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Copper Sulfur Clusters

The Trinuclear Copper(I) Thiolate Complexes$[Cu_3(NGuaS)_3]^{0/1+}$ and their Dimeric Variants $[Cu_6(NGuaS)_6]^{1+/2+/3+}$ with Biomimetic Redox Properties**

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Dedicated to Professor Wolfgang Kaim on the occasion of his 60th birthday

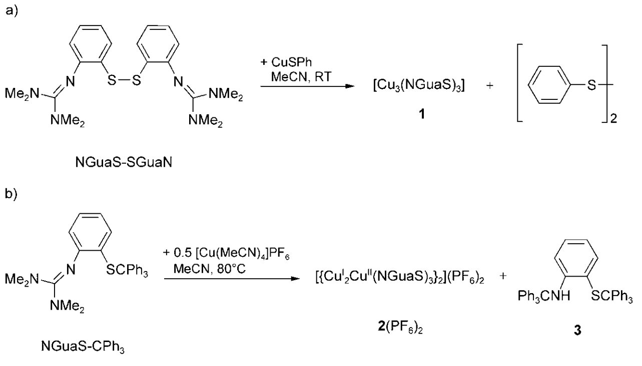
As the active participant of various electron-transport chains, the element copper plays a central role in biology.[1] This privileged position can be traced back to specific redox properties originating in the unique interplay between demands of d^9 and d^{10} copper atoms towards coordination geometries and ligand fields. In this respect, sites for mononuclear coordination (e.g., in azurin and plastocyanin) are conditioned by matrix effects of the protein surroundings.[2] Similar matrix effects are experienced by dinuclear systems, such as Cu_A present in cytochrome-c oxidases or N_2O reductases, which contain copper atoms bridged by two thiolate donor functions.[3]

Artificial reconstruction of these biologically active copper sites to model their characteristic properties in the laboratory failed to date because of difficulties in replacing the natural matrix effects by suitable other influences. This problem also holds for model complexes of Cu_A within cytochrome-c oxidases or N_2O reductases,[4] which—in spite of similarities with respect to coordination numbers and ligand fields—often differ very significantly from their archetypes in their redox properties and the degree of stretching of their central $\{Cu_2S_2\}$ rhombus.[5] In addition, there are numerous other examples of dinuclear thiolate complexes which differ even further from the natural Cu_A.[6]

Searching for solutions to the problem of (biological) matrix packaging[7] we have prepared new thiolate ligands from peralkylated guanidine residues to model the biological N,S donor set and to control the reorganization energies of the corresponding copper complexes as they pass through different metal oxidation states.

In the course of these investigations, we have also encountered polynuclear complexes with rigid geometries. We must assume that these complexes can only respond to changes in individual metal oxidation states by undergoing very small distortions.

In a detailed study, we have examined the influence of the guanidine thiolate ligand $NGuaS^-$ on the structural and electrochemical characteristics of its copper complexes and found that CuSPh reacts with NGuaS–SGuaN giving the cyclic trinuclear Cu^I complex $[Cu_3(NGuaS)_3]$ (**1**) after reductive splitting of the disulfide bridge by thiophenolate ions (Scheme 1a and Figure 1). Complex **1** can be electrochemically oxidized to the monocation $\mathbf{1}^+$ at -0.320 V (reference Fc/Fc^+; $Fc = [(C_5H_5)_2Fe]$). The associated reduction wave of the quasi-reversible process occurs at -0.640 V. Though we were not able to characterize the electrochemically oxidized species further, indications of its structure emerged from the analysis of a trinuclear complex of empirical formula $[Cu_3(NGuaS)_3I]$ (**1I**), which we obtained in the course of investigations using CuI in place of CuSPh. The core of complex **1I** (Figure 2) is arranged in the same way to that of **1** (see below) as a strongly distorted Cu_3S_3 heterocycle, but is characterized



Scheme 1. Syntheses of **1** (a) and $\mathbf{2}(PF_6)_2$ (b).

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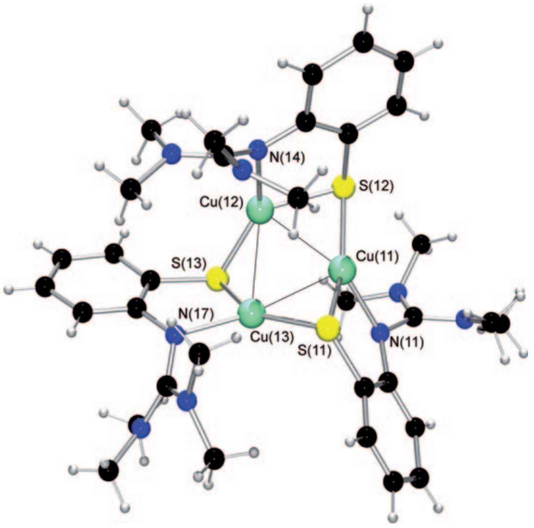

Figure 1. Structure of [$Cu_3(NGuaS)_3$] (**1**) in the crystalline state.

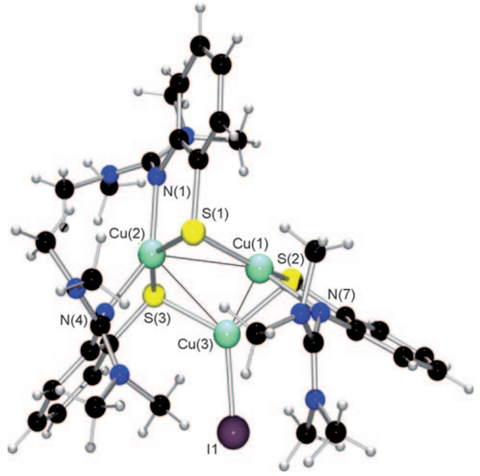

Figure 2. Structure of [$Cu_3(NGuaS)_3I$] (**1I**) in the crystalline state.

by three chemically distinct copper atoms. While the copper center with a S_2N_2 donor set and the coordination number four is assumed to be Cu^{II}, the two copper atoms in trigonal coordination environments with S_2N and S_2I donor sets, respectively, are monovalent. Apparently, **1I** is a mixed-valence complex in which the different metal oxidation states are localized. Presumably, the conditions in the electrochemically generated species $\mathbf{1}^+$ are comparable, because the separation of about 320 mV between the redox waves suggests a chemically rearranged complex with localized Cu^I and Cu^{II} centers.

As we can show in this work, the dimeric variant of $\mathbf{1}^+$ is a complex with complete valence delocalization. The passage through different metal oxidation states is likely not associated with rearrangement processes, because the separations between the redox waves are at $\Delta E = 71$ and 75 mV, very close to the thermodynamically required value (59 mV).

[$Cu_3(NGuaS)_3$] (**1**, Figure 1) crystallizes in the monoclinic space group $P2_1$ with two independent molecules in the unit cell. The copper atoms form a nearly equilateral triangle with a mean edge length of 2.654 Å. They are connected by μ_2-S bridges from the three thiolate groups and coordinated in a distorted trigonal-planar manner. Each copper atom is part of a five-membered chelate ring with a S-Cu-N angle of 88.6° (average). The S-Cu-S angles vary more and are 151.5(2), 145.6(2), and 126.5(2)° for Cu(11), Cu(13), and Cu(12), respectively. The trinuclear complexes [$Cu_3(SC_6H_4NMe_2)_3$] and [$Cu_3(SC_6H_4CH(Me)NMe_2)_3$] with comparable ligand donor sets have different S-Cu-N chelate and S-Cu-S angles.[8]

Reaction of the thioether NGuaS-CPh_3 with [$Cu(MeCN)_4$]PF_6 (Scheme 1 b) leads to the complex cation $[\{Cu^I_2Cu^{II}(NGuaS)_3\}_2]^{2+}$ (**2**), which could be isolated as the hexafluorophosphate salt. This cation formally represents the dimeric variant of the oxidized trinuclear compound $\mathbf{1}^+$ (Figure 5). The mechanism of the complex formation is not completely understood. We suppose that in the first step Cu^I induces a heterolytic cleavage of the S−CPh_3 bond followed by reaction with the thus generated guanidine-thioate ions to form multinuclear precursor complexes (possibly also in form of compound **1**). In the next step, thiyl radicals, as intermediates in a homolytic splitting of other thioether molecules, could initiate partial oxidation of these complexes and their transformation or dimerization to the isolable mixed-valent hexanuclear species **2**. The rearrangement associated with the oxidation of **1** to $\mathbf{1}^+$ would favor the first linking step between two trinuclear complexes through the formation of a μ_3-S bridge and subsequently would result in a reorientation of the nitrogen donor functions in the resulting hexanuclear complex.

Our hypothesis that a homolytic thioether splitting is also occurring finds support in the formation of compound **3**, which is isolated as a by-product and whose existence is compatible with the appearance and the supposed reactivity of intermediate triphenylmethane radicals (see Scheme 1 b).

The higher oxidation state of the copper in $\mathbf{2}(PF_6)_2$ in comparison to the situation in **1** emerges not only indirectly from the charge balance in the crystal, but is also detected directly from the energy of the Cu_K edges in the corresponding X-ray absorption spectra. The experimental values of 8980.1 eV for **1** and of 8981.5 eV for $\mathbf{2}(PF_6)_2$ confirm the interpretation derived from the crystal structural analysis unequivocally. Besides the shifting of the absorption edge which reflects the change of the mean oxidation state of the copper ions, $\mathbf{2}(PF_6)_2$ shows, in comparison to **1**, increasing intensity in the shoulder region of the absorption edge at 8980 eV presumably caused by the higher number of sulfur donor atoms.

Compound $\mathbf{2}(PF_6)_2$ can be recrystallized from acetonitrile without decomposition. In the crystal structure all the copper atoms are identical, in agreement with complete valence delocalization.[9] The UV/Vis/NIR spectrum shows a distinctive absorption band at 1117 nm (Figure 3, black curve) as well as a further transition at 960 nm partly hidden by the first band. The 1117 nm band has an extinction coefficient of $\varepsilon = 6.9\times10^4\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$ with a full width at half maximum (FWHM) of $\Delta\nu_{1/2,\mathrm{exp.}} = 1400\,\mathrm{cm}^{-1}$. This value remains far below the value of $4130\,\mathrm{cm}^{-1}$ which according to Hush is the base for weakly coupled mixed-valent systems.[10] Consequent, **2** should represent a class III system (that is, fully delocalized)

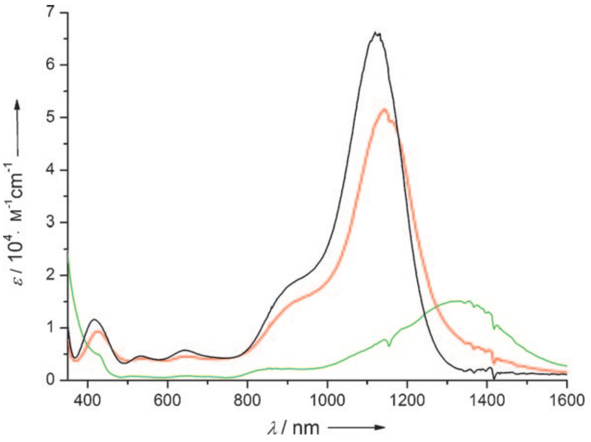

Figure 3. UV/Vis/NIR spectra of **2** (black), **2**$^{\mathrm{ox}}$ (red), and **2**$^{\mathrm{red}}$ (green) (−25 °C, CH_2Cl_2).

according to the classification of Robin and Day.[9] The observed absorption band is therefore assigned to the $\psi\rightarrow\psi^*$ transition in the $[\{Cu^{I}_2Cu^{II}(NGuaS)_3\}_2]^{2+}$ core. The ratio $\Delta\nu_{1/2,\mathrm{exp.}}/\Delta\nu_{1/2,\mathrm{calcd}}$ of 0.33 indicates a fast electron transfer on the time scale of solvent molecule movements.[11] Our interpretation is also confirmed by the fact that the absorption band at 1117 nm shows no solvent or temperature dependence (Figures S10–S12 of the Supporting Information).[10g,h,11]

Like the trinuclear complex **1**, the dimeric variant **2** also has interesting redox properties. The cyclovoltammogram in dichloromethane (Figure 4) shows two reversible redox couples, one at +0.296 V (ΔE = to 71 mV), the other one at −0.652 V (ΔE = 75 mV; all potentials versus Fc/Fc^+). Coulometric measurements confirm two one-electron redox processes. These results demonstrate that the stability range of **2** extends from the mixed-valent $Cu^{+1.5}$ state (**2**$^{\mathrm{ox}}$: $[Cu^{I}_3Cu^{II}_3(NGuaS)_6]^{3+}$) to $Cu^{+1.33}$ (**2**: $[Cu^{I}_4Cu^{II}_2(NGuaS)_6]^{2+}$) to the reduced $Cu^{+1.17}$ species (**2**$^{\mathrm{red}}$: $[Cu^{I}_5Cu^{II}(NGuaS)_6]^{+}$). From the difference of the redox potentials for **2**, a comproportionation constant K_c of $10^{19.8}$ can be calculated in complete accordance with expectations for class III systems.[10g,h,11]

The proof of copper-based redox processes can be provided by spectroelectrochemical measurements. For this purpose, complexes **2**$^{\mathrm{ox}}$ and **2**$^{\mathrm{red}}$ were coulometrically generated at −25 °C, independent of each other, from **2** in quantitative reactions and characterized by their UV/Vis/NIR spectra (Figure 3).

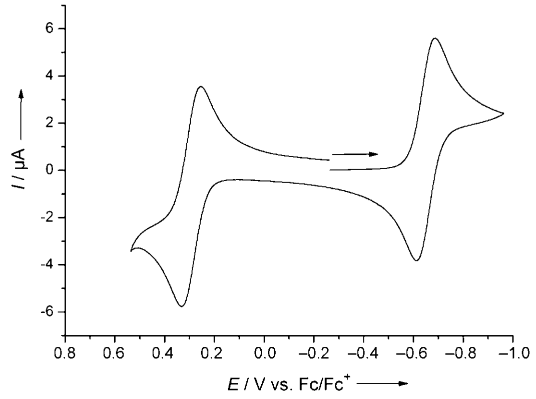

Figure 4. Cyclovoltammogram of **2**$(PF_6)_2$ at 25 °C in CH_2Cl_2.

The spectrum of **2**$^{\mathrm{ox}}$ shows an intensive absorption band at 1145 nm which compared to the band of **2**, is less intense and has a small red shift. In the reduced species **2**$^{\mathrm{red}}$ this band is even less intense and shifted to 1332 nm. Based on the large extinction coefficients as well as the experimentally obtained and calculated FWHMs (**2**$^{\mathrm{ox}}$: $\Delta\nu_{1/2,\mathrm{exp.}} = 1450\ \mathrm{cm^{-1}}$, $\Delta\nu_{1/2,\mathrm{calcd}} = 4090\ \mathrm{cm^{-1}}$; **2**$^{\mathrm{red}}$: $\Delta\nu_{1/2,\mathrm{exp.}} = 1810\ \mathrm{cm^{-1}}$, $\Delta\nu_{1/2,\mathrm{calcd}} = 3790\ \mathrm{cm^{-1}}$), **2**$^{\mathrm{ox}}$ and **2**$^{\mathrm{red}}$ also belong to valence-delocalized class III systems with $\psi\rightarrow\psi^*$ transitions. Compounds **2** and **2**$^{\mathrm{ox}}$ also have sulfur-based ligand-to-metal charge transfer (LMCT) transitions at 420, 530, and 640 nm, after reduction to **2**$^{\mathrm{red}}$ these bands become very weak.

According to the results of SQUID and NMR spectroscopic measurements, **2**$(PF_6)_2$ behaves diamagnetically. The electrochemically generated derivatives **2**$^{\mathrm{ox}}$ and **2**$^{\mathrm{red}}$ should be paramagnetic species. This assumption was confirmed by means of EPR measurements (**2**$^{\mathrm{ox}}$: $g_\perp = 2.06$ and $g_\parallel = 1.98$; **2**$^{\mathrm{red}}$: $g_{\mathrm{iso}} = 2.02$). EPR spectra of **2**$^{\mathrm{ox}}$ and **2**$^{\mathrm{red}}$ show no hyperfine splitting consistent with a valence delocalization over all the copper atoms.

The complex cation **2** (Figure 5) is a molecular wheel with one $\{Cu_6S_6\}$ hub and a virtual axis. This hub consists of three diamond-shaped $\{Cu_2S_2\}$ units, which are linked to each other by a total of six Cu−S bonds. The result is a second set of three other $\{Cu_2S_2\}$ diamonds, which share common Cu–S edges with the diamonds of the first set. These edges extend in approximately parallel directions to the virtual axis of the wheel.

Interestingly, the structural archetype of the $\{Cu_6S_6\}$ framework of **2** is seen in the metal–sulfur scaffoldings of the hexanuclear sulfide–halide complexes of iron with composition $[Fe_6S_6X_6]^{3-/2-}$ (X = Cl, Br, I), for which the term prismane cluster has been adopted.[12] In this complex

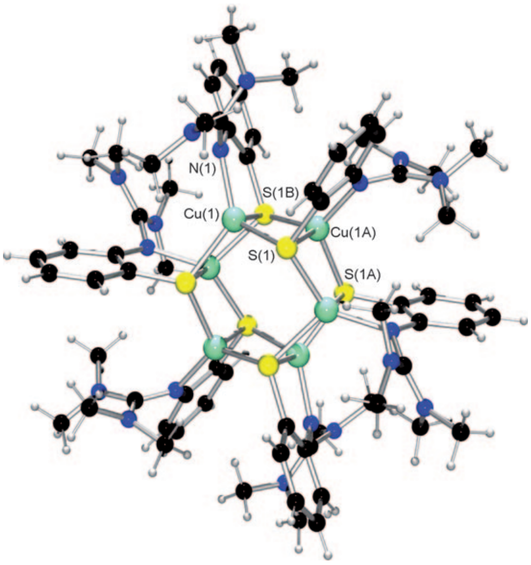

Figure 5. Structure of $[Cu_6(NGuaS)_6]^{2+}$ (**2**) in the crystalline state.

type, the sulfur atoms occupy the corners of an elongated octahedron, whilst the metal atoms form a metal-deficient cube that can be derived from a regular one by removing two corners along a body diagonal. The elongation of the sulfur octahedron takes place along this body diagonal, which at the same time coincides with the virtual axis of the $\{Cu_6S_6\}$ hub.

An interesting variation of paddle-wheel like complexes with $\{Cu_6S_6N_6\}$ cores, in which the six copper atoms are arranged in an approximately octahedral manner, is found if 1,1-bifunctional N,S donor ligands are used.[13] This variant contains only monovalent copper and has—compared to **2**—a slightly modified $\{Cu_6S_6\}$ hub allowing for Cu···S contacts parallel to the virtual axis of the wheel which are now much longer than covalent bonds. Most probably, the very short N···S distance in the ligand prevents chelate ring formation in this case, which is a typical feature of **2** with its 1,2-bifunctional N,S donor ligands. Interestingly, in a recently described hexanuclear Cu^I compound containing 1,3-bifunctional S,S-donor ligands, a $\{Cu_6S_6\}$ core portion similar to that in **2** is present. The basic structural difference between this compound and **2** lies—besides the different metal oxidation state—in the chemical identity and the arrangement of the exogenous bound ligand donor functions which in the Cu^I compound belong to the same Cu_3S_3 ring as the bridging thiolate sulfur functions contrasting the situation in **2**.[14]

The individual $\{Cu_2S_2\}$ unit of **2** is a structural model for the core portion of the Cu_A center of cytochrome-c oxidases (and N_2O reductases), and the oxidation state of the copper atoms in the oxidized form $\mathbf{2}^{ox}$ coincides with the oxidized form of the biological system.[15] This similarity also applies to the Cu···Cu distance of 2.598 Å which is only slightly shorter in the biological system. The coordination environment of the copper atoms within the $\{Cu_2S_2\}$ diamond is completed by two nitrogen donor functions of the exogenously bound guanidine ligands, which take the place of two histidine residues of Cu_A, and by two other sulfur donor functions from neighboring diamonds. These sulfur donors take over the role of ligands from the second co-ordination sphere of Cu_A and replace secondarily bound methionin sulfur and carbonyl oxygen donor functions.

Though by use of terminally bound thiolate ligands, we veer a little bit away from Cu_A, but it must be noted that **2** with the structural characteristics of its $\{Cu_2S_2\}$ diamonds, its metal oxidation stage and its electronic and electrochemical properties resembles the biological Cu_A site more closely than any other compounds known to date.[16] Thus we succeeded for the first time in solving the problem of biological matrix stabilization to produce the desired redox properties of Cu_A by suitable steric restrictions within a synthetic model complex.

Apart from this biologically motivated question, the hexanuclear compound **2** with its unique ability to undergo one-electron-transfer steps between valence delocalized states within the series $[Cu_6(NGuaS)_6]^{3+/2+/1+}$ is a unique functional system in copper–sulfur cluster chemistry.

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