Crystal structure of Tutton's salts $\text{Ti}_2[\text{M}^{\text{II}}(\text{H}_2\text{O})_6](\text{SeO}_4)_2$, $\text{M}^{\text{II}} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$

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Abstract

$\text{H}_{12}\text{MgO}_{14}\text{Se}_2\text{Ti}_2$, monoclinic, $P12_1/a1$ (no. 14), $a = 9.434(2) \text{ \AA}$, $b = 12.634(2) \text{ \AA}$, $c = 6.292(1) \text{ \AA}$, $\beta = 105.72(2)^\circ$, $V = 721.9 \text{ \AA}^3$, $Z = 2$, $R_{\text{gof}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.047$, $T = 295 \text{ K}$.

$\text{H}_{12}\text{MnO}_{14}\text{Se}_2\text{Ti}_2$, monoclinic, $P12_1/a1$ (no. 14), $a = 9.490(1) \text{ \AA}$, $b = 12.734(2) \text{ \AA}$, $c = 6.332(1) \text{ \AA}$, $\beta = 105.57(1)^\circ$, $V = 737.1 \text{ \AA}^3$, $Z = 2$, $R_{\text{gof}}(F) = 0.032$, $wR_{\text{ref}}(F^2) = 0.068$, $T = 295 \text{ K}$.

$\text{H}_{12}\text{CoO}_{14}\text{Se}_2\text{Ti}_2$, monoclinic, $P12_1/a1$ (no. 14), $a = 9.387(2) \text{ \AA}$, $b = 12.600(2) \text{ \AA}$, $c = 6.308(2) \text{ \AA}$, $\beta = 105.70(2)^\circ$, $V = 718.3 \text{ \AA}^3$, $Z = 2$, $R_{\text{gof}}(F) = 0.036$, $wR_{\text{ref}}(F^2) = 0.082$, $T = 295 \text{ K}$.

$\text{H}_{12}\text{NiO}_{14}\text{Se}_2\text{Ti}_2$, monoclinic, $P12_1/a1$ (no. 14), $a = 9.334(1) \text{ \AA}$, $b = 12.572(2) \text{ \AA}$, $c = 6.298(1) \text{ \AA}$, $\beta = 105.70(1)^\circ$, $V = 711.5 \text{ \AA}^3$, $Z = 2$, $R_{\text{gof}}(F) = 0.031$, $wR_{\text{ref}}(F^2) = 0.051$, $T = 295 \text{ K}$.

$\text{H}_{12}\text{CuO}_{14}\text{Se}_2\text{Ti}_2$, monoclinic, $P12_1/a1$ (no. 14), $a = 9.400(2) \text{ \AA}$, $b = 12.539(2) \text{ \AA}$, $c = 6.315(1) \text{ \AA}$, $\beta = 105.01(2)^\circ$, $V = 718.9 \text{ \AA}^3$, $Z = 2$, $R_{\text{gof}}(F) = 0.028$, $wR_{\text{ref}}(F^2) = 0.055$, $T = 295 \text{ K}$.

$\text{H}_{12}\text{O}_{14}\text{Se}_2\text{TiZn}_2$, monoclinic, $P12_1/a1$ (no. 14), $a = 9.383(1) \text{ \AA}$, $b = 12.612(2) \text{ \AA}$, $c = 6.317(1) \text{ \AA}$, $\beta = 105.59(1)^\circ$, $V = 720.1 \text{ \AA}^3$, $Z = 2$, $R_{\text{gof}}(F) = 0.027$, $wR_{\text{ref}}(F^2) = 0.054$, $T = 295 \text{ K}$.

Source of material

The synthesis of all title compounds of the probably isomorphous series $\text{Ti}_2[\text{M}^{\text{II}}(\text{H}_2\text{O})_6](\text{SeO}_4)_2$ was performed by dissolution of equimolar amounts of thallium selenate Ti_2SeO_4 and M^{II} selenate hydrate $\text{M}^{\text{II}}\text{SeO}_4 \cdot n\text{H}_2\text{O}$ in hot distilled water and ensuing evaporation of the solvent. The M^{II} selenate hydrates contained different amounts of crystal water. For the syntheses of the Tutton's salts with $\text{M}^{\text{II}} = \text{Mg}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$, the M^{II} selenate hexahydrates were used, for $\text{M}^{\text{II}} = \text{Mn}$, the M^{II} selenate pentahydrate. Differently coloured, mostly ideomorphous single crystals of dimensions up to 10 mm were obtained.

Experimental details

To reduce errors introduced by insufficient corrections of absorption effects, it was attempted to grind a crystal sphere in order to apply a spherical absorption correction in the course of data processing. The grinding produced an ellipsoid, whose deviation from spherical is characterized by the given max, mid and min crystal dimensions.

Discussion

The so far unknown crystal structures of the compounds of the thallium selenates, constituting one more important series in our studies of crystal chemistry, metal-water interaction and hydrogen bonds in Tutton salts (Rb sulfates [1], Rb selenates [2], Cs sulfates [3], Cs selenates [4], K sulfates [5], K selenates [6], Tl sulfates [7]) by single crystal and powder X-ray diffraction experiments. As all other Tutton salts, they are isotypic. Due to scattering power of Tl and data errors introduced by insufficient correction for the large absorption, the hydrogen positions could not be determined by difference Fourier mapping, as done in [1–6]. Therefore, all hydrogen coordinates were calculated from the linear correlations $x(\text{H}(i))$, $y(\text{H}(i))$, $z(\text{H}(i))$, $i = 1 \dots 6$ vs the cation radius $R(\text{M}^{\text{I}})$ ($\text{M}^{\text{I}} = \text{K}, \text{Rb}, \text{Cs}$), derived for each of the 6 independent hydrogen bonds of the so far studied compounds. The evaluation of the O–H...O bond lengths and angles yielded reasonable hydrogen coordinates. During the structure refinements, these predicted hydrogen coordinates were kept fixed, contrary to a common variable isotropic thermal displacement parameter, assigned to all hydrogens atoms. In all cases, the agreement indices were significantly lowered by introducing the H atoms into the model, for example $R_1^{\text{calc.H}}(\text{M}^{\text{II}} = \text{Mg}) = 0.0284$ to $R_1^{\text{no.H}}(\text{M}^{\text{II}} = \text{Mg}) = 0.0302$. The Tutton salt structure is characterized by irregular $\text{M}^{\text{I}}\text{O}_8$ polyhedral (here with $\text{M}^{\text{I}} = \text{Tl}$), $d(\text{Tl} \cdots \text{O}) = 2.796(5) - 3.362(5) \text{ \AA}$, and $\text{M}^{\text{II}}(\text{H}_2\text{O})_6$ octahedra, which are linked to the SeO_4 groups by a system of hydrogen bonds. According to expectations, the most distorted $\text{M}^{\text{II}}(\text{H}_2\text{O})_6$ octahedron is obtained for $\text{M}^{\text{II}} = \text{Cu}$ (Jahn-Teller distortion) with

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$d(\text{M}^{\text{II}}-\text{O}) = 1.942(5) - 2.295(6) \text{ \AA}$. Compared to the earlier studied isotopic Rb selenates [2], one finds for the present compounds:

1. Except for Mg and Cu, the lattice parameters of all other M^{II} compounds increase on average by 0.3 % for a , but decrease on average by 0.2 %, 0.7 % for b and c , respectively. These small changes follow from the similar sizes of the Tl^+ and Rb^+ cations ($R(\text{Tl}^+) = 1.59 \text{ \AA}$, $R(\text{Rb}^+) = 1.61 \text{ \AA}$ [8]). The unit cell angle β increasing for all compounds, except for $\text{M}^{\text{II}} = \text{Cu}$, by about 0.4° shows the same slope in the linear correlation between β and the M^{II} cation radius. The volume of the unit cell decreases by about 0.7 %. With respect to the exchange of M^{II} , the linear correlations between the lattice parameters and the cation radii exhibit for a , b , c the same slopes, within error limits, as in the Rb selenates.
2. The volumes of the TlO_8 coordination polyhedra in the Tl selenate salts are on average 1.4 % smaller than those in the Rb selenates ($V(\text{TlO}_8)/V(\text{RbO}_8) = 0.986$) [8,9]. This ratio corresponds to the 3rd power of the ratio of the mean $\text{Tl}-\text{O}$ and $\text{Rb}-\text{O}$ distances, $(\bar{d}(\text{Tl}-\text{O})/\bar{d}(\text{Rb}-\text{O}))^3 = 0.988$.
3. Each of the volumes of the $\text{M}^{\text{II}}\text{O}_6$ coordination octahedra agrees with that of the corresponding Rb selenates.
4. 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 $\text{M}^{\text{II}}\text{O}_6$ and the TlO_8 coordination polyhedra increase as the cation radius $R(\text{M}^{\text{II}})$ [8,9] increases. For $V(\text{TlO}_8)$, the increase is more than three times

smaller than that for $V(\text{M}^{\text{II}}\text{O}_6)$, and it is also significantly smaller than that in the analog Rb selenates.

5. As in the Rb selenates, the a lattice parameter of the Mg and Cu compounds deviate significantly from the a vs $R(\text{M}^{\text{II}})$ relation $a[\text{\AA}] = 1.13(5) R(\text{M}^{\text{II}}) + 8.55(4)$. The same holds for the b lattice parameters of the Mg- and Cu-salts, respectively, the former being larger, the latter smaller. Again, for Mg, this can be attributed to the larger M-O electronegativity difference causing somewhat weaker $\text{Tl}-\text{O}$ interactions as reflected by the increased distances, $d(\text{Tl}-\text{O}_5) = 3.362(5) \text{ \AA}$ and $d(\text{Tl}-\text{O}_6) = 3.243(5) \text{ \AA}$, as compared to the other corresponding bond lengths of the other M^{II} compounds of the same series ($\bar{d}(\text{Tl}-\text{O}_5) = 3.301(6) \text{ \AA}$, $\bar{d}(\text{Tl}-\text{O}_6) = 3.145(6) \text{ \AA}$). The distorted shape of the CuO_6 octahedron is caused by the Jahn-Teller effect, the reason for the exceptional behavior of the Cu compound.

6. The oxygen atoms of the SeO_4 group are acceptors of 6 different hydrogen bonds, which provide links to four $\text{M}^{\text{II}}(\text{H}_2\text{O})_6$ octahedra surrounding each selenate anion. Contrary to O1 and O2, O3 and O4 are fixed by bifurcated bonds. Considering all structures of the here studied series, under the reservation that the H positions are derived rather than experimental ones, the hydrogen bond lengths differ negligibly ($\pm 0.025 \text{ \AA}$) from those observed in the Rb selenate analogues, and also the averages over all donor-acceptor distances in the Tl salts structures $\bar{d}(\text{O}-\text{H}\cdots\text{O}) = 2.741(8) \text{ \AA}$ are equal to those in the Rb salts structures $\bar{d}(\text{O}-\text{H}\cdots\text{O}) = 2.734(4) \text{ \AA}$.

1. Thallium hexaaquamagnesium(II) selenate, $\text{Tl}_2[\text{Mg}(\text{H}_2\text{O})_6](\text{SeO}_4)_2$

Table 1. Data collection and handling.

Crystal:	colorless ellipsoid, size $0.31 \times 0.30 \times 0.29 \text{ mm}$
Wavelength:	Mo K_α radiation ($0.71069 \text{ \AA}$)
λ :	274.41 cm^{-1}
Diffractometer, scan mode:	RIGAKU AFC-6R, ω
$2\theta_{\text{max}}$:	50.1°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4908, 1261
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1003
$N(\text{param})_{\text{refined}}$:	90
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.2005	0.0891	0.2837	0.05(1)
H(2)	4e	0.2173	0.1207	0.1119	0.05
H(3)	4e	-0.2442	0.0999	-0.0470	0.05
H(4)	4e	-0.1464	0.1653	0.0056	0.05
H(5)	4e	-0.0725	-0.0588	0.3285	0.05
H(6)	4e	0.0215	-0.1266	0.3350	0.05

Table 3. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	2a	0	0	0	0.016(2)	0.023(2)	0.025(2)	0.001(1)	0.004(2)	0.001(1)
Se	4e	0.40864(7)	0.13604(5)	0.7385(1)	0.0206(3)	0.0253(3)	0.0261(4)	-0.0029(3)	0.0065(3)	-0.0030(3)
O(1)	4e	0.4142(6)	0.2354(4)	0.574(1)	0.053(3)	0.038(3)	0.033(3)	-0.010(3)	0.009(3)	0.005(3)
O(2)	4e	0.5615(6)	0.0704(5)	0.784(1)	0.027(3)	0.062(4)	0.062(5)	0.002(3)	0.003(3)	-0.012(4)
O(3)	4e	0.2743(5)	0.0590(4)	0.6108(9)	0.024(3)	0.036(3)	0.031(3)	-0.007(2)	0.008(2)	-0.006(3)
O(4)	4e	0.3796(6)	0.1795(4)	0.9694(9)	0.051(3)	0.038(3)	0.022(3)	-0.005(3)	0.010(3)	-0.005(2)
O(5)	4e	0.1638(5)	0.1025(4)	0.1655(9)	0.030(3)	0.037(3)	0.025(3)	-0.012(2)	0.010(2)	-0.009(2)
O(6)	4e	-0.1603(5)	0.1096(4)	0.0260(9)	0.025(3)	0.027(2)	0.039(3)	0.005(2)	0.015(2)	0.003(2)
O(7)	4e	-0.0078(5)	-0.0667(4)	0.2915(9)	0.037(3)	0.026(2)	0.033(3)	0.004(2)	0.018(3)	0.004(2)
Tl	4e	0.13099(3)	0.34841(2)	0.35091(6)	0.0394(2)	0.0392(2)	0.0385(2)	-0.0014(2)	0.0137(1)	0.0013(2)

2. Thallium hexaaquamanganese(II) selenate, Tl₂[Mn(H₂O)₆](SeO₄)₂

Table 4. Data collection and handling.

Crystal:	light-pink ellipsoid, size 0.33 × 0.32 × 0.31 mm
Wavelength:	Mo K _α radiation (0.71069 Å)
μ:	276.48 cm ⁻¹
Diffractionmeter, scan mode:	RIGAKU AFC-6R, ω
2θ _{max} :	50.08°
N(hkl) _{measured} , N(hkl) _{unique} :	5022, 1291
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 1014
N(param) _{refined} :	90
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

Table 5. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1)	4e	0.2075	0.0851	0.2837	0.05(1)
H(2)	4e	0.2106	0.1180	0.1156	0.05
H(3)	4e	-0.2506	0.1016	-0.0475	0.05
H(4)	4e	-0.1592	0.1848	-0.0215	0.05
H(5)	4e	-0.0732	-0.0351	0.3569	0.05
H(6)	4e	0.0029	-0.1266	0.3350	0.05

Table 6. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Mn	2a	0	0	0	0.025(1)	0.0267(9)	0.027(1)	-0.0014(7)	0.0051(8)	-0.0003(7)
Se	4e	0.41112(9)	0.13479(6)	0.7388(1)	0.0261(4)	0.0295(4)	0.0300(5)	-0.0028(3)	0.0064(3)	-0.0027(4)
O(1)	4e	0.4152(9)	0.2335(5)	0.574(1)	0.078(5)	0.037(4)	0.040(4)	-0.017(4)	0.015(4)	-0.005(3)
O(2)	4e	0.5613(7)	0.0685(6)	0.783(1)	0.031(4)	0.066(5)	0.069(5)	0.016(3)	0.002(4)	-0.004(4)
O(3)	4e	0.2751(7)	0.0584(5)	0.612(1)	0.028(3)	0.045(4)	0.038(4)	-0.009(3)	0.008(3)	-0.003(3)
O(4)	4e	0.3855(7)	0.1781(5)	0.969(1)	0.055(4)	0.037(3)	0.033(3)	-0.008(3)	0.014(3)	-0.002(3)
O(5)	4e	0.1718(7)	0.1083(5)	0.169(1)	0.035(3)	0.047(4)	0.031(3)	-0.010(3)	0.003(3)	0.002(3)
O(6)	4e	-0.1668(7)	0.1149(5)	0.028(1)	0.030(3)	0.039(3)	0.054(4)	0.002(3)	0.015(3)	-0.001(3)
O(7)	4e	-0.0065(7)	-0.0689(5)	0.304(1)	0.043(4)	0.035(3)	0.033(4)	0.009(3)	0.013(3)	0.006(3)
Tl	4e	0.13509(4)	0.34856(3)	0.35162(6)	0.0462(2)	0.0444(2)	0.0434(2)	-0.0018(2)	0.0152(2)	0.0014(2)

3. Thallium hexaaquacobalt(II) selenate, Tl₂[Co(H₂O)₆](SeO₄)₂

Table 7. Data collection and handling.

Crystal:	red ellipsoid, size 0.34 × 0.33 × 0.32 mm
Wavelength:	Mo K _α radiation (0.71069 Å)
μ:	286.49 cm ⁻¹
Diffractionmeter, scan mode:	RIGAKU AFC-6R, ω
2θ _{max} :	50.08°
N(hkl) _{measured} , N(hkl) _{unique} :	4892, 1259
Criterion for I _{obs} , N(hkl) _{gt} :	I _{obs} > 2 σ(I _{obs}), 1015
N(param) _{refined} :	89
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

Table 8. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(1)	4e	0.1887	0.0875	0.2689	0.07(2)
H(2)	4e	0.2215	0.1255	0.1157	0.07
H(3)	4e	-0.2450	0.1032	-0.0543	0.07
H(4)	4e	-0.1472	0.1730	0.0034	0.07
H(5)	4e	-0.0802	-0.0585	0.3282	0.07
H(6)	4e	0.0134	-0.1201	0.3285	0.07

Table 9. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Co	2a	0	0	0	0.0176(9)	0.0232(9)	0.0228(9)	-0.0018(7)	0.0047(8)	-0.0007(7)
Se	4e	0.4095(1)	0.13539(8)	0.7380(2)	0.0201(5)	0.0266(5)	0.0265(5)	-0.0030(4)	0.0056(4)	-0.0025(4)
O(1)	4e	0.416(1)	0.2352(7)	0.577(1)	0.052(5)	0.041(4)	0.039(4)	-0.012(4)	0.009(4)	-0.001(4)
O(2)	4e	0.5624(9)	0.0664(8)	0.783(2)	0.026(4)	0.060(6)	0.076(7)	0.016(4)	-0.006(4)	-0.010(5)
O(3)	4e	0.2728(8)	0.0590(6)	0.608(1)	0.028(4)	0.038(4)	0.035(4)	-0.009(3)	0.003(3)	-0.011(3)
O(4)	4e	0.3818(9)	0.1790(6)	0.967(1)	0.060(5)	0.038(4)	0.027(4)	-0.003(4)	0.019(4)	-0.002(3)
O(5)	4e	0.1642(8)	0.1074(6)	0.165(1)	0.022(4)	0.044(4)	0.029(4)	-0.004(3)	0.004(3)	-0.003(3)
O(6)	4e	-0.1623(8)	0.1099(6)	0.032(1)	0.024(4)	0.030(4)	0.039(4)	0.006(3)	0.005(3)	0.007(3)
O(7)	4e	-0.0045(8)	-0.0656(6)	0.295(1)	0.030(4)	0.036(4)	0.033(4)	0.002(3)	0.014(3)	0.004(3)
Tl	4e	0.13381(5)	0.34741(4)	0.35069(7)	0.0381(3)	0.0406(3)	0.0393(3)	-0.0012(2)	0.0130(2)	0.0016(2)

4. Thallium hexaaquanickel(II) selenate, $\text{Th}_2[\text{Ni}(\text{H}_2\text{O})_6](\text{SeO}_4)_2$

Table 10. Data collection and handling.

Crystal:	greenish blue ellipsoid, size $0.29 \times 0.28 \times 0.27$ mm
Wavelength:	Mo K_{α} radiation (0.71069 Å)
μ :	290.80 cm^{-1}
Diffraction, scan mode:	RIGAKU AFC-6R, ω
$2\theta_{\text{max}}$:	50.08°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4828, 1240
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1011
$N(\text{param})_{\text{refined}}$:	90
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

Table 11. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4e	0.1941	0.0894	0.2793	0.05(2)
H(2)	4e	0.2165	0.1211	0.1114	0.05
H(3)	4e	−0.2499	0.1019	−0.0654	0.05
H(4)	4e	−0.1442	0.1692	0.0013	0.05
H(5)	4e	−0.0736	−0.0545	0.3257	0.05
H(6)	4e	0.0197	−0.1213	0.3267	0.05

Table 12. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ni	2a	0	0	0	0.0173(8)	0.0212(7)	0.0207(8)	−0.0017(6)	0.0044(6)	0.0001(6)
Se	4e	0.40938(9)	0.13563(6)	0.7381(1)	0.0205(4)	0.0231(4)	0.0253(4)	−0.0024(3)	0.0056(3)	−0.0023(3)
O(1)	4e	0.4204(8)	0.2354(5)	0.578(1)	0.059(4)	0.029(3)	0.032(4)	−0.012(3)	0.012(3)	0.003(3)
O(2)	4e	0.5606(7)	0.0665(6)	0.784(1)	0.026(4)	0.047(4)	0.071(5)	0.006(3)	0.008(3)	−0.008(4)
O(3)	4e	0.2708(6)	0.0585(5)	0.607(1)	0.022(3)	0.036(3)	0.032(3)	−0.008(3)	0.005(3)	−0.004(3)
O(4)	4e	0.3816(7)	0.1794(5)	0.968(1)	0.050(4)	0.034(3)	0.028(3)	−0.009(3)	0.019(3)	−0.006(3)
O(5)	4e	0.1617(6)	0.1064(5)	0.1616(9)	0.027(3)	0.031(3)	0.023(3)	−0.006(3)	0.003(2)	−0.002(3)
O(6)	4e	−0.1605(6)	0.1080(5)	0.030(1)	0.025(3)	0.026(3)	0.034(3)	−0.002(2)	0.008(3)	0.002(3)
O(7)	4e	−0.0015(6)	−0.0628(5)	0.2957(9)	0.028(3)	0.030(3)	0.028(3)	0.002(3)	0.010(3)	0.006(3)
Th	4e	0.13410(4)	0.34738(3)	0.35027(6)	0.0379(2)	0.0379(2)	0.0371(2)	−0.0011(2)	0.0125(2)	0.0012(2)

5. Thallium hexaaquacopper(II) selenate, $\text{Th}_2[\text{Cu}(\text{H}_2\text{O})_6](\text{SeO}_4)_2$

Table 13. Data collection and handling.

Crystal:	light blue ellipsoid, size $0.29 \times 0.28 \times 0.27$ mm
Wavelength:	Mo K_{α} radiation (0.71069 Å)
μ :	289.50 cm^{-1}
Diffraction, scan mode:	RIGAKU AFC-6R, ω
$2\theta_{\text{max}}$:	50.1°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4935, 1270
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1036
$N(\text{param})_{\text{refined}}$:	90
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

Table 14. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1)	4e	0.1932	0.0905	0.2815	0.04(1)
H(2)	4e	0.2220	0.1255	0.1130	0.04
H(3)	4e	−0.2590	0.0970	−0.0530	0.04
H(4)	4e	−0.1673	0.1725	0.0038	0.04
H(5)	4e	−0.0823	−0.0598	0.3191	0.04
H(6)	4e	0.0335	−0.1178	0.3180	0.04

Table 15. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu	2a	0	0	0	0.0201(6)	0.0246(6)	0.0202(7)	−0.0031(5)	0.0043(5)	0.0007(5)
Se	4e	0.39722(7)	0.13751(6)	0.7328(1)	0.0220(4)	0.0254(4)	0.0243(4)	−0.0027(3)	0.0053(3)	−0.0010(3)
O(1)	4e	0.4044(7)	0.2430(5)	0.585(1)	0.054(4)	0.033(3)	0.037(4)	−0.007(3)	0.009(3)	0.004(3)
O(2)	4e	0.5473(6)	0.0685(5)	0.766(1)	0.025(3)	0.056(4)	0.053(4)	0.007(3)	0.001(3)	−0.006(3)
O(3)	4e	0.2592(6)	0.0628(4)	0.6001(9)	0.029(3)	0.037(3)	0.029(3)	−0.010(2)	0.006(2)	−0.002(3)
O(4)	4e	0.3716(6)	0.1738(4)	0.9699(9)	0.044(3)	0.040(3)	0.025(3)	−0.002(3)	0.014(3)	−0.004(2)
O(5)	4e	0.1539(6)	0.1065(4)	0.1590(9)	0.031(3)	0.043(3)	0.027(3)	−0.005(3)	0.003(3)	−0.002(3)
O(6)	4e	−0.1831(6)	0.1144(4)	0.035(1)	0.035(3)	0.036(3)	0.036(4)	−0.002(2)	0.004(3)	0.009(3)
O(7)	4e	−0.0033(5)	−0.0616(4)	0.2808(8)	0.021(3)	0.029(3)	0.025(3)	0.000(2)	0.007(2)	0.006(2)
Th	4e	0.12508(4)	0.35021(3)	0.34890(6)	0.0377(2)	0.0382(2)	0.0360(2)	−0.0005(2)	0.0130(1)	0.0012(2)

6. Thallium hexaaquazinc(II) selenate, Tl₂[Zn(H₂O)₆](SeO₄)₂

Table 16. Data collection and handling.

Crystal:	colorless ellipsoid, size 0.26 × 0.29 × 0.32 mm
Wavelength:	Mo K α radiation (0.71069 Å)
μ :	292.28 cm ⁻¹
Diffraction, scan mode:	RIGAKU AFC-6R, ω
$2\theta_{\max}$:	50.08°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4914, 1263
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1029
$N(\text{param})_{\text{refined}}$:	90
Programs:	SHELXS-97 [10], SHELXL-97 [11], DIAMOND [12]

Table 17. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.2025	0.0881	0.2945	0.04(1)
H(2)	4e	0.2231	0.1219	0.1136	0.04
H(3)	4e	-0.2515	0.1008	-0.0636	0.04
H(4)	4e	-0.1474	0.1688	0.0070	0.04
H(5)	4e	-0.0702	-0.0614	0.3250	0.04
H(6)	4e	0.0218	-0.1276	0.3262	0.04

Table 18. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	2a	0	0	0	0.0174(6)	0.0202(6)	0.0206(7)	-0.0013(4)	0.0049(5)	0.0002(5)
Se	4e	0.40940(8)	0.13556(5)	0.7379(1)	0.0173(4)	0.0194(4)	0.0225(4)	-0.0027(3)	0.0046(3)	-0.0021(3)
O(1)	4e	0.4175(7)	0.2363(4)	0.577(1)	0.058(4)	0.024(3)	0.034(4)	-0.012(3)	0.017(3)	0.005(2)
O(2)	4e	0.5607(6)	0.0668(5)	0.782(1)	0.019(3)	0.054(4)	0.062(5)	0.009(3)	0.003(3)	-0.005(3)
O(3)	4e	0.2722(5)	0.0599(4)	0.6086(9)	0.018(3)	0.030(3)	0.035(3)	-0.009(2)	0.009(2)	-0.012(2)
O(4)	4e	0.3815(6)	0.1786(4)	0.9672(9)	0.044(3)	0.030(3)	0.026(3)	-0.004(3)	0.018(2)	-0.007(2)
O(5)	4e	0.1660(6)	0.1071(4)	0.1647(8)	0.025(3)	0.033(3)	0.024(3)	-0.003(2)	0.005(2)	0.001(2)
O(6)	4e	-0.1634(6)	0.1099(4)	0.0316(9)	0.020(3)	0.024(3)	0.039(3)	-0.001(2)	0.009(2)	0.001(2)
O(7)	4e	-0.0025(6)	-0.0653(4)	0.2960(8)	0.032(3)	0.024(3)	0.028(3)	-0.001(2)	0.017(2)	0.005(2)
Tl	4e	0.13393(4)	0.34767(3)	0.35084(6)	0.0355(2)	0.0338(2)	0.0353(2)	-0.0014(2)	0.0124(1)	0.0013(2)

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