

Crystal structure of dicesium aquapentachlorochromate(III), $\text{Cs}_2[\text{CrCl}_5(\text{H}_2\text{O})]$

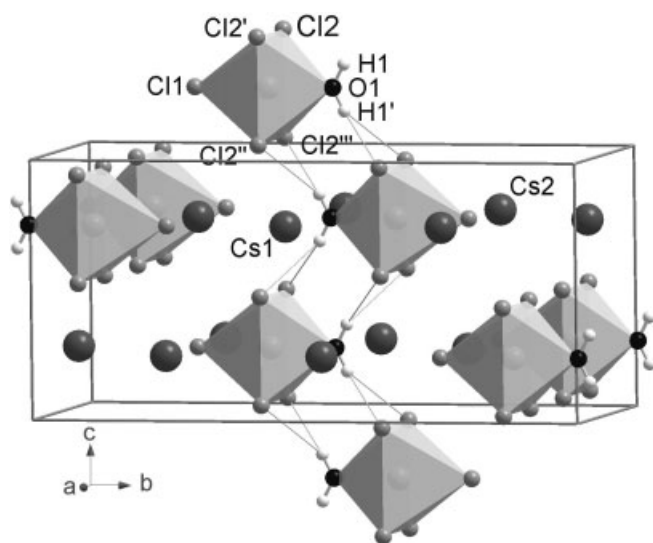
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Received February 5, 2004, accepted and available on-line April 21, 2004; CSD no. 409766



Abstract

$\text{Cl}_5\text{CrCs}_2\text{H}_2\text{O}$, orthorhombic, *Cmcm* (no. 63), $a = 7.4297(6)$ Å, $b = 17.234(1)$ Å, $c = 8.0121(6)$ Å, $V = 1025.9$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.041$, $wR_{\text{ref}}(F^2) = 0.082$, $T = 295$ K.

Source of material

The synthesis of the title compound was carried out as described for $\text{Rb}_2[\text{CrCl}_5(\text{H}_2\text{O})]$ [1] (3.367 g CsCl instead RbCl).

Discussion

There exist two series of alkali aquapentachloride compounds $A_2[M\text{Cl}_5(\text{H}_2\text{O})]$ for $A = \text{K}, \text{NH}_4, \text{Rb}, \text{Cs}$ and $M = \text{In}, \text{Fe}$. Only $\text{Cs}_2[\text{FeCl}_5(\text{H}_2\text{O})]$ compound crystallizes in space group *Cmcm* (no. 63), while seven other compounds crystallize in *Pnma* (no. 62) [2–7]. Here we report the crystal structure of the Cs derivate within the Cr series. This structure, especially hydrogen bonding details, was not yet clarified although the compound has been known for some time [8].

Similar to the structure of $\text{Rb}_2[\text{CrCl}_5(\text{H}_2\text{O})]$ [1], the characteristic feature of the title compound is a distorted octahedral coordination around the Cr atom with the Cr—O distance (2.052 Å) significantly shorter than Cr—Cl distances (2.301 Å to 2.346 Å). Neighboring octahedra are connected via hydrogen bonding forming a one-dimensional chain along [001].

However, instead of a one-to-one bonding between H and Cl in $\text{Rb}_2[\text{CrCl}_5(\text{H}_2\text{O})]$, each H atom in $\text{Cs}_2[\text{CrCl}_5(\text{H}_2\text{O})]$ is equivalently bonded to two Cl atoms with H···Cl distances of 2.740 Å. This distance is significantly longer while the O—H···Cl angle (141.8°) is considerably smaller as compared to the Rb analogue. Moreover, the Cs^+ ions occupy two Wyckoff positions with one surrounded by nine Cl atoms and two O atoms and the other one by ten Cl atoms and one O atom, respectively. The structure preference between space groups *Pnma* and *Cmcm* seems to be correlated to the ratio of ionic radii, $r(A^+)/r(M^{3+})$, but further study on this correlation is nonetheless necessary.

Table 1. Data collection and handling.

Crystal:	dark pink prism, size $0.05 \times 0.06 \times 0.08$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	93.43 cm^{-1}
Diffractometer, scan mode:	Rigaku R-axis RAPID, $D = 127.4$ mm, $2\theta = -60^\circ - 60^\circ$, $\chi = 0^\circ$, $\varphi = 0^\circ$, $\omega = 60^\circ - 180^\circ$, $\Delta\omega = 5^\circ$, $\chi = 30^\circ$, $\varphi = 90^\circ$, $\omega = 60^\circ - 180^\circ$, $\Delta\omega = 5^\circ$
$2\theta_{\text{max}}$:	59.94°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	6660, 851
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 736
$N(\text{param})_{\text{refined}}$:	33
Programs:	SHELXL-97 [9], DIAMOND [10]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	8f	1/2	0.473(5)	0.663(6)	0.03(2)

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cs(1)	4c	0	0.46826(4)	3/4	0.0320(3)	0.0378(3)	0.0219(3)	0	0	0
Cs(2)	4c	0	0.24639(4)	1/4	0.0337(3)	0.0282(3)	0.0464(4)	0	0	0
Cr(1)	4c	1/2	0.61625(7)	3/4	0.0211(6)	0.0186(6)	0.0174(6)	0	0	0
Cl(1)	4c	0	0.2498(1)	3/4	0.033(1)	0.0216(9)	0.042(1)	0	0	0
Cl(2)	16h	0.2784(2)	0.61069(7)	0.5418(2)	0.0328(6)	0.0375(6)	0.0321(6)	-0.0053(4)	-0.0131(4)	0.0013(5)
O(1)	4c	1/2	0.4972(4)	3/4	0.066(5)	0.011(2)	0.020(3)	0	0	0

Acknowledgments. This project was supported by the Fund for Distinguished Young Scholars from the NNSF of China, Fund of the 863 project from the MOST of China, and the Fund of State Key Laboratory of High Performance Ceramics and Superfine Microstructure in Shanghai Institute of Ceramics of CAS. We would also like to thank Dr. Horst Borrmann of Max Planck Institute for Chemical Physics of Solids, Germany, for valuable advices on data collection and structure analysis.

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