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Selenium Rings

A Se_{19} Homocycle Complexed by Two Copper(I) Ions

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Dedicated to Professor Dieter Fenske on the occasion of his 70th birthday

The chemical properties of the homologues sulfur and selenium are closely related owing to their similar covalent radii and electronegativities. However, whereas sulfur is the element with the most allotropes and forms numerous cyclic and molecular modifications (S_n; $n = 6$–15, 18, 20), for selenium only three Se_n homocycles are known ($n = 6$–8) and a Se_{12} ring was observed as a co-crystal.[1–3] Such selenium and sulfur rings serve as neutral ligands in Ag^+ and Cu^+ complexes with weakly coordinating anions. Examples include $\{[AgSe_6]^+\}_\infty$,[4] $[Ag_2Se_6]^{2+}$,[5] $[Ag(S_8)_2]^+$,[6] $[Cu(S_{12})(S_8)]^+$, $[Cu(S_{12})(CH_2Cl_2)]^+$,[7] and also the dicationic complex $[Ag_2Se_{12}]^{2+}$.[3] The existence of $[Ag_2Se_{12}]^{2+}$ demonstrated the straightforward accessibility of chalcogen homocycles, which are otherwise not available in pure form, as their coinage metal complex. Other known or novel Se_n units were found as part of transition-metal complexes; for example, $[PdBr_2Se_6]$,[8] $[Re_2(\mu\text{-}X)_2(CO)_6(Se_7)]$ (X = Br, I),[9] $[Rb_2\{Pd(Se_4)_2\}]\cdot Se_8$,[10] and $[Rh_2Se_9Cl_6]$.[11] Very recently, the first complexes of Te_n ($n = 6$, 8, 9, with Ru as metal) were also reported by Ruck et al.[12]

The motivation for the following work was the assumption that, in analogy to the $[Ag_2Se_{12}]^{2+}$ complex, bare copper(I) ions with very weakly coordinating counterions[7,13–18] might react with selenium to give molecular ions that perhaps include an unknown cyclic allotrope of selenium. To investigate this, two equivalents of the highly soluble Cu^I source $[Cu(dfb)_2][A]$ (dfb = 1,2-$F_2C_6H_4$; $[A] = [Al(OC(CF_3)_3)_4]$)[7] and 19 equivalents of freshly prepared red selenium were mixed in liquid sulfur dioxide and sonicated for 48 h. The color of the solution turned intensely brown-red and some residual dark brown precipitate formed. After filtration and concentration, brown block-shaped crystals of $[Cu_2Se_{19}][A]_2$ (**1**) formed from the filtrate at 2 °C in 73 % yield [Eq. (1)].

$$2[Cu(dfb)_2][A] + 19\,Se_{red} \rightarrow [Cu_2Se_{19}][A]_2 + 4\,dfb \qquad (1)$$

According to the crystal structure of this crystalline material, a complex of the hitherto unknown Se_{19} homocycle formed. This C_2-symmetric ring is of particular interest, because it is the first E_{19} ring of any element E. In further reactions, intensely red-brown-colored solutions and microcrystalline solids were always obtained. Analytically these resembled the single crystalline material. In one reaction, which was sonicated for two days, good crystals of $[Cu_2Se_{19}][A]_2\cdot 0.5\,Na[A]$ (**2**) grew, which also include the $[Cu_2Se_{19}]^{2+}$ dication, but co-crystallized with Na[A].[*] The Na^+ ions probably originate from the glass bulb and were dissolved during the extended sonication. This is in agreement with the ESI-MS spectra that always suggested the presence of some Na^+ ions in the positive-ion mode (see below and the Supporting Information).

The X-ray analyses showed that the bond lengths and angles in the $[Cu_2Se_{19}]^{2+}$ dications in compound **1** and **2** are very similar (Supporting Information, Table S1). Compound **1** crystallizes in the monoclinic space group $P2_1$ (with one interstitial 1,2-$F_2C_6H_4$ molecule in the unit cell), and compound **2** in the tetragonal space group $I4_1/a$. Owing to the better quality of the dataset from the X-ray diffraction measurements, only the structure of **2** will be discussed. The C_2-symmetric dication consists of a 19-membered selenium ring that encloses two Cu^+ ions. The C_2 axis runs vertically through atom Se10 and the midpoint between the two Cu^+ centers. The asymmetric unit of **2** thus only contains half a $[Cu_2Se_{19}]^{2+}$ dication, and the second half is symmetry-generated (Figure 1 a).

From the copper coordination point of view, the dication contains four 5- and two 6-membered $CuSe_{4/5}$ rings that bind to the Cu^+ ions in a distorted-tetrahedral fashion. The MSe_5 rings in boat conformation are also present in the structure of $[Ag_2Se_{12}][Al(OC(CF_3)_3)_4]_2$.[3] The Se–Se bond lengths range from short (231.2(2) pm) to long single bonds (241.1(2) pm) and average to 235.3 pm, which is slightly shorter than those in gray selenium (237.4 pm), as expected from the positive charge.[1] The Se–Se–Se angles lie between 101.7° and 110.1° (av. 104.0°). The Cu–Se distances range from 239.8(2)–244.4(2) pm (av. 241.8 pm) and to our surprise are comparable to those observed in tricoordinate copper(I) selenides with anionic selenide moieties; for example, $d(Cu–Se)_{av.} = 241$ pm in $[(R_3P)_m(CuSePh)_n]$ (R = Me, Et, *i*Pr, *t*Bu).[19] Moreover, all observed structural parameters of the $[Cu_2Se_{19}]^{2+}$ dication are within 0.3 pm (Se–Se) and 6 pm (Cu–Se) in agreement with

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[*] The Na^+ cation is located on a fourfold rotation axis located in the center of four anions. One fluorine atom of each anion interacts weakly with Na^+, so its surrounding is distorted tetrahedral (see the Supporting Information).

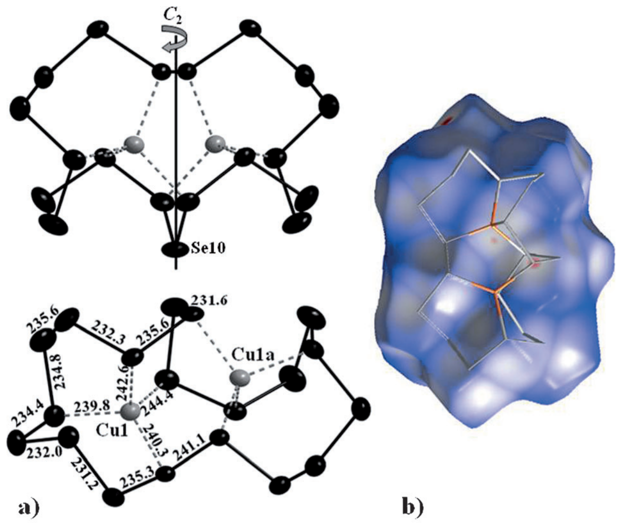

Figure 1. a) Molecular structure of the isolated $[Cu_2Se_{19}]^{2+}$-dication in $[Cu_2Se_{19}][Al(OC(CF_3)_3)_4]_2$·0.5 $Na[Al(OC(CF_3)_3)_4]$ (**2**). The distances are given in pm with an average standard deviation of 0.2 pm for all Se–Se and Cu–Se distances. Ellipsoids are set at 50% probability. b) The Hirshfeld surface of the $[Cu_2Se_{19}]^{2+}$dication in **2**. Red color indicates contact distances below, blue color above the sum of the van der Waals radii. The Hirshfeld surface indicates that the positive charges are delocalized over the entire selenium homocycle.

the calculated dication values at the pbe0/def2-TZVPP level (Supporting Information, Table S2). Eighteen weak Se–F dication–anion contacts between 314.1 and 335.2 pm, and the absence of Cu–F contacts indicate charge transfer from Cu to the Se_{19} ring (sum of the Se–F van der Waals radii 337 pm).[20] In agreement with these rather long contacts, the Hirshfeld analysis[21] of the dication in Figure 1b shows that the charge of the dication is delocalized over the entire Se_{19} ring and is not only located at the copper centers.

Compound **1** was analyzed by IR and far-IR spectroscopy. However, only bands of the isolated intact anion were visible, because of the vanishingly small intensities of the dication vibrations in comparison to the vibrations within the anion (Supporting Information, Figure S6). Repeated attempts to obtain a Raman spectrum of **1** were futile and led to immediate decomposition of the sample, even with low laser energies and at low temperature (100 K).

Two differently synthesized 1,2-difluorobenzene solutions were analyzed by ESI-mass spectrometry. For solution 1, crystals of **2** were dissolved. The main signal at $m/z = 1581$ (monoisotopic) corresponds to the $CuSe_{19}^+$ monocation. Additionally, the copper-selenium monocations $[CuSe_n]^+$ ($n = 12$–17, 20) were observed in the spectra in smaller concentrations.[*] For solution 2, the entire reaction was carried out in 1,2-$F_2C_6H_4$ and the reaction solution was directly used for the ESI without prior crystallization. In contrast to the spectra of solution 1, no $[CuSe_{19}]^+$, but smaller $[CuSe_n]^+$ monocations ($n = 7$–14) were found. No evidence for any copper–selenium dication was observed in all of the MS spectra. To shed light on the energetics of possible dismutation reactions of $[Cu_2Se_{19}]^{2+}$, the geometries of the different species that were observed by ESI-MS were optimized at the pbe0/def2-TZVPP level and calculated in the gas phase and in solution (1,2-$F_2C_6H_4$, COSMO model with $\varepsilon_r = 13.38$;[22] Figure 2).

All of the dismutation reactions of $[Cu_2Se_{19}]^{2+}$ are exothermic and exergonic in the gas phase. In solution, all these reactions but one are endergonic. This implies that if the copper dication formation in the solid state is induced by the high lattice energy of an AB_2 salt, the dissolved Se_{19} ring, as observed by MS, is stable for at least a few hours against further degradation reactions. However, owing to Coulomb repulsion, the second Cu^+ ion is immediately repelled in solution and $[CuSe_{19}]^+$ is mainly formed in solution 1. The driving force for the formation of the dication salt thus appears to be the high lattice energy of solid $[Cu_2Se_{19}][A]_2$. To strengthen this point, the reaction enthalpy and the Gibbs free energy for the formation of solid $[Cu_2Se_{19}][A]_2$ was calculated in a deposited Born–Haber cycle (Supporting Information, Figure S4) as $\Delta_rG° = -200\ \text{kJ mol}^{-1}$ ($\Delta_rH° = -145\ \text{kJ mol}^{-1}$) starting from the higher energy Se_{red} ($\Delta_rH°(Se_{gray} \rightarrow Se_{red}) = +5\ \text{kJ mol}^{-1}$).[22] The same reaction

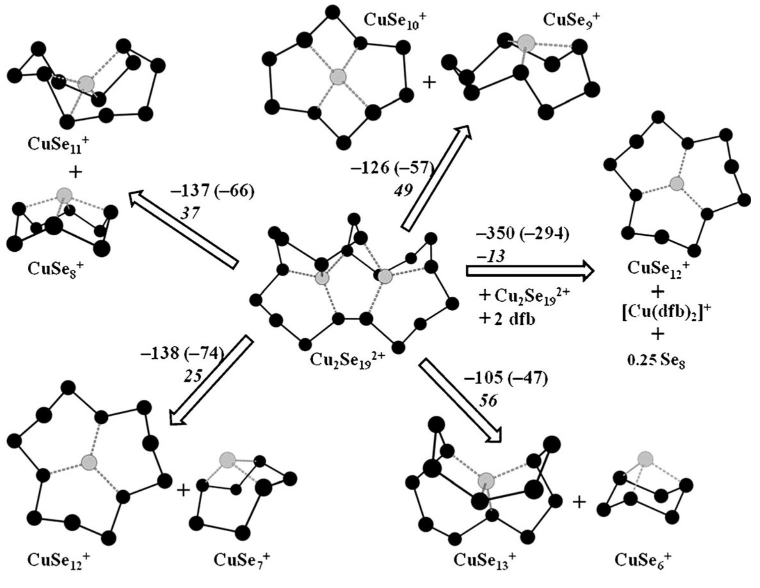

Figure 2. Overview of the species observed by ESI-MS. The structures and the energies of the different $[CuSe_n]^+$ cations that arise owing to the possible dismutation reactions of the $[Cu_2Se_{19}]^{2+}$ cluster never observed in the MS were calculated at the pbe0/def2-TZVPP level. The regular values relate to the gas phase, with the first corresponding to $\Delta_rG°$; the value in parentheses to $\Delta_rH°$ in the gas phase. The values in italics are $\Delta_{solv}G°$ in 1,2-difluorobenzene (solvent used for ESI-MS). All enthalpies/energies are given in kJ mol^{-1}.

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[*] Apart from the copper complexes, silver–selenium cations and lithium and sodium oligosiloxane complexes (from the silicone grease employed) were found in both solutions as contaminations (see the Supporting Information for a detailed assignment and detailed discussion).

starting from Se_{gray} should also work ($\Delta_r G^\circ/\Delta_r H^\circ = -105/-50\,\text{kJ}\,\text{mol}^{-1}$). However, we never observed the intensely colored solution and the dark-brown solid during the reaction with gray selenium. We assume that the reaction starting from gray selenium is kinetically inhibited.

The calculations suggest the formation of $[\text{Cu}_2\text{Se}_{19}][\text{A}]_2$ from $[\text{Cu(dfb)}_2][\text{A}]$ and Se_{red} to be exergonic in solution by $\Delta_{\text{solv}}G^\circ = -70\,\text{kJ}\,\text{mol}^{-1}$. Since in solution 2 only smaller selenium rings as their monocopper complexes were detected, but no $[\text{CuSe}_{19}]^+$,[*] the assumption can be made that $[\text{Cu}_2\text{Se}_{19}]^{2+}$ is not formed in solution without prior crystallization like in solution 1. In agreement with this an—apparently slow—exergonic dismutation reaction of the dissolved dication exists that leads to a degradation of the dication towards smaller monocations, e.g.: $2\,[\text{Cu}_2\text{Se}_{19}]^{2+} + 2\,\text{dfb} \rightarrow 3\,[\text{CuSe}_{12}]^+ + [\text{Cu(dfb)}_2]^+ + 0.25\,\text{Se}_8$; $\Delta_{\text{solv}}G^\circ = -13\,\text{kJ}\,\text{mol}^{-1}$ (Figure 2). The Gibbs free energies for the direct formation of solvated $[\text{CuSe}_n]^+$ ($n = 6$–13) from $n/8\,\text{Se}_8$ and $[\text{Cu(dfb)}_2]^+$ calculated at the pbe0/def2-TZVPP level are negative for almost all reactions ($\Delta_{\text{solv}}G^\circ = -1$ to $-51\,\text{kJ}\,\text{mol}^{-1}$); only the direct formation of the small monocations $[\text{CuSe}_6]^+$ and $[\text{CuSe}_7]^+$ are endergonic ($\Delta_{\text{solv}}G^\circ = +16$ and $+6\,\text{kJ}\,\text{mol}^{-1}$, Figure 3).

Another way to explain the formation of the smaller $[\text{CuSe}_n]^+$ cations is suggested by ESI-MS data and starts from the dissolved $[\text{CuSe}_{19}]^+$, which probably forms from the Coulomb explosion of the freshly dissolved $[\text{Cu}_2\text{Se}_{19}]^{2+}$ dication. As a following step, the dismutation reaction of $[\text{CuSe}_{19}]^+$ according to Equation (2) could lead to smaller soluble copper–selenium monocations and solid Se_{red}.

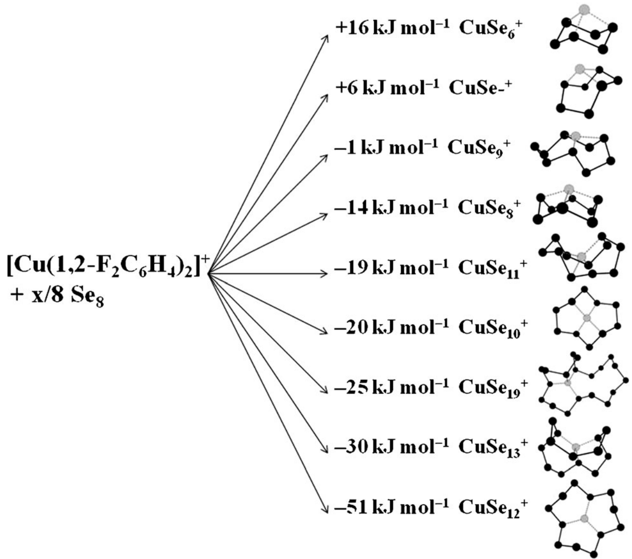

Figure 3. pbe0/def2-TZVPP calculated standard Gibbs free energies $\Delta_r G^\circ_{\text{solv}}$ for the formation of $[\text{CuSe}_n]^+$ from $[\text{Cu(1,2-F}_2\text{C}_6\text{H}_4)_2]^+$ and $n/8\,\text{Se}_8$ in a solution of $1,2\text{-F}_2\text{C}_6\text{H}_4$.

$$\text{CuSe}_{19}{}^{+}{}_{(\text{solv})} \rightarrow \text{CuSe}_{m(\text{solv})}{}^{+} + n\,\text{Se}_{\text{red(s)}} \qquad m = 6-13,\ n = 19-m \tag{2}$$

Our experiments demonstrated that this reaction takes place in equilibrium: After filtration of a freshly prepared difluorobenzene solution of crystalline **1**, and leaving the clear red-brown filtrate standing for several hours, the formation of amorphous red selenium was observed. In agreement with this, all the dismutation reactions in Equation (2) were calculated to be exergonic by −52 to $-81\,\text{kJ}\,\text{mol}^{-1}$ (Supporting Information, Table in Figure S5).

The key to the synthesis of $[\text{Cu}_2\text{Se}_{19}][\text{A}]_2$, featuring the first E_{19} ring of any element E, is the use of freshly prepared red selenium and the copper(I) starting material[7] $[\text{Cu(dfb)}_2][\text{A}]$. This dication and also the underlying odd-membered Se_{19} homocycle is C_2-symmetric and contains five- and six-membered rings in envelope/boat conformation as structural building blocks. This Se_{19} homocycle, the synthesis of which is straightforward and accessible with thermodynamic control, signifies a new selenium modification and is somewhat reminiscent to the related even-membered S_{18} and S_{20} cycles. Interestingly, it is also the largest uneven-membered chalcogen ring currently known and as such a representative of the usually less-stable series of uneven chalcogen homocycles.

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[*] In solution 2, more Na^+ ions were detected, probably because the entire solution in the flask was ultrasonicated for 48 h so that more sodium ions were dissolved from the glass (see the crystal structure of **2**; Supporting Information, Figure S1).

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