Synthesis and structural characterization of [Tp$^{Bu^t_2}$]GaS: a terminal gallium sulfido complex in a system for which the indium counterpart is a tetrasulfido derivative, [Tp$^{Bu^t_2}$]In(η^2-S$_4$)

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The synthesis of the terminal gallium sulfido complex [Tp$^{Bu^t_2}$]GaS *via* the reaction of monovalent [Tp$^{Bu^t_2}$]Ga with elemental sulfur provides a striking contrast with the formation of the tetrasulfido derivative [Tp$^{Bu^t_2}$]In(η^2-S$_4$) in the indium system; such an observation provides a strong indication that gallium exhibits a greater tendency to partake in multiple bonding than does indium.
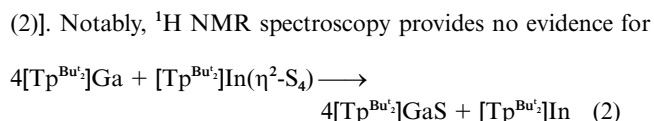
Complexes which exhibit multiple bonding to the heavier p block elements continue to attract considerable attention and provide challenges for the synthetic chemist. We are currently interested in terminal chalcogenido complexes of these elements[1] and have recently employed the sterically demanding tris(3,5-di-*tert*-butyl)pyrazolylhydroborato ligand to isolate the gallium and indium derivatives [Tp$^{Bu^t_2}$]GaE (E = Se or Te)[2] and [Tp$^{Bu^t_2}$]InSe.[3] In this paper, we describe a difference in the chemistry of gallium and indium which clearly indicates that gallium shows a greater tendency to form multiple bonds.

We have previously reported that the terminal indium selenido complex [Tp$^{Bu^t_2}$]InSe is obtained upon reaction of [Tp$^{Bu^t_2}$]-In with elemental selenium;[3] in contrast, the corresponding reaction with elemental sulfur yields the tetrasulfido derivative, [Tp$^{Bu^t_2}$]In(η^2-S$_4$).[4] This difference is quite unexpected in the sense that terminal selenido complexes are generally much less common than their terminal sulfido counterparts.[5] Since gallium and indium frequently show a close correspondence in their chemistry,[6] it was of interest to compare the behavior of the gallium chalcogenido system with that of indium. Significantly, we have discovered that there is a notable difference in their sulfido derivatives. Thus, [Tp$^{Bu^t_2}$]Ga[7] reacts with elemental sulfur at room temperature over a period of 1 d to yield the terminal sulfido complex [Tp$^{Bu^t_2}$]GaS [equation (1)],[8] rather than the tetrasulfido complex [Tp$^{Bu^t_2}$]Ga(η^2-S$_4$).[9]
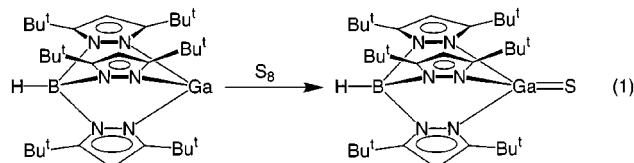
The structure of [Tp$^{Bu^t_2}$]GaS has been determined by X-ray diffraction, as illustrated in Fig. 1.[10] Notably the Ga≈S bond length of 2.093(2) Å is considerably shorter than other Ga–S bond lengths that have been reported, and therefore attests to the multiply bonded character of the interaction.[11] For example, the mean Ga–S bond length for complexes listed in the Cambridge Structural Database is 2.33 Å,[12] with some representative examples listed in Table 1.[13,14]

The terminal sulfido complex [Tp$^{Bu^t_2}$]GaS may also be obtained by reaction of the monovalent gallium complex [Tp$^{Bu^t_2}$]Ga with [Tp$^{Bu^t_2}$]In(η^2-S$_4$) at room temperature [equation (2)]. Notably, ^{1}H NMR spectroscopy provides no evidence for

$$4[Tp^{Bu^t_2}]Ga + [Tp^{Bu^t_2}]In(\eta^2\text{-}S_4) \longrightarrow$$
$$4[Tp^{Bu^t_2}]GaS + [Tp^{Bu^t_2}]In \quad (2)$$

the existence of significant concentrations of possible intermediate species such as [Tp$^{Bu^t_2}$]InS or [Tp$^{Bu^t_2}$]Ga(S$_x$) (x = 2–4) in the above transformation. A further distinction between the gallium and indium systems is that the sulfido ligand of [Tp$^{Bu^t_2}$]-GaS is not abstracted by PR$_3$ (R = Me or Et),[15] whereas [Tp$^{Bu^t_2}$]In(η^2-S$_4$) reacts readily with excess PR$_3$ at room temperature to give the monovalent indium complex [Tp$^{Bu^t_2}$]In.[4,16]

The isolation of [Tp$^{Bu^t_2}$]GaS in preference to [Tp$^{Bu^t_2}$]Ga-(η^2-S$_4$), the counterpart in the indium system, provides convincing evidence that gallium partakes in multiple bonding more readily than does indium. Further support for this notion includes the observations that (*i*) the selenido ligand of [Tp$^{Bu^t_2}$]InSe is readily transferred to [Tp$^{Bu^t_2}$]Ga giving [Tp$^{Bu^t_2}$]GaSe,[2] and (*ii*) the gallium tellurido complex [Tp$^{Bu^t_2}$]-GaTe has been isolated, whereas the indium analog has not.[2]

Of the Group 13 chalcogenido complexes, [Tp$^{Bu^t_2}$]GaE (E = S, Se or Te), [Tp$^{Bu^t_2}$]InSe and [Tp$^{Bu^t_2}$]In(η^2-S$_4$), it is evident that the indium sulfido complex is an anomaly.[17] Such an observation indicates the fine balance that exists in the formation of M≈E multiple *versus* single bonds in these systems. A further illustration of the subtle interplay between M≈E multiple and single bonds is provided by the fact that two closely related germanium sulfido complexes, Tbt(Tip)GeS and [Tbt(Mes)Ge(μ-S)]$_2$, exist as terminal and bridging sulfido complexes, respectively.[18–20]

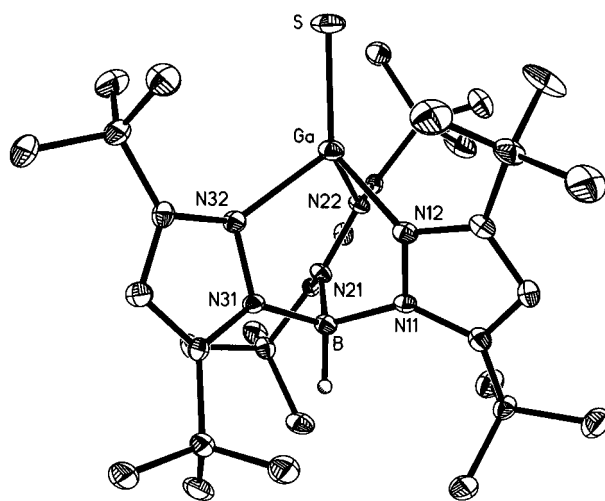**Fig. 1** Molecular structure of [Tp$^{Bu^t_2}$]GaS. Selected bond lengths (Å) and angles (°): Ga–S 2.093(2), Ga–N12 2.056(5), Ga–N22 2.041(4), Ga–N32 2.049(4); S–Ga–N12 131.0(1), S–Ga–N22 119.1(1), S–Ga–N32 123.4(1), N12–Ga–N22 88.2(2), N12–Ga–N32 88.1(1), N22–Ga–N32 97.3(2)

Table 1 Representative Ga–S bond lengths less than 2.4 Å

Complex	$d(\text{Ga–S})_{ave}$/Å	Ref.
[Tp$^{Bu^t}$]GaS	2.093(2)	This work
M$_6$Ga$_2$S$_6$ (M = Na or K)	2.24[1]$_{term}$, 2.34[1]$_{bridge}$	T1
Sr$_2$[Ga$_2$S$_5$]	2.24[2]$_{term}$, 2.31[3]$_{bridge}$	T2
[CsGaS$_2$]$_\infty$	2.28[1]	T3
K$_8$Ga$_4$S$_{10}$·16H$_2$O	2.25[1]$_{term}$, 2.290[9]$_{bridge}$	T4
Ga$_4$I$_4$(μ_2-SMe)$_4$S$_2$	2.204(8), 2.336(7) [Ga–S(C)]	T5
[pyGa(μ-S)Cl]$_3$	2.215[7]	T6
[Et$_4$N]$_3$[Ga$_3$S$_3$Cl$_6$]·THF	2.227[9]	T7
[Bu^{t}Ga(μ_2-S)py]$_3$	2.24[1]	T8
[(Me$_3$Si)$_2$CHGa]$_2$S	2.2197(7)	T9
Ga[S(2,4,6-Bu$^t_3$C$_6$H$_2$)]$_3$	2.205[8]	T10
Bu^{n}Ga[S(2,4,6-Bu$^t_3$C$_6$H$_2$)]$_2$	2.21[1]	T11
(2,4,6-Bu$^t_3$C$_6$H$_2$)Ga(SCH$_3$)	2.271(2)	T12
(Et$_4$N)[Ga(SPh)$_4$]	2.26[2]	T13
(Pr$_4$N)[Ga(SEt)$_4$]	2.264[1]	T13
[Cp(CO)$_2$FeGa(μ_3-S)]$_4$	2.38[2]	T14
[(Me$_4$C$_5$H$_6$N)Ga(μ_3-S)]$_4$	2.36[2]	T15
[(Me$_2$EtC)Ga(μ_3-S)]$_4$	2.356[6]	T16
[Bu^{t}Ga(μ_3-S)]$_4$	2.359(3), 2.365(5)	T17, T18
[Bu^{t}Ga(μ_3-S)]$_6$	2.34[4]	T8
[Bu^{t}Ga(μ_3-S)]$_7$	2.33[4]	T8
[Me$_2$Ga{μ-S(2,6-Me$_2$C$_6$H$_3$)}]$_4$	2.40[1]	T19

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In summary, the terminal gallium sulfido complex [Tp$^{Bu^t}$]-GaS has been synthesized *via* the reaction of [Tp$^{Bu^t}$]Ga with elemental sulfur. Under comparable conditions, the corresponding indium system yields the tetrasulfido complex [Tp$^{Bu^t}$]In(η^2-S$_4$), thereby providing convincing evidence that gallium exhibits a greater tendency to partake in multiple bonding than does indium.

Acknowledgements

Notes and References

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6 A notable difference in their chemistry, however, is the greater tendency of indium to form subvalent derivatives. See, F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988.
7 M. C. Kuchta, J. B. Bonanno and G. Parkin, *J. Am. Chem. Soc.*, 1996, **118**, 10 914.
8 Pentane (*ca.* 10 mL) was added to a mixture of [Tp$^{Bu^t}$]Ga (0.300 g, 0.48 mmol) and sulfur (0.030 g, 0.94 mmol) which was stirred overnight at room temperature. The mixture was filtered and the residue was extracted into toluene (*ca.* 10 mL). The volatile components were removed from the toluene extract under reduced pressure and the solid obtained was washed with pentane (2 × 10 mL) and dried *in vacuo* giving [Tp$^{Bu^t}$]GaS as a white solid (0.065 g, 21% based upon [Tp$^{Bu^t}$]Ga) (Found: C, 58.5; H, 8.4; N, 11.4. Calc. for C$_{33}$H$_{58}$N$_6$BGaS: C, 60.8; H, 9.0; N, 12.9%). IR data: 2644m cm^{-1} [ν(B–H)]. ^{1}H NMR (C$_6$D$_6$): δ 1.19 [s, 27 H, 3C(CH$_3$)$_3$], 1.85 [s, 27 H, 3C(CH$_3$)$_3$], 6.00 [s, 3 H, 3CH] (B–H not observed). ^{13}C NMR (C$_6$D$_6$): δ 30.5 [q, $^1J_{C-H}$ = 126, 3C(*C*H$_3$)$_3$], 31.1 [q, $^1J_{C-H}$ = 126, 3C(*C*H$_3$)$_3$], 32.7 [s, 3*C*(CH$_3$)$_3$], 33.3 [s, 3*C*(CH$_3$)$_3$], 103.5 [d, $^1J_{C-H}$ = 175 Hz, 3CH], 159.7 [s, 3*C*C(CH$_3$)$_3$], 167.9 [s, 3*C*C(CH$_3$)$_3$].
9 ^{1}H NMR spectroscopy indicates that [Tp$^{Bu^t}$]GaS is stable in the presence of excess sulfur and furnishes no evidence for the formation of [Tp$^{Bu^t}$]Ga(η^2-S$_4$).
10 [Tp$^{Bu^t}$]GaS: C$_{33}$H$_{58}$BGaN$_6$S, M = 651.44, triclinic, $P\bar{1}$ (no. 2), a = 10.870(2), b = 13.210(3), c = 13.308(3) Å, α = 95.29(1), β = 100.37(1), γ = 92.67(1)°, U = 1867.7(6) Å^3, Z = 2, μ = 0.822 mm^{-1}, T = 293 K, $R1$ = 0.1021 for 4780 reflections. CCDC reference number 186/1037.
11 The [Ga≈S] interaction may be considered to be a composite of the resonance structures [Ġ–S̈], [G=S] and [Ġ≡S̈]. Of these, it is likely that the polar form [Ġ–S̈] provides an important contribution, in which case the multiple bond is best viewed as being composed of both covalent and ionic interactions, *i.e.* a semipolar double bond. See, L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 3rd edn., 1960, p. 9.
12 The range of Ga–S bond lengths is 2.17–2.55 Å. CSD Version 5.14, *3D Search and Research Using the Cambridge Structural Database*, F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, pp. 1 and 31–37.
13 For recent reviews which include singly bonded chalcogenolate complexes of the Group 13 elements, see, J. P. Oliver, *J. Organomet. Chem.*, 1995, **500**, 269; J. Arnold, *Prog. Inorg. Chem.*, 1995, **43**, 353.
14 For further comparisons, the Ga≈Se and Ga≈Te bond lengths in [Tp$^{Bu^t}$]GaSe and [Tp$^{Bu^t}$]GaTe and 2.214(1) and 2.422(1) Å, respectively. The increments in M≈E bond lengths are comparable to the values predicted by the double bond covalent radii of E: S (0.94), Se (1.07) and Te (1.27 Å). See ref. 2 and L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 3rd edn., 1960.
15 For example, [Tp$^{Bu^t}$]GaS does not react with PMe$_3$ at 80 °C. Furthermore, since the reverse reaction, *i.e.* sulfido transfer from R$_3$PS to [Tp$^{Bu^t}$]Ga, does not occur at temperatures up to 120 °C, it is evident that there is an inaccessible kinetic barrier for sulfido transfer in this system such that it is not possible to infer relative Ga≈S *versus* P≈S bond energies. In contrast, selenido transfer between R$_3$PSe and [Tp$^{Bu^t}$]Ga is facile and equilibrium studies have demonstrated that the Ga≈Se interaction in [Tp$^{Bu^t}$]GaSe is *ca.* 7 kcal mol^{-1} (cal = 4.184 J) stronger than the P≈Se bond in Et$_3$PSe (see ref. 2).
16 This reaction likewise does not yield spectroscopically identifiable quantities of [Tp$^{Bu^t}$]In(S$_x$) (x = 1–3).
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18 N. Tokitoh, T. Matsumoto, H. Ichida and R. Okazaki, *Tetrahedron Lett.*, 1991, **32**, 6877.
19 Tbt = 2,4,6-[(Me$_3$Si)$_2$CH]$_3$C$_6$H$_2$, Tip = 2,4,6-Pr$^i_3$C$_6$H$_2$, Mes = 2,4,6-Me$_3$C$_6$H$_2$.
20 Another noteworthy example of the formation of M≈E multiple *versus* single bonds is provided by the observation that {η^2-[(C$_9$H$_6$N)(Me$_3$Si)CH]}$_2$SnSe exists as a terminal selenido complex, whereas [{(C$_9$H$_6$N)(Me$_3$Si)CH}$_2$Sn(μ-S)]$_2$ is a sulfido-bridged dimer; however, the supporting ligands adopt different co-ordination modes in these particular examples. See, W.-P. Leung, W.-H. Kwok, L. T. C. Law, Z.-Y. Zhou and T. C. W. Mak, *Chem. Commun.*, 1996, 505.

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