inorganic compounds

Dirubidium aquapentachlorochromate(III) and dicaesium aquapentachlorochromate(III)

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The structures of the two novel title compounds, Rb_2-$[CrCl_5(H_2O)]$, (I), and $Cs_2[CrCl_5(H_2O)]$, (II), have been determined by single-crystal X-ray diffraction. Compounds (I) and (II) crystallize with *Pnma* and *Cmcm* symmetry, respectively. In (I), the Cr, three Cl and water O atom lie on a mirror plane; in (II), the Cs, Cr, O and one of the Cl atoms are at sites with *m2m* symmetry. The chromate anions are in a pseudo-cubic environment of eight Rb^+ cations in (I) and in a pseudo-octahedral environment of six Cs^+ cations in (II). The structural arrangement correlates with the r_{anion}/r_{cation} radius ratio.

Comment

Octahedral chromium(III) complexes have attracted increasing interest in the past decade, following the discovery of their catalytic properties. One application of these complexes is in homogeneous catalysis, where CO and CO_2 are converted into organic compounds, such as methanol, under ambient conditions. The conversion into methanol may be of particular importance because it provides a possible way to reduce greenhouse gas emissions (Ogura & Yoshida, 1987). Substitution reactions of ligands are slow in chromium(III) complexes, a fact that corresponds with their considerable stability. Compounds containing the aquapentachlorochromate(III) complex anion, $[CrCl_5(H_2O)]^{2-}$, have been described previously (Ogura & Yoshida, 1987) but have not been structurally characterized.

Two novel compounds were synthesized using the method of Palmer (1954) and were identified as $Rb_2[CrCl_5(H_2O)]$, (I), and $Cs_2[CrCl_5(H_2O)]$, (II), by single-crystal diffraction. Both structures consist of layers of chromate complexes, which are seen to be connected by O—H···Cl hydrogen bonds in (I) (Fig. 1 and Table 2). The position of the H atom could not be

Figure 1
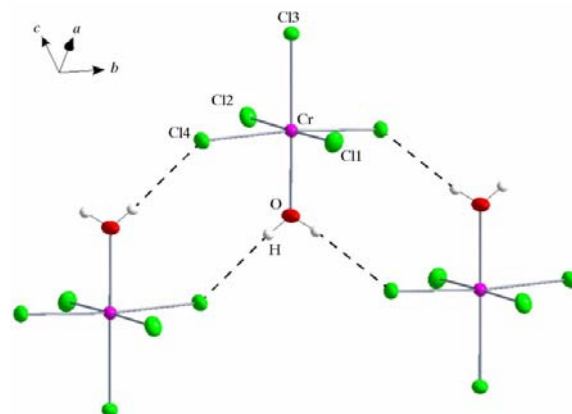The network of $[CrCl_5(H_2O)]^{2-}$ anions in (I), showing the O—H···Cl hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level.

determined in (II). Nevertheless, by analogy with the structure of $Cs_2[FeCl_5(H_2O)]$ (Greedan *et al.*, 1980), the short O···Cl distances [3.380 (5) Å] suggest the existence of bifurcated hydrogen bonds in (II) (Fig. 2).

The chromate anions in (I) and (II) occur in different environments; eight Rb^+ cations form a pseudo-cubic environment in (I), whereas six Cs^+ cations form a pseudo-octahedral environment in (II) (Figs. 3 and 4, and Tables 1 and 3). Coll *et al.* (1987) proposed that the r_{anion}/r_{cation} ratio in alkali aquapentachlorometallates determines the structural type. In the present work, the anionic radius is defined by the average octahedral *M*—*X* distance (*X* = Cl and O). The correlation between the ionic radius ratio and the structure type is shown in Table 4 for aquapentachlorometallates(III), including $Rb_2[MCl_5(H_2O)]$ (*M* = Cr, Fe, In and Tl) and $Cs_2[MCl_5(H_2O)]$ (*M* = Cr, Fe, In, Ir, Rh, Ru and Tl). It is apparent that smaller

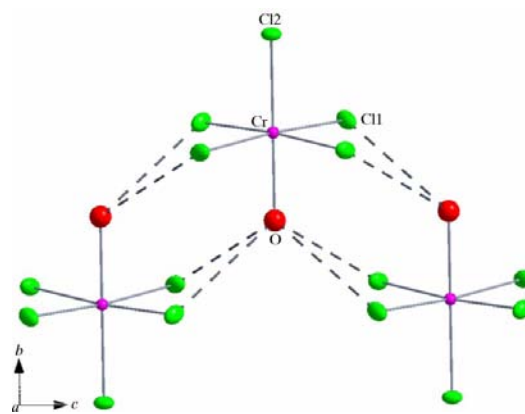**Figure 2**
The network of $[CrCl_5(H_2O)]^{2-}$ anions in (II), showing probable bifurcated hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level.
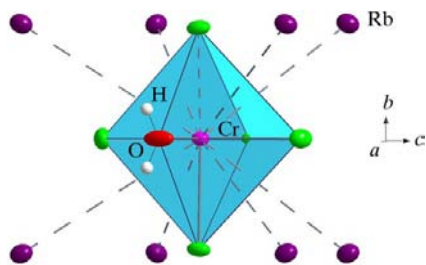
Figure 3
The pseudo-cubic environment of the chromate complex in (I). One atom of each type is labelled.
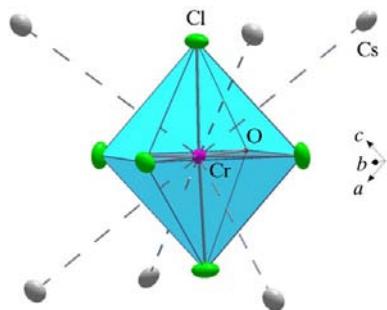

Figure 4
The pseudo-octahedral environment of the chromate complex in (II). One atom of each type is labelled.

radius ratios (1.21–1.24) correspond to the *Cmcm* structure, while larger radius ratios (1.30–1.65) correspond to the *Pnma* structure.

Experimental

The title compounds were synthesized according to the method of Palmer (1954). Stoichiometric proportions of *A*Cl salts (*A* = Rb and Cs) and hexavalent CrO_3 were dissolved in 12 *M* hydrochloric acid (6.0 ml). Ethanol (1.5 ml) was added in small portions. When the exothermal reaction was complete, a saturated solution of *A*Cl salt was added. The solution was first evaporated over a flame and, when crystals started to appear, the solution was evaporated over a boiling water bath. The violet–red products were left to cool in a desiccator over silica gel and were then washed with ethanol. The resulting mixture was dried in an evacuated desiccator over sulfuric acid. Red–violet single crystals were obtained of a size suitable for single-crystal diffraction analysis.

Compound (I)

Crystal data

$Rb_2[CrCl_5(H_2O)]$	Mo $K\alpha$ radiation
$M_r = 418.21$	Cell parameters from 7643
Orthorhombic, *Pnma*	reflections
$a = 13.7558\,(2)$ Å	$\theta = 2.4$–$32.9°$
$b = 9.7484\,(1)$ Å	$\mu = 12.68$ mm^{-1}
$c = 7.1074\,(1)$ Å	$T = 168\,(2)$ K
$V = 953.08\,(2)$ Å^3	Rhombic octahedron, red–violet
$Z = 4$	$0.10 \times 0.06 \times 0.03$ mm
$D_x = 2.915$ Mg m^{-3}	

Data collection

Siemens SMART 1K CCD area-detector diffractometer	1825 independent reflections
ω scans	1465 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.049$
(*SADABS*; Sheldrick, 2002)	$\theta_{max} = 32.9°$
$T_{min} = 0.364$, $T_{max} = 0.702$	$h = -20 \rightarrow 20$
14 988 measured reflections	$k = -14 \rightarrow 14$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2$
$R(F) = 0.038$	$+ 0.3749P]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1825 reflections	$\Delta\rho_{max} = 0.97$ e Å^{-3}
53 parameters	$\Delta\rho_{min} = -1.87$ e Å^{-3}
All H-atom parameters refined	

Table 1
Selected interatomic distances (Å) for (I).

Rb—Cl2^{i}	3.2887 (8)	Rb—Cl4^{i}	3.6180 (11)
Rb—Cl1^{ii}	3.2924 (9)	Rb—Cl4^{ii}	3.7833 (10)
Rb—Cl3^{iii}	3.3358 (8)	Cr—O	2.035 (4)
Rb—Cl3	3.3593 (8)	Cr—Cl3	2.3251 (12)
Rb—Cl2	3.4133 (9)	Cr—Cl1	2.3340 (13)
Rb—Cl4	3.4151 (9)	Cr—Cl4^{iv}	2.3561 (7)
Rb—Cl4^{iii}	3.4619 (11)	Cr—Cl2	2.3603 (14)
Rb—Cl1^{iii}	3.4707 (10)	O—H	0.75 (4)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, 1+z$; (iii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (iv) $x, \frac{1}{2} - y, z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O—H$\cdots$Cl4^{v}	0.75 (4)	2.43 (4)	3.171 (2)	174 (5)

Symmetry code: (v) $-x, -y, -1 - z$.

Compound (II)

Crystal data

$Cs_2[CrCl_5(H_2O)]$	Mo $K\alpha$ radiation
$M_r = 513.09$	Cell parameters from 3038
Orthorhombic, *Cmcm*	reflections
$a = 7.3868\,(3)$ Å	$\theta = 2.4$–$32.9°$
$b = 17.1107\,(7)$ Å	$\mu = 9.50$ mm^{-1}
$c = 7.9848\,(4)$ Å	$T = 173\,(2)$ K
$V = 1009.23\,(8)$ Å^3	Rhombic octahedron, red–violet
$Z = 4$	$0.02 \times 0.02 \times 0.02$ mm
$D_x = 3.377$ Mg m^{-3}	

Data collection

Siemens SMART 1K CCD area-detector diffractometer	883 independent reflections
ω scans	686 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.078$
(*SADABS*; Sheldrick, 2002)	$\theta_{max} = 30.5°$
$T_{min} = 0.833$, $T_{max} = 0.871$	$h = -10 \rightarrow 10$
7414 measured reflections	$k = -24 \rightarrow 24$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$R(F) = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.151$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 2.88$ e Å^{-3}
883 reflections	$\Delta\rho_{min} = -1.40$ e Å^{-3}
28 parameters	

Table 3
Selected interatomic distances (Å) for (II).

Cs1—Cl1[vi]	3.392 (2)	Cs2—Cl2[xi]	3.6938 (2)
Cs1—Cl1[vii]	3.586 (2)	Cs2—Cl2[viii]	3.9934 (2)
Cs1—Cl2[viii]	3.734 (4)	Cr—O	2.064 (10)
Cs2—Cl1[ix]	3.605 (2)	Cr—Cl2	2.308 (4)
Cs2—Cl1[x]	3.665 (2)	Cr—Cl1	2.340 (2)

Symmetry codes: (vi) $x - 1, 1 - y, z - \frac{1}{2}$; (vii) $1 - x, y, z$; (viii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ix) $1 - x, 1 - y, z - \frac{1}{2}$; (x) $\frac{1}{2} - x, y - \frac{1}{2}, z - 1$; (xi) $1 - x, 1 - y, -z$.

Table 4
Correlation between space-group symmetry and r_{anion}/r_{cation} ratio.

Cation radii for eightfold coordination from Shannon (1976).

Compound	Space group	r_{anion}/r_{cation}
Rb2[TlCl5(H2O)]†	Pnma	1.649
Rb2[InCl5(H2O)]‡	Pnma	1.649
Rb2[FeCl5(H2O)]§	Pnma	1.574
Rb2[CrCl5(H2O)]¶	Pnma	1.550
Cs2[TlCl5(H2O)]†	Pnma	1.345
Cs2[InCl5(H2O)]‡	Pnma	1.308
Cs2[FeCl5(H2O)]††	Cmcm	1.239
Cs2[RuCl5(H2O)]‡‡	Cmcm	1.226
Cs2[IrCl5(H2O)]§§	Cmcm	1.224
Cs2[RhCl5(H2O)]¶¶	Cmcm	1.218
Cs2[CrCl5(H2O)]¶	Cmcm	1.217

† Vasil'ev *et al.* (1994). ‡ Solans *et al.* (1988). § O'Connor *et al.* (1979). ¶ This work. †† Greedan *et al.* (1980). ‡‡ Hopkins *et al.* (1966). §§ Coll *et al.* (1987). ¶¶ Thomas & Stanko (1973).

The H-atom position in (I) was located from a Fourier difference map and was refined isotropically without any constraint. The highest peak of residual electron density for (II) is located at (0.0580, −0.0025, 0.2500), 0.43 Å from the O atom, and does not correspond to the missing H atom. An attempt to use the H-atom coordinates determined by Greedan *et al.* (1980) for Cs2[FeCl5(H2O)] led to an unreasonable result.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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