Novel Soluble Cyclic and Polycyclic Polysulfido Species: $[Au_2S_8]^{2-}$, $[Cu_4S_x]^{2-}$ (x = 13–15) and other Copper Clusters

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Introduction

Sulfides of some transition metals, including those *not* forming tetrathioanions as V, Mo and W do, are to some extent soluble in polysulfide solutions. This applies for example to copper and gold sulfides in aqueous polysulfide [1]. No serious explanation has yet been made for this observation, and we suspect that the formation of interesting polynuclear complexes or clusters might be reponsible. In this note we report the isolation of novel cyclic and polycyclic species of copper and gold from polysulfide solutions.

Results and Discussion

By adding ethanolic polysulfide to a solution of $Cu(CH_3COO)_2 \cdot H_2O$ and $[PPh_4]Br$ in CH_3CN an orange-red solution is obtained, though one might have expected the precipitation of 'copper sulfides'*. From this observation it became evident that at least one discrete copper–sulfur aggregate would exist in solution. After keeping the solution for one day the mixed-crystal Cu^I compound $(PPh_4)_2[Cu_4(S_4)(S_5)_2]_{0.4}[Cu_4(S_5)_3]_{0.6}$ (*1*) precipitates. The crystal structure determination (for details see Physical Measurements and Table I) gave the following results: *1* contains the two anions $[Cu_4(S_5)_3]^{2-}$ (*1a*) and $[Cu_4(S_4)(S_5)_2]^{2-}$ (*1b*) (Fig. 1) in 0.6:0.4 ratio, occupying statistically the same site. In both 'species' the Cu atoms form a tetrahedron ($Cu{-}Cu_{av}$ = 274.5 pm), whereby each of six terminal atoms of the three polysulfide groups (*1a*: three S_5^{2-}; *1b* one S_4^{2-} and two S_5^{2-}) represents a bridge for the six edges of the metal tetrahedron ($Cu{-}S_{av}$ = 226.4 pm). The six coordinating S atoms build up a distorted octahedron. A Cu_4S_6 core also occurs in a few other Cu clusters, such as $[Cu_4(\mu_2\text{-}SPh)_6]^{2-}$ [2]). *1a* and *1b* contain four Cu_3S_3 (with chair conformation) and three CuS_x (x = 4, 5) ring systems (Fig. 1).

TABLE I. Results of the Crystal Structure Analyses.

Compound	$(PPh_4)_2[1a]_{0.6}[1b]_{0.4}$	$(PPh_4)_2[1b]_{0.9}[1c]_{0.1}$	$(PPh_4)_2[1b]_{0.8}[1c]_{0.2}$	$(PPh_4)_2[1b]_{0.5}[1c]_{0.5}$	$(PPh_4)_2[Au_2S_8]$
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a [pm]	1330.0(3)	1266.0(3)	1264.4(3)	1254.3(3)	2804.6(12)
b [pm]	1220.6(3)	1307.5(3)	1307.1(3)	1306.4(4)	1124.8(4)
c [pm]	3447.7(8)	3359.0(8)	3357.4(8)	3351.7(8)	2096.9(9)
β [°]	99.34(2)	99.20(3)	99.17(2)	98.97(3)	133.73(3)
V [10^6 pm^3]	5522.8	5488.3	5477.8	5425.0	4779.9
Z	4	4	4	4	4
Number of independent reflections	3354			5652	3666
Number of variables	314			286	103
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.114	[a]	[a]	0.093	0.075
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.079	[a]	[a]	0.120	0.063

[a] The crystal structures were not completely refined, because no further information could be expected and the compounds contain the same ligands as $(PPh_4)_2[1b]_{0.5}[1c]_{0.5}$ in slightly other ratio.

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*A small amount of precipitate is filtered off (1 g $Cu(CH_3COO)_2 \cdot H_2O$; 1 g $[PPh_4]Br$; 60 ml CH_3CN; polysulfide solution as given in ref. [4]).

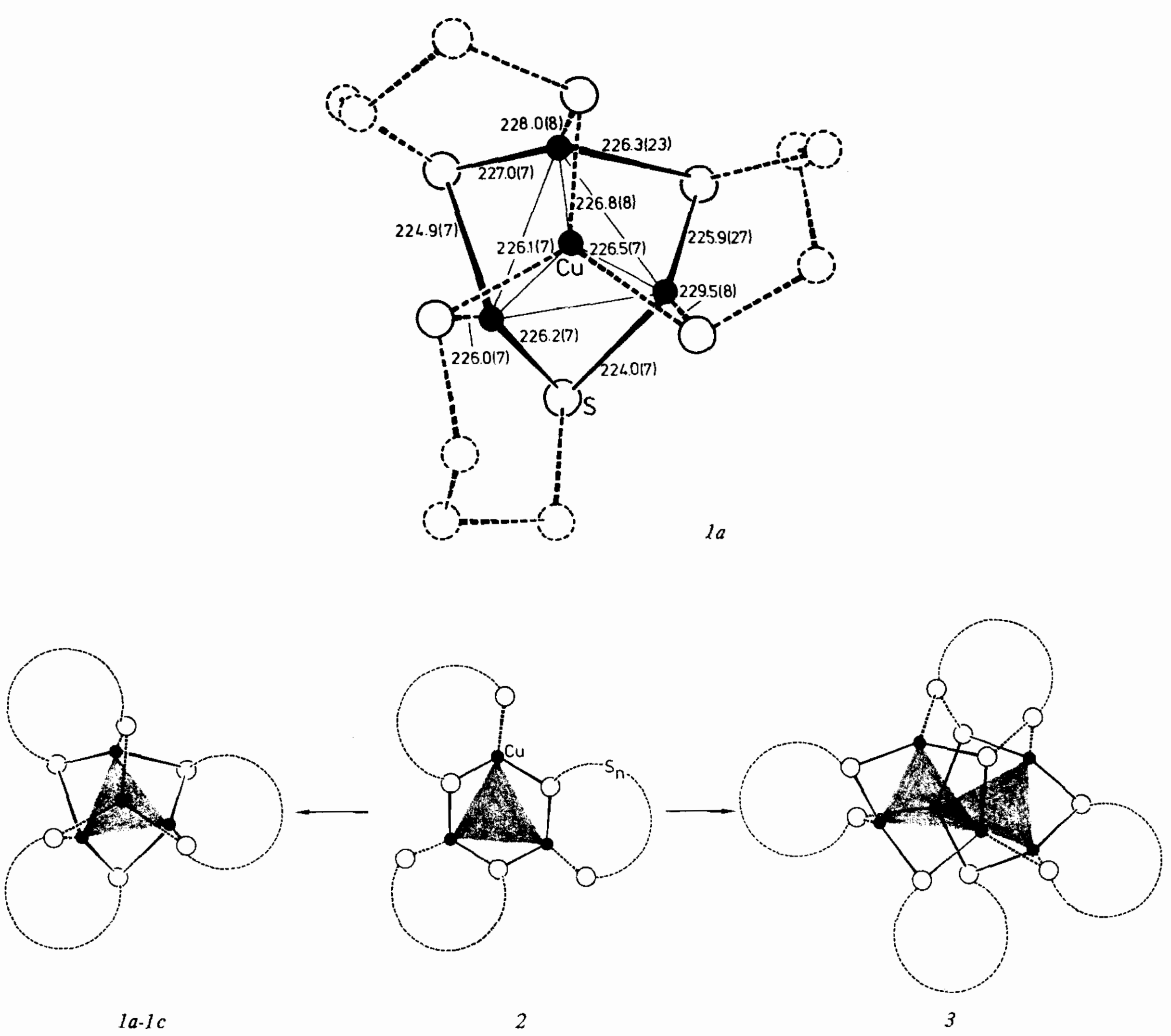

Fig. 1. Structure of *1a* (distances in [pm]) and correlation of the structure of *1a (1b, 1c)* to those of *2* and *3*. (Cu–Cu distances and selected bond angles for *1a*: Cu–Cu 267.5(4)–277.2(4) pm; S–Cu–S 111.5(6)–125.8(3), Cu–S–Cu 72.9(2)–75.3(2)°).

It is interesting to correlate the structure of the tetranuclear clusters with those of other polynuclear polysulfido species of copper, such as $[Cu_3(S_6)_3]^{3-}$ (*2*) [3] and $[Cu_6(S_4)_3(S_5)]^{2-}$ (*3*) [4] (Fig. 1). It turns out that the six-membered $Cu_3(\mu\text{-}S)_3$ ring of *2*, which has a chair conformation, seems to be a paradigmatic unit (see also [5]). The basic structure of *1a* can formally be obtained from *2* by coordination of each of the three 'end-on bonded sulfur atoms' of the three polysulfide ligands to an additional fourth Cu^I, as indicated in Fig. 1. This is a possible description of the structure: the Cu and S of the Cu_4S_6 core are not equivalent, as there are three Cu atoms coordinated to two different S_x^{2-} ligands (those of the marked $Cu_3(\mu\text{-}S)_3$ ring in Fig. 1) and one Cu coordinated to all of the three ligands. The structure of *3* can formally be derived by connecting two $Cu_3(\mu\text{-}S)_3$ units by the four polysulfido ligands (see Fig. 1).

It should also be noted that $Cu_3(\mu\text{-}S)_3$ rings [6] (and in general, $M_3(\mu\text{-}S)_3$ ones [7]) have been incorporated into current models of metallothioneins and low molecular weight proteins, which are believed to play a key role in metal metabolism.

Our investigations show that several different Cu clusters are abundant in polysulfide solutions, depending on the solvent and the concentration of the components. (From an aqueous medium with a high concentration of Cu^{2+} and NH_4^+ ions insoluble NH_4CuS_4, containing a polymeric anion, precipitates upon addition of a polysulfide solution [8].) By changing the concentration and/or solvent of the polysulfide, mixed crystal compounds containing tetranuclear clusters with other ratios of the poly-

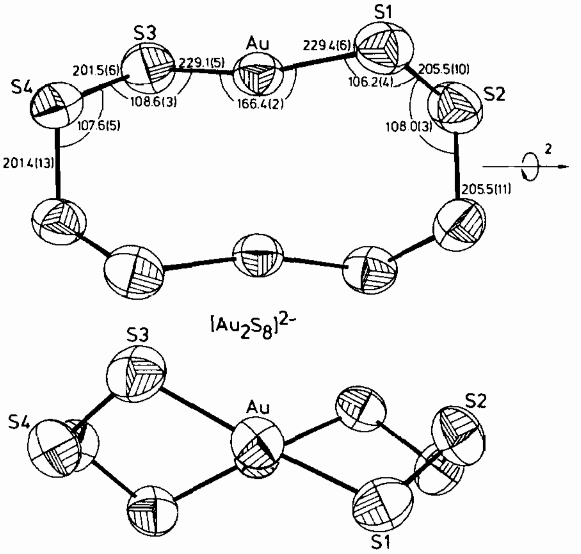

Fig. 2. Structure of the *7a* anion in two projections. (Bond distances and angles are given in [pm] and [°], respectively; Au–Au 312.0(2) pm).

sulfido ligands S_x^{2-} (x = 4, 5) can be obtained. A crystal structure determination has been done for $(PPh_4)_2[Cu_4(S_4)_2(S_5)]_{0.5}[Cu_4(S_4)(S_5)_2]_{0.5}((PPh_4)_2$-$[\mathit{1c}]_{0.5}[\mathit{1b}]_{0.5})$** (*4*), $(PPh_4)_2[Cu_4(S_4)_2(S_5)]_{0.2}$-$[Cu_4(S_4)(S_5)_2]_{0.8}((PPh_4)_2[\mathit{1c}]_{0.2}[\mathit{1b}]_{0.8})$ (*5*) and $(PPh_4)_2[Cu_4(S_4)_2(S_5)]_{0.1}[Cu_4(S_4)(S_5)_2]_{0.9}((PPh_4)_2$-$[\mathit{1c}]_{0.1}[\mathit{1b}]_{0.9})$ (*6*), too (results in Table I). The volume of the unit cell increases with increasing sulfur content, as expected.†

With a comparable preparation method different monocyclic polysulfido ring species of gold such as $[AuS_9]^-$ (dark yellow) and $[Au_2S_8]^{2-}$ (red-brown) can be obtained. By reacting $HAuCl_4 \cdot 4H_2O$ with ethanolic polysulfide *e.g.* the remarkable ten-membered highly-symmetrical $[Au_2S_8]^{2-}$ ring *7a* (Fig. 2) is formed, which can be isolated as diamagnetic red-brown PPh_4^+ salt *7*. The ring has approximately D_2 symmetry (crystallographical site-symmetry C_2). It can be seen from Fig. 2 that there seems to be an attraction between the two Au^I ions in the ring, which have the coordination number 2 with respect to sulfur.

The formation of the soluble clusters is responsible for the fact that some classical analytical separation procedures on the bases of polysulfide solutions (distinguishing between the thioanion forming elements like As, Sb, Sn and others like Cu) sometimes fail.

In general it can be concluded that quite a number of homoleptic mononuclear complexes ($[M(S_4)_2]^{2-}$ (M = Ni, Pd) existing as a spirobicycle [9]; $[Pt(S_5)_3]^{2-}$ [10]; $[Hg(S_6)_2]^{2-}$ [11]) but also polynuclear aggregates (*1a–1c*, *2* [3], *3* [4], *7a*) can be obtained from polysulfide solutions. It seems that metal aggregates can nicely be 'glued' by S_x^{2-} ligands according to their variable number of coordination sites.

Experimental

Physical Measurements

Intensity data were collected on a Syntex $P2_1$ four circle diffractometer (see Table I). The tetranuclear Cu cluster compounds *1*, *4*, *5* and *6* can be identified by the well-defined Raman spectra (λ_e = 647.1 nm; most intense lines below 500 cm^{-1}: 478, 441, ~423(sh) (ν(S–S)); 253; 211 cm^{-1}). With increasing sulfur content (that means higher S_5^{2-} portions) mainly the 423 cm^{-1} line decreases in intensity. *7* can be identified by the Raman lines (λ_e = 514.5 nm): 488, 475, 446 (ν(S–S)); 322, 256; 205; 133 cm^{-1}.

Acknowledgements

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**1c*: $[Cu_4(S_4)_2(S_5)]^{2-}$.

†The CuS_4 rings in *1* and *4–6* have an 'envelope' conformation. Whereas the CuS_5 rings have a distorted 'chair' conformation in *4–6* the situation in *1* is more complicated: The atoms of two S_5^{2-} ligands (those, which are not occupying the same site as the S_4^{2-} ligand) show a disorder in the crystal lattice, generating both distorted 'chair' and 'boat' conformation.