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Rietveld refinement of the Tutton's salt $Rb_2[Cu(H_2O)_6](SO_4)_2$ from parallel-beam X-ray powder diffraction data

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Dirubidium hexaaquacopper(II bis(sulfate), $Rb_2[Cu(H_2O)_6](SO_4)_2$, is characterized by a $\langle Cu—O \rangle$ distance of 2.098 (136) Å. The $Cu(H_2O)_6$ octahedron is strongly distorted because of the Jahn–Teller effect. Rb is eightfold-coordinated by six O atoms and two water molecules with an $\langle Rb—O \rangle$ distance of 3.055 (74) Å.

Key indicators

Powder X-ray study
T = 298 K
Mean σ(S–O) = 0.004 Å
R factor = 0.024
wR factor = 0.034

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

Comment

The title compound, $Rb_2[Cu(H_2O)_6](SO_4)_2$, is a member of the isomorphous series known as Tutton's salts. Their general formula is $M^I_2[M^{II}(H_2O)_6](SO_4)_2$, where M^I and M^{II} are, respectively, a monovalent and a divalent cation. Further salts containing SeO_4^{2-} or CrO_4^{2-} as anion have also been synthesized. The structure of Tutton's salts results from the linking of more or less irregular $M^{II}(H_2O)_6$ octahedra and SO_4^{2-} tetrahedra by the M^I cation, forming sheets parallel to (100). The sheets are linked *via* medium to weak hydrogen bonds acting from the octahedral ligands to the acceptors of the sulfate groups (Fig. 1). The structure of the title compound was determined by van der Zee *et al.* (1972) from single-crystal neutron data. However, during an investigation aiming to rationalize the crystal chemistry of Tutton's salts, we observed

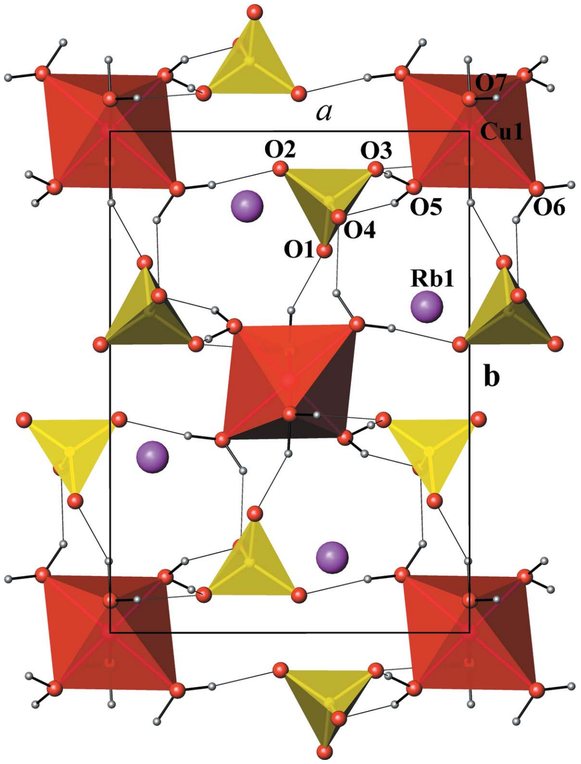

Figure 1
Crystal structure of $Rb_2[Cu(H_2O)_6](SO_4)_2$ as seen along [001].

that reference data of $Rb_2[Cu(H_2O)_6](SO_4)_2$ were characterized by very large standard uncertainties of the unit-cell parameters and fractional coordinates, and by the absence of displacement parameters. Because of the need for precise structural data to determine polyhedral distortions and other geometrical features, we decided to carry out a structure refinement by the Rietveld method from parallel-beam X-ray powder data of the title compound (Fig. 2). The refined ⟨Cu—O⟩ distance within the $Cu(H_2O)_6$ polyhedron is 2.10 (14) Å (the number within parentheses refers to dispersion of bond distances). This value compares favourably with 2.10 (15) Å of reference data (van der Zee *et al.*, 1972), with 2.09 (6) Å reported by Cotton *et al.* (1993) for $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, with 2.10 (14) Å by Robinson & Kennard (1972) for $K_2[Cu(H_2O)_6](SO_4)_2$, and with 2.10 (16) Å by Shields & Kennard (1972) for $Cs_2[Cu(H_2O)_6](SO_4)_2$. The octahedron is strongly distorted as a result of the Jahn–Teller effect. Rb is coordinated by six O atoms and two water molecules with an ⟨Rb—O⟩ distance of 3.06 (7) Å. This value compares favourably with the ⟨Rb—O⟩ distance of 3.04 (9) Å reported by van der Zee *et al.* (1972) and is similar to the ⟨Rb—O⟩ distances of 3.06–3.08 reported by Euler *et al.* (2000) for $Rb_2[M^{II}(H_2O)_6](SO_4)_2$ (M^{II} = Mg, Mn, Fe, Co, Ni and Zn).

Experimental

The title compound was prepared by dissolving Rb_2SO_4 (133.5 mg) and $CuSO_4 \cdot 5H_2O$ (124.8 mg) in distilled water (8 ml) and subsequent slow evaporation of the solvent at 295 K. The product consisted of a fine light-blue powder, with platy morphology, of $Rb_2[Cu(H_2O)_6](SO_4)_2$.

Crystal data

$Rb_2[Cu(H_2O)_6](SO_4)_2$
M_r = 534.68
Monoclinic, $P2_1/a$
a = 9.25625 (5) Å
b = 12.36268 (6) Å
c = 6.22496 (3) Å
β = 105.3090 (4)°
V = 687.06 (1) Å^3
Z = 2
D_x = 2.585 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.541789 Å
μ = 14.34 mm^{-1}
T = 298 K
Specimen shape: cylinder
Specimen prepared at 100 kPa
Specimen prepared at 298 K
Particle morphology: plate, light blue

Data collection

Bruker AXS D8Advance diffractometer
Specimen mounting: 0.3 mm diameter borosilicate glass capillary
Specimen mounted in transmission mode
Scan method: step
Absorption correction: for a cylinder mounted on the φ axis
T_{min} = 0.072, T_{max} = 0.172

Refinement

Refinement on I_{net}
R_p = 0.024
R_{wp} = 0.034
R_{exp} = 0.014
R_B = 0.042
S = 2.46
Excluded region(s): none
Profile function: CW Profile function number 3 with 19 terms; pseudo-Voigt profile coefficients as parameterized by Thompson *et al.* (1987). Asymmetry correction of Finger *et al.* (1994).
118 parameters
Only H-atom coordinates refined
$w = 1/[Y_i]$
$(\Delta/\sigma)_{max}$ = 0.01
Preferred orientation correction: spherical harmonics

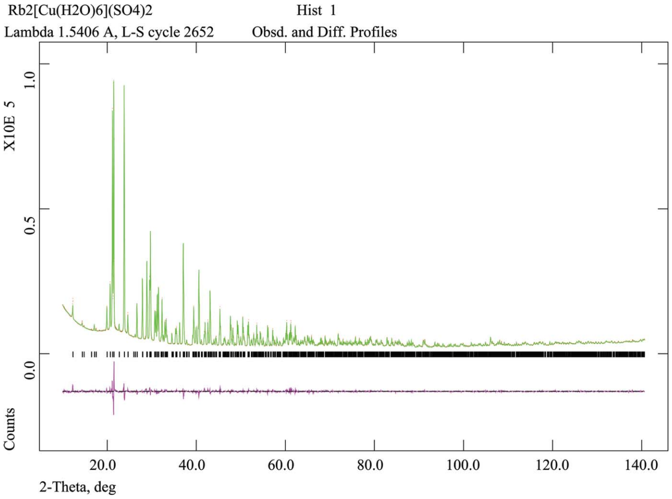

Figure 2
Experimental (dots) and calculated (solid line) intensities of $Rb_2[Cu(H_2O)_6](SO_4)_2$. Difference pattern appears below. Vertical markers refer to calculated positions of Bragg reflections. Parallel-beam X-ray diffraction data on parallel beam using Cu $K\alpha$.

Table 1
Selected geometric parameters (Å, °).

Cu1—O5	2.039 (4)	S1—O4	1.4658 (22)
Cu1—O5^{i}	2.039 (4)	Rb1—O1	3.024 (4)
Cu1—O6	2.285 (4)	Rb1—O1^{ii}	3.027 (4)
Cu1—O6^{i}	2.285 (4)	Rb1—O2^{iii}	3.075 (4)
Cu1—O7	1.969 (4)	Rb1—O2^{ii}	3.074 (4)
Cu1—O7^{i}	1.969 (4)	Rb1—O3^{iii}	2.988 (4)
S1—O1	1.4840 (22)	Rb1—O4^{iv}	2.973 (4)
S1—O2	1.4661 (21)	Rb1—O5	3.229 (5)
S1—O3	1.4771 (22)	Rb1—O6^{v}	3.046 (4)
O5—Cu1—O5^{i}	180	O1—S1—O2	109.27 (22)
O5—Cu1—O7	89.78 (21)	O1—S1—O3	108.25 (23)
O5—Cu1—O7^{i}	90.22 (21)	O1—S1—O4	110.41 (24)
O5^{i}—Cu1—O7	90.22 (21)	O2—S1—O3	108.73 (25)
O5^{i}—Cu1—O7^{i}	89.78 (21)	O2—S1—O4	110.83 (24)
O7—Cu1—O7^{i}	180	O3—S1—O4	109.30 (24)

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O5—H1⋯O3	0.98 (3)	1.85 (4)	2.696 (6)	144 (3)
O5—H2⋯O4^{vi}	0.95 (4)	1.84 (4)	2.746 (6)	159 (3)
O6—H3⋯O2^{vii}	0.97 (4)	1.84 (4)	2.788 (6)	166 (3)
O6—H4⋯O4^{iv}	0.98 (3)	1.90 (4)	2.755 (6)	144 (3)
O7—H5⋯O3^{viii}	0.95 (4)	1.77 (4)	2.669 (6)	156 (3)
O7—H6⋯O1^{ix}	1.01 (2)	1.83 (4)	2.647 (6)	133 (3)

Symmetry codes: (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-1$; (vi) $x, y, z-1$; (vii) $x-1, y, z-1$; (viii) $-x, -y, -z+1$; (ix) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+1$.

Powder diffraction data were analyzed by the Rietveld method using the crystallographic package *GSAS* (Larson & Von Dreele, 1985). Starting atomic positions were those of van der Zee *et al.* (1972). H-atom positions were refined using restraints on O—H, H—H (pseudo-bond) and H⋯O bond distances of, respectively, 0.97 (3), 1.54 (4), and 1.78 (5) Å calculated as an average of reference and unpublished data on the hydrogen network of Tutton's salts. Inclusion of H atoms, besides improving statistical descriptors of the refinement, has been proved to provide a better estimate of both positional and displacement parameters of the O atoms of the water molecules (Ballirano *et al.*, 2003). $U_{iso}(H)$ values were set at 0.04 Å^2.

Data collection: *DiffracPlus* (Bruker, 2004); method used to solve structure: atomic coordinates of van der Zee *et al.* (1972); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 1985); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2006).

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