Third update on compounds with kröhnkite-type chains: the crystal structure of wendwilsonite [Ca$_2$Mg(AsO$_4$)$_2$·2H$_2$O] and the new triclinic structure types of synthetic AgSc(CrO$_4$)$_2$·2H$_2$O and M_2Cu(Cr$_2$O$_7$)$_2$·2H$_2$O (M = Rb, Cs)

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Abstract: As part of a comprehensive crystal-chemical study and classification of minerals and synthetic compounds with kröhnkite-type or -like chains of octahedra bridged by tetrahedra, the crystal structures of wendwilsonite from Schneeberg, Saxony, Germany, with composition Ca$_2$(Mg$_{0.90}$Co$_{0.10}$)(AsO$_4$)$_2$·2H$_2$O, and of three new synthetic double-metal dichromate(VI) dihydrates have been determined from single-crystal X-ray diffraction data.

Wendwilsonite is monoclinic [space group $P2_1/c$ (no. 14), a = 5.806(1), b = 12.923(3), c = 5.628(1) Å, β = 107.49(3)°, V = 402.75(14) Å^3, Z = 2; $R(F)$ = 1.42 %] and adopts type D in the classification of Fleck et $al.$ (2002b); it is isotypic with the three arsenates brandtite, roselite, zincroselite, and the sulphate kröhnkite. Infinite kröhnkite-type tetrahedral-octahedral chains [(Mg,Co)(AsO$_4$)$_2$(H$_2$O)$_2$]$^{2-}$ are separated by Ca^{2+} cations. A very strong hydrogen bond (O···O = 2.5294(18) Å) links adjacent chains.

Hydrothermally synthesised, orange AgSc(CrO$_4$)$_2$·2H$_2$O is triclinic [space group $P\bar{1}$ (no. 2), a = 5.586(1), b = 6.054(1), c = 7.432(1) Å, α = 110.74(3), β = 90.21(3), γ = 117.34(3)°, V = 204.56(6) Å^3, Z = 1; $R(F)$ = 3.48 %] and represents a novel structure type, designated G, among compounds containing kröhnkite-type chains. The structure is metrically pseudo-monoclinic and closely related to those of the monoclinic subtypes F1 ($C2/c$) and F2 ($C2/m$). AgSc(CrO$_4$)$_2$·2H$_2$O also represents the first Ag and Sc compound based on a kröhnkite-type chain. The structure is based on infinite tetrahedral-octahedral chains [Sc(CrO$_4$)$_2$(H$_2$O)$_2$]$^{2-}$ separated by Ag^{1+} cations. The Ag atom exhibits a [4+4]-coordination, with the AgO$_8$ polyhedron closely resembling a strongly sheared cube.

Rb$_2$Cu(Cr$_2$O$_7$)$_2$·2H$_2$O and isotypic Cs$_2$Cu(Cr$_2$O$_7$)$_2$·2H$_2$O were both grown at room temperature as orange blades from slightly acidic aqueous solutions. They represent a new, triclinic structure type containing kröhnkite-like octahedral-tetrahedral chains based on bridging Cr$_2$O$_7$ groups [space group $P\bar{1}$ (no. 2), a = 7.272(1) / 7.462(2), b = 7.648(2) / 7.819(2), c = 7.772(2) / 7.847(2) Å, α = 91.89(3) / 93.19(3), β = 99.72(3) / 99.57(3), γ = 115.79(3) / 116.34(3)°, V = 380.84(15) / 400.23(15) Å^3, Z = 1; $R(F)$ = 3.03 / 2.99 %]. The Cu atoms show a Jahn-Teller-distorted 'octahedral' coordination environment, approaching an unusual [2+2+2]-coordination. Hydrogen bonding is weak. A distinct positive correlation between the size of the alkali cation and the Cr-O-Cr angle in the few known alkali metal dichromates with kröhnkite-like chains is demonstrated.

Key-words: wendwilsonite, crystal structure, kröhnkite, tetrahedral-octahedral chain, dichromate.

Introduction

The crystal structures of minerals and inorganic compounds often contain characteristic fundamental building units such as dimers, trimers, chains, double chains or sheets. One of these units, an infinite chain, is the so-called kröhnkite-type chain as it was first observed in the mineral kröhnkite [Na$_2$Cu(SO$_4$)$_2$·2H$_2$O] (Dahlman, 1952; Hawthorne & Ferguson, 1975). This infinite tetrahedral-octahedral chain has the composition [M(XO_4)$_2$(H$_2$O)$_2$] (M = di- or trivalent cation; X = penta- or hexavalent cation), in which MO_6 octahedra are corner-linked to bridging XO_4 tetrahedra (Fig. 1). In our previous work (Fleck et $al.$, 2002a, b; Fleck & Kolitsch,
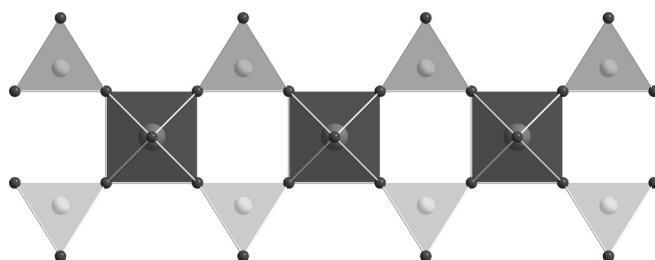

Fig. 1. The idealised kröhnkite-type chain (rod group $pmmm$). Distorted varieties of this chain are found in the eight different structure types of our classification (Fleck et $al.$, 2002b; Fleck & Kolitsch, 2003; this work). All drawings were done with DIAMOND (Brandenburg, 2005).

2003; Kolitsch & Fleck, 2005; Kolitsch, 2006), we have shown that a large number of both natural and synthetic compounds with an $A_nM(XO_4)_2 \cdot 2H_2O$ composition where A = Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Tl$^+$, NH$_4^+$, H$^+$ or Ca^{2+} (n = 1, 2), M = Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} or Al^{3+}, Fe^{3+}, Sc^{3+}, In^{3+}, Tl^{3+}, and X = P^{5+}, As^{5+} or S^{6+}, Se^{6+}, Cr^{6+}, Mo^{6+}, W^{6+} exist that contain kröhnkite-type chains, although the presence of these chains in the compounds was often not recognised as such in the respective original publications. We have proposed a classification scheme for all known compounds with kröhnkite-type chains (Fleck *et al.*, 2002b; Fleck & Kolitsch, 2003; see also Fleck *et al.*, 2002a; Kolitsch & Fleck, 2005), and assigned the compounds to six different structural types (designated type A through F), with either triclinic (types A-C, E) or monoclinic symmetry (types D, F). Type D, for instance, is the structure type adopted by kröhnkite. Minerals are only known to adopt types A, B and D. For comparisons of the kröhnkite-type chain with related chains and structural units, the reader is referred to our previous papers and also to the reviews by Hawthorne (1994), Pushcharovsky *et al.* (1998) and Hawthorne *et al.* (2000).

In the present paper we present a description of the crystal structures of the Ca-Mg-arsenate wendwilsonite and three novel synthetic compounds with kröhnkite-type or kröhnkite-like chains: AgSc(CrO$_4$)$_2 \cdot 2H_2O$ (which represents both the first Ag and Sc compound based on a kröhnkite-type chain, and a novel structure type, designated G), Rb$_2$Cu(Cr$_2$O$_7$)$_2 \cdot 2H_2O$ and isotypic Cs$_2$Cu(Cr$_2$O$_7$)$_2 \cdot 2H_2O$. The latter two also represent a new structure type. The crystal-chemical features of these oxysalts, their hydrogen-bonding schemes and their topological relations with other kröhnkite-type and -like compounds are discussed.

Previous work on wendwilsonite

Wendwilsonite, ideally Ca$_2$Mg(AsO$_4$)$_2 \cdot 2H_2O$, was first described by Dunn *et al.* (1987) on the basis of red to pink, Co-rich material from the Sterling Hill mine, Ogdensburg, New Jersey, Bou Azzer, Morocco, and Coahuila, Mexico. The crystal symmetry was reported as monoclinic, space group $P2_1/c$, with a = 5.806(1), b = 12.912(2), c = 5.623(1) Å, β = 107.40(2)°, V = 402.2(1) Å^3, and Z = 2. Wendwilsonite was shown to be the Mg analogue of roselite, ideally Ca$_2$Co(AsO$_4$)$_2 \cdot 2H_2O$ (Hawthorne & Ferguson, 1977), and Dunn *et al.* (1987) reported chemical analyses evidencing a solid solution series ranging from 82 mol% of wendwilsonite to 89 mol% of roselite. Further occurrences of wendwilsonite were recently reported from Sailauf, Spessart, Germany (Lorenz, 2004), and Aghbar near Bou Azzer, Morocco (Weiß *et al.*, 2002). At the latter locality, the presence of extensive solid solutions and zonations within single crystals was confirmed by quantitative electron microprobe analyses. The extent of solid solutions with isotypic zincroselite, ideally Ca$_2$Zn(AsO$_4$)$_2 \cdot 2H_2O$ (Keller *et al.*, 2004) and brandtite, ideally Ca$_2$Mn(AsO$_4$)$_2 \cdot 2H_2O$ (Hejny *et al.*, 1997) is presently unknown but crystal-chemical experience would suggest a complete solid-solution range between at least the three Mg, Co and Zn end-members.

We note that triclinic dimorphs exist of wendwilsonite, roselite, zincroselite and brandtite; they are named talmessite, roselite-beta (also known as beta-roselite), gaitite and parabrandtite, respectively. The crystal structures of the first three have been reported by Catti *et al.* (1977), Joswig *et al.* (2004) and Keller *et al.* (2004), respectively (note that the use of the mineral name talmessite in the title and text of the second paper is erroneous – the sample is in fact a Mg-rich roselite-beta). No investigation of the crystal structure of parabrandtite has been published yet. The extent of solid solution between the four triclinic end-members has not been studied in detail so far, but studies of samples from Morocco also indicate considerable solid solution ranges between talmessite and roselite (Pekov *et al.*, 2001; Weiß *et al.*, 2002).

According to our classification of compounds with kröhnkite-type chains (Fleck *et al.*, 2002b; Fleck & Kolitsch, 2003), wendwilsonite and its isotypic analogues adopt type D, while talmessite and its isotypic analogues crystallise in type A. Both types represent the most common ones of all types known at present.

Experimental

Synthesis

Rb$_2$Cu(Cr$_2$O$_7$)$_2 \cdot 2H_2O$ crystallised at room temperature on evaporation of a slightly acidic aqueous solution (pH = about 4) containing dissolved rubidium carbonate, copper carbonate hydroxide, chromium(VI) oxide and nitric acid. The isotypic salt Cs$_2$Cu(Cr$_2$O$_7$)$_2 \cdot 2H_2O$ was prepared at room temperature from a nearly neutral aqueous solution (pH 6) containing dissolved caesium carbonate, copper hydroxide dihydrate, chromium(VI) oxide and nitric acid. Both dichromate compounds formed small, orange, elongate (lance-shaped), transparent plates. These orange crystals were the last ones formed in the solutions. The dichromates were accompanied by colourless blocky to prismatic glassy crystals of RbNO$_3$ and CsNO$_3$, respectively. The Cs salt was additionally accompanied by yellow to brown-yellow opaque pseudomorphs of an uninvestigated phase after monoclinic Cs$_2$Cr$_2$O$_7$ (ICDD-PDF 18-350, crystal structure unknown), while the Rb salt was accompanied by uninvestigated thin brownish crusts.

AgSc(CrO$_4$)$_2 \cdot 2H_2O$ was prepared hydrothermally (493 K, 7 d) in a Teflon-lined stainless steel autoclave from a mixture of Ag$_2$CO$_3$, Sc$_2$O$_3$, CrO$_3$, and distilled water (filling height about 75%). Initial and final pH values were about 1.5 and 0.5, respectively. AgSc(CrO$_4$)$_2 \cdot 2H_2O$ formed orange elongate plates which were associated with deep red, corroded prisms of Ag$_2$Sc$_2$(CrO$_4$)$_4$ (new, triclinic structure type; Kolitsch, in preparation) and other, presently unidentified phases (dark red, sharp pseudocubes and black, semimetallic pseudohexagonal-dipyramidal crystals); their correct unit cells could not be determined so far due to apparent twinning and pseudo-symmetries. It is assumed that the dihydrate AgSc(CrO$_4$)$_2 \cdot 2H_2O$ has crystallised upon cooling because it appears to have been the last compound to form within the Teflon vessel.

Single-crystal X-ray diffraction

Selected crystals or crystal fragments of all compounds were studied at room temperature with a Nonius KappaCCD single-crystal X-ray diffractometer equipped with a 300 μm diameter capillary-optics collimator to provide increased resolution. Full spheres were collected from all selected crystals or fragments; the measured intensity data were processed with the Nonius program suite DENZO-SMN and corrected for Lorentz, polarisation, background and absorption effects (for details see Table 1). The programs SHELXS-97 (Sheldrick, 1997a) and SHELXL-97 (Sheldrick, 1997b) were used for the solution and the full-matrix least-squares refinement, respectively, of the crystal structures of all four title compounds.

The wendwilsonite samples showed a primitive-monoclinic unit cell very similar to that reported by Dunn *et al.* (1987). The crystal structure was solved from scratch in space group $P2_1/c$ and a model was obtained which confirmed the kröhnkite-type structure (type D in our classification). Therefore, we used the atomic coordinates of kröhnkite (Hawthorne & Ferguson, 1975) as a starting model for the final refinement steps, which involved anisotropic treatment of the non-H atoms and isotropic, unrestrained refinement of the two H positions. The refinement converged at $R(F) = 1.42\%$. Further details are given in Table 1. The chemical composition of the crystal fragment used for the data collection was subsequently analysed by SEM-EDS. Only Ca, Mg, As and minor Co were detected; possible impurity elements such as Zn, Mn or Fe are therefore not present or below detection limits.

Preliminary single-crystal studies of $AgSc(CrO_4)_2 \cdot 2H_2O$ indicated triclinic symmetry, but with a strongly pronounced monoclinic pseudo-symmetry (see below and also discussion). All crystals investigated were found to be twinned by non-merohedry, the twin plane being parallel to

Table 1. Crystal data, data collection information and refinement details for the title compounds.

Mineral/Compound	Wendwilsonite, $Ca_2(Mg_{0.90},Co_{0.10})(AsO_4)_2 \cdot 2H_2O$	$AgSc(CrO_4)_2 \cdot 2H_2O$ [b]	$Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$	$Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$
Structure type[a]	D	G (new)	kröhnkite-like	kröhnkite-like
Fw [g mol^{-1}]	421.80	420.86	702.51	797.39
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	5.806(1)	5.586(1)	7.272(1)	7.462(2)
b [Å]	12.923(3)	6.054(1)	7.648(2)	7.819(2)
c [Å]	5.628(1)	7.432(1)	7.772(2)	7.847(2)
α [°]	–	110.74(3)	91.89(3)	93.19(3)
β [°]	107.49(3)	90.21(3)	99.72(3)	99.57(3)
γ [°]	–	117.34(3)	115.79(3)	116.34(3)
V [Å^3]	402.75(14)	204.56(6)	380.84(15)	400.23(15)
Z	2	1	1	1
ρ_{calc} [g cm^{-3}]	3.478	3.416	3.063	3.308
μ (Mo$K\alpha$) [mm^{-1}]	9.881	5.772	10.562	8.491
$2\theta_{max}$ [°]	60	70	65	65
Rotat. axis; width [°]	φ, ω; 2	φ, ω; 1	φ, ω; 2	φ, ω; 2
Crystal-detector distance [mm]	30	40	30	30
Total no. of frames	295	1185	516	438
Collect. time/deg. [s]	60	40	55	60
h, k, l ranges	$\bar{8}/8, \bar{18}/18, \bar{7}/7$	$\bar{8}/8, \bar{9}/9, \bar{11}/11$	$\bar{11}/11, \bar{11}/11, \bar{11}/11$	$\bar{11}/11, \bar{11}/11, \bar{11}/11$
Crystal size [mm]	0.07 x 0.10 x 0.15	0.03 x 0.17 x 0.18	0.02 x 0.09 x 0.28	0.01 x 0.07 x 0.22
Absorption correct. [c]	multi-scan	multi-scan	multi-scan	multi-scan
Measured data	2231	3314	5471	5671
Unique data	1164 (R_{int} 1.7%)	1677 (R_{int} 2.5%)	2768 (R_{int} 2.0%)	2893 (R_{int} 2.1%)
Data with $F_o > 4\sigma(F_o)$	1132	1567	2536	2480
Variables	80	76	115	115
Extinction coeff.	0.0171(13)	0.071(8)	0.0186(19)	0.0082(10)
$R1$ [$F_o > 4\sigma(F_o)$]	1.42%	3.48%	3.03%	2.99%
$wR2_{all}$ [all F_o^2]	3.94%	9.05%	8.81%	8.08%
GooF	1.140	1.090	1.038	1.068
Weight. params. a / b	0.016 / 0.27	0.037 / 0.74	0.05 / 0.6	0.04 / 0.6
$\Delta\rho_{min}, \Delta\rho_{max}$ (e/Å^3)	–0.54, 0.48	–0.94, 0.20	–0.93, 1.16	–1.07, 1.26

Note: All measurements done at room temperature. Scattering factors for neutral atoms were used.
[a] According to the classification by Fleck *et al.* (2002b) and Fleck & Kolitsch (2003).
[b] 90 reflections most strongly affected by the non-merohedric twinning of $AgSc(CrO_4)_2 \cdot 2H_2O$ were omitted in the structure refinement (see text).
[c] Otwinowski *et al.* (2003).

Table 2. Fractional atomic coordinates and displacement parameters (in Å^2) for wendwilsonite.

Atom	x	y	z	U_{eq}/U_{iso}
Ca	0.56210(6)	0.12187(2)	0.23138(6)	0.00840(9)
(Mg,Co)^a	0.0	0.0	0.0	0.0078(2)
As	0.21621(3)	0.120488(11)	0.56738(3)	0.00535(7)
O1	−0.05699(18)	0.17409(8)	0.4976(2)	0.0103(2)
O2	0.27852(18)	0.05378(8)	0.83963(19)	0.0085(2)
O3	0.23638(19)	0.03655(8)	0.3426(2)	0.0100(2)
O4	0.43917(19)	0.20566(8)	0.5747(2)	0.0100(2)
Ow5	0.8177(2)	0.13770(10)	0.9649(2)	0.0089(2)
H1	0.881(4)	0.192(2)	0.982(5)	0.022(6)
H2	0.745(5)	0.142(2)	0.838(6)	0.026(7)

Note: The oxygen atom of the water molecule is denoted as Ow. The anisotropic displacement parameters are defined as:
$\exp[-2\pi^2 \Sigma_{i=1}^3 \Sigma_{j=1}^3 U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* h_i h_j]$, U_{eq} according to Fischer & Tillmanns (1988).
^{a} Refined occupany: $Mg_{0.900(3)}Co_{0.100(3)}$.

Table 3. Fractional atomic coordinates and displacement parameters (in Å^2) for $AgSc(CrO_4)_2 \cdot 2H_2O$.

Atom	x	y	z	U_{eq}/U_{iso}
Ag	0.0	0.0	0.5	0.02383(12)
Sc	0.0	0.0	0.0	0.01210(14)
Cr	0.62811(8)	0.22751(9)	0.31352(6)	0.01187(12)
O1	0.6186(6)	0.2954(6)	0.5421(3)	0.0266(5)
O2	0.7735(5)	0.5082(5)	0.2806(4)	0.0248(5)
O3	0.3067(5)	0.0298(5)	0.1809(4)	0.0237(4)
O4	0.8161(5)	0.0662(5)	0.2426(3)	0.0184(4)
Ow5	0.2225(5)	0.4229(5)	0.0674(4)	0.0213(4)
H1	0.21(3)	0.49(2)	−0.012(15)	0.13(4)
H2	0.245(16)	0.537(13)	0.172(8)	0.06(2)

Note: The oxygen atom of the water molecule is denoted as Ow. The anisotropic displacement parameters are defined as:
$\exp[-2\pi^2 \Sigma_{i=1}^3 \Sigma_{j=1}^3 U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* h_i h_j]$, U_{eq} according to Fischer & Tillmanns (1988).

Table 4. Fractional atomic coordinates and displacement parameters (in Å^2) for $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ (upper row) and isotypic $Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ (lower row).

Atom	x	y	z	U_{eq}/U_{iso}
Rb	0.27681(5)	0.74673(4)	0.17355(4)	0.02944(10)
Cs	0.28445(3)	0.75069(3)	0.17853(3)	0.02897(9)
Cu	0.0	0.0	0.5	0.01894(11)
	0.0	0.0	0.5	0.02125(12)
Cr1	0.24356(6)	0.47662(6)	0.66873(5)	0.01863(10)
	0.24420(8)	0.47005(7)	0.66857(7)	0.01997(11)
Cr2	0.29716(6)	0.24535(6)	0.14819(5)	0.01957(10)
	0.29627(8)	0.24521(7)	0.15254(7)	0.02118(12)
O1	0.2715(5)	0.5567(4)	0.4838(3)	0.0444(6)
	0.2664(6)	0.5330(5)	0.4816(4)	0.0488(8)
O2	0.1569(4)	0.5971(3)	0.7771(3)	0.0340(5)
	0.1576(5)	0.5922(4)	0.7686(4)	0.0380(6)
O3	0.0780(3)	0.2417(3)	0.6442(3)	0.0270(4)
	0.0851(4)	0.2370(4)	0.6515(3)	0.0284(5)
O4	0.5109(3)	0.4859(3)	0.2125(3)	0.0243(4)
	0.5129(4)	0.4811(4)	0.2117(3)	0.0277(5)
O5	0.0985(4)	0.2744(4)	0.0605(3)	0.0379(5)
	0.1030(4)	0.2771(4)	0.0745(4)	0.0373(6)
O6	0.2554(4)	0.1313(3)	0.3201(3)	0.0323(4)
	0.2619(4)	0.1358(4)	0.3220(4)	0.0318(6)
O7	0.3545(3)	0.1220(3)	0.0100(3)	0.0291(4)
	0.3377(4)	0.1181(4)	0.0076(3)	0.0305(5)
Ow8	0.2029(4)	−0.0452(3)	0.6713(3)	0.0253(4)
	0.1867(4)	−0.0566(4)	0.6698(3)	0.0262(5)
H1	0.322(6)	0.036(8)	0.653(8)	0.08(2)
	0.303(4)	0.011(5)	0.663(5)	0.012(9)
H2	0.231(9)	0.010(8)	0.780(4)	0.066(16)
	0.220(8)	−0.004(7)	0.773(4)	0.047(15)

Note: The oxygen atom of the water molecule is denoted as Ow. The anisotropic displacement parameters are defined as:
$\exp[-2\pi^2 \Sigma_{i=1}^3 \Sigma_{j=1}^3 U_{ij} \mathbf{a}_i^* \mathbf{a}_j^* h_i h_j]$, U_{eq} according to Fischer & Tillmanns (1988).

the platy face of the crystals. No untwinned fragment could be separated from the platy crystals. Therefore, in order to avoid excessive reflection overlap at low diffraction angles, an increased crystal-detector distance of 40 mm was chosen for the subsequent data collection of a suitable crystal fragment. The intensity data were processed assuming triclinic symmetry (R_{int} = 1.7 %). We note that R_{int} for the C-centred monoclinic pseudo-cell was very high (16 %), the multiscan absorption led to the rejection of 34 % of all reflections, and the structure could not be solved in the proposed space group $C2/m$. Intensity statistics were inconclusive concerning the presence of a centre of symmetry. The crystal structure was determined in space group $P\bar{1}$ (no. 2) by direct methods and subsequent Fourier and difference Fourier syntheses. A subsequent full-matrix least-squares anisotropic refinement on F^2 led to a preliminary $R(F)$ of about 7 %. At this stage, a total of 90 reflections most affected by the twinning ($F_o \gg F_c$) were omitted from the dataset. This allowed location of the two hydrogen atoms, which were subsequently refined isotropically and with a distance restraint (O-H = 0.90(5) Å). Convergence was achieved at $R(F)$ = 3.48 % (see Table 1 for details). The final atomic coordi-

nates were standardised using STRUCTURE TIDY (Gelato & Parthé, 1987). A search for higher symmetry with the program PLATON (Spek, 2003) confirmed that the chosen symmetry and space group are correct. We also note that a refinement in space group $P1$ (no. 1) did not result in an improved model and some of the oxygen atoms showed a 'non-positive-definite' behaviour.

The crystal structure of $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ was solved in space group $P\bar{1}$ (no. 2) by direct methods and subsequent Fourier and difference Fourier syntheses. A preliminary $R(F)$ of about 3.5 % was obtained by a subsequent refinement on F^2. At this stage, the two H atoms were located from a difference-Fourier map and refined isotropically, with the O-H bond distance restrained to 0.95(3) Å. The final $R(F)$ was 3.03 % (for details see Table 1).

The crystal structure of $Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ was refined using the atomic coordinates of $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ as a starting model. The refinement, with anisotropic displacement parameters for all non-H atoms and O-H bond distances restrained to 0.95(3) Å, quickly resulted in convergence at an $R(F)$ index of 2.99 % (details are given in Table 1).

The final positional and displacement parameters of all four compounds are given in Tables 2–4. Anisotropic displacement parameters are listed in Tables 5–7. Selected bond lengths and angles are presented in Tables 8–10, including the hydrogen bonding schemes. A bond-valence analysis of wendwilsonite is presented in Table 11 (results of bond-valence calculations for the three synthetic compounds are given and discussed below). Lists of observed and calculated structure factors can be obtained from the first author.

Results and discussion

Wendwilsonite

The structure refinement of wendwilsonite from Schneeberg yields the formula $Ca_2(Mg_{0.90},Co_{0.10})(AsO_4)_2 \cdot 2H_2O$ and confirms that the mineral is isotypic to brandtite, roselite, zincroselite and kröhnkite (structure type D in the classification of compounds with kröhnkite-type chains by Fleck *et al.*, 2002b and Fleck & Kolitsch, 2003). The funda-

Table 5. Anisotropic displacement parameters (in Å^2) for wendwilsonite.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0.00729(15)	0.00893(16)	0.00946(15)	–0.00153(9)	0.00323(11)	–0.00100(9)
(Mg,Co)*	0.0067(3)	0.0087(3)	0.0077(3)	–0.0023(2)	0.0018(2)	–0.0007(2)
As	0.00518(10)	0.00578(10)	0.00476(10)	0.00012(4)	0.00103(6)	0.00004(4)
O1	0.0070(5)	0.0104(5)	0.0121(5)	0.0001(4)	0.0008(4)	0.0030(4)
O2	0.0088(5)	0.0095(5)	0.0066(5)	0.0027(4)	0.0017(4)	0.0000(4)
O3	0.0103(5)	0.0111(5)	0.0090(5)	–0.0042(4)	0.0035(4)	–0.0014(4)
O4	0.0098(5)	0.0092(5)	0.0118(5)	–0.0015(4)	0.0043(4)	–0.0041(4)
Ow5	0.0110(5)	0.0077(5)	0.0069(5)	0.0003(4)	0.0013(4)	–0.0014(4)

Table 6. Anisotropic displacement parameters (in Å^2) for $AgSc(CrO_4)_2 \cdot 2H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag	0.02924(19)	0.02414(18)	0.02079(17)	0.01060(13)	0.00046(12)	0.01407(14)
Sc	0.0099(3)	0.0140(3)	0.0126(3)	0.0041(2)	0.0025(2)	0.0069(2)
Cr	0.01149(18)	0.0152(2)	0.01031(18)	0.00464(14)	0.00270(13)	0.00803(14)
O1	0.0383(13)	0.0338(13)	0.0126(9)	0.0076(8)	0.0092(9)	0.0228(11)
O2	0.0258(11)	0.0210(10)	0.0309(12)	0.0136(9)	0.0084(9)	0.0116(9)
O3	0.0147(8)	0.0258(11)	0.0279(11)	0.0095(9)	–0.0039(8)	0.0088(8)
O4	0.0207(9)	0.0258(10)	0.0178(9)	0.0106(8)	0.0096(7)	0.0170(8)
Ow5	0.0265(10)	0.0160(9)	0.0173(9)	0.0054(7)	0.0044(8)	0.0083(8)

Table 7. Anisotropic displacement parameters (in Å^2) for $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ and isotypic $Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			$Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$			
Rb	0.03086(15)	0.03187(16)	0.02977(15)	0.01158(11)	0.00945(10)	0.01610(12)
Cu	0.0216(2)	0.01492(19)	0.01746(19)	-0.00175(13)	0.00022(14)	0.00713(15)
Cr1	0.02098(19)	0.01571(18)	0.01814(18)	0.00167(13)	0.00259(13)	0.00776(14)
Cr2	0.01807(18)	0.01995(19)	0.01954(18)	0.00146(13)	0.00345(13)	0.00766(15)
O3	0.0473(14)	0.0556(16)	0.0274(11)	0.0196(11)	0.0070(10)	0.0197(13)
O4	0.0328(11)	0.0255(10)	0.0466(13)	-0.0054(9)	0.0069(9)	0.0168(9)
O5	0.0298(10)	0.0154(8)	0.0286(9)	-0.0046(7)	0.0028(8)	0.0052(7)
O6	0.0224(8)	0.0196(8)	0.0289(9)	0.0043(7)	0.0023(7)	0.0084(7)
O7	0.0265(10)	0.0467(14)	0.0411(12)	-0.0002(10)	-0.0004(9)	0.0198(10)
Ow8	0.0354(11)	0.0299(10)	0.0280(10)	0.0090(8)	0.0123(8)	0.0090(9)
			$Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$			
Cs	0.02984(14)	0.02810(13)	0.03413(13)	0.01217(9)	0.01088(9)	0.01560(10)
Cu	0.0217(3)	0.0173(2)	0.0217(3)	-0.00212(19)	0.00037(19)	0.0084(2)
Cr1	0.0217(2)	0.0172(2)	0.0204(2)	0.00243(17)	0.00327(17)	0.00893(19)
Cr2	0.0189(2)	0.0191(2)	0.0247(2)	0.00247(19)	0.00437(18)	0.0082(2)
O3	0.062(2)	0.055(2)	0.0301(15)	0.0214(14)	0.0124(14)	0.0252(17)
O4	0.0359(15)	0.0296(14)	0.0538(18)	-0.0032(12)	0.0101(13)	0.0206(12)
O5	0.0305(13)	0.0194(11)	0.0296(12)	-0.0020(9)	0.0038(10)	0.0080(10)
O6	0.0228(12)	0.0224(11)	0.0349(13)	0.0061(10)	0.0016(9)	0.0091(10)
O7	0.0262(13)	0.0385(15)	0.0462(17)	0.0013(13)	0.0019(11)	0.0167(12)
Ow8	0.0376(15)	0.0271(13)	0.0316(13)	0.0091(10)	0.0154(11)	0.0123(11)

(a)

c
└─*a*

(b)

b
└─*a*
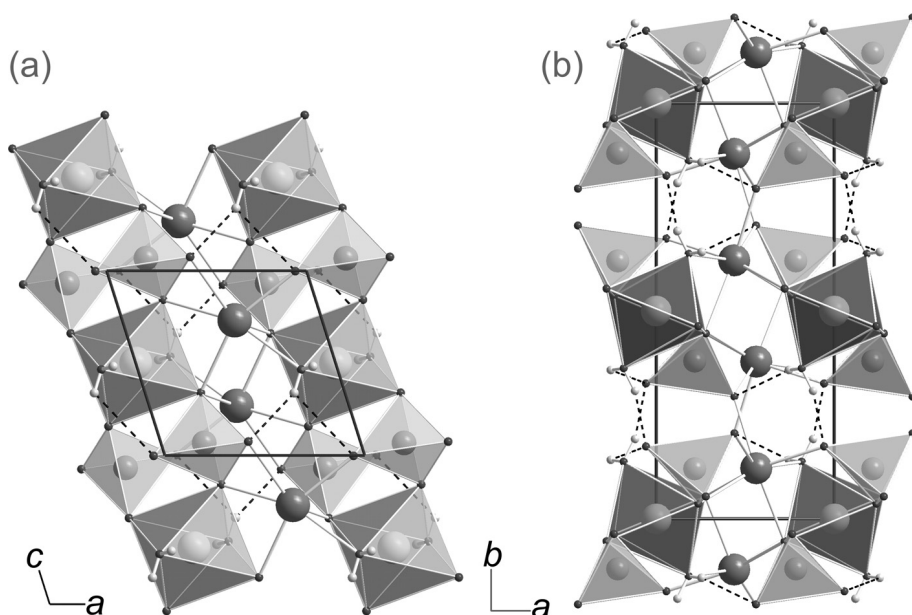
Fig. 2. The crystal structure of wendwilsonite from Schneeberg, $Ca_2(Mg_{0.90},Co_{0.10})(AsO_4)_2 \cdot 2H_2O$. (a) View along [010], perpendicular to the chains; (b) view along [001], parallel to the chains. Ca atoms are shown as large dark spheres. Hydrogen bonds are shown in both views.

Table 8. Selected bond distances (Å) and bond angles (°) for the co-ordination polyhedra in wendwilsonite.

Ca–O1	2.3663(13)	(Mg,Co)–Ow5 x2	2.0494(13)
–O5	2.4149(13)	–O3 x2	2.0577(13)
–O4	2.4241(12)	–O2 x2	2.1886(11)
–O3	2.4281(12)	<(Mg,Co)–O>	2.099
–O2	2.4828(13)		
–O4	2.4988(12)		
–O2	2.5281(12)		
<Ca–O>	2.449		
As1–O1	1.6660(11)	Ow5–H1	0.78(3)
–O4	1.6902(11)	–H2	0.71(3)
–O3	1.6969(11)		
–O2	1.6996(11)		
<As1–O>	1.688		
	Hydrogen bonds		
Ow5···O1	2.5294(18)	Ow5···O4	2.7428(19)
Ow5–H1···O1	165(2)	Ow5–H2···O4	149(3)

mental building unit is an infinite kröhnkite-type tetrahedral-octahedral chain $[(Mg,Co)(AsO_4)_2(H_2O)_2]^{2-}$ whose negative charge is counterbalanced by Ca^{2+} cations (Fig. 2). The chain extends along the *c*-axis at heights of *y* = 0 and 0.5. The coordination number of the Ca atom is seven, with an average Ca-O bond length of 2.449 Å, close to the expected value of 2.50 Å (Baur, 1981); an eighth Ca-O distance, Ca–O3 = 3.1019(13) Å, is too long to be considered a bond.

The $(Mg,Co)O_4(H_2O)_2$ octahedron is characterised by an average (Mg,Co)-O bond length of 2.099 Å which is intermediate between the average [6]Mg-O bond (2.085 Å; Baur, 1981) and [6]Co-O bond (2.112, Wildner, 1992; 2.119 Å, Baur, 1981; 2.111 Å; Trömel, 1984). The shortest intraoctahedral bond is that to the water molecule Ow5 (2.0494(13) Å; Table 8), unlike the situation in roselite where the (Co,Mg)-O3 bond is slightly shorter (2.056(6) Å; Hawthorne & Ferguson, 1977). The $(Mg,Co)O_4(H_2O)_2$ octahedron

shows only a small bond-angle distortion (range of O-Mg-O angles: 83.76(5) to 96.24(5)°). The AsO_4 group is fairly regular, with a small bond-length distortion (Table 8), O-As-O angles ranging between 107.70(6) and 113.76(5)°, and an average As-O bond length of 1.688 Å, very close to the average value in arsenates (<[4]As-O> = 1.682 Å; Baur, 1981).

Bond-valence sums (BVSs) for the atoms in wendwilsonite were calculated using the bond-valence parameters from Brese & O'Keeffe (1991). The results (Table 11) are in good agreement with the expected ideal valencies if additional hydrogen-bond contributions are taken into account (see below).

Hydrogen bonding in wendwilsonite

Hydrogen bonding in wendwilsonite is important for reinforcing the atomic framework. Two hydrogen bonds are donated by the water molecule (Ow5). As can be seen from the data in Table 8, the stronger hydrogen bond is accepted by the strongly underbonded O1 atom (Table 11), having a BVS of only 1.65 valence units (v.u.); the donor-acceptor distance is 2.5294(18) Å. The Ow5···O1 vector roughly extends along [1$\bar{1}$0], providing a strong linkage between adjacent $[(Mg,Co)(AsO_4)_2(H_2O)_2]^{2-}$ chains. The weaker hydrogen bond is accepted by the O4 atom, which is the second most underbonded oxygen ligand. In this case, the donor-acceptor distance is considerably longer (2.7428(19) Å). The hydrogen bonding scheme in wendwilsonite is identical with that in kröhnkite ($Na_2Cu(SO_4)_2 \cdot 2H_2O$, Hawthorne & Ferguson, 1975) and that in its Co analogue roselite (no H atom detected; Hawthorne & Ferguson, 1977), its Zn analogue zincroselite (Keller *et al.*, 2004) and its Mn analogue brandtite (Hejny *et al.*, 1997). However, the strengths of the respective hydrogen bonds differ considerably. The four arsenates wendwilsonite, roselite, zincroselite and brandtite are all characterised by a very strong hydrogen bond (Ow5···O1 = 2.5294(18), 2.517, 2.520(4) and 2.531 Å, respectively), whereas the corresponding bond in kröhnkite is distinctly weaker (Ow5···O1 = 2.626(3) Å).

The new structure type of AgSc(CrO$_4$)$_2$·2H$_2$O

AgSc(CrO$_4$)$_2$·2H$_2$O is unusual because it represents both the first Ag and Sc compound based on kröhnkite-type chains and a novel structure type, which we designate G. The asymmetric unit of this chromate contains one Ag, one Sc, one Cr, five O and two H atoms. Infinite kröhnkite-type tetrahedral-octahedral chains [Sc(CrO$_4$)$_2$(H$_2$O)$_2$]$^{2-}$ run in the direction of the *a*-axis, and are separated by charge-balancing Ag^{1+} cations located on a two-fold position at (0,0,0.5) and symmetry-equivalent positions (Fig. 3).

The Sc atom, located on the origin, is octahedrally coordinated by four oxygen atoms and two water molecules (Table 9). The average Sc-O bond length, 2.095 Å, is slightly shorter than those reported for oxidic Sc compounds (2.105 Å, Baur, 1981; 2.10(7) Å, Serezhkin *et al.*, 2003). The bond-angle distortion is fairly small (range of O-Sc-O angles: 88.53(11) to 91.47(11)°), as is the bond-length distortion (Table 9). In contrast, the CrO$_4$ tetrahedron shows considerable bond-length distortion, with Cr-O bond lengths ranging between 1.608(2) and 1.708(2), but only small deviations of the O-Cr-O angles from the ideal tetrahedral angle (range: 108.90(12) – 110.23(12)°). The average Cr-O bond length (1.654 Å) is nearly identical with that in two other kröhnki-te-type chromates, K$_2$Mg(CrO$_4$)$_2$·2H$_2$O (1.652 Å, Fleck & Kolitsch, 2003) and Rb$_2$Cd(CrO$_4$)$_2$·2H$_2$O (1.650 and 1.652 Å, Kolitsch & Fleck, 2005).

The Ag atom exhibits a [4+4]-coordination, with four short bonds (2x 2.405(2) and 2x 2.492(3) Å) and four long bonds (2.939(3) and 3.026(3) Å). An extensive recent review on oxidic Ag compounds by Müller-Buschbaum (2004) has demonstrated that the coordination number of Ag$^+$ cations is highly variable and spans from 3 to 12, a behaviour quite unlike that observed for alkali cations. The AgO$_8$ polyhedron can be described as a strongly sheared cube (Fig. 4) that shares one of its edges (O3–O4) with the ScO$_4$(H$_2$O)$_2$ octahedron.

BVSs for all atoms were calculated using the bond-valence parameters from Brese & O'Keeffe (1991). The following values were obtained: Ag 0.88, Sc 3.09, O1 1.69, O2 1.74, O3 1.97, O4 1.99 and Ow5 0.47 v.u. These BVSs are all reasonably close to expected ideal valencies. Hydrogen bonding in AgSc(CrO$_4$)$_2$·2H$_2$O is effected by two medium-strong hydrogen bonds that are donated by the water molecule (Ow5). The most underbonded oxygen atom (O1, with 1.69 v.u.) is acceptor of the stronger of the two hydrogen bonds (Ow5···O1 = 2.684(4) Å; Table 9), while the acceptor of the weaker bond is the second most underbonded oxygen ligand, O2 (Ow5···O2 = 2.761(4) Å).

Relation of AgSc(CrO$_4$)$_2$·2H$_2$O to other kröhnkite-type compounds

The new triclinic structure type adopted by AgSc-(CrO$_4$)$_2$·2H$_2$O is closely related to those of the chromates Na*M*(CrO$_4$)$_2$·2H$_2$O (*M* = Fe^{3+}, Al) and *AM*(CrO$_4$)$_2$·2H$_2$O (*A* = K, *M* = Fe^{3+}, Al and *A* = Na, *M* = In), which are both *C*-centred monoclinic and crystallise in type F, subtypes F1 (*C*2/*c*) and F2 (*C*2/*m*), respectively, of our already mentioned classification (Fleck *et al.*, 2002b; Fleck & Kolitsch, 2003; Kolitsch, 2006). A comparative view of these three types is given in Figure 5. The close relation between the types is evident from the pseudo-symmetry of AgSc(CrO$_4$)$_2$·2H$_2$O (already briefly pointed out in the Experimental section): it is metrically pseudo-monoclinic, with a *C*-centred pseudo-cell having the parameters *a* = 10.756, *b* = 5.586, *c* = 7.432 Å, α = 89.79, β = 113.61, γ = 90.13°, *V* = 409.13 Å^3. The tri-

Table 9. Selected bond distances (Å) and bond angles (°) for the co-ordination polyhedra in AgSc(CrO$_4$)$_2$·2H$_2$O.

Ag–O4 x2	2.405(2)	Sc–O3	2.074(2)
–O2 x2	2.492(3)	–O4	2.085(2)
–O3 x2	2.939(3)	–Ow5	2.125(3)
–O1 x2	3.026(3)	<Sc–O>	2.095
<Ag–O>	2.716		
Cr–O1	1.608(2)	Ow5–H1	0.86(5)[a]
–O2	1.623(3)	–H2	0.80(4)[a]
–O3	1.675(2)		
–O4	1.708(2)		
<Cr–O>	1.654		
Hydrogen bonds			
Ow5···O2	2.761(4)	Ow5···O1	2.684(4)
Ow5–H1···O2	148(11)	Ow5–H1···O1	149(8)

[a] O-H distances were restrained (see text).
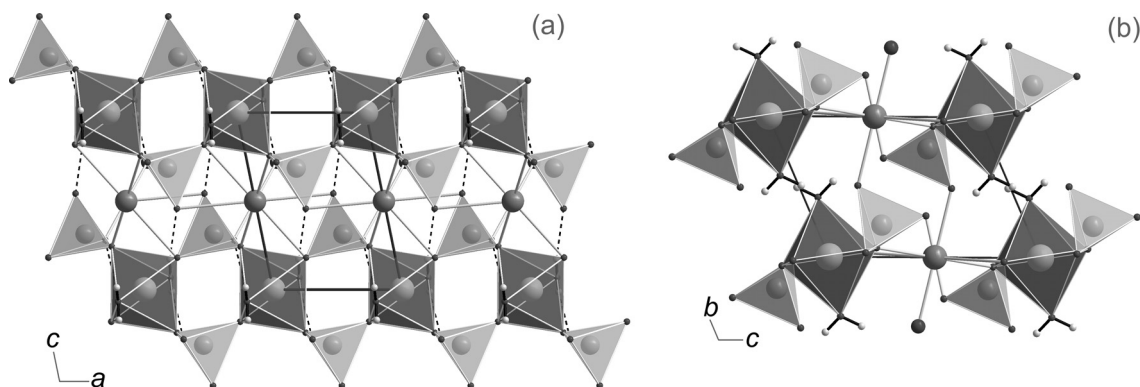
Fig. 3. The crystal structure of AgSc(CrO$_4$)$_2$·2H$_2$O, first representative of a novel triclinic structure type (G) among compounds based on kröhnkite-type infinite octahedral-tetrahedral chains. (a) View along [010], perpendicular to the chains (hydrogen bonding is indicated by dashed lines); (b) view along [100], parallel to the chains. Ag atoms are shown as medium-large dark spheres.
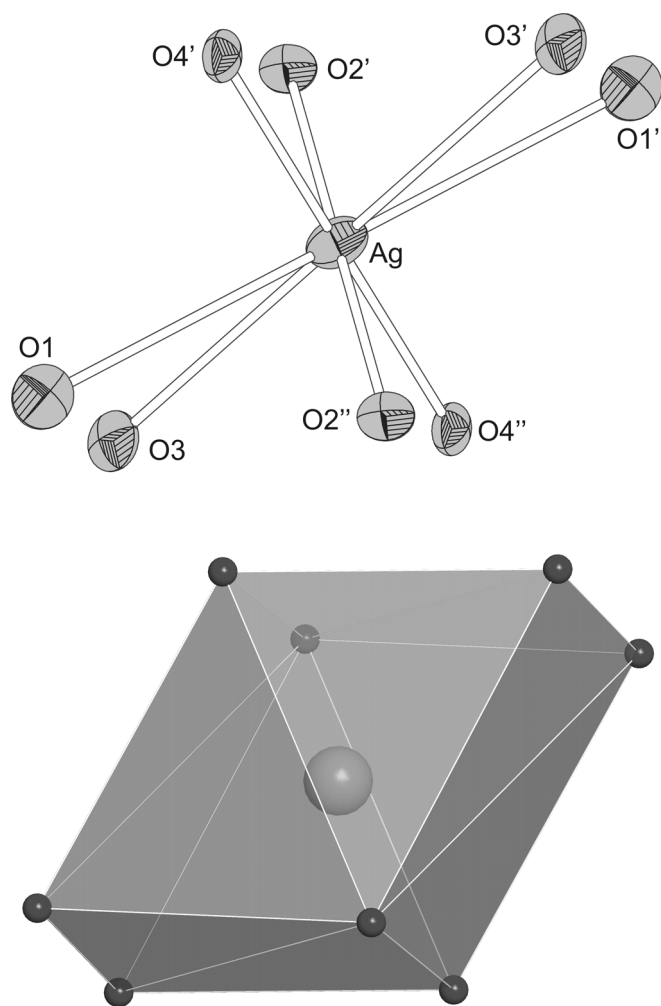
Fig. 4. Two representations of the distorted AgO_8 polyhedron in the crystal structure of triclinic $AgSc(CrO_4)_2 \cdot 2H_2O$ (new type G): a) ellipsoids and Ag-O bonds; b) polyhedron (sheared cube).

clinic cell can be transformed into the pseudo-monoclinic cell *via* the matrix $[120,\bar{1}00,001]$. The pseudo-monoclinic cell parameters of $AgSc(CrO_4)_2 \cdot 2H_2O$ are similar to those of $KAl(CrO_4)_2 \cdot 2H_2O$ (standardised cell: space group $I2/m$, $a = 10.293$, $b = 5.403$, $c = 7.353$ Å, $\beta = 107.41°$, $V = 399.86$ Å^3, $Z = 2$; Cudennec & Riou, 1977). A comparison with NaAl-$(CrO_4)_2 \cdot 2H_2O$ (space group $C2/c$, $a = 14.080$, $b = 5.338$, $c = 10.655$ Å, $\beta = 110.3°$, $V = 750.9$ Å^3, $Z = 4$) also allows one to recognise a distinct similarity: If the a parameter of $NaAl(CrO_4)_2 \cdot 2H_2O$ is halved, it is very similar to the pseudomonoclinic c parameter in $AgSc(CrO_4)_2 \cdot 2H_2O$ (both b parameters are equivalent and $c_{NaAlCr} \sim a_{AgScCr,pseudomon.}$; compare also Fig. 5).

The new structure type of $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ and isotypic $Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$

$Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ and isotypic $Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ represent a novel, triclinic structure type among compounds based on kröhnkite-like chains. Identical to the situ-

ation in other dichromates with kröhnkite-like chains ($K_2Cd(Cr_2O_7)_2 \cdot 2H_2O$, Durif & Averbuch-Pouchot, 1979; $K_2Zn(Cr_2O_7)_2 \cdot 2H_2O$, Fleck & Kolitsch, 2003; $K_2Co(Cr_2O_7)_2 \cdot 2H_2O$ and $Cs_2Cd(Cr_2O_7)_2 \cdot 2H_2O$, Kolitsch & Fleck, 2005; Table 12) the Cr_2O_7 groups in the new structure type assume the role of the bridging XO_4 groups in the chains of kröhnkite-type compounds *sensu strictu* (Fig. 6), as suggested by the structural formula. The asymmetric unit of the two novel compounds contains one alkali atom (Rb or Cs), one Cu, two Cr, eight O and two H atoms. All atoms are in general positions except Cu which is located on a centre of inversion at (0, 0, 0.5). In both dichromates infinite $[Cu^{2+}(Cr_2O_7)_2(H_2O)_2]$-chains running parallel to [110] are linked *via* A^+ cations (A = Rb, Cs) along both the [001] and $[1\bar{1}0]$ directions, as shown in Figure 6.

The Rb$^+$ cation shows an irregular coordination to oxygen within about 3.3 Å; there is no gap in the distribution of Rb-O bond lengths (Table 10), making it difficult to assign a specific coordination number to the Rb atom. An arbitrary distance threshold at 3.3 Å has been chosen, resulting in a coordination number of ten, and a BVS of 1.10 v.u.. The Cs$^+$ cation is also irregularly surrounded by ten oxygen ligands within 3.35 Å. Again, there is no distinct gap in the distribution of Cs-O bond lengths. For an arbitrary distance threshold of 3.3 Å, the coordination number is eight and the BVS amounts to 1.07 v.u.; if two further oxygen neighbours, at distances of 3.312(3) and 3.325(3) Å, are taken into account, a BVS of 1.24 v.u. would be obtained.

The coordination of the Cu^{2+} cation reflects a strong Jahn-Teller distortion. The coordination number, although roughly [4+2], approaches [2+2+2], with two short bond lengths of 1.931(2)/1.926(3) Å (for Rb/Cs), two medium short ones (1.970(2)/1.977(3) Å) and two rather long ones (2.400(2)/2.476(3) Å). Such coordinations are fairly unusual for copper oxysalts (*cf.* Eby & Hawthorne, 1993). In a study of Jahn-Teller effects in Cu^{2+} oxysalt minerals, Burns & Hawthorne (1996) noted that [2+2+2]-distorted Cu$^{2+}O_6$ 'octahedra' are only known to occur in the structures of bayldonite and cyanochroite. These authors attributed the [2+2+2]-coordination to a dynamic Jahn-Teller effect, rather than the static distortion that is usual in CuO$_6$ oxysalt structures. A later study of the crystal structure of turquoise revealed another example of a distorted [2+2+2]-coordination (Kolitsch & Giester, 2000).

Bond-valence analysis and hydrogen bonding in $M_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ ($M = Rb$, Cs)

BVSs for all atoms in novel $M_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ (M = Rb, Cs) were calculated using the bond-valence parameters from Brese & O'Keeffe (1991). The values obtained are as follows (values for $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ given first): Rb/Cs 1.10/1.07 (*vide supra* for discussion of coordination numbers); Cu 2.10/2.13; Cr1 5.93/5.96; Cr2 5.86/5.87; O1 1.93/1.98; O2 1.83/1.78; O3 2.05/2.05; O4 2.17/2.19; O5 1.91/1.83; O6 1.83/1.84; O7 1.82/1.85; Ow8 0.46/0.45 v.u.. These values are all reasonably close to expected ideal valencies, although the oxygen atom bridging the two CrO$_4$ groups (O4) appears somewhat overbonded. However, such
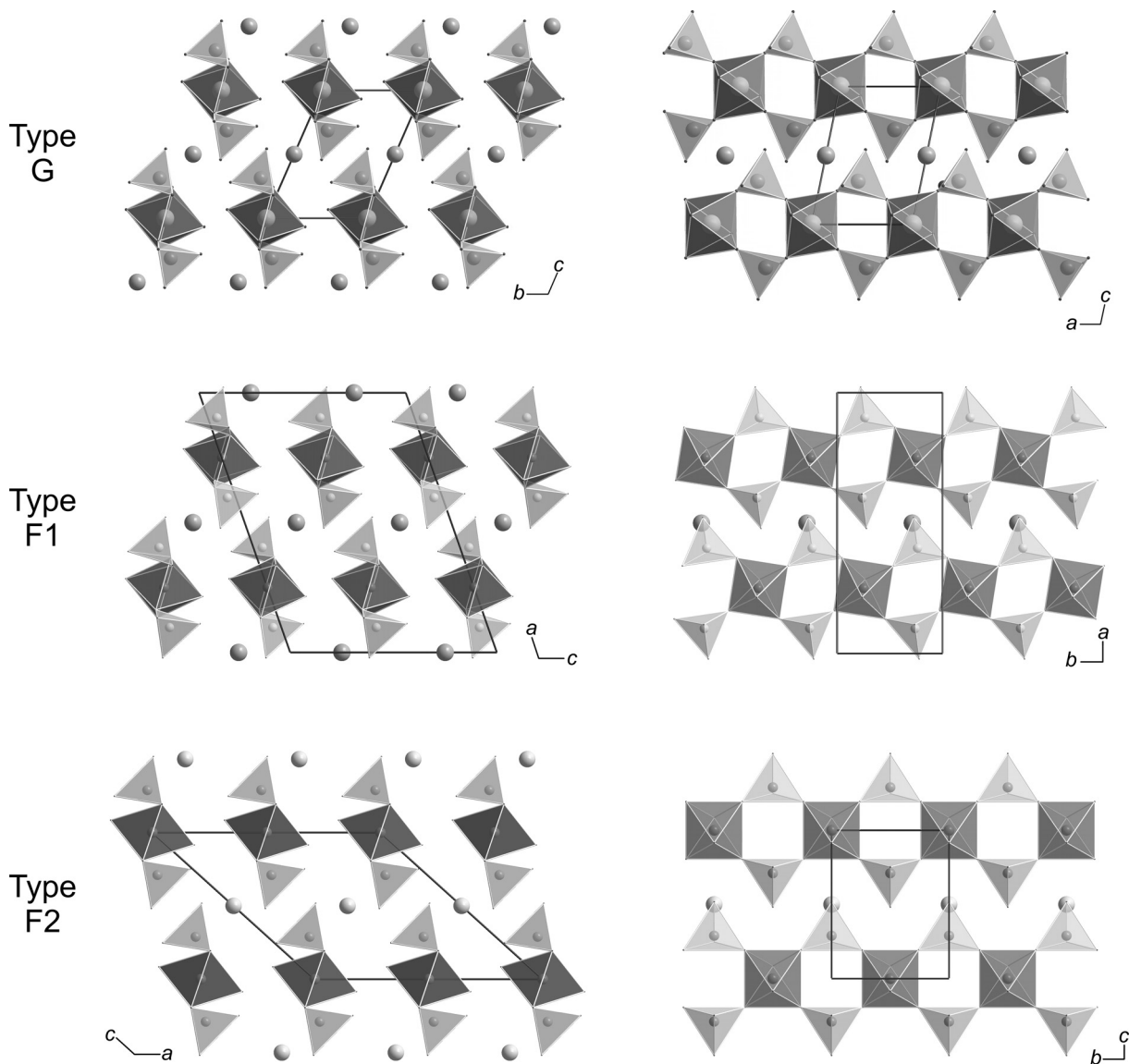
Fig. 5. Comparison of $AgSc(CrO_4)_2 \cdot 2H_2O$ (new type G) with the closely related types F1 (represented by $NaFe(CrO_4)_2 \cdot 2H_2O$) and F2 (represented by $KFe(CrO_4)_2 \cdot 2H_2O$), each shown in two different views; left side: along the kröhnkite-type chains; right side: perpendicular to the kröhnkite-type chains (note that in this case adjacent chains in the types F1 and F2 have been omitted for clarity). Ag, Na and K atoms are shown as dark spheres.

overbonding (with BVSs > 2.00 v.u.) is typical of bridging oxygen atoms in pyro-compounds (diphosphates, diarsenates, dichromates, disilicates *etc.*)

The hydrogen-bonding scheme (Table 10, bottom) shows that in both new dichromates the oxygen atoms O7 is acceptor of the weak hydrogen bond donated by the Ow8-H2 group (the H1 atom is not involved in any hydrogen bonding). In the Rb compound O7 is the most underbonded oxygen atom (BVS 1.82 v.u.), while in the Cs compound other oxygen atoms apart from O7 are also similarly underbonded (bond-valence contributions added from the very long Cs-O bonds would increase their BVSs, however). The refinement of the hydrogen atoms indicated some positional disorder, reflected also by the unexpectedly high U_{iso} values. This observation is in qualitative agreement with, firstly, the low strengths of the hydrogen bonds (as mentioned above,

H1 has no apparent acceptor, and H2 is involved in fairly weak bonds with Ow8···O7 distances > 2.70 Å) and, secondly, the presence of alternative positions for the H1 atom [for both compounds a possible acceptor would be O3, with Ow8···O3 distances of 2.778 Å (Rb) and 2.797 Å (Cs), and with Ow8-H1···O3 bond angles of about 151° (Rb) and 155° (Cs)]. The weak Ow8···O7 bond provides some strengthening of the structure roughly parallel to the *c*-axis (Fig. 6).

Geometry of Cr_2O_7 groups in kröhnkite-like $A_2M(Cr_2O_7)_2 \cdot 2H_2O$ compounds

According to the classification of X_2O_7 groups (X = As, Be, Cr, Ge, P, S, Si, V) in pyro-compounds by Clark & Morley (1976), the Cr_2O_7 groups in kröhnkite-like $A_2M(Cr_2O_7)_2 \cdot 2H_2O$ compounds all show a behaviour that is

(a)

b

c

(b)

c

a — *b*
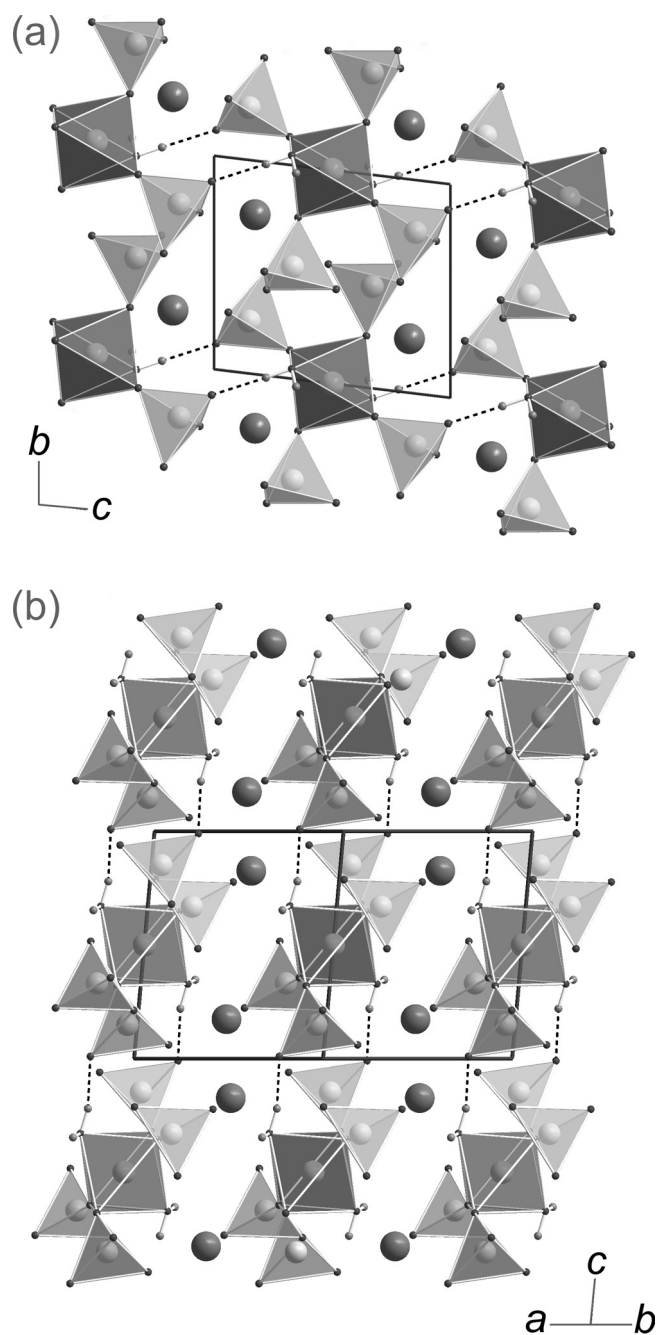
Fig. 6. The crystal structure of $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$, a new triclinic compound based on kröhnkite-like, infinite octahedral-tetrahedral $[Cu^{2+}(Cr_2O_7)_2(H_2O)_2]^{2-}$-chains with bridging Cr_2O_7 groups. (a) View along [100], perpendicular to the chains; (b) view along [110], parallel to the chains. Rb atoms are shown as large dark spheres; hydrogen bonding is indicated by dashed lines.

Table 10. Selected bond distances (Å) and bond angles (°) for the coordination polyhedra in $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ and isotypic $Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$.

Rb–O1	2.854(3)	Cs–O1	2.987(3)
–O5	2.951(3)	–O7	3.131(3)
–O7	3.041(2)	–O5	3.136(3)
–O7	3.045(2)	–O7	3.179(3)
–O2	3.091(3)	–O2	3.206(3)
–O4	3.128(2)	–O6	3.240(3)
–O3	3.178(2)	–O4	3.243(3)
–O6	3.195(3)	–O3	3.292(3)
–O2	3.204(3)	[–O2]	[3.312(3)]
–O5	3.292(3)	[–O5]	[3.325(3)]
[–Ow8]	[3.427(3)]	[–Ow8]	[(3.529(3))]
<Rb–O>	[10]3.098	<Cs–O>	[8]3.177
Cu–O3 (2x)	1.931(2)	Cu–O3 (2x)	1.926(3)
–Ow8 (2x)	1.970(2)	–Ow8 (2x)	1.977(3)
–O6 (2x)	2.400(2)	–O6 (2x)	2.476(3)
<Cu–O>	[4]1.951	<Cu–O>	[4]1.952
	[6]2.100		[6]2.126
Cr1–O1	1.591(2)	Cr1–O1	1.585(3)
–O2	1.609(2)	–O2	1.606(3)
–O3	1.653(2)	–O3	1.658(3)
–O4	1.762(2)	–O4	1.759(3)
<Cr1–O>	1.654	<Cr1–O>	1.652
Cr2–O5	1.599(2)	Cr2–O5	1.600(3)
–O6	1.619(2)	–O6	1.616(3)
–O7	1.626(2)	–O7	1.625(3)
–O4	1.800(2)	–O4	1.800(3)
<Cr2–O>	1.661	<Cr2–O>	1.660

Hydrogen bonds for $Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$		Hydrogen bonds for $Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$	
Ow8–H1	0.86(3) [a]	Ow8–H1	0.80(2) [a]
Ow8–H2	0.88(3) [a]	Ow8–H2	0.83(3) [a]
Ow8···O7	2.711(3)	Ow8···O7	2.720(4)
Ow8–H2···O7	165(6)	Ow8–H2···O7	171(5)

[a] O-H distances were restrained (see text).

Table 11. Results of empirical bond-valence calculations (v.u.) for wendwilsonite.

	Ca	$(Mg,Co)^a$	As	Sum
O1	0.340		1.314	1.65
O2	0.248	0.262 ↓x2	1.200	1.93
	0.219			
O3	0.288	0.373 ↓x2	1.209	1.87
O4	0.291		1.231	1.76
	0.238			
Ow5	0.298	0.382 ↓x2		0.68
Sum	1.92	2.03	4.95	

Note: bond-valence parameters used are from Brese & O'Keeffe (1991).
[a]The Co content on the (Mg,Co) site has not been taken into account since it would decrease the bond-valence sum only marginally.

characteristic of other dichromate compounds, i.e., a (more or less) eclipsed conformation, *X*-O-*X* angles < 140° and an O_{bridge} atom belonging to the coordination sphere of at least one cation.

The $Cr-O_{bridge}-Cr$ angle in the Cr_2O_7 groups in $A_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ (*A* = Rb: 122.13(11)°, *A* = Cs: 124.96(14)°) lie within the range observed for the other di-

chromates mentioned above. However, the data of the two new compounds provide evidence for an obvious positive correlation between the size of the alkali A^+ cation and the Cr-O-Cr angle, as clearly seen from the angle data listed in

Table 12. Comparison of compounds based on kröhnkite-like chains containing dichromate groups.[a]

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å³)	Cr-O-Cr (°)	Ref. [b]
$Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$ structure type									
$Rb_2Cu(Cr_2O_7)_2 \cdot 2H_2O$	7.272(1)	7.648(2)	7.772(2)	91.89(3)	99.72(3)	115.79(3)	380.84(15)	122.13(11)	1
$Cs_2Cu(Cr_2O_7)_2 \cdot 2H_2O$	7.462(1)	7.819(2)	7.847(2)	93.19(3)	99.57(3)	116.34(3)	400.23(15)	124.99(14)	1
$K_2Cd(Cr_2O_7)_2 \cdot 2H_2O$ structure type									
$Cs_2Cd(Cr_2O_7)_2 \cdot 2H_2O$	7.368(1)	8.051(2)	8.047(2)	88.68(3)	81.12(3)	63.81(3)	422.66(16)	125.77(12)	2
$K_2Co(Cr_2O_7)_2 \cdot 2H_2O$	6.801(1)	7.723(1)	7.814(1)	89.23(3)	81.05(3)	64.39(3)	364.93(14)	120.17(7)	2
$K_2Zn(Cr_2O_7)_2 \cdot 2H_2O$	6.794(1)	7.735(1)	7.834(1)	88.97(3)	80.90(3)	64.57(3)	366.5(2)	120.10(13)	3
$K_2Cd(Cr_2O_7)_2 \cdot 2H_2O$ [c]	6.733(3)	7.940(3)	7.999(3)	88.13(5)	80.55(5)	65.06(5)	382.19(5)	120.4	4

[a]All compounds are triclinic, with space group $P\bar{1}$.
[b]1: This work; 2: Kolitsch & Fleck (2005); 3: Fleck & Kolitsch (2003); 4: Durif & Averbuch-Pouchot (1979).
[c]The originally given unit cell for $K_2Cd(Cr_2O_7)_2 \cdot 2H_2O$ ($a = 7.999(3)$, $b = 7.956(3)$, $c = 6.733(3)$ Å, $\alpha = 115.18(5)$, $\beta = 80.55(5)$, $\gamma = 96.11(5)°$; Durif & Averbuch-Pouchot, 1979) is non-reduced; the unit cell has been standardised here using the matrix ($00\bar{1}$, $0\bar{1}\bar{1}$, $\bar{1}00$).

Table 12. This correlation is valid irrespective of the nature of the octahedrally coordinated M^{2+} cation, and is explained by the fact that increasingly larger A^+ cations allow the Cr_2O_7 building units to increasingly relax from steric constraints and to minimize Cr-Cr repulsion.

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