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$NaIn(CrO_4)_2·2H_2O$, the first indium(III) member of the kröhnkite family

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Sodium indium(III) chromate(VI) dihydrate, $NaIn(CrO_4)_2·2H_2O$, synthesized from an aqueous solution at room temperature, is the first indium(III) member of the large family of compounds with kröhnkite $[Na_2Cu^{II}(S^{VI}O_4)_2·2H_2O]$-type chains. The crystal structure is based on infinite octahedral–tetrahedral $[In(CrO_4)_2(H_2O)_2]^-$ chains along [010], linked *via* charge-balancing Na^+ cations. The slightly distorted $InO_4(H_2O)_2$ octahedra are characterized by a mean In—O distance of 2.125 Å. The CrO_4 tetrahedra are strongly distorted (mean Cr—O = 1.641 Å). The Na atom shows an octahedral coordination, unprecedented among compounds with kröhnkite-type chains. The NaO_6 octahedra share opposite edges with the $InO_4(H_2O)_2$ octahedra to form infinite [001] chains. The hydrogen bonds are of medium strength. $NaIn(CrO_4)_2·2H_2O$ belongs to the structural type F2 in the classification of Fleck, Kolitsch & Hertweck [*Z. Kristallogr.* (2002), **217**, 435–443], and is isotypic with $KAl(CrO_4)_2·2H_2O$ and MFe$(CrO_4)_2·2H_2O$ (M = K, Tl or NH_4). All atoms are in special positions except one O atom.

Comment

$NaIn(CrO_4)_2·2H_2O$ was synthesized from an aqueous solution at room temperature as part of a comprehensive study of the crystal chemistry of the large kröhnkite $[Na_2Cu^{II}(S^{VI}O_4)_2·2H_2O]$ family of oxysalts. The title compound is the first In^{III} member of this family, which comprises both natural and synthetic oxysalt compounds based on infinite octahedral–tetrahedral $[M(XO_4)_2(H_2O)_2]$ chains, where M is either divalent (Mg, Mn, Fe, Co, Ni, Cu, Zn or Cd) or trivalent (Al, Fe, Sc, In or Tl), and where X is either pentavalent (P or As) or hexavalent (S, Se, Cr, Mo or W), as discussed in detail in our previous classification (Fleck *et al.*, 2002) and subsequent contributions (Fleck & Kolitsch, 2003; Kolitsch & Fleck, 2005, 2006). In the kröhnkite-type chains, MO_6 octahedra are corner-linked to bridging XO_4 tetrahedra. Very small to very large mono- or divalent A atoms occupy the space between adjacent chains and provide charge balance. The resulting general formula is $A_nM(XO_4)_2·2H_2O$, where A = Na, K, Rb, Cs, Ag, Tl, NH_4, H or Ca and n = 1 or 2.

$NaIn(CrO_4)_2·2H_2O$ belongs to the structural type $F2$ in the classification of Fleck *et al.* (2002), and is isotypic with $KAl(CrO_4)_2·2H_2O$ (Cudennec & Riou, 1977) and MFe$(CrO_4)_2·2H_2O$ (M = K, Tl or NH_4) (Gravereau & Hardy, 1972). Note that the crystal structures of these previously reported chromates have been described in a non-standard setting (same space group, but with $\beta > 120°$); the title compound is described here using a standard setting.

Interestingly, $NaIn(CrO_4)_2·2H_2O$ is not isotypic with the other known sodium metal(III) chromates containing kröhnkite-type chains, *viz*. $NaAl(CrO_4)_2·2H_2O$ (Cudennec & Riou, 1977) and $NaFe(CrO_4)_2·2H_2O$ (Hardy & Gravereau, 1970), although these two crystallize in a closely related structure type (space group $C2/c$; type F1 in the classification of Fleck *et al.*, 2002). Efforts to synthesize the K and Rb analogues of the title compound from aqueous solutions at room temperature have so far been unsuccessful.

The crystal structure of $NaIn(CrO_4)_2·2H_2O$ is based on infinite octahedral–tetrahedral $[In(CrO_4)_2(H_2O)_2]^-$ chains extending along [010], linked *via* charge-balancing Na^+ cations (Figs. 1–3). The slightly distorted $InO_4(H_2O)_2$ octahedra are characterized by a mean In—O distance of 2.125 Å. The CrO_4 tetrahedra show a very strong bond-length distortion (Table 1), with a mean Cr—O distance of 1.641 Å. The Na atom shows a

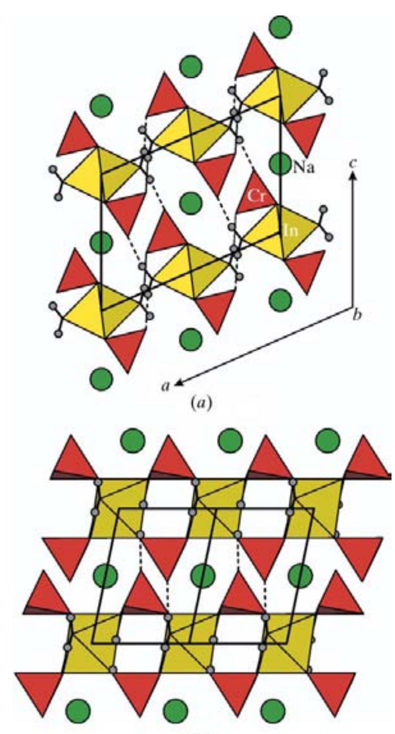

Figure 1
The crystal structure of $NaIn(CrO_4)_2·2H_2O$ in views (*a*) along [010], in the direction of the infinite kröhnkite-type octahedral–tetrahedral $[In(CrO_4)_2(H_2O)_2]^-$ chains, and (*b*) along [110], allowing a suitable top view of the kröhnkite-type chains. $InO_4(H_2O)_2$ octahedra are bridged by CrO_4 tetrahedra. The intercalated Na^+ cations (shown as spheres) are octahedrally coordinated (compare with Fig. 2). The hydrogen bonding is indicated by dashed lines and the unit cell is outlined.

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distinct octahedral coordination, with a mean Na—O bond length of 2.587 Å (Table 1; further O-atom neighbours are at distances greater than 3.16 Å). Such an octahedral coordination of *A* atoms is unprecedented among compounds based on kröhnkite-type chains. The distorted NaO_6 octahedra share opposite edges with the $InO_4(H_2O)_2$ octahedra to form infinite [001] chains (Fig. 2), *i.e.* these octahedral–octahedral chains extend perpendicular to the octahedral–tetrahedral chains. In other kröhnkite-type sodium oxysalts, the Na atoms have one of three coordination types. Firstly, Na may have a distinct [7]-coordination [kröhnkite, $Na_2Cu(SO_4)_2{\cdot}2H_2O$ (monoclinic, type *D*) (Hawthorne & Ferguson, 1975) or $Na_2Mn(XO_4)_2{\cdot}2H_2O$ (*X* = S or Se) (monoclinic, type *D*) (Wildner & Stoilova, 2003)]. Secondly, Na may have a poorly defined [7]- to [8]-coordination [$Na_2M(SeO_4)_2{\cdot}2H_2O$ (*M* = Zn, Co or Ni) (triclinic, type *A*) (Wildner & Stoilova, 2003) or $Na_2Cd(SO_4)_2{\cdot}2H_2O$ (monoclinic, type *D*) (Wildner & Stoilova, 2003)]. Thirdly, Na may have a [6+1]-coordination [$Na_2Cu(SeO_4)_2{\cdot}2H_2O$ (triclinic, type *A*) (Peytavin *et al.*, 1974) or $Na_2Cd(SeO_4)_2{\cdot}2H_2O$ (monoclinic, type *D*) (Wildner & Stoilova, 2003)]. In this last case, even if the seventh oxygen ligand (at about 2.7 Å) were to be neglected, the resulting distorted NaO_6 octahedra would be connected to adjacent octahedra in a different way from that in the title compound, *i.e.* no infinite octahedral–octahedral chains are formed.

Bond-valence sums for all atoms were calculated using the bond-valence parameters from Brese & O'Keeffe (1991). The bond-valence sums are 0.72 (Na), 3.29 (In), 6.09 (Cr), 0.48 (O1 = H_2O), 1.78 (O2), 1.72 (O3), and 2.06 (O4) valence units, and thus are all reasonably close to ideal values. Although the relatively low bond-valence sum for the Na site might indicate that the Na^+ cation is slightly too small for the void in which it is located, the equivalent displacement parameter of the Na atom does not indicate that it 'rattles' within its void. The somewhat undersaturated O3 and O2 ligands are, as expected, acceptors of the two hydrogen bonds (Table 2). These bonds, which both reinforce the atomic arrangement along [001] (Figs. 1 and 2), are of medium strength (Table 2).

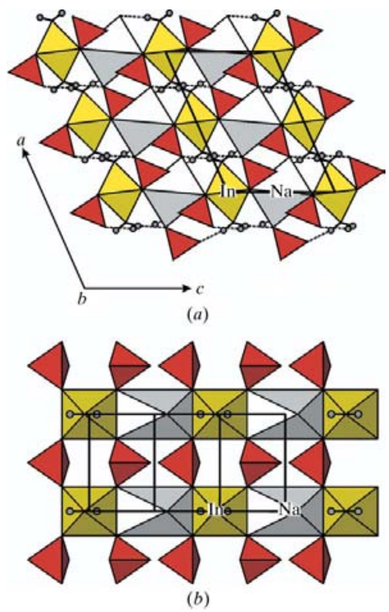

Figure 2
Two views of the octahedral–octahedral chains in $NaIn(CrO_4)_2{\cdot}2H_2O$, *viz*. (*a*) along [001], parallel to the chains, and (*b*) along [201], perpendicular to the chains. Distorted NaO_6 octahedra share opposite edges with $InO_4(H_2O)_2$ octahedra to form infinite [001] chains. Such octahedral–octahedral chains are unprecedented among compounds containing kröhnkite-type chains. The hydrogen bonding is indicated by dashed lines and the unit cell is outlined.

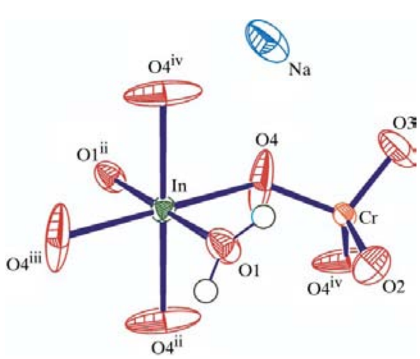

Figure 3
The connectivity in $NaIn(CrO_4)_2{\cdot}2H_2O$, shown with displacement ellipsoids at the 70% probability level. [Symmetry codes: (ii) $-x, y, -z$; (iii) $-x, -y, -z$; (iv) $x, -y, z$.]

Experimental

Tiny orange–yellow pointed prisms of the title compound crystallized at room temperature from an acidic aqueous solution (pH about 3) containing dissolved Na_2CO_3, $In(NO_3)_3{\cdot}H_2O$ and CrO_3 (Na:In:Cr molar ratio unknown, but estimated to be about 2:1:4) in distilled water. The crystals were accompanied by minor quantities of small yellow plates of $Na_2Cr_2O_7{\cdot}2H_2O$ (Kharitonov *et al.*, 1969, 1970; Bulka *et al.*, 1973) and large colourless rounded block-shaped crystals of $NaNO_3$.

Crystal data

$NaIn(CrO_4)_2{\cdot}2H_2O$
M_r = 405.84
Monoclinic, $C2/m$
a = 10.741 (2) Å
b = 5.567 (1) Å
c = 7.497 (1) Å
β = 113.78 (3)°
V = 410.23 (15) Å^3
Z = 2
D_x = 3.286 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 5.48 mm^{-1}
T = 293 (2) K
Prism, orange–yellow
0.06 × 0.02 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski *et al.*, 2003)
T_{min} = 0.735, T_{max} = 0.898
1474 measured reflections
804 independent reflections
708 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 32.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.060
S = 1.07
804 reflections
49 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 1.25P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.90 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0040 (8)

Table 1
Selected bond lengths (Å).

In—O4	2.102 (2)	Cr—O4	1.679 (2)
In—O1	2.172 (3)	Na—O2^{i}	2.531 (3)
Cr—O3	1.594 (3)	Na—O4	2.615 (3)
Cr—O2	1.611 (3)		

Symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D$$\cdots$$A$	D—H$\cdots$$A$
O1—H1$\cdots$O3^{i}	0.86 (4)	1.81 (4)	2.662 (4)	168 (6)
O1—H2$\cdots$O2^{ii}	0.88 (5)	1.92 (6)	2.789 (5)	168 (13)

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

All O—H distances were restrained to a length of 0.90 (5) Å. Isotropic displacement parameters of the H atoms were refined freely; the results show that atom H2 has an anomalously high U_{iso} value and thus appears to be disordered to some extent (it is also involved in the weaker of the two hydrogen bonds). The highest electron-density peak in $NaIn(CrO_4)_2{\cdot}2H_2O$ is 0.42 Å from the O4 site and the deepest hole in the difference map is 0.87 Å from the O4 site.

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *SCALEPACK* and *DENZO* (Otwinowski *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3003). Services for accessing these data are described at the back of the journal.

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