A Novel Aluminium Cage Compound

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We have recently reported the synthesis and crystal structure of the adamantane-like sulphur bridged gallium compound $Ga_4I_4(SCH_3)_4S_2$, which may be synthesized by the reaction between Ga_2I_4 and $(CH_3)_2S_2$ [1]. In this reaction the S-bridged dimer, $Ga_2I_4S(CH_3)_2$ is first formed and this further reacts to give the cage compound.

We have carried out a similar reaction with the mixed metal halide, $GaAlI_4$, and here report the synthesis of the isostructural aluminium analogue.

$GaAlI_4$, which has not been reported previously, was prepared by heating a mixture of Ga, GaI_3, and AlI_3 in the molar ratio 2:1:3 at 200 °C *in vacuo* until complete dissolution of the metal had occurred. The resulting white compound had the characteristic Raman spectrum of the AlI_4^- ion [2].

$Al_4I_4(SCH_3)_4S_2$ was prepared by condensing dry $(CH_3)_2S_2$ onto $GaAlI_4$ *in vacuo*. On removal of excess $(CH_3)_2S_2$ a white crystalline intermediate of composition $GaAlI_4[S(CH_3)_2]_2$ remained. This was dissolved in boiling $(CH_3)_2S_2$ and colourless square crystals of $Al_4I_4(SCH_3)_4S_2$ were deposited on cooling. The gallium and aluminium compounds may be readily distinguished by their Raman spectra; the former has a strong band at 253 cm^{-1} whilst the latter exhibits a strong band at 281 cm^{-1}. The nature of the white intermediate is currently under investigation.

The structure of $Al_4I_4(SCH_3)_4S_2$ was solved by a single crystal X-ray study. Crystal data (20 °C): monoclinic, space group $P2_1/c$, $a = 11.03(1)$, $b = 19.64(2)$, $c = 11.08$ Å, $\beta = 93.9°$, $\mu = 5.48$ mm^{-1}.

Intensity measurements were made on a Stoe STADI-2 diffractometer using Mo Kα radiation. 3854 reflections were measured and after elimination of those for which $I < 3\sigma(I)$ there remained 2081 unique reflections which were used in the final refinement. The structure which was solved using MULTAN [3] and SHELX [4], was refined anisotropically for Al, I and S, and isotropically for C; currently the R value is 0.073. Fractional atomic coordinates are given in Table I.

The molecule (Fig. 1) is isostructural with the gallium analogue; there are few neutral aluminium compounds known with adamantane-like structures, the only other which is directly comparable is Al_4Cl_4-

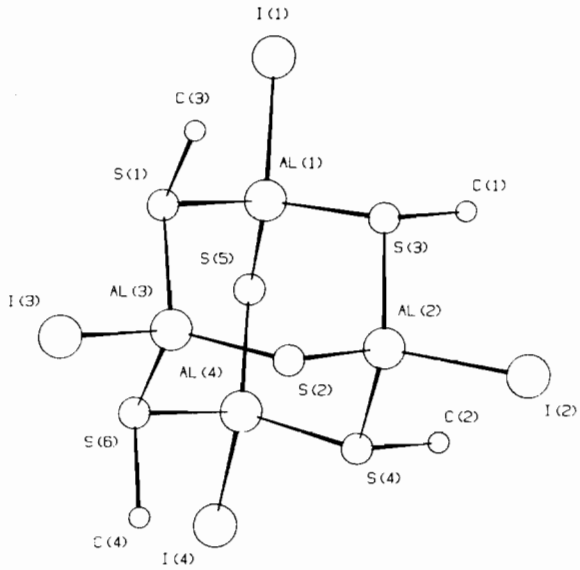

Fig. 1. The molecular structure of $Al_4I_4(SCH_3)_4S_2$.

TABLE I. Fractional Atomic Coordinates (×10^4)

Atom	*x*	*y*	*z*
C(1)	4971(27)	1479(17)	9072(29)
C(2)	4871(23)	−166(16)	7178(32)
C(3)	9755(32)	2209(16)	9303(32)
C(4)	9646(35)	−627(16)	6310(37)
I(1)	7446(2)	1607(1)	11979(2)
I(2)	4982(2)	1638(1)	5350(2)
I(3)	11875(2)	1141(1)	6859(2)
I(4)	7301(2)	−1713(1)	8125(2)
Al(1)	7717(7)	1038(4)	9993(7)
Al(2)	6690(6)	1174(4)	6704(7)
Al(3)	9782(6)	908(4)	7470(7)
Al(4)	7615(7)	−456(4)	8262(8)
S(1)	9651(6)	1263(4)	9440(7)
S(2)	8492(6)	1348(4)	6097(7)
S(3)	6524(6)	1655(4)	8573(7)
S(4)	6421(6)	15(4)	6688(7)
S(5)	7299(7)	−35(4)	10052(8)
S(6)	9591(6)	−242(4)	7800(7)

TABLE II. Selected Bond Distances (Å) in $Al_4I_4(SCH_3)_4S_2$

Al(1)–I(1)	2.503(8)	Al(2)–I(2)	2.498(8)
Al(3)–I(3)	2.493(7)	Al(4)–I(4)	2.495(9)
Al(1)–S(1)	2.30(1)	Al(1)–S(3)	2.32(1)
Al(1)–S(5)	2.16(1)	Al(2)–S(2)	2.17(1)
Al(2)–S(3)	2.29(1)	Al(2)–S(4)	2.30(1)
Al(3)–S(1)	2.30(1)	Al(3)–S(2)	2.19(1)
Al(3)–S(6)	2.30(1)	Al(4)–S(4)	2.31(1)
Al(4)–S(5)	2.20(1)	Al(4)–S(6)	2.31(1)

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$\{N(CH_3)_2\}_4(NCH_3)_2$ [10]. Selected bond distances are given in Table II. The Al–I distances (average 2.497(8) Å) are not significantly different from the terminal distances observed in AlI_3, (average 2.453(9) Å) [5] and 2.468(12) Å in $AlI_3 \cdot SbI_3$ [6]. Two different Al–S distances are observed due to the presence of both two and three coordinate sulphur; the average Al–S(CH_3) distance (2.30(1) Å) is shorter than observed in dimeric (2.370(3) Å [7]) and polymeric (2.348(2) Å [8]) $(CH_3)_2AlSCH_3$. The Al–S distance (average 2.18(1) Å) is not significantly different from that observed in $BaAl_2S_4$ (average 2.23(2) Å) [9].

Supplementary Material

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

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