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Cu₃(SeO₄)₂(SeO₃OH)₂(H₂O)₁₆ – The First Example of a Linear Octahedral–Tetrahedral Heptamer in Inorganic Compounds

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Cu₃(SeO₄)₂(SeO₃OH)₂(H₂O)₁₆ (**1**) is a novel copper selenate hydrate and the first inorganic compound to contain linear octahedral–tetrahedral heptamers. The heptamers are formed by successive polymerization of two SeO₃OH tetrahedra, two SeO₄ tetrahedra, and three Cu(H₂O)₄O₂ octahedra.

The linkages between the octahedra and tetrahedra are in the *trans*-configuration, which is in agreement with the Jahn–Teller distortion of the octahedral coordination geometry of Cu²⁺.

Introduction

The topology of interpolyhedral linkage in inorganic compounds is very diverse and may extend in one, two, or three dimensions, thus forming chain, sheet, or framework topologies, respectively. Zero-dimensional topologies are relatively rare and are usually represented by cyclic, cluster, or cage units. Extended linear units are very rare and, as a rule, are restricted to dimeric or trimeric entities. Herein we report on the highly unusual heptamic unit formed by linear condensation of Jahn–Teller-distorted CuO₆ octahedra ($\phi = \text{O}^{2-}$, H₂O) and SeO₄ tetrahedra, which has been observed in the crystal structure of Cu₃(SeO₄)₂(SeO₃OH)₂(H₂O)₁₆ (**1**), a novel copper selenate hydrate obtained as a byproduct in the synthesis of organically templated uranyl selenate hydrates. In general, inorganic and organically templated metal selenates attract considerable attention due to the diversity of their structural architectures and variable polymorphism.^[1] Copper selenates and selenites are of special interest^[2] due to the interplay of Jahn–Teller deformation and the ability of Se to adopt both 4+ and 6+ oxidation states, often in the same crystal structure. The crystal structures of metal selenates are usually based upon structural units formed as a result of polymerization of metal coordination polyhedra and SeO₄ tetrahedra.^[3]

Results and Discussion

Blue crystals of **1** were prepared by isothermal evaporation of aqueous solutions containing Cu(NO₃)₂, uranyl nit-

rate, and H₂SeO₄. The compound was characterized by single-crystal X-ray diffraction analysis, IR spectroscopy, and thermal gravimetric analysis (TGA) (see Exp. Sect. for more details).

The crystal structure of **1** contains two symmetrically independent Cu²⁺ cations in octahedral coordination with four H₂O molecules and two O_{Se} atoms that belong to the selenate groups. The Cu(H₂O)₄O₂ octahedra are characterized by strong Jahn–Teller distortion, very typical for Cu^{II} oxysalt compounds. For both symmetrically independent octahedra, four Cu–H₂O bonds define equatorial [Cu(H₂O)₄]²⁺ squares with bond lengths varying from 1.945 to 1.979 Å. The Cu–O_{Se} bonds are elongated (2.364–2.414 Å) and define apical axes of the octahedra. There are two Se⁶⁺ cations in the structure, and both are tetrahedrally coordinated by four O atoms. For the Se1 site, the Se–O distances are in the range 1.639–1.643 Å. In contrast, the Se2O₄ tetrahedron contains three relatively short (1.612–1.623 Å) Se–O bonds and one elongated Se–O bond of 1.694 Å. These observations are in total agreement with the values observed for other structures containing both SeO₄ and SeO₃OH units^[4] and point out to the protonation of the O₈ site which leads to the formation of a hydroxyl anion, OH[−].

The most remarkable feature of the crystal structure of **1** is the presence of electroneutral [Cu₃(SeO₄)₂(SeO₃OH)₂(H₂O)₁₂] octahedral–tetrahedral heptamers shown in Figure 1. The heptamers are formed by successive polymerization of two SeO₃OH tetrahedra, two SeO₄ tetrahedra, and three Cu(H₂O)₄O₂ octahedra. The linkages between octahedra and tetrahedra are in the *trans*-configuration, in agreement with the Jahn–Teller distortion of the octahedral coordination geometry of Cu²⁺. From eight crystallographically independent H₂O molecules, six belong to the hepta-

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meric units, whereas two others (H_2O_{15} and H_2O_{16}) are not bonded to Cu^{2+} cations and are located between the adjacent heptamers, providing their three-dimensional linkage via hydrogen bonds. The packing of the heptamers in the crystal structure of **1** is shown in Figure 2.

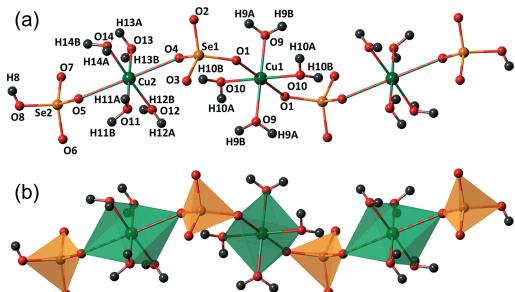


Figure 1. $[\text{Cu}_3(\text{SeO}_4)_2(\text{SeO}_3\text{OH})_2(\text{H}_2\text{O})_{12}]$ octahedral–tetrahedral heptamer in the crystal structure of **1** shown in ball-and-stick (a) and polyhedral (b) representations.

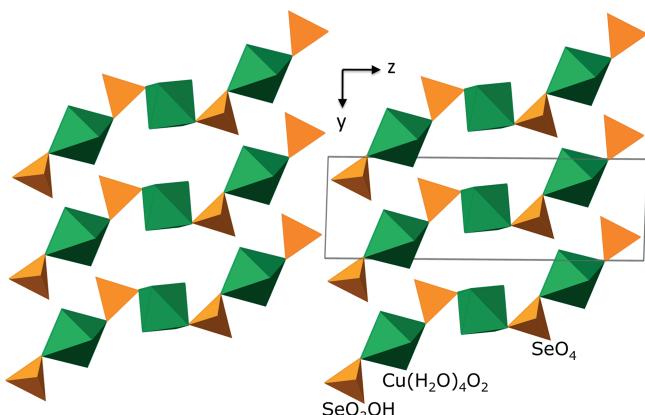


Figure 2. Packing of the $[\text{Cu}_3(\text{SeO}_4)_2(\text{SeO}_3\text{OH})_2(\text{H}_2\text{O})_{12}]$ octahedral–tetrahedral heptamers in the crystal structure of **1**.

Conclusions

The heptameric octahedral–tetrahedral units found in the crystal structure of **1** have never been observed in inorganic or organically templated metal oxysalts so far. In fact, the heptamers can be considered as fragments of extended one-dimensional chains that have been reported, for instance, in the crystal structures of chalcanthite, $\text{Cu}(\text{SO}_4)\text{(H}_2\text{O})_5$,^[5] and $\text{Co}(\text{SeO}_4)(\text{H}_2\text{O})_5$.^[6] In these compounds, $\text{M}(\text{H}_2\text{O})_4\text{O}_2$ octahedra and TO_4 tetrahedra ($\text{M} = \text{Cu}, \text{Co}; \text{T} = \text{S}, \text{Se}$) polymerize to form $[\text{M}(\text{H}_2\text{O})_4(\text{TO}_4)]$ chains. According to the amount of structural information it contains,^[7] the crystal structure of **1** is of intermediate complexity (379.857 bits per cell). However, its Shannon information per atom is quite high and is equal to 5.204 bits. The information-rich character and low entropy of the crystal structure are in agreement with the low-temperature and low-pressure conditions of its formation.

Experimental Section

Synthesis of 1: A mixture of $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 g, Vekton, 99%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.07 g, Vekton, 98%), H_2SeO_4 (40 wt.-% in H_2O , 0.3 mL, Sigma–Aldrich, 99.95%), and deionized distilled water (2 mL) were placed into a steel autoclave with a Teflon capsule and kept at 180 °C for 72 h. After 24 h of cooling to room temperature, the homogeneous liquid was poured onto a watch glass and left to condense. After 5 days, transparent light-blue prismatic crystals were found at the bottom of the watch glass as the main product of the synthesis (yield: 55% based on copper). In the absence of uranyl nitrate, the main crystallization product was $\text{Cu}(\text{SeO}_4)(\text{H}_2\text{O})_5$,^[8] and no crystals of the title phase were observed. Single-crystal X-ray diffraction analysis of **1** was carried out with a Bruker SMART single-crystal X-ray diffractometer equipped with an APEX II CCD planar detector operated with $\text{Mo}-K_\alpha$ radiation at 50 kV and 40 mA. More than a hemisphere of X-ray diffraction data ($\theta_{\max} = 27.50^\circ$) were collected at room temperature with frame widths of 0.5° in ω and exposition times of 10 s spent for each frame. Data were integrated and corrected for background, Lorentz, and polarization effects by using an empirical spherical model with the Bruker programs *APEX2* and *XPREP*. Absorption correction was applied with the *SADABS* program.^[9] The unit cell parameters of **1** [$a = 6.0778(4)$ Å, $b = 6.2781(4)$ Å, $c = 18.8491(12)$ Å, $\alpha = 90.9440(10)^\circ$, $\beta = 91.3230(10)^\circ$, $\gamma = 106.9160(10)^\circ$, $V = 2194.0(7)$ Å³, $Z = 1$] were determined and refined by least-squares techniques on the basis of 7670 reflections with 2θ in the range 4.32–55.00°. From the statistics of reflection distribution, the space group $P\bar{1}$ was determined. The structure was solved by direct methods and refined to $R_1 = 0.028$ ($wR_2 = 0.067$) for 2559 reflections with $|F_o| \geq 4\sigma F$ by using the *SHELXL-97* program incorporated in the *OLEX2* program package.^[10] The final model included coordinates and anisotropic displacement parameters for all non-hydrogen atoms. Positions of H atoms of H_2O molecules and OH⁻ groups were localized from difference Fourier maps and kept fixed during refinement with $U_{\text{iso}}(\text{H})$ set to 1.5 $U_{\text{eq}}(\text{O})$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-429709. IR spectra of **1** were recorded by using KBr pellets with the Bruker Vertex 70 spectrometer in the region 4000–300 cm⁻¹. The IR spectrum of **1** (Figure S1) shows characteristic bands at 396 and 412 cm⁻¹ that can be assigned to v_4 vibrations of $[\text{SeO}_4]^{2-}$ bending modes. Strong bands at 806 and 822 cm⁻¹ are due to v_1 vibrations of symmetric Se–O stretching deformations in $[\text{SeO}_4]^{2-}$ anions, and bands at 880, 916, and 955 cm⁻¹ are attributed to the v_3 vibrations of the asymmetric Se–O stretching modes in $[\text{SeO}_4]^{2-}$ tetrahedra. The sharp band at 496 cm⁻¹ could be attributed to the stretching deformations of the Cu–O bonds. Two sharp bands at 711 and 740 cm⁻¹ are attributed to the symmetric stretching and bending modes of the Se–OH bonds of the hydroselenate ion, respectively. Broad bands at 1260 and 2450 cm⁻¹ are due to the bending and stretching deformations, respectively, of the O–H bond in the $[\text{HSeO}_4]^-$ group. It should be noted that characteristic vibrations of the oxoselenate groups and Cu–O bonds overlap, so they cannot be clearly separated without structure-based calculations. The broad bands with maximum at 3389 cm⁻¹ and the diffuse band at 1652 cm⁻¹ correspond to the O–H stretching and bending vibrations of water molecules, respectively.^[11] Thermal decomposition of **1** (Figure S2) was studied with a Netzsch STA 449F3 TG-DSC instrument by using a protective Ar flow of 30 mL/min and a constant ramp rate of 10 °C/min to 1000 °C. The first three endothermic effects at 75.6, 138.6, and 194.1 °C (total weight loss of

29.2 wt.-%) likely correspond to the water loss (the last peak can be accounted for the release of tightly bound hydrogen selenate water). These results are comparable with the previously reported multistep dehydration behavior of $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$.^[12a] The decomposition of selenate ion with sublimation of SeO_2 occurs between 400 and 700 °C (48.7 wt.-%; endothermic minima at 493.7 and 569.2 °C).^[12b] The weight loss above 800 °C (3.2 wt.-%) can be explained by the decomposition of CuO (tenorite) with the release of oxygen and the formation of Cu_2O (copperite). The powder XRD pattern (Figure S3) of the refractory residue (1000 °C) proves that the latter consists of copperite with the subordinate admixture of tenorite^[12c] and a minor impurity of an unidentified phase.

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