A Novel Cage Compound of Gallium and Sulphur, $Ga_4I_4(SCH_3)_4S_2$

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Although there are now many compounds known with adamantane type structures there are very few examples which contain the group III metals gallium and indium and these are restricted to the recently reported ions $Ga_4S_{10}{}^{8-}$, $In_4S_{10}{}^{8-}$ and $In_4Se_{10}{}^{8-}$ [1]. We report here the first example of a neutral gallium compound.

Dry Me_2S_2 was condensed on to Ga_2I_4 *in vacuo.* On removal of the ligand a white powder remained; this was dissolved in boiling Me_2S_2 and cooled when colourless square crystals of $Ga_4I_4(SCH_3)_4S_2$, suitable for X-ray analysis were formed. The structure was solved by a single crystal X-ray study. *Crystal Data* (20 °C) for $[Ga_4I_4(SCH_3)_4S_2]$: monoclinic, space group $P2_1/c$, $a = 10.85(1)$, $b = 19.62(2)$, $c = 11.18(1)$ Å, $\beta = 94.1(1)°$, $\mu = 9.63$ mm^{-1}. Intensity measurements were made on a Stoe STADI-2 diffractometer using Mo Kα radiation. 4173 reflections were measured and after elimination of those for which $I < 3\sigma(I)$ there remained 2322 unique reflections which were used in the final refinement. The structure was solved using MULTAN [2] and SHELX [3] refined anisotropically for Ga, I and S, and isotropically for C; currently the R value is 0.0621. Fractional atomic coordinates are given in Table I.*

The molecule (Fig. 1) has an adamantane-like cage structure and is the first reported neutral gallium compound of this kind. It has a structure similar to $Ge_4Br_4S_6$ [4] but as gallium has one less electron than germanium there are two types of bridging sulphur, S and S-Me and this is reflected in the Ga–S distances; the two S bridges lie on opposite corners of the sulphur octahedron. Since there are two possible sites for the methyl in the S-Me bridging group, four stereoisomers (plus one optical) are expected. The one observed in this work effectively has C_s symmetry; other possibilities are S_4, C_{2v} and C_1.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$).

	x	*y*	*z*
I(1)	7466(2)	1610(1)	12018(2)
I(2)	4952(2)	1645(1)	5341(2)
I(3)	11893(2)	1153(1)	6844(2)
I(4)	7310(2)	–1722(1)	8123(2)
Ga(1)	7727(3)	1043(2)	10008(3)
Ga(2)	6676(2)	1178(2)	6703(2)
Ga(3)	9787(2)	912(2)	7457(3)
Ga(4)	7629(3)	–455(2)	8279(3)
S(1)	9701(6)	1270(4)	9469(6)
S(2)	8496(6)	1357(4)	6073(6)
S(3)	6515(6)	1675(4)	8599(6)
S(4)	6406(6)	0000(4)	6668(6)
S(5)	7275(7)	–46(4)	10084(7)
S(6)	9619(6)	–247(4)	7807(6)
C(1)	4986(26)	1484(15)	9047(28)
C(2)	4873(29)	–170(17)	7138(30)
C(3)	9756(3)	2189(18)	9274(31)
C(4)	9646(32)	–646(19)	6291(34)

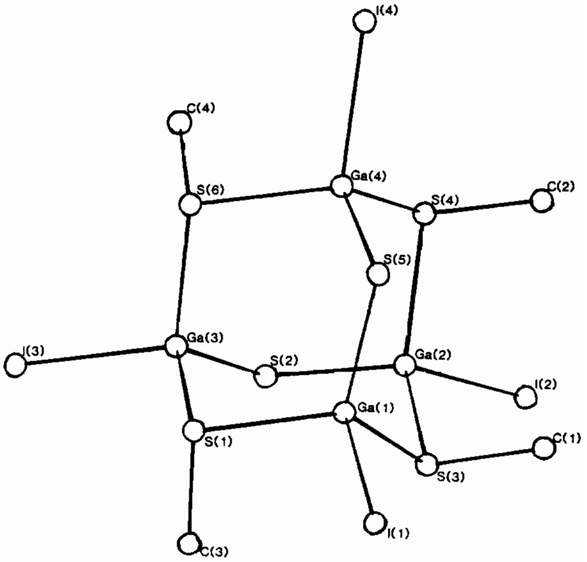

Fig. 1. The molecular structure of $Ga_4I_4(SCH_3)_4S_2$. Average bond distances: Ga–I 2.516(3); Ga–S(C) 2.336(7); Ga–S 2.204(8) Å [Ga–S(bridging) in $Ga_4S_{10}{}^{8-}$ 2.289(2) Å].

The adamantane cage consists of four Ga–S 6-membered rings and each ring has two S-Me groups; an analysis of the conformation of the rings is given below for each isomer.

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*Lists of structure factors are available on request from the authors.

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Symmetry of isomer	*Conformation of methyl groups*			
	Ring 1	2	3	4
C_s	1a,1e	2e	1a,1e	2a
C_{2v}	2e	2a	2e	2a
S_4	1a,1e	1a,1e	1a,1e	1a,1e
C_1	2e	1a,1e	1a,1e	2a

Ring 1 = Ga(1); S(1)[C(3)]; Ga(3); S(2); Ga(2); S(3)[C(1)]
Ring 2= Ga(1); S(1)[C(3)]; Ga(3); S(6)[C(4)]; Ga(4); S(5)
Ring 3= Ga(3); S(6) [C(4)]; Ga(4); S(4) [C(2)]; Ga(2); S(2)
Ring 4 = Ga(4); S(4)[C(2)]; Ga(2); S(3)[C(1)]; Ga(1); S(5)
a = axial; e = equatorial

The interaction between methyl groups in rings containing either 1a, 1e; or 2e will be insignificant because of their large separation; the stronger electron repulsion will occur between two axial methyl groups. This implies that the S_4 isomer will be the most stable; however, the observed distance between two axial C atoms is 3.88(4) Å which is close to the Van der Waals distance (4.0 Å). C–I interatomic distances are also normal and it seems likely that the stabilities of each isomer are similar. Activation energies for isomer interconversion are expected to be high in view of the rigid cage structure and therefore packing effects will not influence the stereochemistry. It is not clear why only the C_s form is produced in the complex reaction and in an attempt to resolve this we are carrying out a detailed study into the mechanism.

The synthetic method has potential for preparing important group III cage compounds with group V and VI elements and we are presently investigating these systems.

References

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