Inorganica Chimica Acta, 65 (1982) L101–L102

Novel Adamantane-like Thio- and Selenoanions from Aqueous Solution: $Ga_4S_{10}^{8-}$, $In_4S_{10}^{8-}$, $In_4Se_{10}^{8-}$

BERNT KREBS, DIETER VOELKER and KURT-OTTO STILLER

Anorganisch-Chemisches Institut der Universitat Münster, D-4400 Munster, F.R.G.

Received April 7, 1982

By reaction of alkali and alkaline earth metal sulfides and selenides with germanium and tin disulfides and dieselenides, a number of monomeric and oligomeric thio- and selenoanions of germanium(IV) and tin(IV) have been prepared from aqueous solutions. They include ions such as $Ge_2S_6^{4-}$ [1], $Ge_4S_{10}^{4-}$ [2], $Ge_8S_{19}^{6-}$ [3, 4], $GeSe_4^{4-}$ [5], $Ge_2Se_6^{4-}$ [6], $Ge_4Se_{10}^{4-}$ [6], $(SnS_3^{2-})_n$ [7], $Sn_2S_6^{4-}$ [1], $Sn_{10}O_4S_{20}^{8-}$ [8], $SnSe_4^{4-}$ [9]. All previous attempts, however, have failed to obtain similar discrete anions from solutions with main group three central atoms.

We have now succeeded to isolate from aqueous solutions three members of a novel group of molecular thio- and selenoanions of gallium and indium. $Ga_4S_{10}^{8-}$ and $In_4S_{10}^{8-}$ are formed as the principal product of nucleophilic degradation of Ga_2S_3 or In_2S_3 with sulfide if the gallium or indium sulfide is reacted at 90 °C/4h with an aqueous solution of a three- or four-fold molar excess of an alkali metal sulfide. The faintly yellow alkali (or alkaline earth) salts are very soluble and can be isolated by slow evaporation of the solvent, excluding atmospheric oxygen. Raman spectra show identical structures of the thioanions in solution and in the solid.

In a similar way $In_4Se_{10}^{8-}$ was prepared from the reaction of In_2Se_3 with a threefold molar excess of alkali metal selenides in water solution. Similar to the corresponding selenogermanates and -stannates [5, 6, 9], this orange-yellow ion is extremely sensitive to oxidation and exclusion of oxygen is necessary throughout preparation and handling.

The thio- and selenoanions were characterized by complete X-ray structural analyses of the hydrated sodium and potassium salts. $K_8Ga_4S_{10}\cdot16H_2O$ (*I*), $K_8In_4S_{10}\cdot16H_2O$ (*II*) and $K_8In_4Se_{10}\cdot16H_2O$ (*III*) are isotypic, space group *Pnma*, with $a = 13.796(2)$, $b = 16.024(2)$, $c = 16.692(2)$ Å for *I*, $a = 14.016(4)$, $b = 16.369(4)$, $c = 16.968(4)$ Å for *II*, and $a = 14.187(4)$, $b = 17.612(4)$, $c = 16.848(4)$ Å for *III*. The structures, which were refined up to $R = 0.052$ (*I*), 0.041 (*II*) and 0.055 (*III*), contain isolated adamantane-like tetrameric $Ga_4S_{10}^{8-}$ (*I*), $In_4S_{10}^{8-}$ (*II*) and $In_4Se_{10}^{8-}$ (*III*) ions with crystallographic C_m symmetry which is, however, very close to the idealized T_d symmetry. In Figs. 1 and 2 the molecular structures are shown, with bond lengths and vibrational ellipsoids (50%). The bond lengths are close to the accepted tetrahedral bond radii sums. In all three ions the terminal bond lengths (average values: 2.252 (*I*), 2.422 (*II*), 2.542 Å (*III*)) are significantly shorter than the bridge bonds (mean: 2.289 (*I*), 2.464 (*II*), 2.571 Å (*III*)). This effect, which is less pronounced than in the isoelectronic $Ge_4S_{10}^{4-}$ [2], indicates slightly stronger bonding to the terminal chalcogen atoms. The bond angles within the central cage are slightly larger than those to the terminal bonds (mean values 110.9° *vs.* 108.0° for *I*, 110.9° *vs.* 107.9° for *II*, 111.7° *vs.* 107.1° for *III*, all ±0.1°).

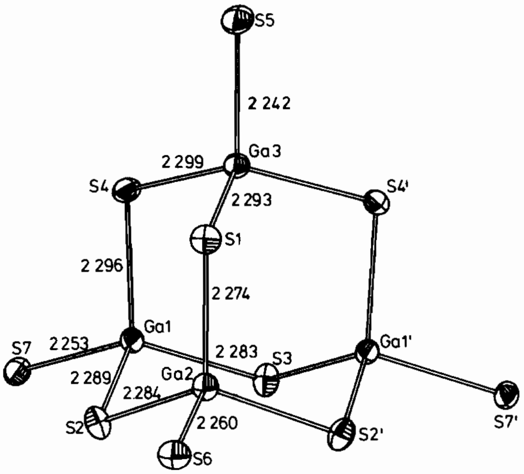

Fig. 1. $Ga_4S_{10}^{8-}$ ion in the structure of $K_8Ga_4S_{10}\cdot16H_2O$ with bond lengths [Å]. Standard deviations 0.002 Å.

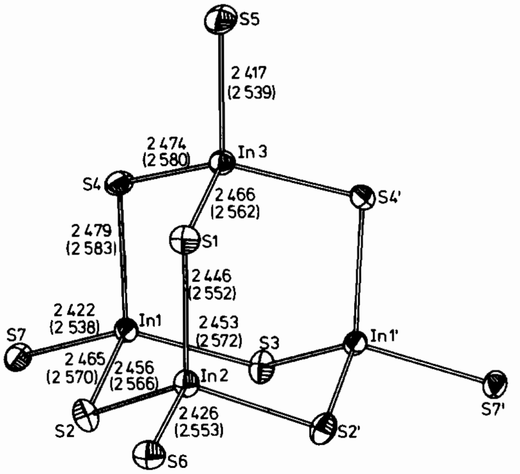

Fig. 2. $In_4S_{10}^{8-}$ ion in the structure of $K_8In_4S_{10}\cdot16H_2O$ with bond lengths [Å]. In parentheses: corresponding values for $In_4Se_{10}^{8-}$. Standard deviations 0.001···0.002 Å.

The present ions extend the isoelectronic series of adamantane-like molecular species from the fifth

0020-1693/82/0000-0000/$02.75

© Elsevier Sequoia/Printed in Switzerland

(P_4O_{10}, P_4S_{10}, P_4Se_{10}) and fourth ($Ge_4S_{10}^{4-}$, $Ge_4Se_{10}^{4-}$) to the third main group*. In view of the high negative charge on the ion, which should be a destabilizing factor, the observed stability of $Ga_4S_{10}^{8-}$, $In_4S_{10}^{8-}$ and $In_4Se_{10}^{8-}$ is remarkable.

The Raman spectra of the aqueous solutions and of the solids show bands in the region of the stretching vibrations at 369(s), 356(s) and 313(s) cm^{-1} for *I* (additional frequencies at 209(w), 170(s), 139(m), 125(m), 110(m), 94(m), 87(m), 80(m), and 66(m) cm^{-1}) and at 337(s), 324(m–s), and 302(s) cm^{-1} for *II* (additional bands at 230(w), 209(w), 189(w), 134(s), 104(s), 62(m) cm^{-1}) to be assigned to $\nu_1(A_1)$, $\nu_{10}(F_2)$, and $\nu_2(A_1)$, respectively. An estimation of the stretching force constants from the vibrational data affords values of *ca.* 1.7 mdyn/Å for $Ga_4S_{10}^{8-}$ and *ca.* 1.6 mdyn/Å for $In_4S_{10}^{8-}$, which are well below the values of 2.07 and 1.67 mdyn/Å to be predicted for single bonds according to Siebert's approximation.

Acknowledgements

Financial support for this research by the Minister fur Wissenschaft und Forschung NRW and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

1 B. Krebs, S. Pohl and W. Schiwy, *Angew. Chem.*, *82*, 884 (1970); *Angew. Chem. Int. Ed. Engl.*, *9*, 897 (1970); *Z. Anorg. Allg. Chem.*, *393*, 241 (1972).
2 B. Krebs and S. Pohl, *Z Naturforsch.*, *26b*, 853 (1971); S. Pohl and B. Krebs, *Z. Anorg. Allg Chem.*, *424*, 265 (1976).
3 B. Krebs, H.-J Wallstab and D. Voelker, *VI. European Crystallographic Meeting*, Barcelona, 1980, Abstracts p. 96.
4 B. Krebs, H.-U. Hürter, D. Voelker and H.-J. Wallstab, *Z. Krist.*, *154*, 63 (1980).
5 B. Krebs and H.-J. Jacobsen, *Z. Anorg. Allg. Chem.*, *421*, 97 (1976).
6 B. Krebs and H. Müller, *Z Anorg. Allg Chem.*, in the press.
7 W. Schiwy, Ch. Blutau, D. Gaethje and B. Krebs, *Z. Anorg. Allg. Chem.*, *412*, 1 (1975).
8 W. Schiwy and B. Krebs, *Angew. Chem.*, *87*, 451 (1975); Angew. Chem. Int. Ed. Engl., 14, 261 (1975).
9 B Krebs and H.-U. Hürter, *Z. Anorg Allg. Chem.*, *462*, 143 (1980).
10 A. Hardy, *Bull. Soc Fr. Min. Crist.*, *91*, 111 (1968).
11 D. Müller and H. Hahn, *Z. Anorg. Allg. Chem.*, *438*, 258 (1978)
12 B. Krebs and K.-O. Stiller, *Z. Naturforsch* b, in press.

---

*In $Pb_2B_2S_5$ [10], B_4S_{10} groups are present, which, however, cannot be brought into solution. As parts of polymeric $(GaSe_2^-)_n$ and $(InSe_2^-)_n$ units, adamantane-like Ga_4Se_{10} and In_4Se_{10} groups are observed in $TlGaSe_2$ [11] and $KInSe_2$ [12]