

SHORT STRUCTURAL PAPERS

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The Cooperative Jahn–Teller Distorted Structure of γ -Rubidium Chromium(II) Trichloride*

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Abstract. γ -RbCrCl₃ (at ~ 100 K), monoclinic, $C2$, $a = 12.109$ (3), $b = 6.962$ (4), $c = 12.438$ (8) Å, $\beta = 93.94$ (4)°, $V = 1046.08$ (94) Å³, $Z = 8$, $D_x = 3.09$ Mg m⁻³. γ -RbCrCl₃ undergoes a transition to the previously determined β -RbCrCl₃ phase at 201 K [Crama, Maaskant & Verschoor (1978), *Acta Cryst.* B **34**, 1973–1974]. It has a slightly distorted hexagonal perovskite structure, which is related to the β phase and consists of chains of elongated face-sharing octahedra.

Introduction. The preparation of RbCrCl₃ has been described earlier (Crama, Maaskant & Verschoor, 1978). Single-crystal measurements were performed on a three-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation; 3068 reflections were measured at 100 ± 5 K. From systematic absences

* Dedicated to Professor E. Havinga on the occasion of his 70th birthday.

Table 1. Comparison of the cell constants of γ -RbCrCl₃ and β -RbCrCl₃

	γ -RbCrCl ₃	β -RbCrCl ₃
a (Å)	12.109 (3)	12.224 (4)
b (Å)	6.962 (4)	7.040 (3)
c (Å)	12.438 (8)	6.250 (3)
β (°)	93.94 (4)	93.34 (5)

(hkl ; $h + k = 2n + 1$) the space group could be $C2/m$, $C2$ or Cm . The cell constants are given in Table 1. From Patterson analyses, the existence of a mirror plane could be excluded and therefore the space group is $C2$. The positional parameters of γ -RbCrCl₃ were refined with starting values from β -RbCrCl₃ (Crama *et al.*, 1978). The final discrepancy indices are $R = 0.0947$ and $R_w = 0.1107$ † (1403 significant reflections, 64 parameters). We refined Cr²⁺ and Rb⁺ with anisotropic and Cl⁻ with isotropic temperature factors. The final difference Fourier synthesis had no peaks larger than 1.5 times the standard deviation and no physical meaning could be connected with these peaks. The positional parameters of this refinement are given in Table 2.‡

Discussion. As has been stated earlier (Crama *et al.*, 1978), RbCrCl₃ exhibits an $E \otimes \epsilon$ cooperative effects.§

† The calculations were carried out on the Leiden University IBM 370/158 computer using programs written or modified by Mrs E. W. M. Rutten-Keulemans and Dr R. A. G. de Graaff.

‡ Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34389 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

Table 2. The positional parameters of γ -RbCrCl₃

The labeling of the atoms is the same as in the β phase. Cl(2) splits into Cl(2) and Cl(3) because of the disappearance of the mirror plane.

$$z_{\text{Rb}(a)} \approx z_{\text{Rb}(b)} - 0.5 \text{ etc.}$$

		x	y	z		x	y	z	
Rb(a)	4(c)	0.3375 (2)	0.0447 (9)	0.3779 (2)	Rb(b)	4(c)	0.3304 (2)	0.0093 (9)	0.8796 (2)
Cr(1 a)	2(a)	0.0	0.0	0.0	Cr(1 b)	2(b)	0.0	0.0647 (7)	0.5
Cr(2)	4(c)	0.0025 (3)	0.0339 (12)	0.2477 (3)	Cl(1 b)	4(c)	0.1637 (3)	0.0411 (13)	0.6597 (4)
Cl(1 a)	4(c)	0.1688 (5)	0.0111 (16)	0.1555 (5)	Cl(2 b)	4(c)	0.0773 (4)	0.2396 (12)	0.8924 (4)
Cl(2 a)	4(c)	0.0886 (5)	0.2978 (13)	0.4001 (5)	Cl(3 b)	4(c)	0.0796 (4)	-0.2441 (12)	0.8886 (4)
Cl(3 a)	4(c)	0.0800 (5)	-0.1884 (13)	0.3902 (6)					

Below 470 K this results in a monoclinic structure (β phase). Another phase transition at 201 K at which the c axis doubles was detected by DTA. We have determined the structure below 201 K (γ phase). This γ phase contains chains of face-sharing elongated CrCl_6 octahedra. There are three possible elongations: along the $x(x')$, $y(y')$ and $z(z')$ directions, defined in Fig. 1(b). The elongation sequence we have found in $\gamma\text{-RbCrCl}_3$ is: z, x', z, y', z etc. (see Fig. 1 and Table 3). The fact that for the first transition (α - β) there are three possibilities (one of the three twofold axes perpendicular to the c axis in the α phase is preserved in the β phase) and for the second (β - γ) another two possibilities (z, x', z, y' etc. and z, y', z, x' etc.) is probably the reason why no single crystal of $\gamma\text{-RbCrCl}_3$ without disorder could be obtained. This is reflected in the relatively high R indices. We have tried several models which lead to small differences in the final parameters, but always give the same elongated-octahedra configuration.

Table 3. Cr-Cl distances (\AA) in $\gamma\text{-RbCrCl}_3$

Octahedra around Cr(1a) and Cr(1b) are elongated along the z direction. Octahedra around Cr(2) are alternately elongated along the x' and y' directions.

Cr(1a)-Cl(1a)	2.72 (2)	Cr(1b)-Cl(1b)	2.71 (2)
Cr(1a)-Cl(2b)	2.37 (4)	Cr(1b)-Cl(2a)	2.35 (5)
Cr(1a)-Cl(3b)	2.43 (4)	Cr(1b)-Cl(3a)	2.46 (6)
Cr(2)-Cl(1a)	2.39 (6)	Cr(2)-Cl(2b)	2.41 (5)
Cr(2)-Cr(1b)	2.39 (6)	Cr(2)-Cl(3a)	2.48 (6)
Cr(2)-Cl(2a)	2.79 (4)	Cr(2)-Cl(3b)	2.71 (3)

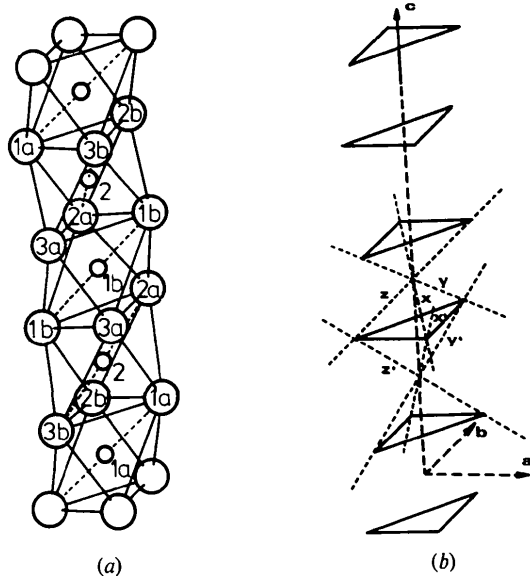


Fig. 1. (a) Part of the unit cell of $\gamma\text{-RbCrCl}_3$. Small circles are Cr^{2+} ions and large circles are Cl^- ions. Broken lines inside the CrCl_6 octahedra show the positions of the long axes. (b) The unit-cell axes and labeling of the octahedral axes in the two differently orientated octahedra.

Probably the less intense reflections are more influenced by the amount of disorder. When we refined the reflection set by restricting ourselves to reflections with $F > 40$ and $F > 60$ the values $R_w = 0.0874$ and $R_w = 0.0730$, respectively, are found (with a non-significant change of the parameters).

One can describe the Jahn-Teller distortion of a regular octahedron by two variables q and φ (see Fig. 2). The variable q is a measure of the magnitude of the distortion. $q = (q_\theta^2 + q_\epsilon^2)^{1/2}$, $\varphi = \text{tg}^{-1}(q_\epsilon/q_\theta)$, $q_\theta = 1/(12)^{1/2}(2Z - X - Y)$ and $q_\epsilon = \frac{1}{2}(X - Y)$ [X , Y and Z are the distances between the Cl^- ions along the $x(x')$, $y(y')$ and $z(z')$ directions, respectively, within the octahedron].

In Table 4 the variable q is given for the three different octahedra, where it is assumed that oppositely placed Cl^- ions lie on three orthogonal axes. The distortions of the three octahedra are all of about the same magnitude. The q value of the compressed octahedron in the β phase [Cr(2)] is almost half the value found in the γ phase (see Table 4). It is very probable (see Fig. 2) that the β phase is an averaged or dynamical structure of the γ phase, in a similar way to that described by Mullen, Heger & Reinen (1975) and Reinen (1977). In $\beta\text{-RbCrCl}_3$ the elongations along the x' and y' directions become averaged to an apparent compression along the z' direction around Cr(2), whereas the deformation around Cr(1) remains an elongation along the z direction; it is possible that this is not completely independent of the Cr(2) neighbour. The smaller q value of Cr(1) in the β phase should therefore be noted. Averaging of the γ positional

Table 4. q values (\AA) of the distorted octahedra in RbCrCl_3

	γ -Phase	β' -Phase	β -Phase	β -Phase (CsCrCl_3)
Cr(1a)	0.37 (5)	0.37 (7)	0.30 (4)	0.28 (6)
Cr(1b)	0.35 (7)	0.37 (7)	0.30 (4)	0.28 (6)
Cr(2)	0.38 (8)	0.23 (8)	0.22 (4)	0.22 (6)

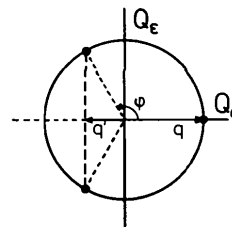


Fig. 2. Description of the magnitude (q) and the angular variable (φ) of the Jahn-Teller distorted octahedron (Eng'lman, 1971). $\varphi = 0, 120$ and 240° means elongation along the z, x and y directions respectively. The result of averaging over two octahedra elongated along x and y , respectively, is apparently a compressed octahedron with $\varphi = 180^\circ$ and $q' = \frac{1}{2}q$.

parameters does indeed give a β phase (β') with the correct q value for the 'compressed' octahedron.

The super-reflections induced by the doubling of the c axis are difficult to find in the powder diffraction patterns. It is therefore possible that CsCrCl_3 (Crama *et al.*, 1978) at 5 K also has a doubled c axis or all elongated octahedra, again on the basis of the magnitude of the distortion of the 'compressed' octahedron.

So it seems that the Cr^{2+} compounds, like the Cu^{2+} compounds, possess only elongated CrCl_6 octahedra. Unlike CsCuCl_3 (Schlueter, Jacobson & Rundle, 1966), however, the elongated axes do not form a screw-like configuration.

Details of the theoretical background of this type of ordering of ' D_{4h} ' octahedra, in comparison with CsCuCl_3 , will be published elsewhere.

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Structure of Scolecite from Poona, India

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Abstract. $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$, monoclinic, Cc , $a = 6.5174$ (4), $b = 18.956$ (2), $c = 9.7647$ (9) Å, $\beta = 108.860$ (8)°, $V = 1141.6$ Å³, $Z = 4$, $D_m = 2.28$, $D_c = 2.28$ Mg m⁻³, $R = 0.032$. The aluminosilicate framework of scolecite is isotypical with the framework of natrolite, except for a small monoclinic distortion. The Ca ion coordinates three water and four framework O atoms in a distorted pentagonal bipyramid.

Introduction. Scolecite is a widespread fibrous zeolite in the natrolite group and generally occurs in the cavities of basaltic rocks, in schists and in contact zones.

Proposals for the scolecite crystal structure have been made by Pauling (1930), Taylor, Meek & Jackson (1933) and Ivleva & Gabuda (1972). Our study was undertaken to determine the structure of scolecite and its relation to natrolite, since no study based on sufficient experimental data was found.

The material was taken from a specimen containing clear prismatic crystals of scolecite and some laumontite. The composition $\text{Ca}_{0.98}\text{Al}_{1.93}\text{Si}_{3.07}\text{O}_{10}\cdot 3.01\text{H}_2\text{O}$ (plus traces of Na) was obtained by AA spectrophotometry (Perkin–Elmer 306) and a determination of the water loss (300 mg zeolite, 1323 K for 1 h). The cell dimensions were refined by least squares from 42 single indexed lines of a powder pattern obtained in a

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Guinier–Hägg focusing camera with Cu $K\alpha_1$ radiation. This powder pattern differed from published data (JCPDS Powder Diffraction File 26-1048) mainly in the indexing of the reflexions. The unit cell of Smith & Walls (1971) was redefined to give the conventional space group Cc .

Owing to extensive twinning the crystals were crushed and a thin plate (0.110 × 0.080 × 0.020 mm) was selected with the Weissenberg technique. Systematic absences were $hkl: h + k = 2n + 1$ and $h0l: l = 2n + 1$.

Information concerning the collection and reduction of the intensities and the refinement are given in Table 1. A CAD-4 four-circle diffractometer was used. A refinement of 49 accurately measured θ values confirmed the cell parameters.

During the data collection no systematic variation was observed in two standard reflexions which were checked every 2 h. I and $\sigma_c(I)$ (based on counting statistics) were corrected for Lorentz and polarization effects.

It was assumed that the aluminosilicate frameworks of scolecite and natrolite are identical and consequently the five independent positions of Al and Si in the $Fdd2$ cell of natrolite (Meier, 1960) were transformed into the scolecite cell. Full-matrix least-squares