

We believe that the $E \otimes \varepsilon$ Jahn–Teller interaction is responsible for this structure. Apparently the warping term and second-order Jahn–Teller effect, which tend to a three-state model, are less effective than in $CsCuCl_3$ (Kroese, 1976).

The strain components e_{xz}, e_{yz} (E_{1g} in D_{6h}) in combination with orbital overlap seem to determine the phase transition.

If we try to explain the α phase of $RbCrCl_3$ and $CsCrCl_3$ as a time averaging of the three possibilities of the β phase, we would expect a $P6_3/mmc$ (D_{6h}^4) structure with large anisotropic motions of the Cl ions along the *c* axis.

It should be remarked that no indication of magnetic ordering in $CsCrCl_3$ has been found at 5 K.

We are performing further structural and magnetic investigations of the phases of these compounds.

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