

# Synthesis and structural characterization of $[\text{Tp}^{\text{Bu}_t}]_2\text{GaS}$ : a terminal gallium sulfido complex in a system for which the indium counterpart is a tetrasulfido derivative, $[\text{Tp}^{\text{Bu}_t}]_2\text{In}(\eta^2\text{-S}_4)$

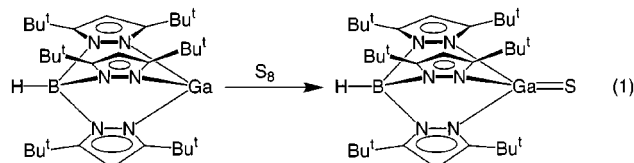
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The synthesis of the terminal gallium sulfido complex  $[\text{Tp}^{\text{Bu}_t}]_2\text{GaS}$  via the reaction of monovalent  $[\text{Tp}^{\text{Bu}_t}]\text{Ga}$  with elemental sulfur provides a striking contrast with the formation of the tetrasulfido derivative  $[\text{Tp}^{\text{Bu}_t}]_2\text{In}(\eta^2\text{-S}_4)$  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.

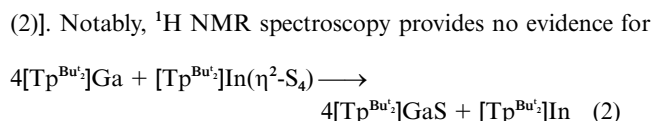
Complexes which exhibit multiple bonding to the heavier p block elements continue to attract considerable attention and provide challenges for the synthetic chemist. We are currently interested in terminal chalcogenido complexes of these elements<sup>1</sup> and have recently employed the sterically demanding tris(3,5-di-*tert*-butyl)pyrazolylhydroborato ligand to isolate the gallium and indium derivatives  $[\text{Tp}^{\text{Bu}_t}]\text{GaE}$  (E = Se or Te)<sup>2</sup> and  $[\text{Tp}^{\text{Bu}_t}]\text{InSe}$ .<sup>3</sup> 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  $[\text{Tp}^{\text{Bu}_t}]\text{InSe}$  is obtained upon reaction of  $[\text{Tp}^{\text{Bu}_t}]\text{In}$  with elemental selenium;<sup>3</sup> in contrast, the corresponding reaction with elemental sulfur yields the tetrasulfido derivative,  $[\text{Tp}^{\text{Bu}_t}]_2\text{In}(\eta^2\text{-S}_4)$ .<sup>4</sup> This difference is quite unexpected in the sense that terminal selenido complexes are generally much less common than their terminal sulfido counterparts.<sup>5</sup> Since gallium and indium frequently show a close correspondence in their chemistry,<sup>6</sup> 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,  $[\text{Tp}^{\text{Bu}_t}]\text{Ga}$ <sup>7</sup> reacts with elemental sulfur at room temperature over a period of 1 d to yield the terminal sulfido complex  $[\text{Tp}^{\text{Bu}_t}]_2\text{GaS}$  [equation (1)],<sup>8</sup> rather than the tetrasulfido complex  $[\text{Tp}^{\text{Bu}_t}]_2\text{Ga}(\eta^2\text{-S}_4)$ .<sup>9</sup>



The structure of  $[\text{Tp}^{\text{Bu}_t}]_2\text{GaS}$  has been determined by X-ray diffraction, as illustrated in Fig. 1.<sup>10</sup> 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.<sup>11</sup> For example, the mean Ga-S bond length for complexes listed in the Cambridge Structural Database is 2.33 Å,<sup>12</sup> with some representative examples listed in Table 1.<sup>13,14</sup>

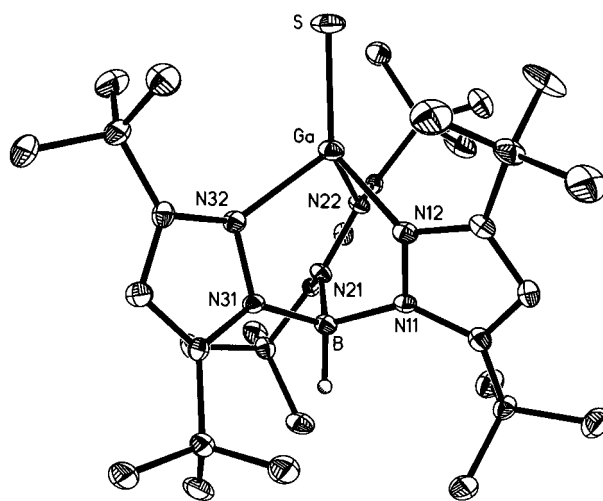
The terminal sulfido complex  $[\text{Tp}^{\text{Bu}_t}]_2\text{GaS}$  may also be obtained by reaction of the monovalent gallium complex  $[\text{Tp}^{\text{Bu}_t}]\text{Ga}$  with  $[\text{Tp}^{\text{Bu}_t}]\text{In}(\eta^2\text{-S}_4)$  at room temperature [equation



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

The isolation of  $[\text{Tp}^{\text{Bu}_t}]_2\text{GaS}$  in preference to  $[\text{Tp}^{\text{Bu}_t}]\text{Ga}(\eta^2\text{-S}_4)$ , 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  $[\text{Tp}^{\text{Bu}_t}]\text{InSe}$  is readily transferred to  $[\text{Tp}^{\text{Bu}_t}]\text{Ga}$  giving  $[\text{Tp}^{\text{Bu}_t}]\text{GaSe}$ ,<sup>2</sup> and (ii) the gallium tellurido complex  $[\text{Tp}^{\text{Bu}_t}]\text{GaTe}$  has been isolated, whereas the indium analog has not.<sup>2</sup>

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



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

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In summary, the terminal gallium sulfido complex [Tp<sup>Bu<sub>3</sub></sup>]-GaS has been synthesized *via* the reaction of [Tp<sup>Bu<sub>3</sub></sup>]Ga with elemental sulfur. Under comparable conditions, the corresponding indium system yields the tetrasulfido complex [Tp<sup>Bu<sub>3</sub></sup>]In(η<sup>2</sup>-S<sub>4</sub>), thereby providing convincing evidence that gallium exhibits a greater tendency to partake in multiple bonding than does indium.

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## Notes and References

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- 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.
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- Pentane (*ca.* 10 mL) was added to a mixture of [Tp<sup>Bu<sub>3</sub></sup>]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<sup>Bu<sub>3</sub></sup>]GaS as a white solid (0.065 g, 21% based upon [Tp<sup>Bu<sub>3</sub></sup>]Ga) (Found: C, 58.5; H, 8.4; N, 11.4. Calc. for C<sub>33</sub>H<sub>58</sub>N<sub>6</sub>BGaS: C, 60.8; H, 9.0; N, 12.9%). IR data: 2644 cm<sup>-1</sup> [ν(B–H)]. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.19 [s, 27 H, 3C(CH<sub>3</sub>)<sub>3</sub>], 1.85 [s, 27 H, 3C(CH<sub>3</sub>)<sub>3</sub>], 6.00 [s, 3 H, 3CH] (B–H not observed). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 30.5 [q, <sup>1</sup>J<sub>C–H</sub> = 126, 3C(CH<sub>3</sub>)<sub>3</sub>], 31.1 [q, <sup>1</sup>J<sub>C–H</sub> = 126, 3C(CH<sub>3</sub>)<sub>3</sub>], 32.7 [s, 3C(CH<sub>3</sub>)<sub>3</sub>], 33.3 [s, 3C(CH<sub>3</sub>)<sub>3</sub>], 103.5 [d, <sup>1</sup>J<sub>C–H</sub> = 175 Hz, 3CH], 159.7 [s, 3CC(CH<sub>3</sub>)<sub>3</sub>], 167.9 [s, 3CC(CH<sub>3</sub>)<sub>3</sub>].
- <sup>1</sup>H NMR spectroscopy indicates that [Tp<sup>Bu<sub>3</sub></sup>]GaS is stable in the presence of excess sulfur and furnishes no evidence for the formation of [Tp<sup>Bu<sub>3</sub></sup>]Ga(η<sup>2</sup>-S<sub>4</sub>).
- [Tp<sup>Bu<sub>3</sub></sup>]GaS: C<sub>33</sub>H<sub>58</sub>BGaNS, *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<sup>3</sup>, *Z* = 2, *μ* = 0.822 mm<sup>-1</sup>, *T* = 293 K, *R*1 = 0.1021 for 4780 reflections. CCDC reference number 186/1037.
- The [Ga≈S] interaction may be considered to be a composite of the resonance structures [G<sup>-</sup>S<sup>-</sup>], [G=S] and [G<sup>+</sup>S<sup>+</sup>]. Of these, it is likely that the polar form [G<sup>-</sup>S<sup>-</sup>] 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.
- 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.
- 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.
- For further comparisons, the Ga≈Se and Ga≈Te bond lengths in [Tp<sup>Bu<sub>3</sub></sup>]GaSe and [Tp<sup>Bu<sub>3</sub></sup>]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.
- For example, [Tp<sup>Bu<sub>3</sub></sup>]GaS does not react with PMe<sub>3</sub> at 80 °C. Furthermore, since the reverse reaction, *i.e.* sulfido transfer from R<sub>3</sub>PS to [Tp<sup>Bu<sub>3</sub></sup>]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<sub>3</sub>PSe and [Tp<sup>Bu<sub>3</sub></sup>]Ga is facile and equilibrium studies have demonstrated that the Ga≈Se interaction in [Tp<sup>Bu<sub>3</sub></sup>]GaSe is *ca.* 7 kcal mol<sup>-1</sup> (cal = 4.184 J) stronger than the P≈Se bond in Et<sub>3</sub>PSe (see ref. 2).
- This reaction likewise does not yield spectroscopically identifiable quantities of [Tp<sup>Bu<sub>3</sub></sup>]In(S<sub>x</sub>) (*x* = 1–3).
- Other complexes containing the [In(η<sup>2</sup>-S<sub>4</sub>)] moiety are known. See, for example, P. P. Paul, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 1993, **115**, 3316; S. Dhingra and M. G. Kanatzidis, *Polyhedron*, 1991, **10**, 1069; S. S. Dhingra and M. G. Kanatzidis, *Inorg. Chem.*, 1993, **32**, 3300; D. L. Reger and P. S. Coan, *Inorg. Chem.*, 1995, **34**, 6226; W. Bubenheim and U. Müller, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1607.
- N. Tokitoh, T. Matsumoto, H. Ichida and R. Okazaki, *Tetrahedron Lett.*, 1991, **32**, 6877.
- Tbt = 2,4,6-[(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Tip = 2,4,6-Pr<sup>t</sup><sub>3</sub>C<sub>6</sub>H<sub>2</sub>, Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.
- Another noteworthy example of the formation of M≈E multiple versus single bonds is provided by the observation that {η<sup>2</sup>-[(C<sub>9</sub>H<sub>6</sub>N)(Me<sub>3</sub>Si)CH]}<sub>2</sub>SnSe exists as a terminal selenido complex, whereas {[(C<sub>9</sub>H<sub>6</sub>N)(Me<sub>3</sub>Si)CH]}<sub>2</sub>Sn(μ-S)<sub>2</sub> 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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