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## Key indicators

Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{Cr}-\text{O}) = 0.002\text{ \AA}$   
 $R$  factor = 0.028  
 $wR$  factor = 0.079  
Data-to-parameter ratio = 19.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Redetermination of potassium chloro-  
chromate,  $\text{KCrO}_3\text{Cl}$ 

$\text{KCrO}_3\text{Cl}$ , potassium trioxochlorochromate(VI), has been redetermined from room-temperature single-crystal X-ray data. The Cr atom is tetrahedrally coordinated by three O atoms (average Cr–O bond length 1.597 Å) and one Cl atom at 2.1916 (8) Å, with nearly ideal tetrahedral angles. The K ion is coordinated by eight O and three Cl atoms. Isolated  $\text{CrO}_3\text{Cl}$  tetrahedra and K ions are connected *via* common ligands. All atoms are in general positions.

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## Comment

The crystal structure of  $\text{KCrO}_3\text{Cl}$ , a compound first described by Peligot (1833) and therefore labeled Peligot's salt by Bostrup (1985), has been studied by Helmholz & Foster (1950), who reported atomic coordinates but no  $R$  value. A statement in the ICSD entry for the compound, and on the corresponding ICDD-PDF card (ICDD, 2001) advises that 'coordinates are those given in the paper but are obviously wrong'.

Crystals of  $\text{KCrO}_3\text{Cl}$  were obtained in an attempt to prepare potassium metal(II) chromates containing kröhnkite-type chains [for review, see Fleck *et al.* (2002) and Fleck & Kolitsch (2002)]. The redetermination shows that the structural model of Helmholz & Foster (1950) is basically correct, although it reports unreliable unit-cell parameters and metal-anion bond distances.

The structure contains isolated  $\text{CrO}_3\text{Cl}$  groups connected to 11-coordinated K ions *via* common ligands (Figs. 1 and 2). The Cr atom in  $\text{KCrO}_3\text{Cl}$  is tetrahedrally coordinated by three O atoms (average Cr–O bond length 1.597 Å) and one Cl atom at 2.1916 (8) Å, with nearly ideal tetrahedral angles (Fig. 2 and

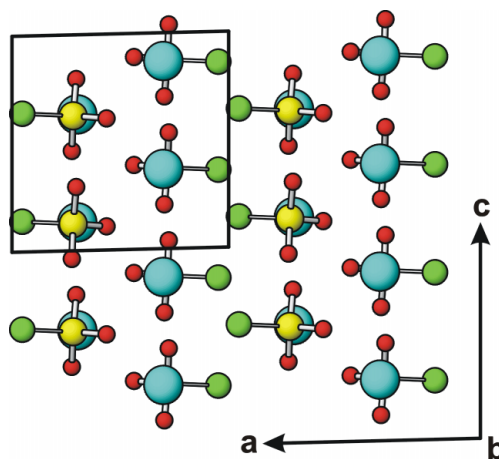
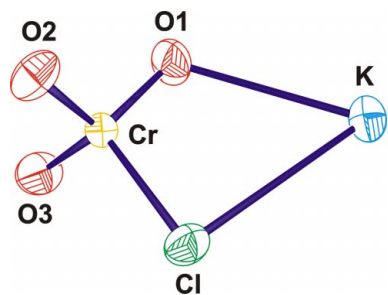


Figure 1

Packing in the structure of  $\text{KCrO}_3\text{Cl}$ , viewed along  $[010]$ . Isolated  $\text{CrO}_3\text{Cl}$  tetrahedra (Cr yellow, Cl green and O red) are connected to K ions (turquoise) *via* common ligands (K–anion bonds have been omitted for clarity). The unit cell is outlined.



**Figure 2**  
Anisotropic displacement ellipsoids (50% probability level) of the atoms in the asymmetric unit of  $\text{KCrO}_3\text{Cl}$ .

Table 1). Originally reported Cr–O and Cr–Cl distances were 1.53 (5) and 2.16 (4) Å (Helmholz & Foster, 1950), whereas corresponding distances calculated from X-ray powder diffraction data by Diemann (1976), of 1.62 (2) and 2.18 (4) Å, are closer to the new values.

The coordination sphere of the K ion comprises eight O atoms and three Cl atoms, the latter being at distances between 3.3 and 3.6 Å. Bond-valence sums for all atoms were calculated using the metal–O parameters from Brese & O’Keeffe (1991) and the metal–Cl parameters from Brown (1996). They amount to 1.03 (K), 5.91 (Cr), 2.03 (O1), 1.96 (O2), 1.96 (O3) and 1.00 (Cl) valence units. The atomic arrangement is characterized by an approximately layered arrangement of K ions parallel to (110).

By comparison to commonly observed average Cr–O distances in  $\text{CrO}_4$  groups in oxy-salts (1.64–1.66 Å), the respective distance in  $\text{KCrO}_3\text{Cl}$  is shortened by about 0.05 Å in order to maintain the bond-valence requirements of the  $\text{Cr}^{\text{VI}}$  cation. This is also reflected in the IR and Raman spectra; upon substitution of one of the O atoms in a  $\text{CrO}_4$  group by a halogen atom, the stretching frequencies of the remaining three Cr–O bonds strongly increase (Balicheva & Petrova, 1974).

$\text{KCrO}_3\text{Cl}$  is isostructural with both  $\text{RbCrO}_3\text{Cl}$  (Foster & Sterns, 1974) and  $\text{NH}_4\text{CrO}_3\text{Cl}$  (Hanic & Madar, 1956), whereas  $\text{CsCrO}_3\text{Cl}$  crystallizes in the  $\text{BaSO}_4$  structure type (Foster & Sterns, 1974). A reversible phase transition of  $\text{KCrO}_3\text{Cl}$  was reported to occur at about 420 (Mahieu *et al.*, 1972) and 429 K (Foster & Hambly, 1977) (see also ICDD-PDF cards 31–996 and 31–997). A more detailed study of the phase transition was conducted by De Benyacar *et al.* (1994) using optical microscopy, X-ray diffraction and differential scanning calorimetry. They measured a transition temperature of about 430–437 K, and noted the existence of at least one intermediate metastable phase, hysteresis effects, the development of strong mechanical stresses in single crystals during the phase transition, and a complicated dependence of the thermal behavior on the previous thermal history. For the high-temperature phase, they reported orthorhombic symmetry and the cell parameters  $a = 8.04$ ,  $b = 6.57$  and  $c = 9.48$  Å.

Both  $\text{RbCrO}_3\text{Cl}$  and  $\text{CsCrO}_3\text{Cl}$ , although not being isostructural with  $\text{KCrO}_3\text{Cl}$ , also show phase transitions, at 437

and 496 K, respectively (Foster & Hambly, 1977). The crystal structures of the high-temperature modifications of all three alkali chromochlorates apparently have not been determined yet. An attempt to determine the structure of the high-temperature modification of the title compound using the same crystal measured already at room temperature was unsuccessful; at 443 (5) K, the primitive monoclinic cell was still present, whereas at a temperature close to 453 K, the still transparent crystal yielded only diffraction patterns similar to incomplete X-ray powder diffraction rings. This transformation was not reversible on slow cooling; a retransformation was also not observed after keeping the crystal at room temperature for two weeks. It is unclear if the observed transformation involved a change of the chemical composition. According to Foster & Hambly (1977), decomposition of  $\text{KCrO}_3\text{Cl}$  and evaporation of gaseous chlorine is not expected to start at the temperatures used for the present studies.

A determination of the unit-cell parameters at 120 K during the present work indicated no structural change in the title compound below room temperature.

## Experimental

The title compound was prepared by controlled evaporation at room temperature of an aqueous solution (pH about 4) containing dissolved  $\text{K}_2\text{CrO}_4$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and some drops of  $\text{HNO}_3$ . Elongated tabular, transparent brown–orange crystals of  $\text{KCrO}_3\text{Cl}$  up to several mm in length formed. According to single-crystal studies of their orientation, they are elongated along [100] and tabular on (001). The crystals were accompanied by minor amounts of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (pale-green pseudo-rhombohedra, quickly dehydrating in air) and very minor amounts of KCl (colourless octahedra).

### Crystal data

$\text{KCrO}_3\text{Cl}$	$D_x = 2.528 \text{ Mg m}^{-3}$
$M_r = 174.55$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1435 reflections
$a = 7.838$ (2) Å	$\theta = 2.0\text{--}30.0^\circ$
$b = 7.493$ (1) Å	$\mu = 3.84 \text{ mm}^{-1}$
$c = 7.812$ (2) Å	$T = 293$ (2) K
$\beta = 91.40$ (3)°	Tabular, brown–orange
$V = 458.66$ (18) Å <sup>3</sup>	$0.20 \times 0.10 \times 0.02 \text{ mm}$
$Z = 4$	

### Data collection

Nonius KappaCCD diffractometer	1102 independent reflections
$\omega$ scans	924 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.015$
( <i>HKL SCALEPACK</i> ;	$\theta_{\text{max}} = 27.9^\circ$
Otwinowski & Minor, 1997)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.514$ , $T_{\text{max}} = 0.927$	$k = -9 \rightarrow 9$
2117 measured reflections	$l = -10 \rightarrow 10$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.08P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.079$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.16$	$\Delta\rho_{\text{max}} = 0.57 \text{ e \AA}^{-3}$
1102 reflections	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$
56 parameters	Extinction correction: <i>SHELXL97</i>
	Extinction coefficient: 0.015 (2)

**Table 1**Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

K—O3 <sup>i</sup>	2.7798 (18)	K—O2 <sup>v</sup>	3.368 (2)
K—O1 <sup>ii</sup>	2.847 (2)	K—Cl <sup>vi</sup>	3.4023 (13)
K—O2 <sup>iii</sup>	2.8485 (18)	K—Cl <sup>vii</sup>	3.5505 (14)
K—O3 <sup>iv</sup>	2.979 (2)	Cr—O1	1.5938 (18)
K—O1	3.0210 (19)	Cr—O2	1.5977 (16)
K—O2 <sup>iv</sup>	3.037 (2)	Cr—O3	1.5997 (17)
K—O1 <sup>v</sup>	3.063 (2)	Cr—Cl	2.1916 (8)
K—Cl	3.3297 (9)		
O1—Cr—O2	110.70 (11)	O1—Cr—Cl	106.59 (7)
O1—Cr—O3	111.70 (11)	O2—Cr—Cl	109.13 (7)
O2—Cr—O3	109.29 (10)	O3—Cr—Cl	109.38 (7)

Symmetry codes: (i)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (ii)  $1 - x, 1 - y, 2 - z$ ; (iii)  $x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (iv)  $x, 1 + y, z$ ; (v)  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (vi)  $-x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (vii)  $-x, 1 - y, 2 - z$ .

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999) and *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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## References

- Balicheva, T. G. & Petrova, G. A. (1974). *Zh. Neorg. Khim.* **19**, 723–728.
- Bostrup, O. (1985). *Dan. Kem.* **66**, 44.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. (1996). *J. Appl. Cryst.* **29**, 479–480.
- De Benyacar, M. A. R., Bompadre, S., Casal, M., Lanza, H. & Parisi, F. (1994). *Phase Transitions*, **50**, 199–204.
- Diemann, E. (1976). *Z. Naturforsch. Teil B*, **31**, 1468–1471.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fleck, M. & Kolitsch, U. (2002). In preparation.
- Fleck, M., Kolitsch, U. & Hertweck, B. (2002). *Z. Kristallogr.* **217**, 435–443.
- Foster, J. J. & Hambly, A. N. (1977). *Aust. J. Chem.* **30**, 251–260.
- Foster, J. J. & Sterns, M. (1974). *J. Cryst. Mol. Struct.* **4**, 149–164.
- Hanic, F. & Madar, J. (1956). *Chem. Zvesti*, **10**, 82–90. (In German.)
- Helmholz, L. & Foster, W. R. (1950). *J. Am. Chem. Soc.* **72**, 4971–4974.
- ICDD (2001). PDF-2: The Powder Diffraction File. International Centre for Diffraction Data, 12 Campus Boulevard, Newtown Square, PA 19073–3273, USA.
- Mahieu, B., Ladrerie, J., Cambier, J., Apers, D. & Capron, P. (1972). *Bull. Soc. Chim. Belg.* **81**, 343–349. (In French.)
- Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Peligo, E. (1833). *Ann. Chim. Phys.* **52**, 267–275. (In French.)
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Shape Software (1999). *ATOMS* for Windows and Macintosh. Version 5.0.4. Shape Software, Kingsport, TN 37663, USA.