Isolation of the First Gallium Hydrosulphido Complex and its Facile Conversion to a Ga_4S_4 Cubane: X-Ray Structures of $[(Bu^t)_2Ga(\mu\text{-}SH)]_2$ and $[(Bu^t)GaS]_4$

Michael B. Power and Andrew R. Barron*

Department of Chemistry, Harvard University, Cambridge, MA 02138, USA

The reaction of $(Bu^t)_3Ga$ with an excess of H_2S in pentane at ambient temperature results in the formation of the hydrosulphido bridged dimer $[(Bu^t)_2Ga(\mu\text{-}SH)]_2$, **1**, which upon mild thermolysis is converted to the cubic tetramer $[(Bu^t)GaS]_4$ **2**. Compounds **1** and **2** have been characterized by IR, NMR and mass spectroscopy and their molecular structures have been determined by X-ray crystallography.

The controlled reaction of group 13 alkyls, R_3M, with water is often extremely exothermic, however, in many instances it is possible to obtain the intermediate hydroxide complex which on thermolysis at moderate temperatures (25–60 °C) results in the formation of an oxide [eqn.(1)].[1] In contrast, the reaction with H_2S results in the direct formation of other insoluble polymeric sulphides, presumably *via* unstable hydrosulphido complexes.[2] Our recent isolation of an exceptionally stable hydroxide complex $[(Bu^t)_2Ga(\mu\text{-}OH)]_3$,[3] whose decomposition to the oxide only occurs above 140 °C, has prompted us to investigate the possible synthesis, and isolation, of its sulphur analogue. In addition, the presence of the sterically hindered *tert*-butyl ligand should limit oligomerization of the sulphide, allowing for its isolation and structural characterization.

$$R_3M \xrightarrow[-RH]{+H_2O} [R_2MOH]_n \xrightarrow[-RH]{\text{heat}} (RMO)_x \qquad (1)$$

The interaction of a cooled (−10 °C) pentane solution of $(Bu^t)_3Ga$[4] with an excess of H_2S yields a small quantity of an insoluble sulphide (see below), and a colourless solution from which may be obtained in moderate yield the crystalline complex $[(Bu^t)_2Ga(\mu\text{-}SH)]_2$ **1**. The dimeric nature of **1** was established by mass spectrometry (MS),† while IR and NMR spectroscopic data† are consistent with the presence of a single isomer, in which the bridging hydrosulphido ligands adopt an *anti* conformation.[5] The molecular structure of **1** has been confirmed by X-ray crystallography.‡

Compound **1** exists as a centrosymmetric dimer as shown in Fig. 1. One of the *tert*-butyl groups [C(2)] on each gallium shows a rotational disorder about the Ga(1)–C(2) bond, and only the major isomer (*ca.* 55%) is shown in the Figure. The heavy atom core geometry of **1** is similar to that found in $[(Ph)_2Ga(\mu\text{-}SEt)]_2$,[6] with a slight increase in the C–Ga–C and Ga–S–Ga bond angles, consistent with the increased Bu^t–Bu^t *vs.* Ph–Ph and reduced H–Bu^t *vs.* Et–Ph steric interactions. The Ga–S bond distances are within the ranges reported previously for alkylthio and dithiolato complexes of gallium (2.26–2.46 Å).[6,7] The hydrosulphido hydrogen was located, freely refined, and the ligand adopts the *anti* conformation indicated by ^1H NMR and IR spectroscopy.

Although an increasing number of hydrosulphido complexes have been reported in recent years,[8] compound **1** is not only the first isolated group 13 complex, but is, to the best of our knowledge, the only example with only σ-bound organic groups as ancillary ligands. Since the dimeric structure of **1** is undoubtedly similar to that of the less hindered, non-isolable methyl and ethyl derivatives,[2] the remarkable thermal stability of **1** suggests that the condensation reaction is intermolecular rather than intramolecular. We presume, therefore, that this enhanced stability is due to the steric bulk of the *tert*-butyl substituents on the gallium, which hinders the close approach of two molecules of **1** required for condensation/elimination to occur.

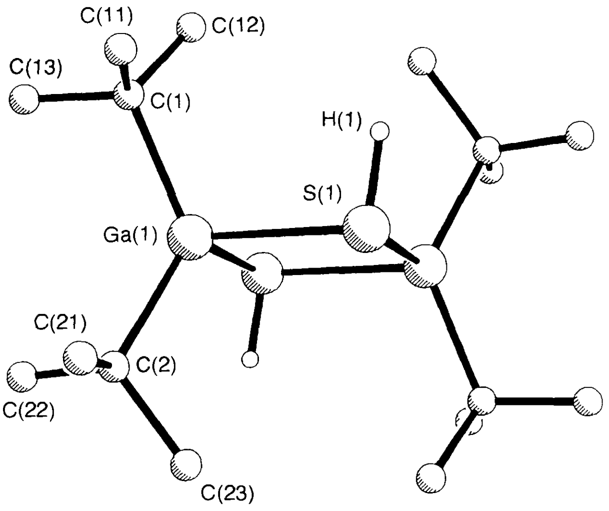

Fig. 1 The molecular structure of $[(Bu^t)_2Ga(\mu\text{-}SH)]_2$ **1** showing the atom numbering scheme; all the organic hydrogen atoms and the *tert*-butyl methyls of the minor isomer have been omitted for clarity. Bond lengths: Ga(1)–S(1) 2.444(4), Ga(1)–S(1A) 2.421(4), Ga(1)–C(1) 2.018(9), Ga(1)–C(2) 2.00(1), S(1)–H(1) 1.2(1) Å; bond angles: S(1)–Ga(1)–S(1A) 90.5(1), S(1)–Ga(1)–C(1) 107.3(4), S(1)–Ga(1)–C(2) 109.9(4), C(1)–Ga(1)–C(2) 123.9(5), Ga(1)–S(1)–Ga(1A) 89.5(1), Ga(1)–S(1)–H(1) 98(5), Ga(1A)–S(1)–H(1) 95(5)°.

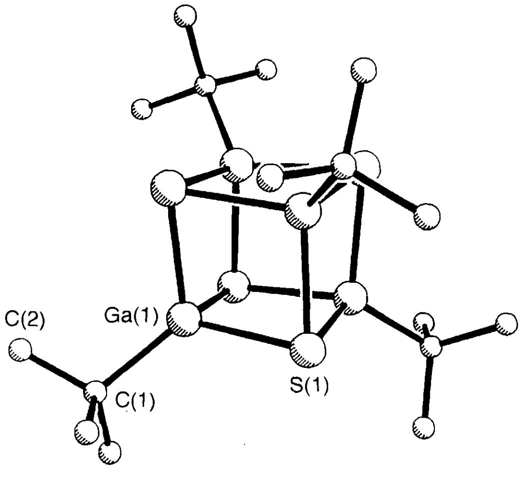

Fig. 2 The molecular structure of $[(Bu^t)GaS]_4$ **2** showing the atom numbering scheme; all the hydrogen atoms and the *tert*-butyl methyls of one of the isomers have been omitted for clarity. Bond lengths: Ga(1)–S(1) 2.359(3), Ga(1)–C(1) 1.978(6) Å; bond angles: S(1)–Ga(1)–C(1) 119.9(5), S(1)–Ga(1)–S(1A) 97.3(1), Ga(1)–S(1)–Ga(1A) 82.1(1)°.

Thermogravimetric analysis data indicate that compound **1** slowly decomposes in the solid state above 45 °C. Heating a sample of **1** at this temperature results in a 27.1% mass loss (equivalent to loss of Bu^tH, calculated 26.8%), and the formation of a white powder **2**, with a composition corresponding to $(Bu^t)GaS$.† This material is spectroscopically identical to that obtained as a side product in the formation of

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† *Selected physical data* for **1**: colourless plates; m.p. 145–147 °C (dec.) partial conversion to oligomer **2** occurs prior to melting. MS, *m/z* (EI, %) 401 ($2M^+ - SH$, 100%), 287 ($2M^+ - SH - 2Bu^t$, 20%), 183 (Bu^t_2Ga, 90%); IR $\nu_{S\text{-}H}/cm^{-1}$ (Nujol mull): 2552; NMR ($CDCl_3$ relative to external $SiMe_4$), ^1H δ 1.11 [18 H, s, $C(CH_3)_3$], 0.642 (1H, s, S-H); ^{13}C δ 30.56 [$C(CH_3)_3$], 26.24 [$C(CH_3)_3$]. **2**: colourless cubes; m.p. >250 °C, MS (*m/z*) (EI, %): 636 ($4M^+$, 40%) 579 ($4M^+\text{-}Bu^t$, 100%), 523 [$4M^+ - Bu^t - CH_2{=}C(CH_3)_2$, 20%], 465 ($4M^+ - 3Bu^t$, 15%), 408 ($4M^+ - 4Bu^t$, 20%) 69 (Ga, 25%); (*m/z*, CI, isobutane, %): 635 ($4M^+$, 100%), 579 ($4M^+\text{-}Bu^t$, 15%); NMR (C_6D_6, relative to external $SiMe_4$). ^1H δ 1.16 [$C(CH_3)_3$]; ^{13}C δ 26.85 [$C(CH_3)_3$ and $C(CH_3)_3$].

‡ *Crystal data*: **1** $C_{16}H_{38}Ga_2S_2$, $M = 434.0$, triclinic, space group $P1$ (No. 2), $a = 6.573(4)$, $b = 8.373(5)$, $c = 11.056(5)$ Å, $\alpha = 103.49(4)$, $\beta = 103.56(5)$, $\gamma = 102.16(5)$, $V = 552.1(5)$ Å³, $D_c = 1.305$ g cm^{-3}, $Z = 1$, $F(000) = 228$, Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 2.607$ mm^{-1}. Nicolet R3mV four circle diffractometer, 1148 reflections collected, 2θ range 4–40°, semi-empirical absorption correction, 846 unique reflections with $F > 4\sigma(F)$. Structure solved by direct methods (Ga and S atoms) and Fourier difference synthesis. Refined by full-matrix least-squares with Ga, S, and C atoms anisotropic. Hydrosulphide H atom located and refined isotropically. Organic ligand H atoms AFIXed and refined with $U_{iso}(H) = 1.2\,[U_{iso}(C)]$, converged $R = 0.054$, $R_w = 0.068$. **2** $C_{16}H_{36}Ga_4S_4$, $M = 635.6$, cubic, space group $P23$ (No. 195), $a = b = c = 8.626(1)$ Å, $V = 641.8(5)$ Å³, $D_c = 1.644$ g cm^{-3}, $Z = 1$, $F(000) = 320$, Mo-Kα radiation, $\lambda = 0.71073$ Å, $\mu = 4.454$ mm^{-1}. Nicolet R3mV four circle diffractometer, 909 reflections collected, 2θ range 4–55°, semi-empirical absorption correction, 266 unique reflections with $F > 4\sigma(F)$. Structure solved by direct methods (Ga and S atoms) and Fourier difference synthesis. Refined by full-matrix synthesis. Refined by full-matrix least-squares with Ga, S and C atoms anisotropic. Hydrogen atoms AFIXed and refined with $U_{iso}(H) = 1.2\,[U_{iso}(C)]$, converged $R = = 0.079$, $R_w = 0.098$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

1. Similarly, if a pentane solution of **1** is warmed to reflux, **2** is formed almost quantitatively as an insoluble white powder with the concomitant liberation of *iso*-butane. The mass spectrum of **2**† exhibits a peak due to the tetramer [(Bu^t)-GaS]$_4$, while the ^{1}H and ^{13}C NMR spectra are consistent with a single gallium coordinated *tert*-butyl environment. Crystals of **2** suitable for X-ray diffraction may be formed *via* recrystallization from hot benzene.‡ Compound **2** is air-stable, shows no further reaction in the presence of an excess of H_2S, and may be sublimed without decomposition at 225 °C, atmospheric pressure.

The molecular structure of **2** is shown in Fig. 2, and consists of a distorted cubane core of four gallium atoms and four μ_3-sulphido groups. The pseudo-tetrahedral coordination sphere at each gallium is completed by a terminally bonded *tert*-butyl group. As was observed for **1** the *tert*-butyl methyls are rotationally disordered about the Ga(1)–C(1) bond, and only one of the isomers is shown in the Figure. The Ga(1)–S(1) bond length in **2** is shorter than those in **1**, but longer than the μ_2-sulphido bridges in the adamantane-like $Ga_4I_4(SMe)_4S_2$ [2.204(8) Å][9] and $Ga_4S_{10}{}^{8-}$ [2.289(2) Å],[10] consistent with the strain inherent in the cubane structure.

While cubane structures have been reported for aluminium imides[11] and phosphides[12] and indium hydroxide,[13] compound **2** is the first group 13-chalcogenide cubane, previous examples being adamantane-like structures. Finally we note that **2** is isostructural to the Fe_4S_4 cubes present in iron-sulphur electron transfer proteins[14] whose synthetic representations have been studied in considerable detail.[15]

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References

1 See, for example, M. E. Kenney and A. W. Laubengayer, *J. Am. Chem. Soc.*, 1954, **76**, 4839; G. S. Smith and J. L. Hoard, *J. Am. Chem. Soc.*, 1959, **81**, 3907; S. J. Dzugan and V. L. Goedken, *Inorg. Chem.*, 1986, **25**, 2858; A. M. Arif and A. R. Barron, *Polyhedron*, 1988, **7**, 2091.

2 See, for example. M. Boleslawski, S. Pasynkiewicz, A. Kunicki and J. Smola, *J. Organomet. Chem.*, 1974, **65**, 161; T. Hirabayashi, K. Inoue, K. Yokota and Y. Ishii, *J. Organomet. Chem.*, 1975, **92**, 139.

3 M. B. Power, W. M. Cleaver, A. W. Apblett, A. R. Barron and J. W. Ziller, submitted to *Polyhedron*.

4 R. A. Kovar, H. Derr, D. Brandau and J. O. Callaway, *Inorg. Chem.*, 1975, **14**, 2809.

5 W. Beck, W. Danzer and R. Höfer, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 77.

6 G. G. Hoffman and C. Burschlea, *J. Organomet. Chem.*, 1984, **267**, 229.

7 See, for example, K. Dymock, G. J. Palenik, J. Slezak, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 28; E. Uhleman and P. Thomas, *Z. Anorg. Allg. Chem.*, 1967, **356**, 71.

8 A. Müller and E. Diemann, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford 1988, Chapter 16.1.

9 A. Boardman, S. E. Jeffs, R. W. H. Small and I. J. Worrall, *Inorg. Chim. Acta*, 1984, **83**, L39.

10 B. Krebs, D. Voelker and K. Stiller, *Inorg. Chim. Acta*, 1982, **65**, L101.

11 G. Del Piero, M. Cesari, G. Dozzi and A. Mazzei, *J. Organomet. Chem.*, 1977, **129**, 281.

12 A. H. Cowley, R. A. Jones, M. A. Mardones, J. L. Atwood and S. G. Bott, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1409.

13 A. M. Arif and A. R. Barron, *Polyhedron*, 1988, **7**, 2091.

14 *Iron-Sulfur Proteins*, ed. W. Lovenberg, Academic Press, New York, 1973, vols. 1 and 2.

15 R. H. Holm, *Chem. Soc. Rev.*, 1981, 455.