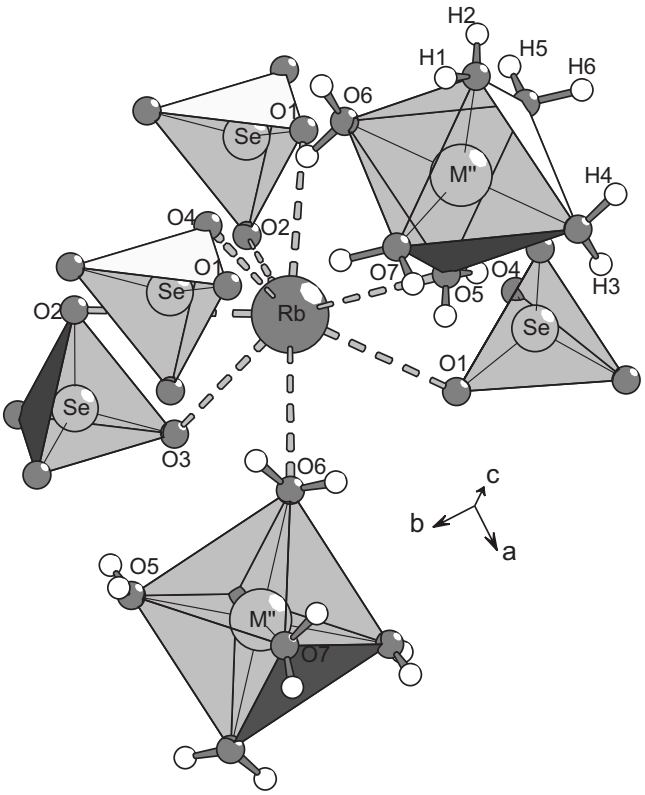
Crystal structure of Tutton's salts, $Rb_2[M^{II}(H_2O)_6](SeO_4)_2$, M^{II} = Mg, Co, Mn, Zn

H. Euler*, B. Barbier, A. Meents and A. Kirfel

Universität Bonn, Mineralogisch-Petrologisches Institut, Poppelsdorfer Schloss, D-53115 Bonn, Germany

Received April 3, 2003, accepted and available on-line July 25, 2003; CSD-No. 409719, 409720, 409721, 409722



Abstract

$H_{12}MgO_{14}Rb_2Se_2$, monoclinic, $P12_1/a1$ (No. 14), a = 9.401(1) Å, b = 12.658(2) Å, c = 6.339(1) Å, β = 105.25(1)°, V = 727.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.020, $wR_{ref}(F^2)$ = 0.040, T = 293 K.

$CoH_{12}O_{14}Rb_2Se_2$, monoclinic, $P12_1/a1$ (No. 14), a = 9.363(1) Å, b = 12.618(1) Å, c = 6.3562(7) Å, β = 105.238(9)°, V = 724.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.018, $wR_{ref}(F^2)$ = 0.037, T = 293 K.

$H_{12}MnO_{14}Rb_2Se_2$, monoclinic, $P12_1/a1$ (No. 14), a = 9.4496(8) Å, b = 12.760(1) Å, c = 6.3794(7) Å, β = 105.189(7)°, V = 742.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.056, T = 293 K.

$H_{12}O_{14}Rb_2Se_2Zn$, monoclinic, $P12_1/a1$ (No. 14), a = 9.352(1) Å, b = 12.626(2) Å, c = 6.360(1) Å, β = 105.195(8)°, V = 724.7 Å^3, Z = 2, $R_{gt}(F)$ = 0.024, $wR_{ref}(F^2)$ = 0.048, T = 293 K.

Source of material

All compounds of the isomorphous series $Rb_2[M^{II}(H_2O)_6](SeO_4)_2$ (M^{II} = Mg, Mn, Co, Zn) were prepared by dissolution of equimolar amounts of rubidium selenate Rb_2SeO_4 and M^{II}-selenate-hydrate $M^{II}SeO_4 \cdot nH_2O$ in hot destilled water and ensuing evaporation of the solvent H_2O. The M^{II}-selenate-hydrates contained different amounts of crystal water. For the syntheses of the Tutton's salts with M^{II} = Mg, Co, Zn, the M^{II}-selenate-hexahydrates, and for M^{II} = Mn, the Mn(II)-selenate-pentahydrate was used. Differently coloured, in most cases ideomorphous single crystals of dimensions up to 10 mm were obtained.

Discussion

The structure is characterized by irregular RbO_8 polyhedra (d(Rb–O) = 2.881(2) Å – 3.384(4) Å) and $M^{II}(H_2O)_6$ octahedra ($d(M^{II}–O)$ = 2.030(2) Å – 2.203(3) Å), the latter being linked to SeO_4 tetrahedra by hydrogen bonds. Compared to the isotypic sulfates [1], and the own structure analyses of Tutton's salts of the same isomorphous series with M^{II} = Ni, Cu, found in excellent agreement with [2], one finds: 1. The lattice constants increase, a and c by about 1.9%, b by about 1.5%, due to the larger volume of the $(SeO_4)^{2-}$ anion [3]. The ratio of the TO_4 volumes (T = S, Se), $V(SeO_4)/V(SO_4)$ = 1.37, is in perfect agreement with the ratio of the Se—O and S—O bond lengths, d(Se—O)/d(S—O) = 1.111. The angle β decreases for all compounds by about 0.8°. With respect to the exchange of M^{II}, the linear correlations between the different lattice constants and the cation radii exhibit the same slope. 2. The volumes of the $M^{II}O_6$ coordination octahedra agree with those of the sulfates. 3. The volumes of the RbO_8 coordination polyhedra increase by 4.4%. 4. While, in agreement with chemical expectation, the selenate group is practically invariant against the M^{II} cation exchange in the hexahydrate complex, the volumes of both the $M^{II}O_6$ and RbO_8 coordination polyhedra increase as the cation radius $R(M^{II})$ [4] increases. However, for $V(RbO_8)$, the rate of increase is about three times smaller than for $V(M^{II}O_6)$. 5. a, b and $V(RbO_8)$ of the Mg compound are, as in the sulfate series and in [5] significantly larger than expected from the linear lattice constant correlations observed for the other structures. This finding can be attributed to the smaller electronegativitiy of Mg, causing a somewhat weaker electrostatic Rb-O interaction, as reflected by increased distances d(Rb—O5) = 3.263(3) Å and d(Rb—O6) = 3.185(2) Å. 6. For the individual selenate compounds, the respective distributions of the hydrogen bonds differ from those observed in the sulfates, but no significant differences are found for the mean distances $\bar{d}$(O–H···O).

* Correspondence author (e-mail: h.euler@uni-bonn.de)

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

Table 1. Data collection and handling.

Crystal:	colorless sphere, size 0.24 × 0.25 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	118.30 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-6R, ω
$2\theta_{max}$:	50.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5006, 1287
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1125
$N(param)_{refined}$:	113
Programs:	SHELXS-97 [6], DIAMOND [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.204(4)	0.093(3)	0.291(6)	0.04(1)
H(2)	4*e*	0.213(4)	0.123(3)	0.109(6)	0.03(1)
H(3)	4*e*	–0.246(4)	0.100(3)	–0.055(6)	0.04(1)
H(4)	4*e*	–0.144(4)	0.169(3)	0.004(6)	0.04(1)
H(5)	4*e*	–0.065(4)	–0.059(3)	0.342(6)	0.05(1)
H(6)	4*e*	0.024(4)	–0.130(3)	0.336(6)	0.05(1)

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}
Mg	2*a*	0	0	0	0.0175(6)	0.0200(6)	0.0195(6)	–0.0009(5)	0.0057(5)	0.0004(5)
Se	4*e*	0.40531(3)	0.13879(2)	0.73205(4)	0.0183(2)	0.0217(2)	0.0215(2)	–0.0022(1)	0.0052(1)	–0.0015(1)
O(1)	4*e*	0.4118(2)	0.2389(2)	0.5717(3)	0.049(1)	0.026(1)	0.028(1)	–0.010(1)	0.014(1)	0.0017(9)
O(2)	4*e*	0.5582(2)	0.0720(2)	0.7790(4)	0.023(1)	0.048(1)	0.057(2)	0.009(1)	0.002(1)	–0.003(1)
O(3)	4*e*	0.2703(2)	0.0617(2)	0.6035(3)	0.022(1)	0.032(1)	0.029(1)	–0.0080(9)	0.0065(9)	–0.0048(9)
O(4)	4*e*	0.3755(2)	0.1813(2)	0.9611(3)	0.043(1)	0.028(1)	0.022(1)	–0.0058(9)	0.0117(9)	–0.0039(8)
O(5)	4*e*	0.1616(2)	0.1063(2)	0.1636(4)	0.025(1)	0.034(1)	0.023(1)	–0.0081(9)	0.005(1)	–0.0002(9)
O(6)	4*e*	–0.1636(2)	0.1082(2)	0.0226(4)	0.022(1)	0.024(1)	0.036(1)	0.0004(9)	0.008(1)	0.0002(9)
O(7)	4*e*	–0.0070(3)	–0.0655(2)	0.2894(3)	0.030(1)	0.028(1)	0.026(1)	0.0031(9)	0.015(1)	0.0041(9)
Rb	4*e*	0.13224(3)	0.34520(2)	0.34107(5)	0.0337(2)	0.0330(2)	0.0336(2)	–0.0011(1)	0.0121(1)	0.0010(1)

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

Table 4. Data collection and handling.

Crystal:	dark red sphere, size 0.29 × 0.30 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	129.45 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-6R, ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4974, 1279
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1114
$N(param)_{refined}$:	113
Programs:	SHELXS-97 [6], DIAMOND [7]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.195(4)	0.086(3)	0.282(6)	0.05(1)
H(2)	4*e*	0.220(4)	0.122(2)	0.109(5)	0.019(9)
H(3)	4*e*	–0.250(4)	0.100(3)	–0.054(6)	0.03(1)
H(4)	4*e*	–0.148(5)	0.175(3)	–0.006(6)	0.06(1)
H(5)	4*e*	–0.073(5)	–0.054(3)	0.342(7)	0.06(1)
H(6)	4*e*	0.020(5)	–0.124(4)	0.336(7)	0.06(1)

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}
Co	2*a*	0	0	0	0.0199(3)	0.0210(3)	0.0212(3)	–0.0010(2)	0.0061(2)	0.0005(2)
Se	4*e*	0.40610(3)	0.13784(2)	0.73214(4)	0.0208(2)	0.0228(2)	0.0233(2)	–0.0022(1)	0.0056(1)	–0.0016(1)
O(1)	4*e*	0.4147(3)	0.2392(2)	0.5744(3)	0.049(1)	0.029(1)	0.029(1)	–0.009(1)	0.014(1)	0.0028(9)
O(2)	4*e*	0.5583(2)	0.0691(2)	0.7769(4)	0.025(1)	0.047(1)	0.059(2)	0.008(1)	0.003(1)	–0.005(1)
O(3)	4*e*	0.2685(2)	0.0625(2)	0.6027(3)	0.023(1)	0.034(1)	0.030(1)	–0.0084(9)	0.0055(9)	–0.0066(9)
O(4)	4*e*	0.3772(3)	0.1801(2)	0.9615(3)	0.045(1)	0.030(1)	0.024(1)	–0.004(1)	0.012(1)	–0.0030(8)
O(5)	4*e*	0.1626(3)	0.1099(2)	0.1644(4)	0.029(1)	0.035(1)	0.024(1)	–0.009(1)	0.005(1)	0.000(1)
O(6)	4*e*	–0.1671(3)	0.1095(2)	0.0267(4)	0.024(1)	0.028(1)	0.037(1)	0.0005(9)	0.008(1)	0.0008(9)
O(7)	4*e*	–0.0052(3)	–0.0650(2)	0.2920(3)	0.032(1)	0.029(1)	0.029(1)	0.0030(9)	0.0144(9)	0.0038(9)
Rb	4*e*	0.13381(3)	0.34461(2)	0.34269(5)	0.0360(2)	0.0339(2)	0.0350(2)	–0.0009(1)	0.0128(1)	0.0009(1)

3. Rubidium hexaaquamanganese(II) selenate, $Rb_2[Mn(H_2O)_6](SeO_4)_2$

Table 7. Data collection and handling.

Crystal:	light pink sphere, size 0.25 × 0.26 × 0.29 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	123.67 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-6R, ω
$2\theta_{max}$:	50.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5106, 1312
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1122
$N(param)_{refined}$:	113
Programs:	SHELXS-97 [6], DIAMOND [7]

Table 8. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.207(5)	0.088(4)	0.297(8)	0.03(1)
H(2)	4*e*	0.214(5)	0.120(4)	0.115(7)	0.02(1)
H(3)	4*e*	–0.251(6)	0.102(4)	–0.048(8)	0.04(1)
H(4)	4*e*	–0.159(7)	0.182(5)	–0.02(1)	0.07(2)
H(5)	4*e*	–0.075(6)	–0.061(4)	0.350(9)	0.06(2)
H(6)	4*e*	0.008(6)	–0.127(5)	0.332(9)	0.05(2)

Table 9. 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}
Mn	2*a*	0	0	0	0.0219(4)	0.0225(4)	0.0238(4)	–0.0016(3)	0.0051(3)	0.0006(3)
Se	4*e*	0.40781(4)	0.13726(3)	0.73275(6)	0.0228(2)	0.0236(2)	0.0245(2)	–0.0023(2)	0.0054(2)	–0.0020(2)
O(1)	4*e*	0.4148(4)	0.2366(2)	0.5733(5)	0.060(2)	0.028(1)	0.031(2)	–0.013(2)	0.015(1)	0.002(1)
O(2)	4*e*	0.5588(3)	0.0701(3)	0.7760(6)	0.028(2)	0.056(2)	0.064(2)	0.008(2)	0.002(2)	–0.006(2)
O(3)	4*e*	0.2720(3)	0.0621(2)	0.6072(4)	0.030(2)	0.035(2)	0.034(2)	–0.010(1)	0.009(1)	–0.008(1)
O(4)	4*e*	0.3800(3)	0.1800(2)	0.9618(5)	0.048(2)	0.032(1)	0.027(2)	–0.006(1)	0.014(1)	–0.006(1)
O(5)	4*e*	0.1700(4)	0.1106(3)	0.1699(6)	0.032(2)	0.038(2)	0.028(2)	–0.008(1)	0.008(2)	0.001(1)
O(6)	4*e*	–0.1705(3)	0.1136(2)	0.0243(5)	0.030(2)	0.029(2)	0.041(2)	0.001(1)	0.010(1)	0.002(1)
O(7)	4*e*	–0.0067(4)	–0.0690(3)	0.3007(5)	0.040(2)	0.029(2)	0.034(2)	0.004(1)	0.019(1)	0.006(1)
Rb	4*e*	0.13588(5)	0.34537(3)	0.34444(7)	0.0394(3)	0.0357(2)	0.0365(2)	–0.0014(2)	0.0133(2)	0.0011(2)

4. Rubidium hexaaquazink(II) selenate, $Rb_2[Zn(H_2O)_6](SeO_4)_2$

Table 10. Data collection and handling.

Crystal:	colorless sphere, size 0.25 × 0.26 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	134.51 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC-6R, ω
$2\theta_{max}$:	50.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4970, 1277
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1100
$N(param)_{refined}$:	113
Programs:	SHELXS-97 [6], DIAMOND [7]

Table 11. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.209(6)	0.091(4)	0.31(1)	0.06(2)
H(2)	4*e*	0.221(6)	0.120(4)	0.111(8)	0.03(1)
H(3)	4*e*	–0.255(6)	0.094(4)	–0.066(8)	0.04(1)
H(4)	4*e*	–0.149(6)	0.171(4)	0.000(9)	0.05(2)
H(5)	4*e*	–0.068(5)	–0.061(3)	0.329(7)	0.02(1)
H(6)	4*e*	0.022(6)	–0.121(4)	0.329(9)	0.04(2)

Table 12. 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}
Zn	2*a*	0	0	0	0.0195(3)	0.0219(3)	0.0199(3)	–0.0014(2)	0.0053(3)	0.0006(2)
Se	4*e*	0.40640(4)	0.13808(3)	0.73315(6)	0.0184(2)	0.0211(2)	0.0207(2)	–0.0022(2)	0.0044(2)	–0.0015(2)
O(1)	4*e*	0.4148(3)	0.2391(2)	0.5758(4)	0.046(2)	0.030(2)	0.028(2)	–0.009(1)	0.014(1)	0.003(1)
O(2)	4*e*	0.5584(3)	0.0690(3)	0.7769(6)	0.026(2)	0.046(2)	0.058(2)	0.008(1)	0.005(2)	–0.005(2)
O(3)	4*e*	0.2677(3)	0.0632(2)	0.6042(4)	0.024(2)	0.030(2)	0.029(2)	–0.008(1)	0.004(1)	–0.007(1)
O(4)	4*e*	0.3785(3)	0.1809(2)	0.9625(5)	0.043(2)	0.029(1)	0.021(1)	–0.005(1)	0.011(1)	–0.004(1)
O(5)	4*e*	0.1629(3)	0.1100(2)	0.1644(5)	0.026(2)	0.033(2)	0.024(2)	–0.009(1)	0.006(1)	–0.002(1)
O(6)	4*e*	–0.1672(3)	0.1091(2)	0.0274(5)	0.024(2)	0.024(2)	0.034(2)	0.001(1)	0.009(1)	0.000(1)
O(7)	4*e*	–0.0029(4)	–0.0643(3)	0.2931(5)	0.027(2)	0.029(2)	0.026(2)	0.003(1)	0.012(1)	0.003(1)
Rb	4*e*	0.13440(5)	0.34497(3)	0.34379(7)	0.0332(2)	0.0323(2)	0.0320(2)	–0.0009(2)	0.0114(2)	0.0008(2)

References

1. Euler, H.; Barbier, B.; Klumpp, S.; Kirfel A.: Crystal structure of Tutton's salts, $Rb_2[M^{II}(H_2O)_6](SO_4)_2$, M^{II} = Mg, Mn, Fe, Co, Ni, Zn. Z. Kristallogr. NCS **215** (2000) 473-476.
2. Fleck, M.; Kolitsch, U.: 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, $Rb_2[Cu(H_2O)_6](SeO_4)_2$. Z. Kristallogr. NCS **217** (2002) 15-16.
3. Zunic, T. B.; Vickovic, I.: IVTON-program for the calculation of geometrical aspects of crystal structures and some crystal chemical applications. J. Appl. Crystallogr. **29** (1996) 305-306.
4. Shannon, R.D.: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. A**32** (1976) 751-767.
5. Micka, Z.; Prokopova, L.; Cisarova, I.; Havlicek, D.: Crystal structure, thermoanalytical properties and infrared spectra of double magnesium selenates. Collect. Czech. Chem. Comm. CCCCA **61** (1996) 1295-1306.
6. Sheldrick G. M.: SHELXL-97. Program for refining crystal structures. University of Göttingen 1997.
7. Diamond: Visual Crystal Structure Information System, Version 2.1, Crystal Impact, Postfach 1251, D-53002 Bonn.