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Acid and base assisted topological reorganization of gallium sulfido clusters

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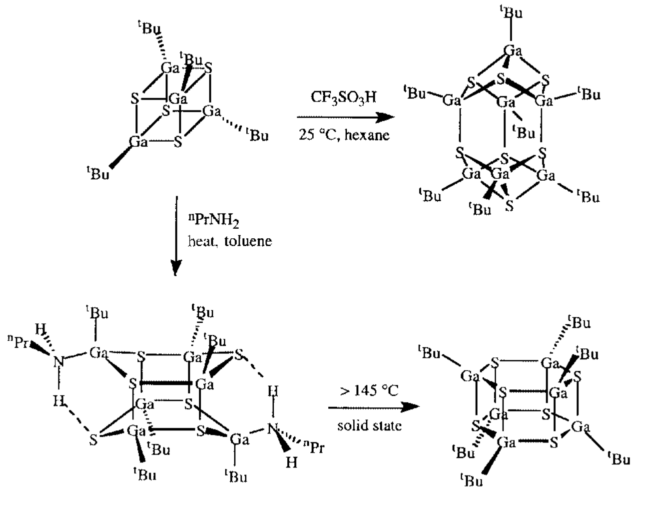
The reaction of $[(^{t}Bu)Ga(\mu_3\text{-}S)]_4$ with $^{n}PrNH_2$ in toluene solution yields $[(^{t}Bu)_6Ga_6(\mu_3\text{-}S)_4(\mu\text{-}S)_2(NH_2{}^{n}Pr)_2]$ (1), whose thermolysis in the solid state (110 °C), results in the stoichiometric conversion to $[(^{t}Bu)Ga(\mu_3\text{-}S)]_6$ ($\Delta H^{\ddagger} = 136$ kJ mol^{-1}); in contrast, the reaction of $[(^{t}Bu)Ga(\mu_3\text{-}S)]_4$ with triflic acid at room temperature yields $[(^{t}Bu)Ga(\mu_3\text{-}S)]_7$.

We have previously reported that the gallium sulfido cubane, $[(^{t}Bu)Ga(\mu_3\text{-}S)]_4$,[1,2] undergoes a topological reorganization to higher oligomers upon prolonged thermolysis in solution.[3] The identity of the product was found to be dependent on the choice of solvent. Thermolysis in pentane gave the octamer, $[(^{t}Bu)Ga(\mu_3\text{-}S)]_8$, in low yield (<25%), while in hexane the heptamer, $[(^{t}Bu)Ga(\mu_3\text{-}S)]_7$, is formed (80%).[3] In addition, we have found that the hexameric derivative, $[(^{t}Bu)Ga(\mu_3\text{-}S)]_6$, may be prepared, along with $[(^{t}Bu)Ga(\mu_3\text{-}S)]_8$, by the reaction of $[(^{t}Bu)Ga(\mu_3\text{-}S)]_4$ with pyridine to give $[(^{t}Bu)Ga(\mu\text{-}S)(py)]_3$, and subsequent solid state thermolysis (50%). The observation that strong Lewis bases, such as pyridine, cause core cleavage prompted an investigation of the reactivity of $[(^{t}Bu)Ga(\mu_3\text{-}S)]_4$ with amines. In addition, the original synthesis of $[(^{t}Bu)Ga(\mu_3\text{-}S)]_7$ was carried out in water, and the chemical inertness of the gallium–alkyl bond, suggested that protic reagents may also cause cage reorganization.

The reaction of $[(^{t}Bu)Ga(\mu_3\text{-}S)]_4$ with a small excess of $^{n}PrNH_2$ in toluene solution allows for the isolation, in high yield, of the hexa-gallium compound, $[(^{t}Bu)_6Ga_6(\mu_3\text{-}S)_4(\mu\text{-}S)_2(NH_2{}^{n}Pr)_2]$ (**1**), Scheme 1.† The molecular structure of compound **1** has been determined by X-ray crystallography, and is shown in Fig. 1.‡ The molecular structure is similar to $[(^{t}Bu)_6Al_6(\mu_3\text{-}O)_4(\mu\text{-}O)_2(NH_2{}^{n}Bu)_2]$,[4] and other Group 13/16 open hexamers.[5,6] The Ga_6S_6 core structure consists of two fused boat conformation Ga_3S_3 rings and can be described as being derived from the opening of two opposing edges of a hexagonal prism. The geometries and bond distances around the Ga and S atoms, in compound **1**, are similar to those we have previously reported for other *tert*-butyl gallium sulfido compounds,[1,2] in particular, the bridging sulfido-ligands in **1** are comparable to those observed in $[(^{t}Bu)Ga(\mu\text{-}S)(py)]_3$ [2.231(3)–2.253(3) Å].[3] The Ga–N bond distance [2.04(1) Å] is similar to those expected for a gallium amine interactions (1.98–2.24 Å), and considerably longer than that expected from the range reported for terminal gallium amide moieties (1.82–1.97 Å).[7] Unfortunately, the hydrogen atoms bonded to N(1) could not be located in the difference map and were fixed in ideal positions. However, the N(1)···S(1) distance (3.47 Å) is within the range appropriate for N–H···S hydrogen bonding in comparison with the related distance associated with N–H···O hydrogen bonding.[8] The presence of a sharp band in the IR spectrum (3298 cm^{-1}), characteristic of an amine ν(N–H) stretch (3300–3100 cm^{-1}),[9] and lack of a band associated with an S–H stretch (2580–2500 cm^{-1}),[10] along with the X-ray structure and ^{1}H NMR spectrum † are consistent with the formation of a gallium amine complex, and not the formation of an amide/thiol compound, *i.e.*, the formation of $[(^{t}Bu)_6Ga_6(\mu_3\text{-}S)_4(\mu\text{-}S)_2(NH_2{}^{n}Pr)_2]$ as opposed to $[(^{t}Bu)_6Ga_6(\mu_3\text{-}S)_4(\mu\text{-}SH)_2(NH^{n}Pr)_2]$.



Scheme 1 Summary of acid and base promoted topological reorganization of $[(^{t}Bu)Ga(\mu_3\text{-}S)]_4$.

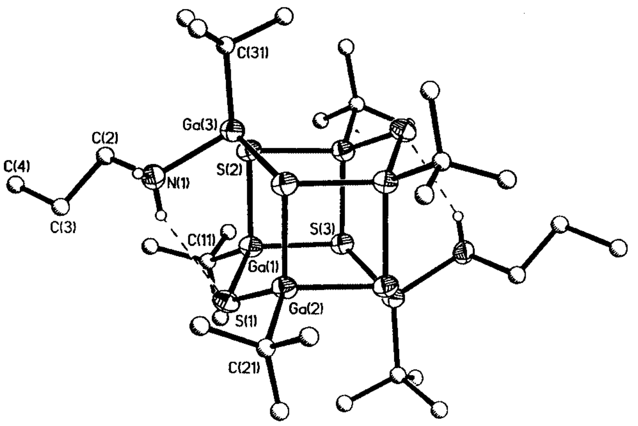


Fig. 1 Molecular structure of $[(^{t}Bu)_6Ga_6(\mu_3\text{-}S)_4(\mu\text{-}S)_2(NH_2{}^{n}Pr)_2]$. Thermal ellipsoids are shown at the 25% level. Carbon atoms are shown as shaded spheres and non-amine hydrogen atoms are omitted for clarity. Ga(1)–S(1) 2.234(4), Ga(1)–S(2) 2.363(4), Ga(1)–S(3) 2.366(4), Ga(2)–S(1) 2.237(4), Ga(2)–S(2′) 2.368(4), Ga(2)–S(3′) 2.380(4), Ga(3)–S(2) 2.281(4), Ga(3)–S(3′) 2.266(4), Ga(3)–N(1) 2.04(1) Å; S(1)–Ga(1)–S(2) 112.0(2), S(1)–Ga(1)–S(3) 116.7(2), S(2)–Ga(1)–S(3) 92.9(1), S(1)–Ga(2)–S(2′) 116.9(2), S(1)–Ga(2)–S(3′) 112.5(2), S(2′)–Ga(1)–S(3′) 92.4(1), N(1)–Ga(3)–S(2) 100.1(4), N(1)–Ga(3)–S(3′) 95.5(3), S(2)–Ga(3)–S(3′) 118.2(2), Ga(1)–S(1)–Ga(2) 112.3(2), Ga(1)–S(2)–Ga(3) 110.8(2), Ga(1)–S(2)–Ga(2′) 87.2(1), Ga(2′)–S(2)–Ga(3) 108.9(2), Ga(1)–S(3)–Ga(3′) 109.3(2), Ga(1)–S(3)–Ga(2′) 86.9(1), Ga(2′)–S(3)–Ga(3′) 109.9(2)°.

The mass spectrum of a sample of compound **1** only shows peaks due to $[(^{t}Bu)Ga(\mu_3\text{-}S)]_6$ ($m/z = 897$, $M^{+} - {}^{t}Bu$) and $^{n}PrNH_2$ ($m/z = 59$) suggesting the labile loss of the coordinated

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amines. The thermogravimetric/differential thermal analysis of compound **1** shows a mass loss between 145 and 188 °C consistent with the loss of two equivalents of $^n\mathrm{PrNH}_2$ (calc., 11.0%; exp., 11.7%). On a larger scale, thermolysis of compound **1** in the solid state at 110 °C under vacuum (10^{-2} Torr) for 2 days, results in its stoichiometric conversion to $[(^t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-S})]_6$. Based upon TG/DTA data at atmospheric pressure the ΔH‡ for the reaction shown in eqn. (1) is 136 kJ mol^{-1}.

$$[(^t\mathrm{Bu})_6\mathrm{Ga}_6(\mu_3\text{-S})_4(\mu\text{-S})_2(\mathrm{NH}_2{}^n\mathrm{Pr})_2] \xrightarrow{\text{heat}} [(^t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-S})]_6 + 2\ {}^n\mathrm{PrNH}_2 \tag{1}$$

In contrast to the reaction with $^n\mathrm{PrNH}_2$, the reaction of $[(^t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-S})]_4$ with triflic acid ($\mathrm{CF_3SO_3H}$) at room temperature yields the heptamer, $[(^t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-S})]_7$ in good yield (>70%), see Scheme 1. Since the heptamer was originally shown to form through heating $[(^t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-S})]_4$ in hexane,[3] this suggests the reorganization is catalyzed by acid. As was noted above, the synthesis of $[(^t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-S})]_7$ may also be carried out by thermolysis in water over a significantly shorter reaction time than is required for the same conversion to occur in hydrocarbon solution. Given relative rates of tetramer to heptamer conversion ($\mathrm{CF_3SO_3H}$ > heating in $\mathrm{H_2O}$ > heating in hexane), we propose that the topological reorganization is catalyzed by protonolysis of the cage.

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Notes and references

† To a solution of $[(^t\mathrm{Bu})\mathrm{Ga}(\mu_3\text{-S})]_4$ (500 mg, 0.79 mmol) in toluene (30 cm^3) was added $^n\mathrm{PrNH}_2$ (0.15 cm^3, 1.82 mmol). The resulting solution was then refluxed overnight. After cooling, the volatiles were removed under vacuum yielding a white solid. Clear colorless crystals suitable for X-ray structure determination were grown from a hexane/toluene solution at −20 °C. Yield: 0.45 g, 80%. IR (Nujol mull, KBr plates, cm^{-1}): 3298 (w), 2725 (w), 1581 (w), 1173 (s), 1090 (m), 1009 (w), 957 (m), 811 (s), 728 (m), 665 (s). ^{1}H NMR (Bruker AM-250, $\mathrm{C_6D_6}$): δ 3.78 (2H, m, NH), 2.40 [4H, m, J(H-H) = 7.3 Hz, NCH_2], 1.49 [36H, s, C(CH_3)$_3$], 1.23 [18H, s, C(CH_3)$_3$], 0.95 [4H, q, J(H-H) = 7.3 Hz, $\mathrm{NCH_2}$CH_2], 0.50 [6H, t, J(H-H) = 7.3 Hz, $\mathrm{NCH_2CH_2}$CH_3].

‡ Crystal data for $[(^t\mathrm{Bu})_6\mathrm{Ga}_6(\mu_3\text{-S})_4(\mu\text{-S})_2(\mathrm{NH}_2{}^n\mathrm{Pr})_2]\cdot 2(\mathrm{C_6H_5CH_3})$. $\mathrm{C_{44}H_{86}Ga_6N_2S_6}$, $M = 1253.83$, monoclinic, space group $P2_1/c$, $a = 12.452(3)$, $b = 20.312(4)$, $c = 12.348(3)$ Å, $\beta = 103.30(3)°$, $U = 3041(1)$ Å^3, $Z = 2$, $D_\mathrm{c} = 1.370$ g cm^{-3}, $T = 298$ K, $\mu(\text{Mo-K}_\alpha) = 2.85$ mm^{-1}, $F(000) = 1292$, $R = 0.0747$, $R_\mathrm{w} = 0.1504$ for 1505 independent observed reflections $[|F_\mathrm{o}| > 4.0\sigma|F_\mathrm{o}|, 3.4 \le 2\theta \le 46.7°]$ and 257 parameters, largest residual = 0.78 e Å^{-3}. Data collected on a Bruker CCD Smart System Diffractometer. CCDC reference number 186/1938.

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