Redox Active Complexes

DOI: 10.1002/anie.201102714

A Halide-Induced Copper(I) Disulfide/Copper(II) Thiolate Interconversion**

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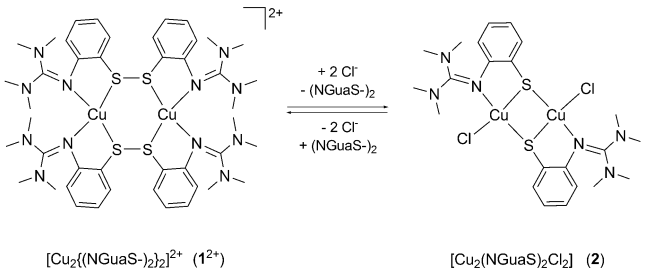
Dedicated to Professor Bernhard Lippert on the occasion of his 65th birthday

Shortly after their discovery as protein active sites, copper sulfur complexes entered the stage of modern synthetic coordination chemistry.[1] In this respect, the combination of copper (II) and potentially reducing thiolate ligands appears especially attractive owing to its relevance to the Cu_A within cytochrome-c oxidase and N_2O reductase.[2] Despite extensive research efforts, dinuclear copper(II) or mixed-valent copper-(I/II) thiolate complexes with protein active site properties are rare.[3]

This situation can be traced back to the ligands under investigation, which are not capable of preventing Cu^{II} from being reduced to Cu^{I} along with the formation of organo-disulfides. On the other hand, the selective and reversible oxidation of thiols/thiolates to organo-disulfides (e.g., cysteine to cystine) is one of the most important biological reactions resulting in the formation of disulfide bridges within peptides and proteins. In addition, the reaction system thiol–disulfide is an important electron source for a number of redox processes in biological systems, making it an indispensable component of basic regulatory processes during signal transduction and enzyme activity.[4] Nevertheless, disulfide–thiolate redox processes are largely unexplored in an inorganic context, although they were investigated in terms of the participation of copper(II) ions in kinetic studies more than 50 years ago.[5] Quite recently, further reports have been published on this subject,[6] and in 2002 a unique model system was described which—under the influence of copper and controlled by halide ions—is able to shift the thiolate–disulfide equilibrium reversibly and completely from the one side to the other.[3a] This surprising discovery indicates an enormous but largely unrecognized potential for such reaction systems to act as novel electron sources and sinks, which has motivated us to explore this topic more deeply.

We report herein a previously unknown chloride-induced disulfide–thiolate interconversion, leading from the copper(I) disulfide complex cation $[Cu^{I}_2\{(NGuaS\text{-})_2\}_2]^{2+}$ ($\mathbf{1}^{2+}$) to the electrically neutral copper(II) thiolate species $[Cu^{II}_2(NGuaS)_2Cl_2]$ (**2**; there is no longer an S–S bond in the NGauS ligands, thus it is no longer written as $(NGuaS\text{–})_2$). Both compounds ($\mathbf{1}^{2+}$ as $\mathbf{1}[OTf]_2$) were characterized by X-ray crystallography. The proposed oxidation states of the Cu ions were confirmed by K-edge measurements. The reverse reaction can be initiated by removal of the chloride ligands from the corresponding thiolate complex (Scheme 1).



$[Cu_2\{(NGuaS\text{-})_2\}_2]^{2+}$ ($\mathbf{1}^{2+}$) $[Cu_2(NGuaS)_2Cl_2]$ (**2**)

Scheme 1. Chloride-induced disulfide–thiolate interconversion.

During studies on the influence of polyfunctional ligands containing guanidine- and sulfur-donor functions on the structural and electrochemical properties of copper complexes we were recently able to isolate the disulfide 2′,2′-(2,2′-dithiodiphenyl)bis(1,1,3,3-tetramethylguanidine) (NGuaSS-GuaN or $(NGuaS\text{-})_2$).[3k,7] Reaction of $[Cu(MeCN)_4]OTf$ with a yellow suspension of $(NGuaS\text{-})_2$ (ratio 1:1) in acetonitrile resulted in a deep red solution, from which, after filtration and subsequent treatment with diethyl ether, red crystals of $[Cu^{I}_2\{(NGuaS\text{-})_2\}_2][OTf]_2$ ($\mathbf{1}[OTf]_2$; Scheme 2, route A) separated in the course of one week.

The cationic component $\mathbf{1}^{2+}$ is a helicate[9] of the monovalent copper centers. In this double-stranded dinuclear complex cation, both disulfide ligands are bound to both Cu^{I} atoms in a multidentate manner. The center of this molecule is surrounded by a heterocyclic six-membered ring, which consists of four sulfur and two copper atoms in a "twist" conformation (Figure 1). The two sulfur atoms attached to each copper participate in a tetrahedral coordination sphere together with two further nitrogen atoms. The Cu–S bonds are 2.288 Å on average with mean S-Cu-S- and N-Cu-N

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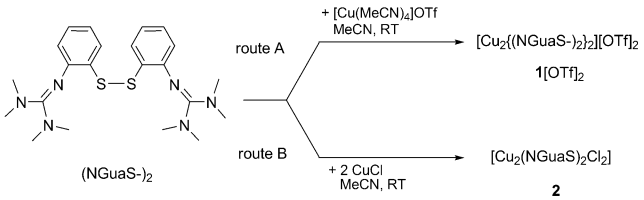
[**] We thank the German research council (DFG) and the German Federal Ministry of education and research (BMBF) for the continuous support of our work. A.N. and R.H. thank the University of Paderborn and the Evonik Foundation for doctoral fellowships. We also thank HASYLAB/DESY for providing beamtime within the scope of the project I-20090150 and Dr. Edmund Welter as well as Dr. Dariusz A. Zajac for their support during the measurement periods.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201102714.



Scheme 2. Synthesis of **1**[OTf]$_2$ and **2**.

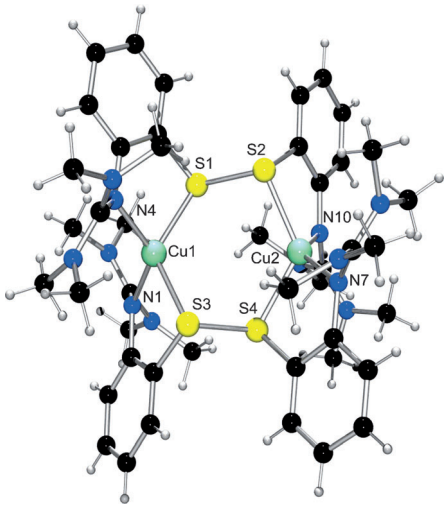


Figure 1. Crystal structure of **1**$^{2+}$.

valence angles of 125.1 and 132.2°, respectively, which are comparable to corresponding values of other dinuclear copper(I) disulfide complexes.[3j,6a–c,8]

The UV/Vis spectrum of **1**[OTf]$_2$ in dichloromethane features an intense absorption band at 417 nm ($\varepsilon =$ 8000 $M^{-1}cm^{-1}$) (Figure 4, red lines) which possibly originates from a $Cu^{I}\rightarrow S$ metal-to-ligand charge transfer (MLCT) transition.[8a–c]

The ESI-MS spectrum of **1**[OTf]$_2$ in dichloromethane shows an intense signal at m/z 507.1, which—from its isotopic distribution—could originate from the fragment [Cu^{I}-(NGuaS-)$_2$]$^+$ and thus can be regarded as a "monomer" of the divalent complex cation **1**$^{2+}$. Another possibility could be formulated as [Cu^{III}(NGuaS)$_2$]$^+$.

A copper-centered electrochemical oxidation of the complex in different solvents up to a potential of +1.2 V (reference: Ag/$AgNO_3$; Figure S1 in the Supporting Information) could not be observed.

Parallel to the synthesis of **1**$^{2+}$, the reaction of (NGuaS-)$_2$ with CuCl in place of [Cu(MeCN)$_4$]OTf in acetonitrile (ratio 1:0.5) led to a blue suspension (Scheme 2, route B). From the filtered solution deep dark blue crystals of [Cu^{II}_2(NGuaS)$_2$Cl$_2$] (**2**) were obtained within a few days by vapor diffusion of diethyl ether. An X-ray structure analysis confirmed the assumed reductive cleavage of the disulfide used and the formation of a copper(II) thiolate species.

In the center of the molecule there is a heterocyclic folded ring of four alternately arranged copper and sulfur atoms. As in **1**$^{2+}$, the copper atoms are surrounded by four ligands, albeit the geometry is more distorted and one of the ligands is a chloride substituent (Figure 2). The N-Cu-S and Cl-Cu-S bond angles range from 141.69(5) to 145.39(2)°.

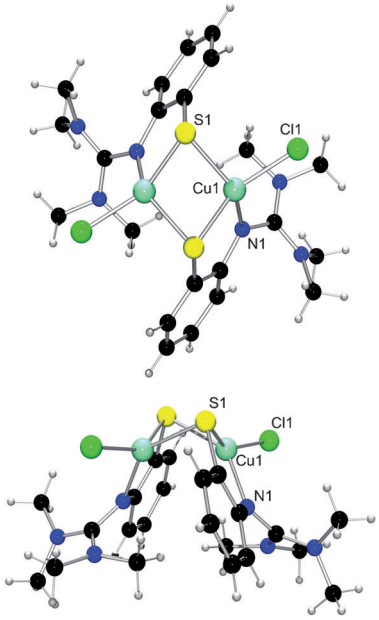


Figure 2. Crystal structure of **2**.

The distortion from the ideal type for tetrahedral geometry leads towards a square-planar coordination. The Cu_2S_2 unit has two longer and two shorter Cu–S bonds (mean 2.220 and 2.336 Å). The Cu-S-Cu and S-Cu-S angles are at 73.69(2) and 88.96(3)°. The relatively strong folding of the four-membered ring along the S–S axis (57.8°) results in a characteristic 'butterfly' structure (Figure 2, bottom).

The positions of the Cu-K absorption edges differ for **1**$^{2+}$ and **2** by 1.59 eV, confirming our assumption that **2** is a Cu^{II} complex (Figure 3). The shoulder in the absorption edge of **1**$^{2+}$ is typical for Cu^{I} containing compounds, while the shift of the first minimum behind the absorption edge from about 9020 to 9028 eV indicates a change in the average ligand distance. This change has to be expected due to the binding of

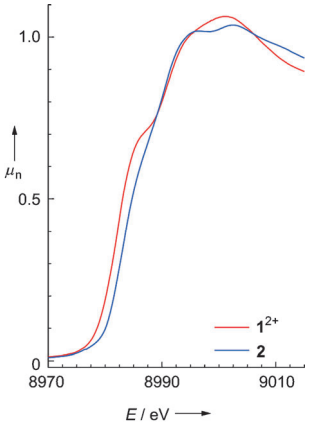


Figure 3. Cu-K edges (XANES regions) of **1**$^{2+}$ and **2**.

the chlorine ligands (Figure S10 in the Supporting Information).

Solutions of **2** in dichloromethane are deep blue. The UV/Vis spectrum is characterized by two intense $S \rightarrow Cu^{II}$ ligand-to-metal charge transfer (LMCT) transitions at 590 nm ($\varepsilon = 6300\,M^{-1}cm^{-1}$) and 708 nm ($\varepsilon = 8400\,M^{-1}cm^{-1}$), and a weaker $S \rightarrow Cu^{II}$ band at 419 nm ($\varepsilon = 4600\,M^{-1}cm^{-1}$) (Figure 4, blue lines).[3j,10] Reference values in the literature are lacking, since the known dinuclear thiolate-bridged complexes have deviating chromophores.[3a–g]

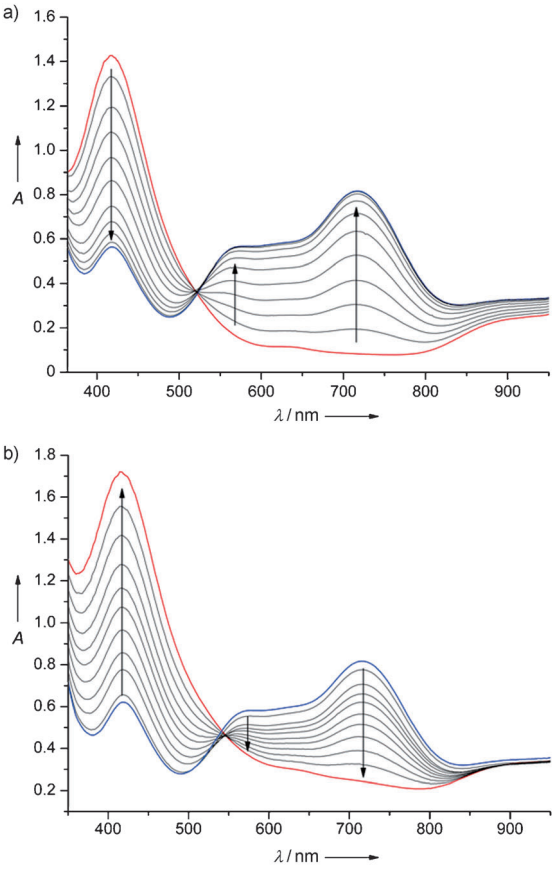


Figure 4. Spectroscopic titrations (CH_2Cl_2, −40 °C). a) From **1**-$[OTf]_2$ (red) with Et_4NCl to **2** (blue). b) From **2** (blue) with $AgBF_4$ to **1**$[BF_4]_2$ (red).

The ^1H NMR spectrum of **2** shows sharp signals, indicating a strong antiferromagnetic coupling of the two Cu^{II} atoms, which was confirmed by magnetic measurements. However, it was not possible to convert **2** into either a mixed-valence $\{Cu^ICu^{II}\}$ species or into a completely reduced Cu^I form by means of electrochemistry (up to a potential of −2 V and in various solvents). We attribute this behavior to the strong folding of the Cu_2S_2 diamond, as all mixed-valence copper complexes known to date have planar frames.[2,3h,k,11]

In the cyclic voltammogram, a reduction wave at −2.2 V (reference: $Ag/AgNO_3$) cannot be assigned unambiguously; as an alternative to a ligand-based process, a metal-centered reduction would also be possible (see Figure S2 in the Supporting Information).

However, reduction of copper in **2** takes place chemically if the chloride ions are removed with silver(I) tetrafluoroborate or silver(I) trifluoromethanesulfonate. This process is based on an intramolecular shift of two electrons from the thiolate ligands to the copper atoms, resulting in the formation of the disulfide complex $\mathbf{1}^{2+}$. As a prerequisite for this conversion, additional disulfide ligands have to be present which replace the chloride ions and one half of the thiolate bridges in the starting material.

A direct route from $\mathbf{1}^{2+}$ to **2** is also possible and opens up when **1**$[OTf]_2$ is treated with Et_4NCl in dichloromethane. From the deep blue reaction solution, blue crystals of compound **2** separate after several days. To characterize the shift of electrons from the disulfide to the copper during the conversion from $\mathbf{1}^{2+}$ into **2** unambiguously, solutions of **1**$[OTf]_2$ were titrated with Et_4NCl and the progress of the reaction was monitored by means of UV/Vis spectroscopy (Figure 4a). The stepwise decrease of the absorption band at 417 nm of the starting compound correlates with the stepwise increase of the bands at 419, 590, and 708 nm of compound **2**. The reversibility of this reaction is shown by the formation of $\mathbf{1}^{2+}$ after titration of **2** with $AgBF_4$ (Figure 4b).

The existence of an isosbestic point in the titration of $\mathbf{1}^{2+}$ with Et_4NCl (Figure 4a) indicates that no further intermediates or byproducts are involved. This situation is true for the reverse reaction (Figure 4b), although no clean isosbestic point is observed probably because of the formation of solid AgCl.

The shift of electrons is not only driven by chloride ions, but also takes place when $\mathbf{1}^{2+}$ is treated with Et_4NBr resulting in the formation of the corresponding bromo derivative $[Cu_2(NGuaS)_2Br_2]$, whose properties do not differ significantly from the chlorine-containing **2**.[12]

In conclusion, we have discovered a hitherto unknown facet of the redox behavior of copper sulfur clusters. The results presented clearly emphasize the unique potential of copper as a redox mediator not only in biomimetic systems. Though the complexes developed by us have no direct biological meaning, significant parallels can be recognized to biorelevant systems in which the protein matrix exerts a similar influence on the redox behavior as the specific layout of the ligands in the artificial compounds.

Experimental Section

Spectra were recorded with the following instruments: UV/Vis: PerkinElmer Lambda 45 in combination with the Hellma UV/Vis low-temperature fiber-optic interface (1 cm path length cell); NMR: Bruker Avance 300 and Avance 500; IR: Nicolet P510; ESI-MS: Bruker Esquire 3000. The elemental analysis was performed with the Elementar vario MICRO Cube. Temperature dependent magnetic susceptibilities of powdered samples were measured by using a SQUID magnetometer (Quantum Design MPMS-7) at 1 T. Cyclic voltammetry was performed with an EG&G 273A potentiostat/galvanostat using a three-electrode arrangement with a glassy carbon working electrode (2 mm diameter), an Ag/0.01 M $AgNO_3$ reference electrode and a Pt wire counter electrode in CH_2Cl_2/0.2 M NBu_4PF_6 or NBu_4Cl. All manipulations were carried out under an anaerobic and anhydrous atmosphere of nitrogen by employing standard Schlenk techniques or working in a glove box. All solvents were dried and degassed prior to use.

1[OTf]$_2$: The reaction of (NGuaS-)$_2$[3k,7] (1.1 mmol, 444 mg) and [Cu(MeCN)$_4$]OTf[13] (1 mmol, 376 mg) in MeCN (10 mL) leads to a suspension of a red solid. The reaction mixture was stirred for 1 h at room temperature. After cooling, Et_2O (ca. 70 mL) was added. The red precipitate was collected by filtration and washed with Et_2O. Yield: 1.1 g (85%). Single crystals of **1**[OTf]$_2$ were obtained by slow diffusion of Et_2O into the red mother liquor.

UV/Vis (CH_2Cl_2, RT): λ_{max} (ε) = 417 (8000), 286 (32400), 235 nm (64200 $M^{-1}cm^{-1}$). ^{1}H NMR (500 MHz, CD_2Cl_2, 25°C, TMS): δ = 2.64 (48H, CH_3), 6.75 (1H, CH), 7.14 (1H, CH), 7.56 (1H, CH), 7.70 ppm (1H, CH). ESI-MS (CH_2Cl_2): *m/z*: 507.1 [Cu(NGuaS-)$_2$]$^+$. IR (KBr): $\tilde{\nu}$ = 3056w, 2927w, 2879w, 2800w, 1560m (ν (C=N)), 1525vs (ν (C=N)), 1457s, 1396s, 1268s, 1155m, 1029s, 856w, 808w, 754w, 636s, 518w cm^{-1}. Elemental analysis (%) calculated for $C_{46}H_{64}Cu_2F_6N_{12}O_6S_6$: C 42.03, H 4.91, N 12.79, S 14.64; found: C 41.67, H 4.91, N 12.68; S 14.76.

2: The reaction of (NGuaS-)$_2$ (0.5 mmol, 222 mg) and CuCl (1 mmol, 99 mg) in MeCN (10 mL) led to a suspension of a blue solid. The reaction mixture was heated under reflux for 30 min. After cooling to room temperature, Et_2O (ca. 70 mL) of was added. The blue precipitate was collected by filtration and washed with Et_2O. Yield: 0.57 g (90%). Single crystals of **2** were obtained by gas-phase diffusion of Et_2O into the cold mother liquor or from the slow cooling of a hot, saturated MeCN solution.

UV/Vis (CH_2Cl_2, RT): λ_{max} (ε) = 708 (8400), 590 (6300), 419 (4600), 275 (25200), 243 nm (28100 $M^{-1}cm^{-1}$). ^{1}H NMR (500 MHz, CD_2Cl_2, 25°C, TMS): δ = 2.79 (12H, CH_3), 6.48 (1H, CH), 6.81 (1H, CH), 7.06 (1H, CH), 7.43 ppm (1H, CH). ESI-MS (CH_2Cl_2): *m/z*: 607.04 [(*M*−Cl)$^+$]. IR (KBr): $\tilde{\nu}$ = 3050*w*, 2195m, 2861m, 2784w, 1585s (ν (C=N)), 1509vs, 1442s, 1394vs, 1321s, 1290m, 1228m, 1164m, 1033m, 860m, 808m, 742m, 686w, 449m cm^{-1}. Elemental analysis (%) calculated for $C_{22}H_{32}Cu_2Cl_2N_6S_2$: C 41.12, H 5.02, N 13.08, S 9.98; found: C 40.91, H 5.06, N 13.13, S 9.90.

Crystal Structure Analysis: Bruker-AXS SMART APEX CCD diffractometer, graphite monochromator, $\lambda(Mo_{K\alpha})$ = 0.71073 Å, *T* = 120(2) K. Data reduction and absorption correction were performed with SAINT and SADABS.[14] All non hydrogen atoms were refined anisotropically. H atoms were derived from difference Fourier maps and placed at idealized positions, riding on their parent C atoms, with isotropic displacement parameters $U = 1.5\,U_{iso}$(methyl-C) or $1.2\,U_{iso}$(C).

1[OTf]$_2$: $C_{46}H_{64}Cu_2F_6N_{12}O_6S_6$; M_r = 1314.53, orthorhombic, space group Aba2, *a* = 37.270(4), *b* = 28.138(3), *c* = 11.7614(14) Å, *V* = 12334(2) Å^3, *Z* = 8, D_x = 1.416 g cm^{-3}, *F*(000) = 5440, μ = 0.964 mm^{-1}, 48739 reflections with 1.09° ≤ θ ≤ 27.88°. The structure was solved by direct methods [SHELXTL][14] and refined by full-matrix least-squares[14] on F^2 with 14645 independent reflections (R_{int} = 0.0996). As it was not possible to model one of the disordered triflate anion molecules in an adequate manner, the data set was eventually treated with the SQUEEZE facility of PLATON.[15 Refinement then converged smoothly. 647 parameters, *R*1 ($I > 2\sigma(I)$) = 0.073, *wR*2 (all data) = 0.144. Min./max. difference electron density −0.73/0.80 e Å^3.

2: $C_{22}H_{32}Cl_2Cu_2N_6S_2$; M_r = 642.64, monoclinic, space group *C*2/*c*, *a* = 21.456(3), *b* = 6.9394(9), *c* = 20.219(3) Å, β = 117.037(2)°, *V* = 2681.5(6) Å^3, *Z* = 4, D_x = 1.592 g cm^{-3}, *F*(000) = 1320, μ = 1.965 mm^{-1}, 11398 reflections with 2.13° ≤ θ ≤ 27.86°. Structure solving and refinement as for **1**[OTf]$_2$ with 3190 independent reflections (R_{int} = 0.049), 154 parameters, *R*1 ($I > 2\sigma(I)$) = 0.034, *wR*2 (all data) = 0.082. Min./max. difference electron density −0.37/0.88 e Å^3.

CCDC 809966 (**1**[OTf]) and 809965 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

XAS Spectroscopy: Configuration and conduction of the measurements as well as the analysis of the resulting data are described in the literature.[16] **1**[OTf]$_2$ and **2** were homogenized with boron nitride and measured in transmission mode at room temperature.

Received: April 19, 2011
Revised: September 14, 2011
Published online: January 10, 2012

Keywords: bioinorganic chemistry · copper · copper sulfur complexes · disulfide–thiolate interconversion · structure elucidation

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[12] Form the reaction of CuBr with $(NGuaS\text{-})_2$ (molar ratio 1:0.5) in MeCN we also obtained the copper(II) complex $[Cu_2(NGuaS)_2Br_2]$. The molecular structure as well as the spectroscopic signature is similar to **2**.

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