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$(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$: a new structure type with kröhnkite-like chains

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Tetraammonium cadmium dihydrogenselenite(IV) diselenate(VI), $(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$, is the third example of a compound containing both hydrogen selenite and selenate anions, and has a new structure type. It contains kröhnkite-like heteropolyhedral chains in which CdO_6 octahedra are linked *via* bridging $HSeO_3$ groups, having their remaining two *trans* apices decorated by SeO_4 groups. The charge-balancing NH_4 groups are involved in weak hydrogen bonding, whereas the H atom of the $HSeO_3$ group provides a strong hydrogen bond [O$\cdots$O = 2.614 (5) Å]. The average Cd—O bond length is 2.298 Å. All atoms are on general positions except Cd (on $\bar{1}$). Relations to the kröhnkite-type compounds $Na_2Mg(SO_3)\cdot2H_2O$, $Ba_2CoCl_2(SeO_3)_2$ and $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$, and to the mineral curetonite are discussed. Unit-cell data are given for an isotypic Mn^{II} analogue.

Comment

The title compound has a new triclinic structure type. However, a topological analysis shows that it contains heteropolyhedral chains similar to those in kröhnkite, $Na_2Cu^{II}(S^{VI}O_4)_2\cdot2H_2O$ (Dahlman, 1952; Hawthorne & Ferguson, 1975). In our recent review and classification of natural and synthetic oxysalt compounds with kröhnkite-type and kröhnkite-like chains (Fleck *et al.*, 2002), and in an update (Fleck & Kolitsch, 2003), we showed that all kröhnkite-type compounds contain infinite $[M(XO_4)_2(H_2O)_2]$ chains, where M is divalent (Mg, Mn, Fe, Co, Ni, Cu, Zn or Cd) or trivalent (Al, Fe, In or Tl) and X is pentavalent (P or As) or hexavalent (S, Se, Cr, Mo or W). In these chains, MO_6 octahedra are corner-linked to bridging XO_4 tetrahedra. Large cations occupy the spaces between adjacent chains and provide charge balance. Several compounds were also recognized which contain kröhnkite-like chains, *i.e.* chains which differ in some respects from the strictly kröhnkite-type topology (Fleck *et al.*, 2002; Fleck & Kolitsch, 2003). Among these is one sulfite, $Na_2Mg(SO_3)\cdot2H_2O$ (Lutz & Buchmeier, 1983), in which the SO_3 groups assume the role of the bridging SO_4 groups in kröhnkite-type sulfates, and $Ba_2CoCl_2(SeO_3)_2$ (Johnston & Harrison, 2002), which, as subsequently pointed out by Fleck & Kolitsch (2003), is topologically very similar to $Na_2Mg(SO_3)\cdot2H_2O$ in that it contains SeO_3 groups bridging between CoO_4Cl_2 octahedra to form kröhnkite-like chains.

$(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$ contains one crystallographically unique Cd atom, two Se, two N, seven O and nine H atoms in its asymmetric unit. It represents the first example of a compound containing kröhnkite-like chains in which an $HSeO_3$ group connects MO_6 (M is Cd^{II}) octahedra (Fig. 1). The additional SeO_4 groups decorate these chains by being attached *via* common ligands to the remaining two apices of the CdO_6 octahedra in a *trans* arrangement (Figs. 1 and 2). The two non-equivalent charge-balancing NH_4^+ cations are located in the voids between the decorated chains (Figs. 1–3). A single-crystal study of the morphological elongation of the prismatic crystals of the title compound demonstrated that their elongation is along the chain direction. The cell metric is pseudo-monoclinic, having a C-centred pseudo-cell with a = 13.68, b = 5.79 and c = 11.76 Å, and α = 90.8, β = 118.9 and γ = 89.6°. The closeness to the higher symmetry explains the pervasive twinning in the title compound. Twinning is very commonly observed in kröhnkite-type and kröhnkite-like compounds (*e.g.* Fleck & Kolitsch, 2003).

Bond-valence summations for the metal atoms, calculated using the parameters of Brese & O'Keeffe (1991), give 2.07 v.u. (valence units) for Cd, 6.08 v.u. for Se1 (Se^{VI}) and 4.14 v.u. for Se2 (Se^{IV}), *i.e.* values close to the theoretical valences. Bond-valence sums for the O atoms were calculated taking into account the contributions from the NH_4^+ cations and using bond-valence parameters recently proposed by García-Rodríguez *et al.* (2000). The values obtained are 1.94 (O1), 1.76 (O2), 1.96 (O3), 2.06 (O4), 2.04 (O5), 2.03 (O6) and 1.42 v.u. (O7). Atom O2 is underbonded, but accepts a strong hydrogen bond from the O7—H9 group (see below). The two NH_4^+ cations have nine (N1) and seven + one (N2) next-nearest O neighbours and are involved in weak hydrogen bonds, with N$\cdots$O distances all longer than 2.86 Å (Table 2). These features of the NH_4^+ cations agree with the conclusions of Khan & Baur (1972) that NH_4^+ cations with large coordination numbers (seven to nine) have a pseudo-alkali character and do not show a pronounced tendency for hydrogen bonding. By contrast, the hydrogen bond involving the OH ligand of the $HSeO_3$ group is fairly short, with an O$\cdots$O distance of 2.614 (5) Å (Table 2). The acceptor of the strong hydrogen bond is the underbonded atom O2, and the bond strengthens the connection between two adjacent chains along the b axis (Fig. 2).

In the title compound, the $HSeO_3$ and SeO_4 groups show the characteristic pyramidal geometry for the Se^{IV}-based anion and tetrahedral geometry for the Se^{VI}-based anion. The average Se—O bond length in the SeO_4 tetrahedron (1.633 Å) and the average Cd—O bond length in the CdO_6 octahedron (2.298 Å) are close to the commonly observed values. The hydrogen selenite ($HSeO_3$) group exhibits an elongated Se—O bond [1.735 (3) Å] to the protonated O atom (O7), a typical

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feature of this group for the optimization of the bond-valence sums incident at the involved atoms (*e.g.* Koskenlinna, 1996). The average Se—O bond length (1.693 Å) and the average O—Se—O angle (102°) show good agreement with the average values reported in reviews of hydrogen selenites [1.709 (10) Å and 100.1 (13)° (Hawthorne *et al.*, 1987), 1.70 (5) Å and 101 (3)° (Loub, 1995), and 1.702 (20) Å and 100.1 (26)° (Koskenlinna, 1996)].

As also briefly pointed out by Fleck *et al.* (2002), there exist two kröhnkite-like compounds in which the heteropolyhedral chains are, similar to the situation in the title compound, also additionally decorated with either H_2XO_4 or XO_4 groups; these two compounds are $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$ (Toumi *et al.*, 1997) and the mineral curetonite, $Ba[(Al,Ti^{IV})(PO_4)(OH,O)F]$ (Cooper & Hawthorne, 1994), respectively. In $Ba_2Ca(HPO_4)_2(H_2PO_4)_2$, CaO_6 octahedra and H_2PO_4 tetrahedra are corner-linked to form kröhnkite-like infinite chains. Unlike kröhnkite-type chains in the strictest sense, the *trans* apices of the CaO_6 octahedron are not formed by water molecules but are decorated with additional H_2PO_4 tetrahedra, thus giving an overall composition of $[Ca(H_2PO_4)_2(HPO_4)_2]^{4-}$ for these chains. The charge-balancing Ba^{2+} cations are located in the voids between the chains. The H atoms of the protonated PO_4 groups have the role of providing hydrogen bonds to reinforce the structure. In curetonite, $Ba[(Al,Ti^{IV})(PO_4)(OH,O)F]$ (Cooper & Hawthorne, 1994), which contains kröhnkite-type chains composed of $(Al,Ti)O_6$ octahedra and PO_4 tetrahedra, an additional corner-linkage between these chains is achieved *via* AlO_4F_2 octahedra. The resulting heteropolyhedral layers are separated by Ba atoms. It is also worth noting that kröhnkite-based chains involving carbonate anions are found in the mineral sahamalite, $(Mg,Fe^{II})Ce_2(CO_3)_4$ (Pertlik & Preisinger, 1983). In that structure, the CO_3 groups play a dual role: they link $(Mg,Fe^{II})O_6$ octahedra into a kröhnkite-like chain, but also decorate the two remaining *trans* apices of the octahedra.

The title compound is a rare example of an oxysalt containing both $HSeO_3$ and SeO_4 groups. In fact, only about eight compounds with mixed-valent selenium(IV/VI) anions are known (Weil & Kolitsch, 2002), and only two of them have the same types of anions as the title compound. The first of these two examples is $La(HSeO_3)(SeO_4)\cdot 2H_2O$ (Harrison & Zhang, 1997), which is built up from a densely packed network of irregular LaO_9 groups, $HSeO_3$ pyramids and SeO_4 tetrahedra, sharing vertices and edges *via* La—O—La and La—O—Se bonds. The second example is $Fe(HSeO_3)(SeO_4)\cdot H_2O$ (Giester, 1992), which is based on sheets formed by $FeO_5(H_2O)$ octahedra sharing five of their corners with $HSeO_3$ pyramids and SeO_4 tetrahedra; these sheets are interconnected *via* hydrogen bonds only.

A determination of the unit-cell parameters of the title compound at 120 and 100 K indicated no change in symmetry upon cooling. An Mn^{II} analogue of $(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$ has been prepared by the controlled evaporation at room temperature of an acidic aqueous solution (of unknown pH) of manganese(II) carbonate, selenic acid and ammonia. The Mn^{II} analogue formed sheaves of pale-rose-coloured elongated tabular pseudo-orthorhombic crystals, which were

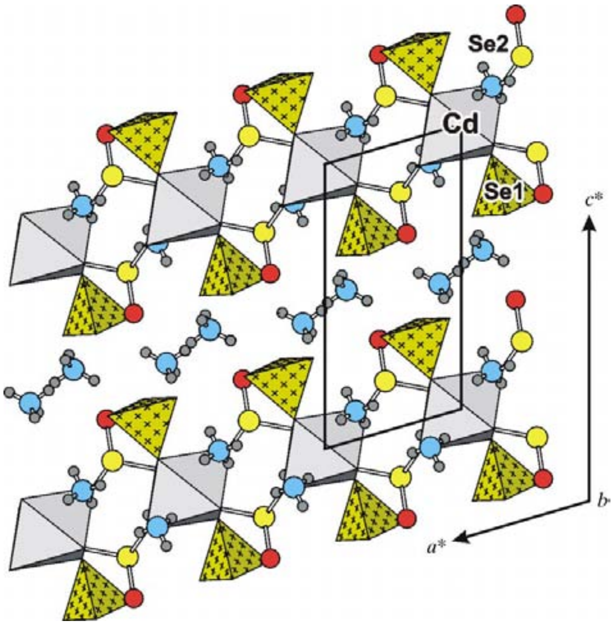

Figure 1
The crystal structure of $(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$ projected along [010]. CdO_6 octahedra are linked *via* bridging $HSeO_3$ groups to form heteropolyhedral infinite chains running along [100]. Each CdO_6 octahedron has two *trans* O vertices decorated with SeO_4 tetrahedra (marked with crosses). The two NH_4 groups are involved in weak hydrogen bonding (see text).

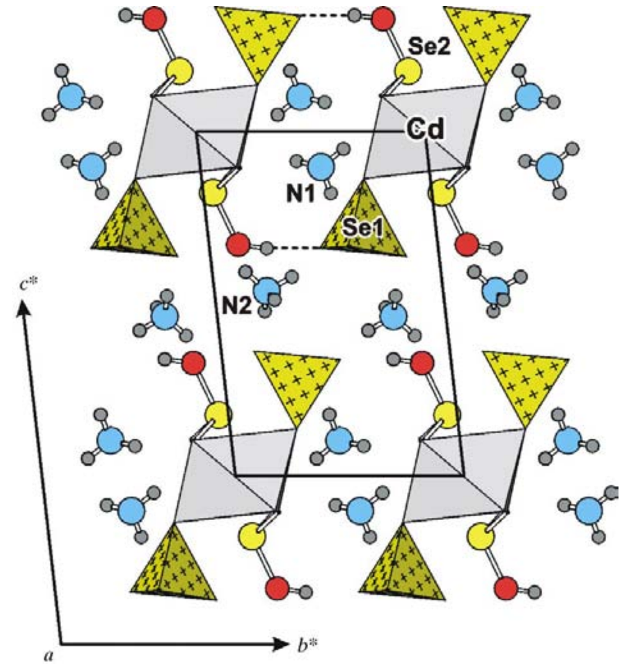

Figure 2
A view of the crystal structure of $(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$ along [100], *i.e.* the direction of the kröhnkite-like chains. The key is as in Fig. 1. The strong hydrogen bonds involving atoms O7 (donor), H9 and O2 (acceptor) are shown as dashed lines in the upper half of the figure.

also invariably twinned. A structure refinement was performed using a data set collected from a non-merohedrally twinned crystal at a large crystal-to-detector distance. Although the final R_F value was only *ca* 0.09 and H atoms could not be located (insufficient quality of the data set due to the influence of twinning), the refinement confirmed that $(NH_4)_4Mn(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$ is isotypic with $(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$. The refined unit-cell parameters of the Mn^{II} analogue are a = 5.700 (1), b = 7.397 (1) and c = 10.740 (2) Å, α = 90.63 (3), β = 104.45 (3) and γ = 112.73 (3)°, and V = 401.51 (12) $Å^3$. As expected, the unit-cell volume is distinctly smaller than that of the Cd analogue.

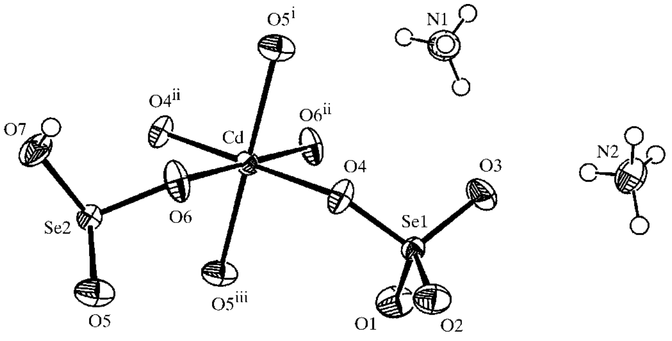

Figure 3
A view of the main building units in $(NH_4)_4Cd(HSe^{IV}O_3)_2(Se^{VI}O_4)_2$, shown with ellipsoids at the 50% probability level. All atoms of the asymmetric unit are included, and H atoms are represented as small spheres of arbitrary radii [symmetry codes: (i) $1 + x, y, z$; (ii) $-x, 2 - y, 2 - z$; (iii) $-1 - x, 2 - y, 2 - z$].

Experimental

The title compound was prepared by the controlled evaporation at room temperature of an acidic aqueous solution (of unknown pH) of cadmium carbonate, selenic acid and ammonia. The title compound crystallized as sheaves of colourless pseudo-orthorhombic invariably twinned prismatic crystals. On further evaporation, large colourless twinned prisms of $(NH_4)_2SeO_4$ crystallized.

Crystal data

$(NH_4)_4Cd(HSeO_3)_2(SeO_4)_2$
M_r = 726.42
Triclinic, $P\overline{1}$
a = 5.7910 (10) Å
b = 7.4110 (10) Å
c = 10.736 (2) Å
α = 90.05 (3)°
β = 105.02 (3)°
γ = 112.61 (3)°
V = 408.20 (17) $Å^3$
Z = 1
D_x = 2.955 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2196 reflections
θ = 2.0–30.0°
μ = 10.33 mm^{-1}
T = 293 (2) K
Prism, colourless
0.18 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ψ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.258, T_{max} = 0.747
4514 measured reflections
2368 independent reflections
2003 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 30.0°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.101
S = 1.07
2368 reflections
143 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.1P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.85 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.22 e $Å^{-3}$
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0173 (19)

Table 1
Selected geometric parameters (Å, °).

Cd—O6	2.275 (3)	Se1—O3	1.641 (3)
Cd—O4	2.309 (4)	Se1—O4	1.651 (3)
Cd—O5^{i}	2.311 (3)	Se2—O5	1.665 (4)
Se1—O1	1.612 (4)	Se2—O6	1.678 (3)
Se1—O2	1.629 (4)	Se2—O7	1.735 (3)
O1—Se1—O2	109.8 (2)	O3—Se1—O4	107.38 (19)
O1—Se1—O3	111.2 (2)	O5—Se2—O6	101.24 (19)
O2—Se1—O3	111.0 (2)	O5—Se2—O7	103.65 (5)
O1—Se1—O4	110.7 (2)	O6—Se2—O7	100.96 (19)
O2—Se1—O4	106.62 (19)		

Symmetry code: (i) $x + 1, y, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3	0.87 (5)	2.03 (5)	2.866 (6)	163 (8)
N1—H2···O5^{i}	0.86 (5)	2.34 (6)	3.099 (6)	147 (7)
N1—H2···O6^{i}	0.86 (5)	2.38 (6)	3.105 (7)	142 (7)
N1—H3···O4^{i}	0.78 (4)	2.43 (5)	3.078 (6)	141 (6)
N1—H4···O5^{ii}	0.83 (5)	2.17 (5)	2.958 (6)	160 (7)
N2—H5···O1^{iii}	0.90 (5)	2.13 (7)	2.868 (6)	138 (8)
N2—H6···O3	0.87 (4)	2.11 (4)	2.947 (7)	161 (5)
N2—H7···O3^{iv}	0.86 (4)	2.26 (5)	2.919 (6)	133 (5)
N2—H8···O1^{v}	0.90 (4)	2.02 (4)	2.915 (7)	172 (5)
O7—H9···O2^{ii}	0.88 (5)	1.75 (5)	2.614 (5)	167 (8)

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

All N—H and O—H distances were constrained to a maximum of 0.90 (5) Å. The deepest hole is 0.86 Å from the Cd site and the highest peak is 0.86 Å from the Se1 site.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1663). Services for accessing these data are described at the back of the journal.

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