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The Jahn–Teller Effect in the Structures of Caesium Chromium(II) Trichloride and Casesium Chromium(II) Triiodide

BY W. J. CRAMA AND H. W. ZANDBERGEN

Gorlaeus Laboratoria, PO Box 9502, Leiden, The Netherlands

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Abstract

α -CsCrCl₃ and α -CsCrI₃ (at 295 K) are hexagonal, space group $P6_3/mmc$ (D_{6h}^4), with respectively, $a = 7.257$ (3), $c = 6.238$ (2) Å, $V = 284.5$ (3) Å³, $D_c = 3.412$ (3) Mg m⁻³, $\mu(\text{Mo } K\alpha) = 9.49$ mm⁻¹ and $a = 8.107$ (3), $c = 6.917$ Å, $V = 393.7$ (5) Å³, $D_c = 4.788$ (4) Mg m⁻³, $\mu(\text{Mo } K\alpha) = 17.31$ mm⁻¹; $Z = 2$. Final R values are 0.034 and 0.027 for 421 and 289 significant reflexions respectively. These high-temperature phases have a slightly distorted BaNiO₃ structure. This distortion is predominantly related to the local Jahn–Teller effect, which leads to elongated octahedra. The elongation can occur along one of the three principal axes of the octahedron. A new model is introduced, which takes into account the existence of octahedra with randomly distributed elongation directions.

Introduction

Most of the ABX_3 compounds ($A = \text{Rb, Cs}$; $X = \text{Cl, Br, I}$ and $B = 3d$ transition element) have the BaNiO₃ structure (without a Jahn–Teller-active B ion, e.g. CsNiCl₃, Tishenko, 1955). When B is a Jahn–Teller-active ion, Cr²⁺ or Cu²⁺, small but definite distortions from this type of structure at lower temperatures are known (CsCuCl₃: Schlueter, Jacobson & Rundle, 1966; RbCrCl₃ and CsCrCl₃: Crama, Maaskant & Verschoor, 1978; Crama, Bakker, Maaskant & Verschoor, 1979; and CsCrI₃: Zandbergen & IJdo,

1980). The high-temperature phases (α phases) of these compounds seem to possess hexagonal symmetry. In all known cases (CsCrCl₃: McPherson, Kistenmacher, Folkers & Stucky, 1972; CsCrBr₃: Li & Stucky, 1973; CsCrI₃: Guen, Marchand, Jouini & Verbaere, 1979; and CsCuCl₃: Kroese, Maaskant & Verschoor, 1974) the space group is not uniquely determined. Two possibilities have been reported: $P6_3/mmc$, as found for instance for the undistorted CsMgCl₃ (McPherson, Kistenmacher & Stucky, 1970), or $P6_3mc$ in which Cu and Cr are irregularly surrounded by X ions and which has been reported to be the most probable arrangement. In both space groups a strongly anisotropic thermal motion of the X ions along the c axis has been found. This is not usual for X ions in the BaNiO₃ structure, e.g. CsMgCl₃ and CsNiCl₃.

In connexion with the interest of our department in the cooperative Jahn–Teller effect, we redetermined the crystal structure of α -CsCrCl₃ and isomorphous α -CsCrI₃, with the assumption that the α phases are still Jahn–Teller distorted. Strong indications for this thesis were found in the description of the ligand-field spectra of CsCrCl₃ and RbCrCl₃ (Köhler, 1976) and other measurements of spectra (McPherson *et al.*, 1970; Alcock, Putnik & Holt, 1976). γ -CsCrCl₃* and γ -RbCrCl₃ contain tetragonal distorted CrCl₆ octahedra, which implies a more complicated ligand-field

* Recent investigations have revealed a doubling of the c axis of CsCrCl₃ below its transition temperature. This phase is analogous to γ -RbCrCl₃ rather than to β -RbCrCl₃.

spectrum than for regularly surrounded Cr ions. This is indeed found, but the spectra do not change on going from the γ or β phase to the α phase. Our interpretation is that the CrCl₆ octahedra in the α phase are still tetragonal (D_{4h}) distorted, in contradiction to the results of the structure reported for α -CsCrCl₃ and α -CsCrI₃.

Taking into account the low-temperature structures together with the above-mentioned arguments, we have redetermined the structures of α -CsCrCl₃ and α -CsCrI₃, using a new model.

Experimental

Single crystals of CsCrCl₃ and CsCrI₃ were grown using the Bridgman method. The compounds were prepared by melting a stoichiometric mixture of the binary compounds. CrI₂ was prepared and sublimated in an almost horizontal evacuated glass tube with a temperature region of 1223 K (Cr-side)–473 K (I₂-side). CrCl₂ was prepared by passing dry hydrogen chloride over Cr flakes at approximately 1143 K.

The crystal symmetries of the hexagonal unit cells were determined from zero and upper-level Weissenberg photographs. Systematically absent reflexions show the space group to be $P6_3/mmc$, $P6_2c$ or $P6_3mc$ for both compounds.

The crystals were mounted along the [001] direction on an Enraf–Nonius three-circle diffractometer. Single-crystal data are given in the *Abstract* and details of intensity-data collection in Table 1. All crystallographic calculations were carried out on the Leiden University IBM 370/158 computer using a set of computer programs written or modified by Rutten-Keulemans and de Graaff. A correction for absorption

Table 1. *Details of intensity-data collection for α -CsCrCl₃ and α -CsCrI₃ (295 K)*

	CsCrCl ₃	CsCrI ₃
λ (Mo K α)	0.71069 Å	
Bragg angle (°)	4–40	4–30
Scan type	ω	
Scan angle (°)	$1.9 + 1.0 \tan \theta$	$1.2 + 0.8 \tan \theta$
Monochromator	Graphite	
Reflections used for absorption correction	002, 004, 006	002, 004
Crystal dimensions (mm)	0.1 × 0.2 × 0.5	0.1 × 0.1 × 0.35
Systematically absent reflexions	$hh2hl:l = 2n + 1$	
Measured reflexions	3197	2574
Independent reflexions		
Significant	421	289
Non-significant	84	104
Independent reflexions with averaging of the reflexions hkl and $\bar{h}\bar{k}\bar{l}$		
Significant	343	211
Non-significant	35	59

was made with a program developed by de Graaff (1973). Scattering factors and anomalous-dispersion corrections for all ions were taken from *International Tables for X-ray Crystallography* (1962). After correction for Lorentz and polarization effects the intensities were reduced to F_o values. The function minimized during the least-squares refinement process was $w_F(F_o - F_c)^2$ using the weighting scheme $w_F = 1/\sigma_F^2$ (σ_F : standard deviation of F_o).

In the refinements two models are introduced to try to describe the effect of the Jahn–Teller distortion, *viz.* model *A*, derived theoretically and related to β -CsCrI₃ (disordered over three *X* ion sites, space group $P6_3/mmc$), and model *B*, more related to γ -CsCrCl₃ (disordered over four *X* ion sites, space group $P6_3/mmc$). Furthermore a model *C* was introduced, which has already been used in the refinements of α -CsCrCl₃ by McPherson (disordered over two *X* ion sites, space group $P6_3/mmc$). Finally, models *D* (ordered, space group $P6_3/mmc$) and *E* (ordered, space group $P6_3/mc$) were refined for comparison of the results.

The refinements were carried out in such a way that all parts of the Cl[−] ion have the same isotropic thermal parameter. As can be seen from Table 4, no significant changes in the *R* values of the models *A* and *B* occur, if we allow the thermal parameter to be anisotropic. In the case of α -CsCrI₃ a considerable lowering of the *R* indices has been found by the introduction of anisotropic thermal parameters for the I[−] ion, probably because of the higher polarizability of the I[−] ion. In Table 5 we give only the results for the anisotropic refinement.

The results of the full-matrix refinement of all parameters and extinction correction of the best fitting models, *viz.* models *A* and *B* in space group $P6_3/mmc$, are given in Tables 2 and 3. Refinements of models *A* and *B* in the other possible space groups give no

Table 2. *Positional parameters of α -CsCrCl₃ of models A and B (with isotropic thermal parameters for the parts of the Cl[−] ion)*

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Model
Cs	2(<i>d</i>)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	2.87 (2)	<i>A, B</i>
Cr	2(<i>a</i>)	0	0	0	1.98 (3)	<i>A, B</i>
Cl(1)	12(<i>k</i>)	0.1613 (1)	−0.1613 (1)	0.2873 (3)	2.30 (3)	<i>A</i>
	12(<i>k</i>)	0.1647 (5)	−0.1647 (5)	0.2978 (13)	2.33 (3)	<i>B</i>
Cl(2)	6(<i>h</i>)	0.1501 (3)	−0.1501 (3)	0.25	2.30 (3)	<i>A</i>
	12(<i>k</i>)	0.1543 (2)	−0.1543 (2)	0.2688 (9)	2.33 (3)	<i>B</i>

Table 3. *Positional parameters of α -CsCrI₃ of models A and B*

		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Model
Cs	2(<i>d</i>)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.87 (3)	<i>A, B</i>
Cr	2(<i>a</i>)	0	0	0	2.07 (5)	<i>A, B</i>
I(1)	12(<i>k</i>)	0.1677 (2)	−0.1677 (2)	0.2840 (5)	2.48 (9)	<i>A</i>
	12(<i>k</i>)	0.1707 (11)	−0.1707 (11)	0.2946 (11)	2.66 (9)	<i>B</i>
I(2)	6(<i>h</i>)	0.1555 (5)	−0.1555 (5)	0.25	2.48 (9)	<i>A</i>
	12(<i>k</i>)	0.1597 (5)	−0.1597 (5)	0.2672 (8)	2.66 (9)	<i>B</i>

Table 4. Discrepancy indices resulting from different models for α -CsCrCl₃ (%)

Model	(a)			(b)		
	R_w	R	N	R_w	R	N
A	3.67	3.40	9	3.31	3.10	12
B	3.77	3.47	10	3.46	3.21	13
C	4.89	4.08	8	3.47	3.26	11
D	10.94	8.23	7	5.40	4.50	8
E	7.78	6.08	9	3.71	3.55	12

The values (a) represent the isotropic thermal Cl⁻ ion refinements and (b) the anisotropic thermal Cl⁻ ion refinements. N represents the number of parameters.

Table 5. Discrepancy indices resulting from different models for α -CsCrI₃ (%)

Model	R_w	R	N
A	2.84	2.67	12
B	2.80	2.64	13
C	6.03	4.25	11
D	6.44	4.69	8
E	3.75	3.49	12

significant lowering of the final discrepancy indices and are not reported. After averaging of the reflexions hkl and $\bar{h}\bar{k}\bar{l}$, refinements of all parameters converged for α -CsCrCl₃ to $R_w = 0.037$ and $R = 0.034$ and for α -CsCrI₃ to $R_w = 0.028$ and $R = 0.027$ in model A or B. The final discrepancy indices of the different model refinements are listed in Tables 4 and 5.*

Discussion

From visual-near-infrared (VIS-NIR) spectra of CsCrCl₃ as a function of temperature, we find evidence that locally Jahn-Teller-distorted CrCl₆ octahedra are present in the α phase. McPherson *et al.* attributed the difference between the structures of CsCrCl₃ and CsMgCl₃ to the Jahn-Teller effect. However, their conclusion that the space group of α -CsCrCl₃ is $P6_3mc$ (our model E) is not logical in relation to a Jahn-Teller effect. No simple explanation in connexion with a Jahn-Teller effect can be given for the high-temperature structures with space group $P6_3mc$ (three short and three long Cr-X distances).

A difference Fourier analysis of the results of the refinement of model D showed positive peaks on both sides of the mirror plane (001) near the position of the X ion at $z = 0.25$. This result suggests the existence of

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35908 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

a (001) mirror plane and the space group $P6_3mc$ reported for α -CsCrCl₃ (McPherson *et al.*) and α -CsCrI₃ (Guen *et al.*) not to be correct.

Because in the low-temperature phases only elongated octahedra have been found and the VIS-NIR spectra of γ or β and α phases seem identical, we assume the existence of elongated octahedra also above the phase transition, where the α phase is the phase in which each elongation direction has an equal chance to appear. To show how one can account for the Jahn-Teller effect in the α phase, we first explain model A. Assuming that only tetragonally elongated octahedra are present, having two long (L) and four short (S) Cr-X bonds, three identical distortions can occur, which can be represented by the axes which are elongated, *viz.* x , y or z , all being distortions of the Q_3 type (Fig. 1).* The principal x , y and z axes of the CrX₆ octahedra are defined in Fig. 2.

In the case of a random distribution of elongated octahedra four possible situations can appear around an X ion: two long axes are intersecting on X: xx (Fig. 3d), two short axes are intersecting on X: yy, yz, zy, zz (Fig. 3a), a long and a short axis are intersecting on X: xy, xz (Fig. 3b) and a short and a long axis are intersecting on X: yx, zx (Fig. 3c), where, for example, zx means the upperlying octahedron is elongated

* The elongations of the Q_3 type along the x , y and z axes can be described by $Q_x = (-Q_3 + \sqrt{3}Q_2)/2$, $Q_y = (-Q_3 - \sqrt{3}Q_2)/2$ and $Q_z (=Q_3)$.

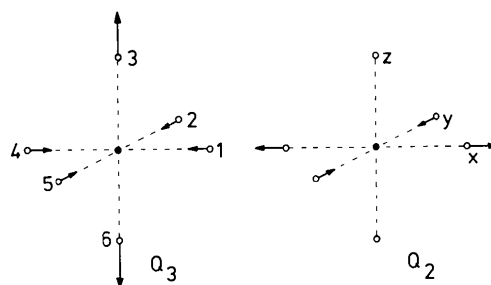


Fig. 1. Q_3 and Q_2 types of distortion of an octahedron.

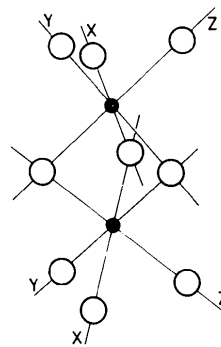


Fig. 2. Definition of the local x , y and z axes of the face-sharing octahedra. The x axes of neighbouring CrX₆ octahedra are intersecting on the same X ion.

along its z axis and the underlying along its x axis. We omit the possibility shown in Fig. 3(d) (e.g. xx , but also yy and zz), in the first place on crystallographic grounds, since this X shift results in a very small Cs– X distance, and secondly because no significant electron density was found in a difference Fourier analysis of models A , B and D at that position.

In the case of a random distribution of the long octahedron axes, excluding xx , yy and zz , six configurations are left yielding three possible X ion positions (see Fig. 4a) which are equally occupied (model A) [Fig. 3(a): yz, zy , $X(2)$ ion position: $x_2, \bar{x}_2, 0.25$, Fig. 3(b): xy, xz , $X(1)$ ion position: $x_1, \bar{x}_1, 0.25 + \delta$ and Fig. 3(c): yx, zx , $X(1)$ ion position: $x_1, \bar{x}_1, 0.25 - \delta$].

In the undistorted structure the face-sharing octahedra are built up from triangles of X ions equidistant between the Cr^{2+} ions. Since one triangle of X ions is part of two octahedra, the displacements of the X ions will be a combination of the distortion mode of the Q_3 type of the underlying as well as the upperlying Cr^{2+} ion. The local deformation around the Cr^{2+} ion in model A can be approximated by a canting of the triangles around $[100]$ (see Fig. 5). This deformation is characteristic (Crama, 1980) for one component of the symmetry mode transforming as E_{1g} ($k = 0,0,0$) or B_{3g} ($k = \pi/a, 0,0$), which becomes static in β -CsCrI₃. In γ -CsCrCl₃ the other component with E_{1g} symmetry, which is a canting of the triangle orthogonal to the one described above (around $[110]$; see Fig. 5), is partly present (Crama, 1980). Model B tries to describe an average X ion distribution, which is related to that component. In model B two thirds of the X ions are situated at $x_2, \bar{x}_2, 0.25 \pm \delta_2$ and one third is at $x_1, \bar{x}_1, 0.25 \pm \delta_1$ (Fig. 4b). Combinations of these types of distortion lead also to compressed CrX_6 octahedra and

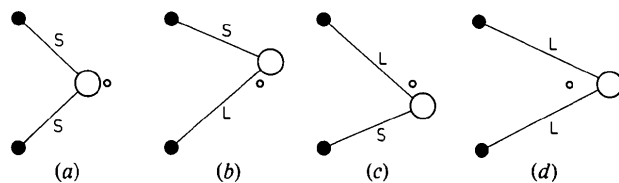


Fig. 3. The four possibilities which can occur around an X ion concerning the long and short axes of the elongated octahedra. The filled circles represent Cr^{2+} ions, the open circles an X ion and the small open circles the X ion position without a Jahn–Teller distortion. L represents a long octahedron axis and S a short octahedron axis.

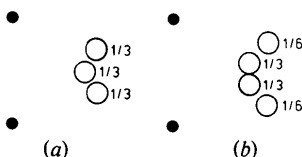


Fig. 4. Schematic picture of the models (a) A and (b) B .

therefore are an indication whether other (Q_2, Q_3) distortions than those of the Q_3 type are present.

Comparison of the R values of the five models (see Tables 4 and 5) favours models A and B , because of their lower R indices. Also the almost isotropic description of the X ions in the models A and B , in contrast to models E and D , favours models A and B , which shows that the large anisotropic motion as found in previous studies can be fully ascribed to the locally distorted Jahn–Teller octahedra.

Both models A and B are able to describe the Jahn–Teller distortions with about the same discrepancy indices.

It is difficult to discriminate between models A and B , though model A is preferred because it is theoretically expected. Because of the large thermal overlap of the X ion contributions, model B resembles model A . A continuous distribution of (Q_2, Q_3)

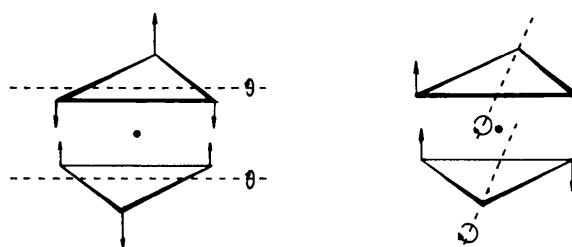


Fig. 5. Canting of the two X triangles of a CrX_6 octahedron around $[110]$ for γ -CsCrCl₃ (left) and $[100]$ for β -CsCrI₃ (right). The Cr^{2+} ion is represented by a filled circle.

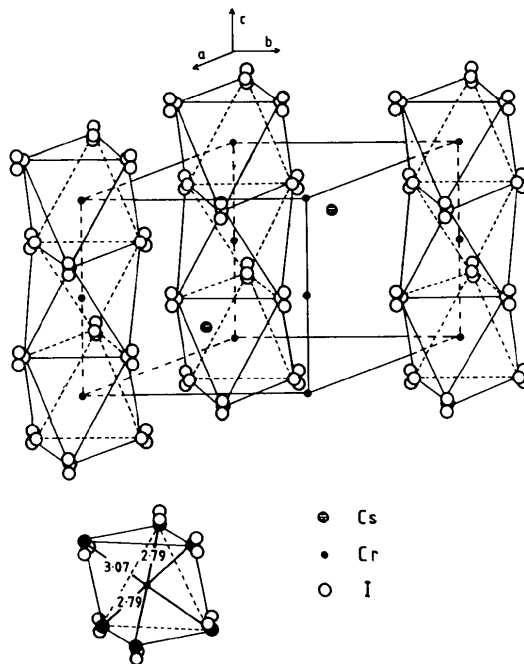


Fig. 6. The unit cell of α -CsCrI₃ with the I^- ions distributed over three positions (model A). One of the chains is omitted for the sake of clarity. Below, an example of the distortion is given.

Table 6. x and z parameters of the Cl^- ions in $\gamma\text{-RbCrCl}_3$ and the I^- ions in $\beta\text{-CsCrI}_3$ transformed to the hexagonal unit cell

	x	z		x	z
$\text{Cl}(1)$	0.161	0.289	$\text{I}(1)$	0.167	0.283
$\text{Cl}(2)$	0.158	0.269	$\text{I}(2)$	0.156	0.25

solutions of the linear Jahn–Teller problem is also possible, yielding a banana-shaped distribution. However, the ligand-field spectra of RbCrCl_3 and CsCrCl_3 point to model *A* having the highest probability (Crama, 1980). In Fig. 6 the structure, found from refinement of model *A*, is depicted.

It is worth noting the very good correspondence of the x and z parameters of the disordered X ions with the positions found in the low-temperature structures (Table 6).

It can be concluded that $\alpha\text{-CsCrCl}_3$ and $\alpha\text{-CsCrI}_3$ have a disordered Jahn–Teller distorted structure, which is evident from displacements of the halide ions particularly along the c axis. We expect the same type of structures for e.g. $\alpha\text{-RbCuCl}_3$, $\alpha\text{-CsCrBr}_3$, $\alpha\text{-RbCrCl}_3$, $\alpha\text{-RbCrBr}_3$, $\alpha\text{-RbCrI}_3$ and $\alpha\text{-CsCuCl}_3$. As to CsCuCl_3 , the main displacements of the Cl^- ions in the β phase are just perpendicular to the c axis, but in $\alpha\text{-CsCuCl}_3$ Kroese *et al.* (1974) found also a large anisotropic motion of the Cl^- ions along the c axis. A similar structure redetermination of $\alpha\text{-CsCuCl}_3$ (Crama, 1981) gives comparable results and points unambiguously to model *A*. Also in $\alpha\text{-Ti}_4\text{CrI}_6$ a disordered phase with respect to the Jahn–Teller elongation direction has been found (Zandbergen, 1979).

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Structure de l'Hydroxysulfate de Chrome Monohydraté

PAR AMÉDÉE RIOU ET ANDRÉ BONNIN

Laboratoire de Cristallographie Minérale, Institut National des Sciences Appliquées, 35043 Rennes CEDEX, France

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Abstract

The basic chromium sulfate $\text{Cr}(\text{OH})\text{SO}_4 \cdot \text{H}_2\text{O}$ has been studied by single-crystal X-ray structure analysis with an automatic diffractometer and $\text{Mo K}\alpha$ radiation. It crystallizes in the non-centrosymmetric monoclinic

space group Cc with $a = 12.477(7)$, $b = 7.259(5)$, $c = 14.382(7)$ Å, $\beta = 93.99(4)^\circ$, $V = 1299$ Å³, $D_m = 2.80$, $D_c = 2.807$ Mg m⁻³ for $M_r = 183.08$ and $Z = 12$. All atoms, except the H atoms, were located, the final discrepancy index being $R_{hkl} = 8.5\%$ for the 2132 reliable reflexions. Each Cr atom is octahedrally

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