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$(PPh_4)_4[Ag_2S_{20}]\cdot S_8$, an Unusual Very Sulfur-Rich Compound

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It is now evident that S_x^{2-} ions are fascinating and versatile ligands from the structural point of view (this is also the case for S_2^{2-} [1]) and that metal aggregates can be 'glued' by these ligands according to their flexible and high number of coordination sites [2–4]. We report here the isolation of $[(S_6)Ag(S_8)Ag(S_6)]^{4-}$ (**1**), the first complex with an S_8^{2-} ligand. To our knowledge salts containing this discrete ion have not been reported so far.

Red–brown $(PPh_4)_4[(S_6)Ag(S_8)Ag(S_6)]\cdot S_8$ (**1a**), characterised by an X-ray structure analysis (Table I) and by its Raman spectrum, can be obtained by the reaction of $AgNO_3$ with a polysulfide solution (for details see Experimental). The disorder of **1** and the S_8 unit in the crystal lattice causes crystallographically a center of inversion.

The binuclear anion (**1**) has a very interesting structure. It contains two bidentate S_6^{2-} ligands $(d(SS)_{av} = 205.0$ pm) and a bridging S_8^{2-} ligand $(d(SS)_{av} = 196.0$ pm) (see Fig. 1). The structure and the bond lengths correspond to one component of **1** in the crystal lattice. As a result of the disorder, the S–S distances in the S_8^{2-} bridge are less accurate. The structures of the AgS_6 heterocycles have roughly twisted chair conformation (see [5]) and the structure of the S_6^{2-} group is comparable to the corresponding ones in $[Hg(S_6)_2]^{2-}$ [6]. The Ag atoms in these metallocycles are linked by the S_8^{2-} ligand, causing a trigonal planar coordination of the metal centers $(d(AgS)_{av} = 247.1$ pm).

Another remarkable feature of **1a**, a transition metal compound with one of the highest sulfur contents known so far, is the abundance of S_8 units in the crystal lattice.

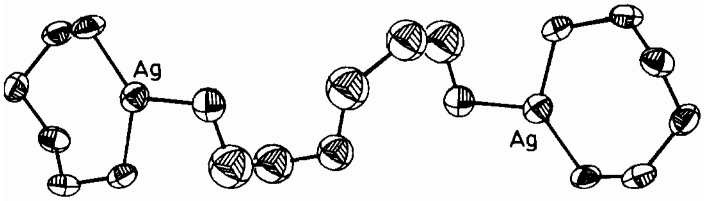

Fig. 1. Structure of **1**.

TABLE I. Results of the Crystal Structure Determination for 1a.

Space group	$P\bar{1}$
a [pm]	1091.6(4)
b [pm]	1361.5(6)
c [pm]	1937.5(8)
α [°]	86.15(3)
β [°]	83.89(3)
γ [°]	67.97(3)
V [10^6 pm^3]	2653.1
Z	1
Data collection instrument	Syntex $P2_1$
Radiation	Mo–Kα (graphite monochromator)
Crystal dimensions [mm]	0.1 × 0.4 × 0.4
μ [cm^{-1}]	9.8
Number of independent reflections $F_o > 3.92\sigma(F_o)$	4550
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$	0.099
$Rw = (\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2)^{1/2}$	0.066

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1a can be easily identified by its Raman spectrum (λ_e = 647.1 nm), showing the most intense bands of the S_8 unit in the lattice (at 472, 218 and 152 cm^{-1}) and bands of **1** with medium intensity (at 490, 454, 442, 411, 394 ($\tilde{\nu}$ (S–S)); 243, 202, 189, 113 cm^{-1}).

Experimental

*Preparation of **1a***

A stream of NH_3 was passed through a solution of 2.0 g $AgNO_3$ in 50 ml CH_3CN for 10 sec. While stirring, this mixture was added to 200 ml of a freshly prepared polysulfide solution (see below). The mixture was heated quickly up to 50 °C and the filtrate kept in a closed beaker at 5 °C in an Ar atmosphere. After about three weeks the red–brown crystals of **1a** were filtered off and washed several times with toluene (to remove the co-precipitated sulfur). Yield: 0.15 g.

Polysulfide Solution

A stream of NH_3 was passed through 200 ml CH_3CN for 20 min. After addition of 5.0 g (PPh_4)-Br and of 2.0 g S_8 a stream of H_2S was passed for ½ min through the mixture (colour change to greenish–brown) and stirred for 1 min.

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