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$[Ag_2(S_6)_2]^{2-}$ (with a Novel Cyclic Inorganic Ring System), $[Ag(S_9)]^-$ and $(PPh_4)(NH_4)S_7 \cdot CH_3CN$ with an Unusual Conformation of the Heptasulfide Ion

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A variety of discrete transition metal clusters and complexes with polysulfido ligands can be isolated from polysulfide solutions [1]. We report here a new cyclic and a novel polycyclic species of silver, but also a salt with an unusual conformation of the heptasulfide ion.

The complexes $[Ag_2(S_6)_2]^{2-}$ (1) and $[Ag(S_9)]^-$ (2) (orange PPh_4^+ salts **1a**, **2a**) were isolated from solutions of $AgNO_3$ and polysulfide in CH_3CN (into which NH_3 and afterwards for a very short time H_2S was bubbled in presence of $(PPh_4)Br$ and S_8), respectively**. With this method generally long chain type polysulfide ions are formed. The rather unstable orange-red heptasulfide $(PPh_4)(NH_4)S_7 \cdot CH_3CN$ (**3a**) is obtained under similar conditions (by heating the reaction mixture without the presence of the metal salt). If the reaction mixture is not heated, the stable $(PPh_4)_2S_7$ (see below) precipitates in high yield. Details of the crystal structure determinations of all new compounds are given below and in Table I.

1 represents a novel inorganic condensed ring system with a central, exactly planar, four-membered ring and two seven-membered ones with a distorted chair conformation (Fig. 1, with distances, bond- and torsion angles). **1** has C_i symmetry.

The results of a crystal structure analysis of **2a** (all Ag and S atoms are disordered in the crystal lattice and could, in contrary to the cation, not be refined completely) and the vibrational spectra (IR and Raman) support the presence of a monocyclic $[Ag(S_9)]^-$ complex in this compound. The spectra are very similar to those of $(PPh_4)[Au(S_9)]$ [1–3].

Raman spectra can be used for identification of polysulfide species and as a probe for purity, as they give well defined sharp, very intense and characteristic bands.

The structural chemistry of the polysulfido complexes of silver is obviously governed by AgS_x ring units, which can exist as monocycles (see **2**) or which may be linked by a bridging polysulfide ligand (for example $[Ag_2(S_6)_2(S_8)]^{4-}$ [4]) or which can be condensed, as in **1**. The coordination number of silver is either two or three.

In contrast to the described coordination of silver, copper always shows a trigonal planar coordination in all known polysulfido complexes and clusters ($[Cu_6(S_4)_3(S_5)]^{2-}$, $[Cu_4(S_5)_3]^{2-}$, $[Cu_4(S_5)_2(S_4)]^{2-}$, $[Cu_4(S_5)(S_4)_2]^{2-}$, $[Cu_4(S_4)_3]^{2-}$, [Cu$_3$-

TABLE I. Results of the Crystal Structure Determinations.

Compound	$(PPh_4)_2[Ag_2(S_6)_2]$	$(PPh_4)[AgS_9]$	$(PPh_4)(NH_4)S_7 \cdot CH_3CN$[b]
Space group	$P2_1/c$	$P2/n$	$P\bar{1}$
a [pm]	1093.8(4)	1239.7(3)	795.3(2)
b [pm]	1397.7(5)	728.7(1)	1359.1(3)
c [pm]	1701.7(6)	1700.9(4)	1424.2(3)
α [°]			93.94(2)
β [°]	105.11(3)	109.60(2)	95.37(2)
γ [°]			95.21(2)
V [10^6 pm^3]	2511.6	1447.5	1521.7
Z	2	2	2
No. of independent reflections ($F_o > 3.92\ \sigma(F_o)$)	4013	1661	3524
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.062	a	0.079

[a] The PPh_4^+ cation could be refined, but not the anion, which is strongly disordered in the crystal lattice. [b] The last Difference Fourier maps showed a maximum near S(5) and S(6), which might be due to a disorder caused by the presence of ions with different conformation and/or stoichiometrics. Further investigations are in progress.

****1a** and **2a** were obtained by using different amounts of the reagents according to their stoichiometries.

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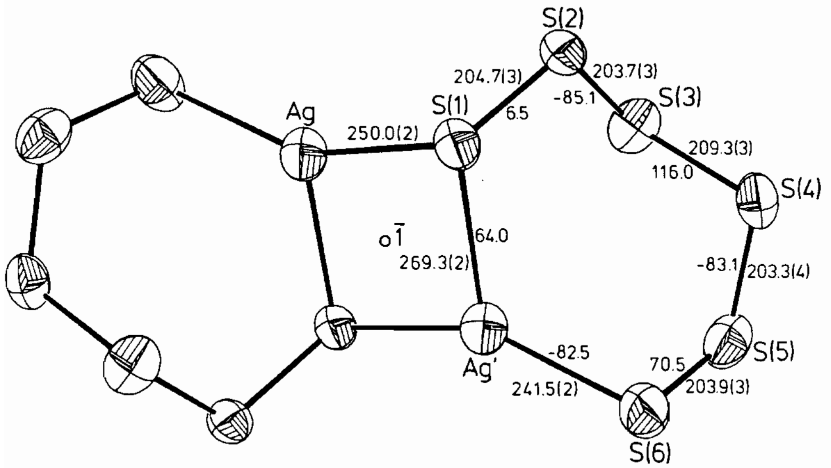

Fig. 1. Structure of **1** with bond distances (pm, Ag–Ag 344.2(1)) and torsion angles (°). Bond angles (°): S(1)–Ag–S(1)' 97.1(1), S(1)–Ag–S(6)' 148.1(1), S(1)'–Ag–S(6)' 114.6(1), Ag–S(1)–Ag' 82.9(1), Ag–S(1)–S(2) 112.9(1), Ag'–S(1)–S(2) 108.6(1), Ag'–S(6)–S(5) 102.9(1), S–S–S 106.7(1)–111.7(1).

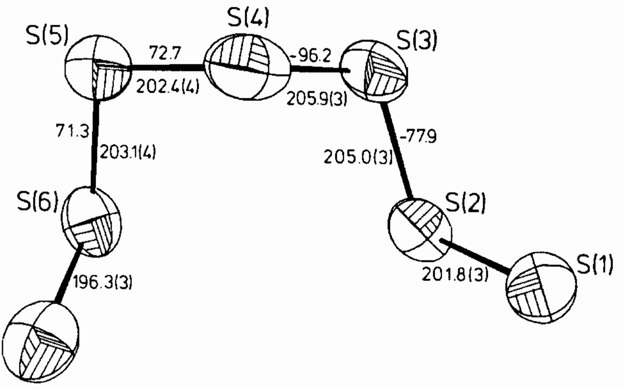

Fig. 2. Structure of **3** with bond distances (pm) and torsion angles (°). The bond angles (°) vary between 105.5(2) and 108.6(1).

$(S_x)_3]^{3-}$ (x = 4, 6), and $[Cu_2(S_6)_2(S_8)]^{4-}$ [1, 5]), in which the Cu_3S_3 ring with chair conformation is a paradigmatic unit (exception: the binuclear complex).

Whereas the polysulfide chains in $(PPh_4)_2S_7$†, Cs_2S_6 [6] and Cs_2S_5 [7] (with all-*trans* conformation [8]) correspond to portions of an infinite helical chain, the array of the five central sulfur atoms of S_7^{2-} in **3a** (with *cis* conformation [8]) corresponds to a part of the cyclo-octa-sulfur ring (from which three atoms have been removed; see Fig. 2, with distances, bond- and torsion angles). The *cis* conformation is obviously unusual for polysulfides, for which the helical chain is regarded as normal [8].

X-ray Structure Analysis and Vibrational Spectra

The data for all compounds were collected at 21 °C with a Syntex $P2_1$ four circle diffractometer. Empirical absorption corrections were applied for **1a** and **2a**. All structures were solved by conventional heavy atom and direct methods using SHELXTL. Crystal data and details concerning intensity measurement and structure refinement are given in Table I.

The Raman spectra of the new compounds **1a** and **2a** were measured with a Spex Ramalog spectrometer (excitation with a krypton laser, λ_e = 647.1 nm): **1a**: 484, 458, 396, 294, 255, 230, 200. **2a**: 492, 465, 452, 410, 279, 246, 184, 160. **3a**: A reasonable Raman spectrum could not be obtained until now (only weak ν(S–S) IR bands at 502, 465, 455, 436, 423 cm^{-1}).

[†] The structure of $(PPh_4)_2S_7$, which was prepared earlier from $[MoS(S_4)_2]^{2-}$, is known [9].

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