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$[Cu_3S_{18}]^{3-}$, a Novel Sulfur Rich Complex with Different Kinds of Puckered Copper Sulfur Heterocycles, a Central Cu_3S_3 and Three Outer CuS_6 Ones

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Only a few discrete pure polynuclear transition metal sulfur complexes and clusters are known. We were able to prepare in pure form the clusters $[Mo_3S(S_2)_6]^{2-}$ (formed at 90 °C) and $[Mo_2(S_2)_6]^{2-}$ (formed at room temperature) by reaction of MoO_4^{2-} with an aqueous solution of polysulfide [1]. Because of the high affinity of Cu^{n+} to S_x^{2-} ions and because of the variety of binary and ternary copper sulfur minerals and their variety of structures [2], we expected the formation of discrete copper sulfur aggregates under similar conditions as given above.

By reacting $Cu(CH_3COO)_2 \cdot 2H_2O$ with a solution of polysulfide in ethanol in presence of $[(C_2H_5)_4N]I$ red $[(C_2H_5)_4N]_3[Cu_3S_{18}]$ (*1*) was obtained in reasonable yield and pure form. It is interesting to note that in aqueous solution in the presence of NH_4^+ ions the compound NH_4CuS_4 with S_4^{2-} 'ligands' and a catena structure (i.e. with no discrete species) was obtained [3].

1 was characterized by elemental analysis as well as by IR, Raman, ESCA, UV/VIS spectroscopy and X-ray structure analysis. The compound crystallizes in the space group $P2_12_12_1$ and contains the novel trinuclear $[Cu_3S_{18}]^{3-}$ complex *2* (Fig. 1) with a novel type of S_6^{2-} ligand forming a condensed ring system consisting of a central puckered Cu_3S_3 (Cu–S = 220 pm; SCuS = 106.0, CuSCu = 107.7° (mean values)) and three seven-membered CuS_6 heterocycles (Cu–S = 221, S–S ≈ 205 pm; SCuS = 134.3°). Cu has a distorted trigonal planar coordination sphere (further details given below).

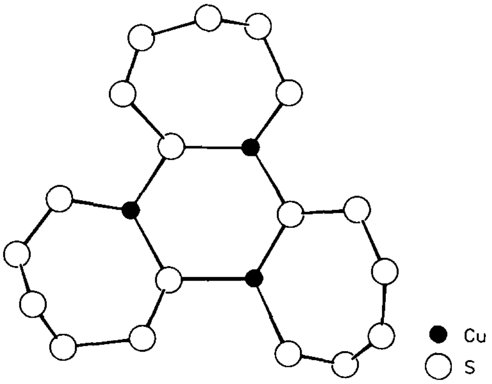

Fig. 1. Structure of *2* in crystals of *1*.

1 gives, as expected, only weak IR bands (CsI pellet: 453 (ν(S–S)) and 254 cm^{-1} (ν(Cu–S))).

The UV/VIS spectrum (solid state reflectance; bleached cellulose) shows bands at 285 (sh), 350 and 430 (sh) nm.

The structural variety of copper sulfide minerals (cf. for instance the different types of coordinated Cu in Anilithe, Cu_7S_4, [2]) implies that quite a number of different discrete species also exist. We intend to investigate these systematically, as for the molybdenum sulfur clusters.

Crystal Structure Determination

The molecular structure of *2* was determined by single crystal X-ray structure analysis of *1* (Syntex $P2_1$ four-circle diffractometer; Mo-K_α; λ = 71.069 pm; graphite monochromator; ω-scan; $4° \leq 2\theta \leq 40°$; a strong decline of the intensities was observed for higher 2θ-values). The unit cell parameters were obtained at 21 °C by a least squares refinement of the angular setting of 15 high-angle reflections ($13° < 2\theta < 19°$) [Crystal dimensions 0.3 × 0.2 × 0.18 mm^3, space group $P2_12_12_1$, a = 1349.1(6), b = 1731.7(8), c = 2161.9(10) pm, $V = 5050.7 \times 10^6$ pm^3, $Z = 4$, $d_{exp} = 1.52$, $d_{calc} = 1.52$ gcm^{-3}, 1204 independent reflections ($F_o > 3.92\sigma(F_o)$)].

The central Cu_3S_3 ring was located from a three dimensional Patterson synthesis and by direct methods using MULTAN 80. The remaining positional parameters were deduced from successive difference Fourier syntheses. The outer sulfur atoms in the puckered CuS_6 rings are highly disordered and show strong thermal vibrations. This explains the difficulties in measuring intensities at higher 2θ-values, the resulting small number of observed reflections, and the obtained rather high R value of 0.15. A further refinement of the structure will be taken out after collecting a new data set at low temperature.

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