Crystal structure of the Tutton's salts rubidium hexaaquanickel(II) selenate, $Rb_2[Ni(H_2O)_6](SeO_4)_2$, and rubidium hexaaquacopper(II) selenate, $Rb_2[Cu(H_2O)_6](SeO_4)_2$

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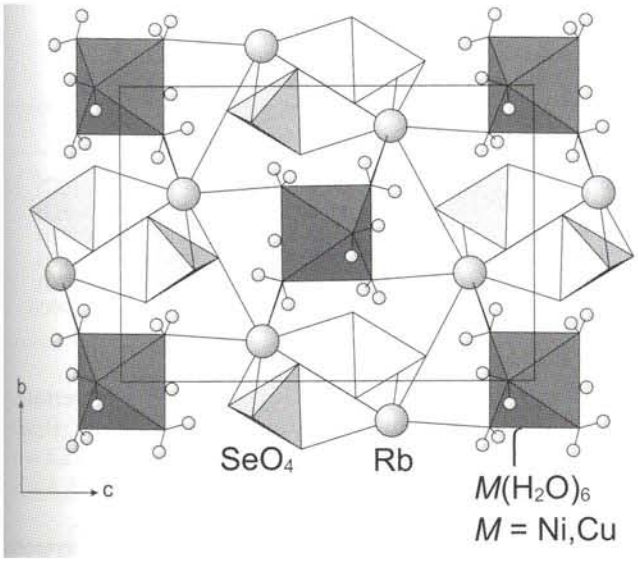

Abstract

$H_{12}NiO_{14}Rb_2Se_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 6.339(1)$ Å, $b = 12.595(3)$ Å, $c = 9.307(2)$ Å, $\beta = 105.33(3)°$, $V = 716.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.025$, $wR_{ref}(F^2) = 0.064$, $T = 293$ K.

$H_{12}CuO_{14}Rb_2Se_2$, monoclinic, $P12_1/c1$ (No. 14), $a = 6.351(1)$ Å, $b = 12.551(3)$ Å, $c = 9.398(2)$ Å, $\beta = 104.70(3)°$, $V = 724.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.021$, $wR_{ref}(F^2) = 0.056$, $T = 293$ K.

Source of material

Prismatic crystals of the title compounds up to several mm in size were obtained by controlled evaporation from aqueous solutions of selenic acid, rubidium carbonate and M^{II}-carbonate (M = Ni, Cu) in water at a temperature of 353 K.

Discussion

The crystal structures of the title compounds, $Rb_2[Ni(H_2O)_6](SeO_4)_2$ and $Rb_2[Cu(H_2O)_6](SeO_4)_2$, consist of isolated $M^{II}O_6$-octahedra (M = Ni, Cu) located on the centre of symmetry. All six coordinating oxygen atoms belong to the water molecules. Each octahedron is surrounded by isolated SeO_4-tetrahedra as well as [8]-coordinated rubidium atoms (range 2.88 Å to 3.33 Å for M = Ni and 2.95 Å to 3.23 Å for M = Cu). The polyhedra are connected by a system of medium-strong hydrogen bonds (range 2.67 Å to 2.80 Å).

The title compounds are isostructural with the large family of Tutton's salts $A^{I}_2[M^{II}(H_2O)](X^{VI}O_4)_2$ (A = Na, K, Rb, Cs, Tl, NH_4; M = Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ru, Cd; X = S, Se, Cr). A comparison of the Jahn-Teller distortion of the $Cu(H_2O)_6$ polyhedron in $Rb_2[Cu(H_2O)_6](SeO_4)_2$ with that in other copper Tutton's salts, $K_2[Cu(H_2O)_6](SO_4)_2$ [1], $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$ [2,3], $Rb_2[Cu(H_2O)_6](SO_4)_2$ [4], $Cs_2[Cu(H_2O)_6](SO_4)_2$ [5], $Tl_2[Cu(H_2O)_6](SO_4)_2$ [6], $(NH_4)_2[Cu(H_2O)_6](SeO_4)_2$ [7], and $K_2[Cu(H_2O)_6](SeO_4)_2$ [8], shows that Cu is always [4+2]-coordinated, and that Cu—O bond lengths are within a restricted range (short bonds: 1.94 Å to 2.08 Å; long bonds: 2.23 Å to 2.32 Å). It is noteworthy that the orientation of the longest Cu—O bonds in the $Cu(H_2O)_6$ polyhedron can depend on temperature, pressure and deuteration (e.g., [2,3]). The longest Cu—O bond in sulphate Tutton's salts is generally larger than that in the selenate analogues. An exception is $(NH_4)_2[Cu(H_2O)_6](SO_4)_2$, possibly due to the influence of the ammonium group and its hydrogen bonds. The geometry of the $Ni(H_2O)_6$ octahedron in $Rb_2[Ni(H_2O)_6](SeO_4)_2$ is almost identical to that in $Rb_2[Ni(H_2O)_6](SO_4)_2$ [9].

1. Rubidium hexaaquanickel(II) selenate, $Rb_2[Ni(H_2O)_6](SeO_4)_2$

Table 1. Data collection and handling.

Crystal:	light green prism, size 0.04 × 0.06 × 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	132.43 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa-CCD, 773 frames, $\Delta\varphi = 1°$
$2\theta_{max}$:	61.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4141, 2178
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1980
$N(param)_{refined}$:	113
Programs:	SHELXS-97 [10], SHELXL-97 [11], ATOMS [12]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1W1)	4e	–0.333(6)	0.125(3)	–0.025(4)	0.04(1)
H(2W1)	4e	–0.333(6)	0.060(3)	0.079(4)	0.05(1)
H(1W2)	4e	0.110(5)	0.126(3)	0.220(4)	0.035(9)
H(2W2)	4e	0.268(6)	0.088(3)	0.192(4)	0.05(1)
H(1W3)	4e	–0.009(4)	0.165(2)	–0.141(3)	0.022(7)
H(2W3)	4e	–0.054(5)	0.093(3)	–0.240(4)	0.040(9)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	4*e*	0.65709(4)	0.65525(2)	-0.13516(3)	0.0333(2)	0.0331(2)	0.0332(2)	0.00080(9)	0.0116(1)	-0.00098(9)
Ni	2*a*	0	0	0	0.0181(2)	0.0188(2)	0.0164(2)	0.0004(1)	0.0048(1)	-0.0012(1)
Se	4*e*	0.26716(3)	0.63790(2)	0.09357(2)	0.0210(1)	0.0212(1)	0.0176(1)	0.00149(7)	0.00429(8)	0.00208(7)
O(1W)	4*e*	-0.2932(3)	0.0631(2)	0.0018(2)	0.0239(7)	0.0265(9)	0.0266(8)	0.0030(7)	0.0105(6)	0.0017(7)
O(2W)	4*e*	0.1608(3)	0.1084(2)	0.1594(2)	0.0224(8)	0.0307(9)	0.0224(8)	-0.0009(7)	0.0037(7)	-0.0064(7)
O(3W)	4*e*	0.0282(3)	0.1073(2)	-0.1632(2)	0.0303(8)	0.0247(9)	0.0203(8)	0.0002(7)	0.0060(6)	0.0012(7)
O(1)	4*e*	0.2206(3)	0.5687(2)	-0.0591(2)	0.053(1)	0.045(1)	0.0225(8)	0.0052(9)	0.0025(8)	-0.0081(8)
O(2)	4*e*	0.4247(3)	0.7389(1)	0.0830(2)	0.0291(8)	0.0269(9)	0.047(1)	-0.0011(7)	0.0138(7)	0.0084(8)
O(3)	4*e*	0.3979(3)	0.5626(1)	0.2322(2)	0.0263(8)	0.0339(9)	0.0225(7)	0.0061(7)	0.0057(6)	0.0084(7)
O(4)	4*e*	0.0374(3)	0.6809(1)	0.1233(2)	0.0237(8)	0.0277(9)	0.043(1)	0.0041(7)	0.0129(7)	0.0052(8)

2. Rubidium hexaaquacopper(II) selenate, $Rb_2[Cu(H_2O)_6](SeO_4)_2$

Table 4. Data collection and handling.

Crystal:	light blue prism, size 0.22 × 0.23 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	132.66 cm^{-1}
Diffractometer, scan mode:	Nonius Kappa-CCD, 567 frames, $\Delta\varphi = 1°$
$2\theta_{max}$:	60.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4045, 2107
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1978
$N(param)_{refined}$:	113
Programs:	SHELXS-97 [10], SHELXL-97 [11], ATOMS [12]

Table 5. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1W1)	4*e*	-0.320(6)	0.128(3)	-0.019(4)	0.05(1)
H(2W1)	4*e*	-0.315(6)	0.060(3)	0.080(5)	0.06(1)
H(1W2)	4*e*	0.109(6)	0.125(3)	0.212(4)	0.05(1)
H(2W2)	4*e*	0.265(6)	0.096(3)	0.190(4)	0.05(1)
H(1W3)	4*e*	0.001(6)	0.171(3)	-0.167(4)	0.05(1)
H(2W3)	4*e*	-0.052(6)	0.099(3)	-0.250(4)	0.040(9)

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb	4*e*	0.65540(4)	0.65319(2)	-0.12413(3)	0.0291(1)	0.0296(1)	0.0304(1)	0.00035(8)	0.01037(9)	0.00016(8)
Cu	2*a*	0	0	0	0.0161(2)	0.0182(2)	0.0177(2)	0.0011(1)	0.0042(1)	-0.0026(1)
Se	4*e*	0.26980(3)	0.63929(2)	0.10431(2)	0.0185(1)	0.0196(1)	0.0181(1)	0.00068(6)	0.00415(8)	0.00227(6)
O(1W)	4*e*	-0.2806(2)	0.0614(1)	0.0033(2)	0.0216(7)	0.0232(7)	0.0241(7)	0.0036(6)	0.0087(6)	0.0004(6)
O(2W)	4*e*	0.1608(3)	0.1099(2)	0.1523(2)	0.0211(8)	0.0358(9)	0.0274(8)	0.0014(7)	0.0048(7)	-0.0061(7)
O(3W)	4*e*	0.0298(3)	0.1117(2)	-0.1830(2)	0.0342(9)	0.0273(9)	0.0274(9)	0.0028(7)	0.0046(7)	-0.0024(7)
O(1)	4*e*	0.2371(3)	0.5698(2)	-0.0459(2)	0.049(1)	0.040(1)	0.0220(8)	0.0027(8)	0.0035(7)	-0.0073(7)
O(2)	4*e*	0.4178(3)	0.7445(1)	0.0957(2)	0.0268(7)	0.0232(7)	0.045(1)	-0.0026(6)	0.0104(7)	0.0080(7)
O(3)	4*e*	0.4022(2)	0.5654(1)	0.2428(2)	0.0245(7)	0.0315(8)	0.0217(7)	0.0049(6)	0.0064(6)	0.0090(6)
O(4)	4*e*	0.0345(2)	0.6760(1)	0.1308(2)	0.0197(7)	0.0313(8)	0.0412(9)	0.0032(6)	0.0109(7)	0.0046(7)

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