Cyclosulfur Ligands

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Cyclododecasulfur as a Ligand: From Gas-Phase Experiments to the Crystal Structures of $[Cu(S_{12})(S_8)]^+$ and $[Cu(S_{12})(CH_2Cl_2)]^+$**

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Sulfur is the element with the largest number of modifications and usually exists as S_n ring molecules; those with $n = 6$–14, 18, and 20[1,2] have been structurally characterized. Thermodynamically, the two most stable rings are D_{4d} S_8 and D_{3d} S_{12}.[1a,2] In contrast to the rich structural chemistry of elemental sulfur, the coordination chemistry of neutral sulfur molecules is underdeveloped and, to our knowledge, limited to $[Ag(S_8)]^+$, $[Ag(S_8)_2]^+$,[3] $[\{Rh_2(O_2CCF_3)_4\}_n(S_8)_m]$[4a] and $[Re_2(\mu\text{-}X)_2(CO)_6(S_8)]$ (X = Br, I).[4b] The coordination chemistry of the other chalcogens, Se and Te, is also restricted[5a] to few examples including $[(OSO)AgSe_6Ag(OSO)]^{2+}$ and $[(Se_6Ag^+)_n]$.[5b] In agreement with this, the sulfur ring molecules usually undergo redox degradation when treated with transition metal cations, leading to simpler metal (poly-)sulfide complexes, rather than forming coordination compounds.[6] However, Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) gas phase investigations of transition metal monocations M^+ with sulfur vapor (mainly S_8) detected strong signals for $[MS_n]^+$ complexes ($n = 2$–4, 6–8, 10, 12, and 14), suggesting that such coordination complexes can exist.[7] However, it remains unclear, if the observed compounds are true coordination compounds of the S_n molecule or if M^+ oxidatively added to the S–S bond, forming a $(n+1)$-heterocycle. Recent quantum chemical studies on $[MS_n]^+$ complexes (M = Li, Ca, V, Cu) suggested complexation of the metal cation to the ring structures.[8] Another open question from the pioneering mass spectrometric study[7] is whether the $[MS_n]^+$ complexes contain a single S_n molecule or two (or more) smaller molecules S_x and S_y ($x + y = n$). For Ag^+ and S_8, the mass spectrum showed two main signals, for $[AgS_8]^+$ and $[AgS_{16}]^+$, both of which were also fully characterized as $[Ag(\eta^4\text{-}S_8)]^+$ and $[Ag(\eta^4\text{-}S_8)_2]^+$ incorporated in the corresponding salts in the solid state,[3] using large and weakly coordinating anions (WCAs).[9] These large WCAs create pseudo-gas-phase conditions in the solid state and the gas-phase reactivity was reproduced in the condensed phase. However, the reaction of Cu^+ with S_8 vapor is more challenging:[7a,b] MS experiments showed that the "natural" S_8 complexes $[CuS_8]^+$ and $[CuS_{16}]^+$ were only observed within the first ten seconds of the experiment, after which $[CuS_{12}]^+$ was the major peak. From the mass spectra it was not clear, if the S_{12} ring was present as a ligand or if the detected mass corresponded to one S_4 and one S_8, two S_6, or even three S_4 units. Figure 1 gives an overview of PBE0/TZVPP calculated $[Cu(S_x)(S_y)]^+$ ($x + y = 12$) species. These calculations indicate that that C_{3v} $[Cu(S_{12})]^+$ is the most stable cation in the gas phase.[10]

To examine whether $[Cu(S_{12})]^+$ is also the global minimum in the condensed phase, we studied the reaction of cyclooctasulfur S_8 with Cu^+ salts of WCAs. Reactions of $Cu[AsF_6]$ with S_8 in solution in SO_2 immediately gave an insoluble compound, which was fully characterized by Raman spectroscopy.[12] By comparison with the structurally characterized homologues $[Ag(\eta^2\text{-}S_8)_2]^+[EF_6]^-$ (E = As,[3a] Sb[3b]), this material was assigned as $[Cu(\eta^2\text{-}S_8)_2]^+[AsF_6]^-$ (see the Supporting Information). Thus, using the classical weakly coordinating $[AsF_6]^-$ anion, the gas-phase behavior[7] is not reproduced, probably as a result of the insolubility of $[Cu(\eta^2\text{-}S_8)_2]^+[AsF_6]^-$, which may kinetically stabilize the S_8 complex over the S_{12} complex.

Larger WCAs of the type $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$)[9a] are less coordinating than $[SbF_6]^-$ or $[AsF_6]^-$ and induce higher solubility. Therefore, they are more suitable for the isolation of complexes of weakly bound ligands, such as $[Ag(\eta^2\text{-}P_4)_2]^+$,[13a] $[Ag(\eta^4\text{-}S_8)_2]^+$,[3b] $[Ag(\eta^2\text{-}C_2H_4)_3]^+$,[13b] or $[Ag(\eta^2\text{-}C_2H_2)_4]^+$.[13c] We also isolated and characterized related Cu^+ complexes, such as $[Cu(\eta^2\text{-}P_4)_2]^+$ and $[Cu(\eta^2\text{-}C_2H_4)_3]^+$, which were obtained by sonicating $Ag[Al(OR^F)_4]$, the corresponding ligand and CuI in CH_2Cl_2 solution [Eq. (1); $L = P_4$, C_2H_4].[14]

$$Ag[Al(OR^F)_4] + n\,L + CuI \rightarrow [Cu(L)_n]^+[Al(OR^F)_4]^- + AgI \qquad (1)$$

The analogous reaction of CuI and $Ag[Al(OR^F)_4]$ with $L = S_8$ only led to the formation of $[Ag(S_8)_2]^+[Al(OR^F)_4]^-$, independently of the solvent used (more than five independent reactions).[15] Therefore, a different approach was necessary. Our recently prepared Cu^I complex $[Cu(1,2\text{-}F_2C_6H_4)_2]^+[Al(OR^F)_4]^-$[16] is a good source of "naked" Cu^+. This species was dissolved in a 2:1 mixture of CH_2Cl_2 and CS_2, and an excess of elemental sulfur (approximately 2.5 equivalents) was added [Eq. (2) and the Supporting Information].

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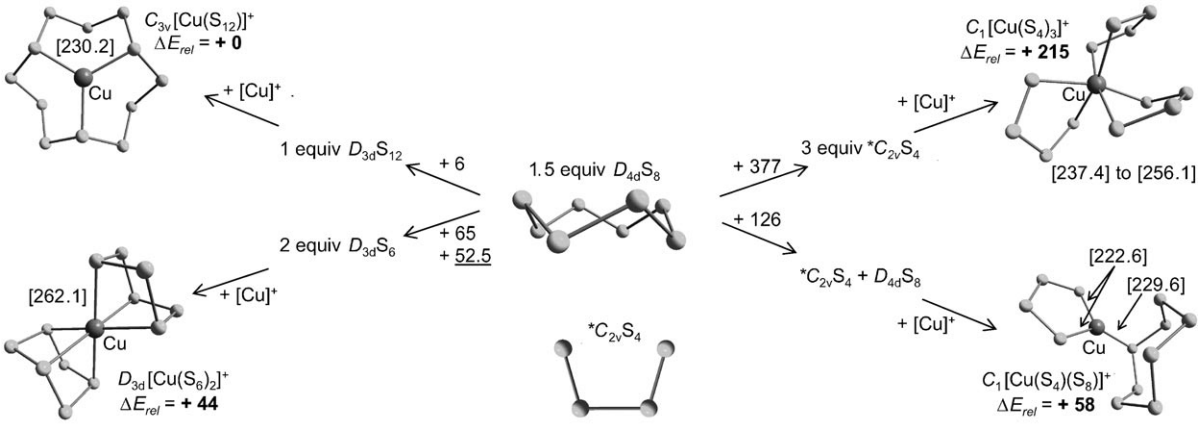

Figure 1. Calculated energies (PBE0/TZVPP, $\Delta H°_{(g)}$/kJ mol^{-1})[10] and experimental values:[11] Interconversion of cyclooctasulfur into other S_n species and possible $[Cu(S_x)(S_y)]^+$ ($x+y=12$) structures: underlined. Relative energies to C_{3v} $[Cu(S_{12})]^+$ (the most favorable complex): **bold**. Cu–S bond lengths [pm]: [brackets]. *C_{2v} S_4 was recently described as the global minimum structure of all possible S_4 isomers. See ref. [8b]. All unlabelled atoms are S.

$$[Cu(1,2\text{-}F_2C_6H_4)_2]^+[Al(OR^F)_4]^- + (\text{excess})\ S_8 \rightarrow [Cu(S_{12})(L)]^+[Al(OR^F)_4]^-$$
$$\mathbf{1}:\ L = S_8$$
$$\mathbf{2}:\ L = CH_2Cl_2 \qquad (2)$$

Depending on the sonication time, single crystals of $[(\eta^1\text{-}S_8)Cu(1,5,9\text{-}\eta^3\text{-}S_{12})]^+[Al(OR^F)_4]^-$ (**1**)[17,18] or $[(CH_2Cl_2)Cu(1,5,9\text{-}\eta^3\text{-}S_{12})]^+[Al(OR^F)_4]^-$ (**2**) were isolated from several independent reactions; yet the reactions could never be driven to completion. Along with the product crystals, a few of cyclooctasulfur were detected by Raman spectroscopy, unit cell determinations, and crystallography.[22] Complexes **1** and **2** both contain almost undistorted coordinated D_{3d} S_{12} and provide the first examples of any metal–S_{12} complex. Additionally, **1** is the first example of a complex in which two modifications of an element are bound to a metal atom. Complex **2**, which contains a very weakly bound CH_2Cl_2 molecule, is probably a structural approximation of gaseous C_{3v} $[CuS_{12}]^+$ (see below).

In **1**, the S_{12} ring coordinates to Cu^+ with an almost trigonal planar geometry, with Cu residing 33 pm above the S_3 plane, giving an almost C_{3v}-symmetric $[CuS_{12}]^+$ ion with an average Cu–S bond length of 232.3(2) pm (or 0.317 valence units)[10d] and a sum of the S-Cu-S bond angles of 354.9° (Figure 2). Compared to free cyclo-S_{12} (S–S 205.2 pm),[19a] the Cu^+-coordination leads to elongation of the S–S bonds around the tricoordinate sulfur atoms by approximately 2.5 pm, whereas the other S–S bond lengths remain almost unchanged (Figure 2). The η^1-S_8 ring coordinates perpendicular to the trigonal plane, with a Cu–S bond length of 243.3(1) pm (or 0.236 valence units),[10d] so that the resulting coordination geometry of the copper cation is trigonal pyramidal and the total valency around Cu^+ reaches 1.19 valence units. Structurally related complexes with a $\{Cu^IS_4\}$ core are known.[20,21] Compared to free cyclo-S_8, with an average S–S bond length of 205.29(2) pm (in the range 204.79(3)–205.59(2) pm),[22] the coordinated S–S bond is elongated by approximately 2 pm, whereas the uncoordinated S–S bonds remain almost unchanged (as in Figure 2).

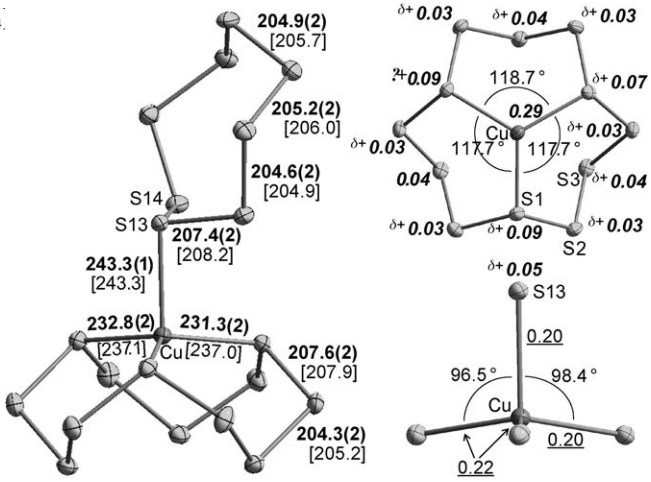

Figure 2. Crystal structure of the cation $[Cu(S_{12})(S_8)]^+$ in **1**. The anion $[Al(OR^F)_4]^-$ has been omitted for clarity. Left: Experimental average bond lengths [pm]: **bold**; calculated values [pm] (PBE0/TZVPP):[10] [brackets]. Thermal ellipsoids are set at 50% probability. Right: PABOON partial charges:[10c] ***bold italics***; shared electron numbers (SEN):[10c] underlined. All unlabelled atoms are S.

Quantum-chemical calculations[10] at the PBE0/TZVPP level reproduced the structural parameters of the crystal structure within 4.9 pm for Cu–S and 0.8 pm for S–S.

In **2**, cyclo-S_{12} also coordinates in a η^3 fashion with an almost trigonal planar $\{CuS_3\}$ core. The Cu^+ cation lies approximately 21 pm above the S_3 plane, with an average Cu–S bond length of 228.4 (4) pm (or 0.352 valence units,[10d] Figure 3). The apical position is now occupied by a weakly bound CH_2Cl_2 molecule (Cu–Cl 256.4(3) pm, 0.141 valence units[10d]). The sum of the S-Cu-S bond angles is 357.5°. In **2**, the Cu–S bond lengths are approximately 4 pm shorter than in **1**, and in good agreement to related complexes.[20,21] The Cu–Cl bond length is significantly longer than in $[(CH_2Cl_2)Cu[Al(OR^F)_4]$ ($R^F = C(CH_3)(CF_3)_2$)[16] (by approximately 40 pm) and $[Cu(CO)(CH_2Cl_2)_3]^+[Al(OR^F)_4]^-$[23] (by

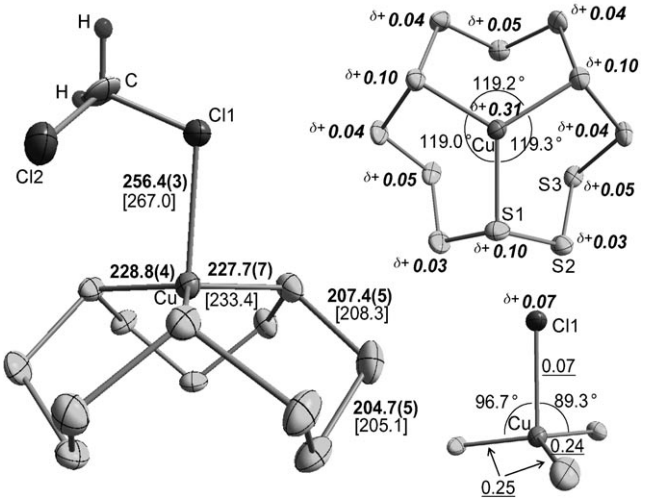

Figure 3. Crystal structure of the cation $[Cu(S_{12})(CH_2Cl_2)]^+$ in **2**. The anion $[Al(OR^F)_4]^-$ has been omitted for clarity. Left: Experimental average bond lengths [pm]: **bold**; theoretical average values [pm] (PBE0/TZVPP):[10] [brackets]. Thermal ellipsoids are set at 50% probability. Right: PABOON partial charges:[10c] ***bold italics***; shared electron numbers (SEN):[10c] underlined. All unlabelled atoms are S.

approximately 20 pm) suggesting a very weak Cu–Cl interaction.

The cation in the crystallographically determined structure of $[(CH_2Cl_2)Cu(1,5,9\text{-}\eta^3\text{-}S_{12})]^+[Al(OR^F)_4]^-$ (**2**) is in agreement with the PBE0/TZVPP calculation, within approximately 5 pm for Cu–S and 0.6 pm for S–S[10] (Figure 3). The anion is heavily disordered (see the Supporting Information).

An AIM analysis[10e] for $[Cu(S_{12})]^+$ gives electron densities of 0.49 e Å^{-3} at the bond critical points (BCPs) for the Cu–S bonds and 0.95–1.00 e Å^{-3} for the S–S bonds. The value of 0.49 e Å^{-3} at the Cu–S BCP is in a similar range to the experimental value calculated earlier for very weak complexes on the borderline between electrostatic and covalent bonding, such as $[Ag(\eta^2\text{-}C_2H_2)]^+$ (0.48 e Å^{-3}),[13c] or as was calculated for $[Cu(\eta^2\text{-}P_4)_2]^+$ (0.44 e Å^{-3}; PBE1PBE/6-311G(2df)).[10e] Similar values were also calculated for $[Cu(S_{12})(S_8)]^+$ (Cu–S_{12} bonds: 0.43 e Å^{-3}; Cu–S_8 bond: 0.38 e Å^{-3}). Molecular orbital (MO) and natural bond orbital (NBO) analyses[10c,e] suggested that cyclododecasulfur is a better ligand for Cu^+ than cyclooctasulfur (see the Supporting Information).

Calculated reaction energies (PBE0/TZVPP) and dispersion-corrected values ((RI)-BP86/TZVPP, values in italics)[10a] in the gas phase for the formation of $[Cu(S_n)]^+$ moieties from $[Cu(1,2\text{-}F_2C_6H_4)_2]^+$ [Eq. (3)–(7)] confirm the thermodynamically preferred bonding to S_{12}. Ligand exchange between $C_6F_2H_4$ and cyclo-S_n ($n = 8$ or 12) is favored in all of these cases by at least 32 kJ mol^{-1}. Dispersion-corrected energetics[10a] favor ligand exchange to an even greater extent [Eq. (3)–(9)]. The coordination of one S_{12} and one S_8 ring is favored over the coordination of two S_8 rings by at least 42 kJ mol^{-1} [Eq. (3) and (4)]. The formation of $[Cu(S_{12})(S_8)]^+$ and $[Cu(S_{12})]^+$ or $[Cu(S_{12})(CH_2Cl_2)]^+$ is favored by at least 34 kJ mol^{-1} over the formation of two $[Cu(S_8)_2]^+$ moieties [Eq. (8) and (9)]. A Born-Fajans-Haber (BFH) cycle [Eq. (10)] supports these results and indicates that solid $[Cu(S_{12})(S_8)]^+[Al(OR^F)_4]^-$ and $[Cu(S_{12})(CH_2Cl_2)]^+[Al(OR^F)_4]^-$ are favored by 66 kJ mol^{-1} over two molecules of solid $[Cu(S_8)_2]^+[Al(OR^F)_4]^-$ and liquid CH_2Cl_2 (see the Supporting Information).

We postulate the following pathway for the formation of **1** and **2**: $[Cu(S_8)(S_8)]^+$ is formed first [Eq. (3) and Supporting Information], as evident from the synthesis of insoluble $[Cu(S_8)_2]^+[AsF_6]^-$. BFH cycles also support the kinetic argument (see the Supporting Information). However, $[Cu(S_8)_2]^+[Al(OR^F)_4]^-$ is soluble and the $[Cu(S_8)_2]^+$ ion remains in solution, allowing an intermolecular rearrangement to give the thermodynamically more stable cations, $[Cu(S_{12})(S_8)]^+$ and $[Cu(S_{12})(CH_2Cl_2)]^+$ [Eq. (8) and (9) and the Supporting Information]. Another possibility is that an interconversion of S_8 into S_{12} is driven by the energy supplied by the ultrasonic bath [Eq. (10)]. With cyclododecasulfur present in the reaction mixture, the formation of $[Cu(S_{12})(S_8)]^+$ [Eq. (5)], $[Cu(S_{12})]^+$ [Eq. (6)] or $[Cu(S_{12})(CH_2Cl_2)]^+$ [Eq. (7)] would be thermodynamically favored in either case.

$$[Cu(1,2\text{-}F_2C_6H_4)_2]^+ + 2\ S_8 \xrightarrow{\Delta H^\circ_{(g)} = -34\ kJ\ mol^{-1}\ [-43\ kJ\ mol^{-1}]} [Cu(S_8)(S_8)]^+ + 2\ (1,2\text{-}F_2C_6H_4) \quad (3)$$

$$[Cu(1,2\text{-}F_2C_6H_4)_2]^+ + 2.5\ S_8 \xrightarrow{\Delta H^\circ_{(g)} = -76\ kJ\ mol^{-1}\ [-103\ kJ\ mol^{-1}]} [Cu(S_{12})(S_8)]^+ + 2\ (1,2\text{-}F_2C_6H_4) \quad (4)$$

$$[Cu(1,2\text{-}F_2C_6H_4)_2]^+ + S_{12} + S_8 \xrightarrow{\Delta H^\circ_{(g)} = -82\ kJ\ mol^{-1}\ [-100\ kJ\ mol^{-1}]} [Cu(S_{12})(S_8)]^+ + 2\ (1,2\text{-}F_2C_6H_4) \quad (5)$$

$$[Cu(1,2\text{-}F_2C_6H_4)_2]^+ + S_{12} \xrightarrow{\Delta H^\circ_{(g)} = -32\ kJ\ mol^{-1}\ [-31\ kJ\ mol^{-1}]} [Cu(S_{12})]^+ + 2\ (1,2\text{-}F_2C_6H_4) \quad (6)$$

$$[Cu(1,2\text{-}F_2C_6H_4)_2]^+ + S_{12} + CH_2Cl_2 \xrightarrow{\Delta H^\circ_{(g)} = -67\ kJ\ mol^{-1}\ [-81\ kJ\ mol^{-1}]} [Cu(S_{12})(CH_2Cl_2)]^+ + 2\ (1,2\text{-}F_2C_6H_4) \quad (7)$$

$$2\ [Cu(S_8)(S_8)]^+ \xrightarrow{\Delta H^\circ_{(g)} = -34\ kJ\ mol^{-1}\ [-41\ kJ\ mol^{-1}]} [Cu(S_{12})(S_8)]^+ + [Cu(S_{12})]^+ \quad (8)$$

$$2\ [Cu(S_8)(S_8)]^+ + CH_2Cl_2 \xrightarrow{\Delta H^\circ_{(g)} = -69\ kJ\ mol^{-1}\ [-99\ kJ\ mol^{-1}]} [Cu(S_{12})(S_8)]^+ + [Cu(S_{12})(CH_2Cl_2)]^+ \quad (9)$$

$$1.5\ S_8 \xrightarrow{\Delta H^\circ_{(g)} = +6\ kJ\ mol^{-1}} S_{12} \quad (10)$$

Raman spectra of $[Cu(S_8)_2][AsF_6]$, $[Ag(S_8)_2][SbF_6]$, and S_8, experimental procedures, ESI-MS data, MO and NBO theoretical calculations, Born–Fajans–Haber cycles, total energies and dispersion-energy corrections, coordinates for all calculated species, crystallographic tables, and CIF files are contained in the Supporting Information.

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[17] All structures were solved (SHELX 6.14 8/6/00) by the Patterson heavy atom or direct methods and successive interpretation of the difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. Data collection was performed at 98 K for **1** and 100 K for **2** on a Bruker APEX II CCD equipped with a Kappa goniometer ($Mo_{K\alpha}$ 0.70173 Å radiation). Colorless needles, sensitive to air and moisture were mounted at low temperature using a stream of cold gaseous N_2. **1**: space group $P\bar{1}$; $a = 12.6222$, $b = 14.6972$, $c = 14.7126$ Å; $\alpha = 91.417$, $\beta = 90.537$, $\gamma = 114.487°$; $V = 2482.48$ Å^3; $\rho_{calcd} = 2.237$ g cm^{-3}; $Z = 2$; 47691 reflections measured; 14307 unique reflections; $R1 = 0.0614$ for $F_o > 4\sigma(F_o)$ and 0.0928 for all data and 703 parameters; $wR2 = 0.1836$; GoF = S = 1.079; restrained GoF = 1.079 for all data. Max/min largest residual peak 2.26/−0.75 e Å^{-3}. **2**: space group $P\bar{1}$; $a = 11.0023$, $b = 14.2097$, $c = 14.8746$ Å; $\alpha = 90.313$, $\beta = 98.926$, $\gamma = 90.022°$; $V = 2297.33$ Å^3; $\rho_{calcd} = 2.169$ g cm^{-3}; $Z = 2$; 14204 reflections measured; 6578 unique reflections; $R1 = 0.0740$ for $F_o > 4\sigma(F_o)$ and 0.1266 for all data; $wR2 = 0.1679$; GoF = S = 1.031; restrained GoF = 1.033 for all data. Max/min largest residual peak 0.95/−1.01 e Å^{-3}.

[18] The structural parameters of the anions in **1** and **2** do not differ from published data.

[19] a) cyclo-S_{12}: S–S 205.2 pm; S-S-S 107.1°. J. Steidel, R. Steudel, *Z. Anorg. Allg. Chem.* **1981**, *476*, 171 – 178; A. Kutoglu, E. Hellner, *Angew. Chem.* **1966**, *78*, 1021; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 965; b) Value was calculated based on the reported crystal structure of cyclo-S_{12}.

[20] For example, $[(\eta^1\text{-TTCN})Cu(\eta^3\text{-TTCN})]^{+[21b]}$ or $[Cu(\eta^4\text{-18-ane-}S_6)]^{+[21b]}$ (TTCN = 1,4,7-trithiacyclononane, 18-ane-S_6 = hexathia-18-crown-6); Cu–S ranges from 222 to 236 pm. Tripodal $N(R_nSR')_3$ ligands, such as tris(methylthioethyl)amine (TMMEA) or tris(ethylthioethyl)amine (TEMEA), lead to almost trigonal planar $\{Cu^IS_3\}$ cores (Cu–S approximately 226 pm) with a fourth ligand in an apical position.[21c] Three monodentate S-ligands, such as 2(1*H*)-pyridinethione[21d] or 1,3-dithiane,[21e] adopt also a trigonal planar conformation around the copper cation (Cu–S 221–230 pm). Four 1,4-thioxane ligands (1,4-TOX)[21f] also coordinate to Cu in a trigonal pyramidal arrangement with an almost planar base ($Cu–S_{plane}$ 228–231 pm, $Cu–S_{apical} \approx 234$ pm).

[21] Selected examples for $\{Cu^{I}S_n\}$ cores and their references: a) TTCN: K. K Snaullah, R. S. Glass, G. S. Wilson, *J. Am. Chem. Soc.* **1993**, *115*, 592 – 600; K. K. Sanaullah, H. Hungerbühler, C. Schöneich, M. Morton, D. G. Vander Velde, G. S. Wilson, K.-D. Asmus, R. S. Glass, *J. Am. Chem. Soc.* **1997**, *119*, 2134 – 2145; b) 18-ane-6: J. A. R. Hartman, S. R. Cooper, *J. Am. Chem. Soc.* **1986**, *108*, 1202 – 1208; c) TMMEA/TEMEA: T. H. Cooper, M. J. Mayer, K.-H. Leung, L. A. Ochrymowycz, D. B. Rorabacher, *Inorg. Chem.* **1992**, *31*, 3796 – 3804; E. A. Ambundo, M.-V. Deydier, A. J. Grall, N. Aguera-Vega, L. T. Dressel, T. H. Cooper, M. J. Heeg, L. A. Ochrymowycz, D. B. Rorabacher, *Inorg. Chem.* **1999**, *38*, 4233 – 4242; J. M. Baumeister, R. Alberto, K. Ortner, B. Spingler, P. A. Schubiger, T. A. Kaden, *J. Chem. Soc. Dalton Trans.* **2002**, 4143 – 4151; d) pyridinethione: S. C. Kokkou, S. Fortier, P. J. Rentzeperis, *Acta Cryst.* **1983**, *C39*, 178-180; e) 1,3-dithiane: J. M. Knaust, S. W. Keller, *Cryst. Eng. Comm.* **2003**, *5*, 459 – 465; f) 1,4-TOX: M. M. Olmstead. W. K. Musker, R. M. Kessler, *Transition Met. Chem.* **1982**, *7*, 140 – 146.

[22] Cyclo-S_8 measured at 100 K with high resolution ($R1 = 0.0158$, $2\theta_{max} = 80°$). Further details on the crystal structure investigations 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-391460.

[23] G. Santiso-Quiñones, I. Krossing, unpublished results.

