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$K_4(CrO_4)(NO_3)_2$, the first chromate(VI)-nitrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(O–N) = 0.004 Å
R factor = 0.038
wR factor = 0.106
Data-to-parameter ratio = 20.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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$K_4(CrO_4)(NO_3)_2$ is the first chromate(VI)-nitrate to be reported. It contains isolated CrO_4^{2-} tetrahedra and NO_3^- groups linked together by K^+ ions. The latter show a layered arrangement approximately parallel to the (001) plane. The average Cr—O, N—O and K—O bond lengths are 1.645, 1.242, and 2.905 Å, respectively. All atoms are on general positions.

Comment

We are currently investigating and classifying crystal structure types of both natural and synthetic kröhnkite [$Na_2Cu(SO_4)_2\cdot 2H_2O$]-type oxysalts and related compounds (Fleck, Kolitsch & Hertweck, 2002; Fleck, Kolitsch, Hertweck, Giester *et al.*, 2002). In our recent research we have also included chromate compounds (Fleck & Kolitsch, 2002), which are environmentally important because of the toxicity of hexavalent chromium. The title compound, the first chromate(VI)-nitrate to be reported, was obtained as an unexpected by-product during synthesis from aqueous solutions at room temperature. Because it crystallized from an approximately

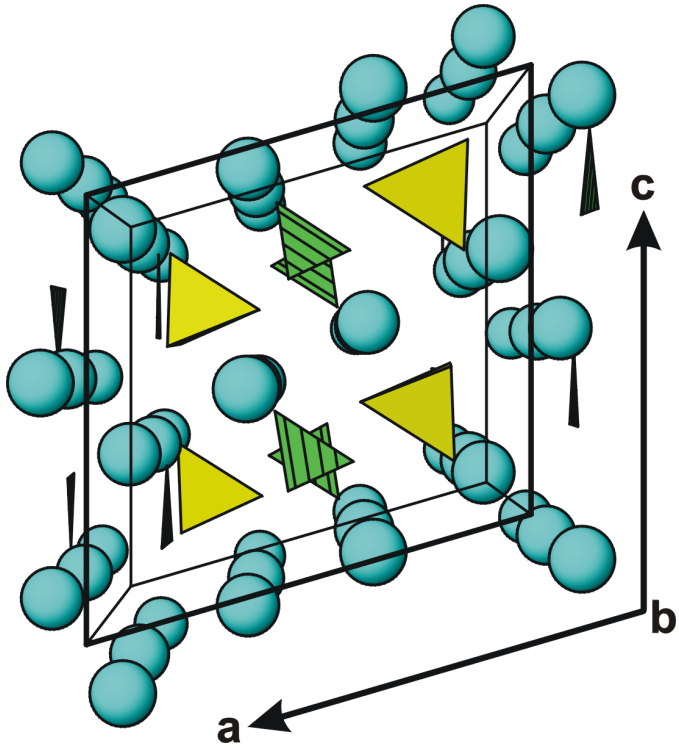

Figure 1
Perspective view of $K_4(CrO_4)(NO_3)_2$ along [010]. Isolated CrO_4^{2-} tetrahedra (yellow) are linked to isolated NO_3^- groups (green, striped) *via* bonds to K^+ ions (bluish).

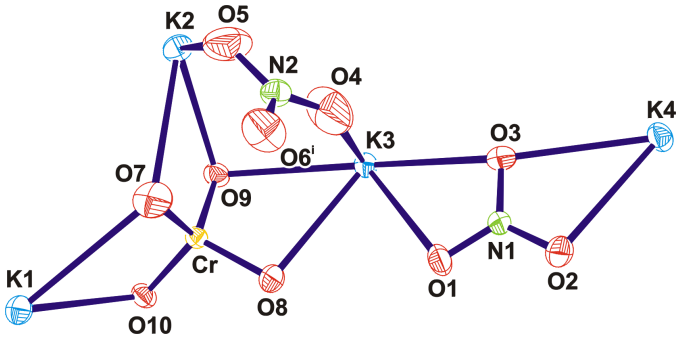

Figure 2
Anisotropic displacement ellipsoids (50% probability level) of the atoms in the asymmetric unit of $K_4(CrO_4)(NO_3)_2$ [Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$].

neutral aqueous solution and was accompanied by the synthetic analogue of tarapacáite (naturally occurring K_2CrO_4), it might also occur in K-rich natural environments.

The asymmetric unit of $K_4(CrO_4)(NO_3)_2$ contains four K, one Cr, two N and ten O atoms, all located in general positions. The structure is characterized by isolated CrO_4^{2-} tetrahedra and NO_3^- groups which are linked together by K^+ ions (Figs. 1, 2). The latter show a layered arrangement, approximately parallel to the (001) plane (Fig. 1). The overall linkage is weak, and explains the low hardness and tenacity of the compound.

The K^+ ions show coordination numbers between eight and ten, with an overall mean K—O distance of 2.905 Å. The unique CrO_4^{2-} tetrahedron, although isolated, shows a slight angular distortion, with O—Cr—O angles ranging from 108.43 (10) to 111.21 (10)°. The oxygen ligands of the N2-centred NO_3 group, O4, O5 and, to a lesser extent, O6, show somewhat increased displacement parameters (unlike those of the N1-centred NO_3 group), and therefore may indicate slight positional disorder.

The chemical composition of the title compound makes it unique. However, it is chemically related to the following four alkali sulfate nitrates, all with unknown crystal structures: $K(NH_4)_3(SO_4)(NO_3)_2$ (ICDD-PDF 20-853), $K_2(NH_4)_2(SO_4)(NO_3)_2$ (ICDD-PDF 20-852), $K_4H_2(NO_3)_2(SO_4)_2$ (Orlova *et al.*, 1986; ICDD-PDF 39-722), and $Na_2CrO_2F_2(NO_3)_2$ (Brown & Gard, 1973; ICDD-PDF 30-1179). The first two of these compounds might be isostructural with the title compound, in view of their equivalent stoichiometries.

Experimental

The title compound was prepared by slow evaporation at room temperature of an approximately neutral aqueous solution containing dissolved HNO_3, K_2CrO_4, KOH, $ZrCl_4$ and Co(II)$(OH)_2$. It formed yellow, transparent, thin platelets with indistinct or pseudohexagonal outline. The platelets were arranged in rosette-shaped to spheroidal aggregates, and were accompanied by large prismatic to block-shaped crystals of yellow K_2CrO_4 [synthetic tarapacáite], minor amounts of colourless KNO_3, and uninvestigated lilac grainy aggregates of a Co-compound.

Crystal data

$CrK_4N_2O_{10}$	D_x = 2.466 Mg m^{-3}
M_r = 396.42	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3227 reflections
a = 10.143 (2) Å	θ = 2.0–30.0°
b = 11.149 (2) Å	μ = 2.68 mm^{-1}
c = 9.837 (2) Å	T = 293 (2) K
β = 106.31 (3)°	Thin platelet, pale yellow
V = 1067.6 (4) Å^3	0.20 × 0.10 × 0.01 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	3107 independent reflections
φ and ω scans	2139 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)	R_{int} = 0.027
	θ_{max} = 30.1°
T_{min} = 0.617, T_{max} = 0.974	$h = -14 \rightarrow 14$
6048 measured reflections	$k = -15 \rightarrow 15$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.43P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.038	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.106	$\Delta\rho_{max}$ = 0.52 e Å^{-3}
S = 1.01	$\Delta\rho_{min}$ = −0.84 e Å^{-3}
3107 reflections	Extinction correction: *SHELXL*97
155 parameters	Extinction coefficient: 0.0020 (4)

Table 1
Selected geometric parameters (Å, °).

K1—O7^{i}	2.657 (2)	K3—O1	2.932 (2)
K1—O10^{ii}	2.6952 (18)	K3—O4	2.986 (3)
K1—O3^{iii}	2.7923 (19)	K3—O2^{ix}	3.0416 (19)
K1—O5^{iv}	2.834 (2)	K3—O3^{x}	3.172 (2)
K1—O2^{v}	2.8934 (19)	K4—O9^{xi}	2.7900 (17)
K1—O6^{iii}	2.931 (2)	K4—O9^{x}	2.808 (2)
K1—O4^{iii}	2.978 (3)	K4—O3	2.8422 (19)
K1—O7^{ii}	3.162 (2)	K4—O2	2.8800 (19)
K1—O5^{i}	3.178 (3)	K4—O8^{viii}	2.9125 (19)
K2—O8^{vi}	2.698 (2)	K4—O10^{xi}	2.9131 (18)
K2—O9	2.7129 (18)	K4—O2^{iii}	2.918 (2)
K2—O5	2.811 (3)	K4—O1^{iii}	2.921 (2)
K2—O6^{vii}	2.849 (2)	K4—O1^{viii}	3.089 (2)
K2—O1^{vi}	2.8598 (19)	Cr—O7	1.6395 (19)
K2—O6^{i}	2.895 (3)	Cr—O8	1.6434 (17)
K2—O7	3.061 (2)	Cr—O9	1.6468 (16)
K2—O4^{vi}	3.156 (3)	Cr—O10	1.6494 (16)
K3—O10^{viii}	2.8239 (18)	N1—O1	1.246 (2)
K3—O10^{vi}	2.8637 (18)	N1—O2	1.250 (2)
K3—O8	2.8710 (19)	N1—O3	1.261 (3)
K3—O9	2.8939 (18)	N2—O4	1.209 (3)
K3—O3	2.9037 (19)	N2—O5	1.231 (3)
K3—O8^{vi}	2.9148 (19)	N2—O6^{xii}	1.253 (3)
O7—Cr—O8	111.21 (10)	O1—N1—O2	120.52 (19)
O7—Cr—O9	108.43 (10)	O1—N1—O3	119.75 (19)
O8—Cr—O9	109.16 (9)	O2—N1—O3	119.64 (19)
O7—Cr—O10	109.43 (10)	O4—N2—O5	123.1 (3)
O8—Cr—O10	109.22 (9)	O4—N2—O6^{xii}	119.5 (3)
O9—Cr—O10	109.37 (8)	O5—N2—O6^{xii}	117.1 (2)

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

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO, SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular

graphics: *ATOMS* (Shape Software, 1999); *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97).

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