DALTON
FULL PAPER

Electronic structure of tris(pyrazolyl)hydroborato [Tp] gallium complexes: density functional studies of monovalent Ga[Tp], terminal chalcogen complexes, Ga[Tp]E (E = O, S, Se or Te) and a GaI_3 adduct, $Ga_2[Tp]I_3$

Jennifer C. Green and James L. Suter

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.
E-mail: jennifer.green@chem.ox.ac.uk

Received 6th July 1999, Accepted 24th September 1999

Density functional theory calculations have been made on gallium complexes supported by the tris(pyrazolyl)-hydroborato ligand [Tp], Ga[Tp] **I**, Ga[Tp]E **II** (E = O **a**, S **b**, Se **c** or Te **d**) and $Ga_2[Tp]I_3$ **III** aimed at modelling the bonding in the recently reported tris(3,5-di-*tert*-butylpyrazolylhydroborato ($[Tp^{Bu^t_2}]$) gallium complexes, $Ga[Tp^{Bu^t_2}]$ **1**, the terminal chalcogen complexes $Ga[Tp^{Bu^t_2}]E$ **2** (E = S **b**, Se **c** or Te **d**), and the adduct $Ga_2[Tp^{Bu^t_2}]I_3$ **3**. The calculated and observed structures are in good agreement. The gallium "lone pair" in Ga[Tp] has Ga–N antibonding character. The decrease in Ga–N bond lengths between Ga[Tp] and its adducts is associated with relief of this antibonding character. The bonding in Ga[Tp]E (E = O, S, Se or Te) is found to be almost entirely semipolar $[[Tp]Ga^+–E^-]$ irrespective of the nature of the chalcogen element although the polarisation of charge decreases on descending the group. The GaI_3 adduct is also best described by the resonance structure $[Tp]Ga^+–Ga^-I_3$.

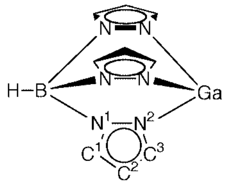
Introduction

Heavier elements of Group 13–16 form complexes which exhibit the "inert pair effect", where the elements form the subvalent ($N - 2$) oxidation state. For the heavier metals (*e.g.* Tl, Pb) this subvalent oxidation state is well established. However for the lighter elements it is much rarer.[1,2]

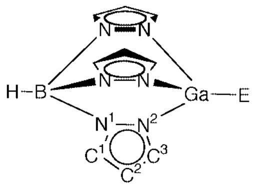
Monovalent complexes of B, Al, Ga are extremely rare, while for the heavier elements of Group 13 they are well known. However, the bulky tris(3,5-di-*tert*-butylpyrazolyl)hydroborato ligand, $Tp^{Bu^t_2}$, provides an environment which stabilises monovalent gallium, $Ga[Tp^{Bu^t_2}]$ **1**.[3] This is the first monovalent gallium complex to be synthesized which does not have a reduced oxidation state by virtue of Ga–Ga bonds[4] or mixed valence compounds (*e.g.* $[Ga^I][Ga^{III}X_4]$)[5] and has been structurally characterised by X-ray diffraction.

Monovalent $Ga[Tp^{Bu^t_2}]$ reacts with elemental sulfur to form $Ga[Tp^{Bu^t_2}]S$ **2b**.[6] This is in contrast to $In[Tp^{Bu^t_2}]$ which reacts with sulfur to form $In[Tp^{Bu^t_2}](\eta^2\text{-}S_4)$.[7] The structure of $Ga[Tp^{Bu^t_2}]S$ has been determined by X-ray diffraction.[6] The Ga–S bond length was significantly shorter than other Ga–S bond lengths reported,[6] from which multiple bond character might be inferred. Resonance structures $M–E^-$, M=E, and $M^-\equiv E^+$ were proposed. Similar reactions occur between $Ga[Tp^{Bu^t_2}]$ and Se and Te at room temperature, producing the terminal chalcogen complexes, $Ga[Tp^{Bu^t_2}]E$ (E = Se or Te) **2c**, **2d**.[8] While multiple bonding between Group 14 and 16 elements is well established,[9,10] that between gallium and chalcogen elements is less studied. Monovalent $Ga[Tp^{Bu^t_2}]$ also forms an adduct with GaI_3, $Ga_2[Tp^{Bu^t_2}]I_3$.[3] It was noted that this compound had Ga–N bond lengths more akin to those of a gallium(III) complex than those of Ga^I in $Ga[Tp^{Bu^t_2}]$. The nature of the Ga–Ga bond is especially relevant as recently multiple bonds between Ga atoms have been proposed[11] with bond lengths only marginally shorter than Ga–Ga single bonds, although the formal assignment of the bond order in these compounds is still open to debate.[12,13]

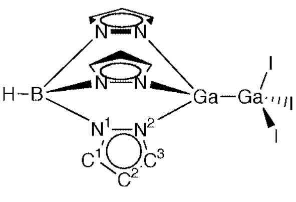
In order to understand the bonding in these gallium complexes we have carried density functional theory (DFT) calculations on the model systems Ga[Tp], Ga[Tp]E (E = O, S, Se or Te) and $Ga_2[Tp]I_3$, where Tp is the tris(pyrazoyl)borato ligand, in which the tertiary butyl groups are replaced by hydrogen atoms.



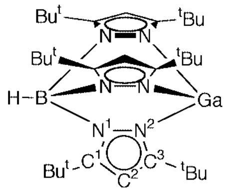
I



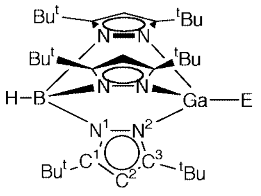
II; E = O(a), S(b), Se(c), Te(d)



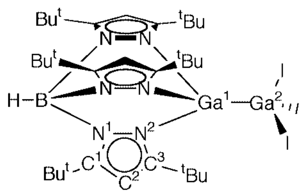
III



1



2; E=S(b), Se(c), Te(d)



3

Computational methods

Calculations were performed using density functional methods of the Amsterdam Density Functional Package (Version 2.3).[14] Type IV basis sets used triple-ζ accuracy sets of Slater type orbitals, with a single polarisation function added; 2p on H,

Table 1 Comparison of selected structural parameters (Å) between the optimised geometries with type IV basis sets of Ga[Tp] **I**, Ga[Tp]E **II** (E = O **a**, S **b**, Se **c** or Te **d**) and $Ga_2[Tp]I_3$ **III** under C_{3v} symmetry and their experimental analogues, **1**,[3] **2b**,[6] **2c**,[8] **2d**[8] and **3**,[3] as determined by X-ray diffraction. For **2b**–**2d** and **3** the experimental structural parameters listed in Table 2 are the average values of the structural parameters determined by X-ray diffraction

	Ga[Tp]		Ga[Tp]O	Ga[Tp]S		Ga[Tp]Se		Ga[Tp]Te		$Ga_2[Tp]_2I_3$	
Parameter	Calc.	Exptl.	Calc.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.
Ga–$N^{1,2}$	2.18	2.240(6)	2.03	2.01	2.05	2.01	2.05	2.01	2.06	1.99	2.05
N^2–C^3	1.34	1.326(9)	1.33	1.33	1.35	1.33	1.34	1.33	1.34	1.33	1.35
C^3–C^2	1.38	1.377(10)	1.39	1.39	1.38	1.39	1.38	1.39	1.39	1.39	1.36
C^2–C^2	1.39	1.377(9)	1.33	1.38	1.38	1.38	1.38	1.38	1.37	1.38	1.43
C^1–N^1	1.33	1.343(8)	1.38	1.34	1.36	1.34	1.36	1.34	1.36	1.35	1.39
N^1–B	1.52	1.553(8)	1.34	1.53	1.56	1.53	1.56	1.53	1.56	1.53	1.54
N^1–N^2	1.34	1.384(7)	1.34	1.35	1.39	1.35	1.39	1.35	1.39	1.35	1.38
Ga–E			1.67	2.05	2.093(2)	2.17	2.2139(7)	2.36	2.4222(5)		
Ga^1–Ga^2										2.36	2.506(3)
Ga^2–I										2.54	2.57

and 3d on C and 4d on Ga. The cores of the atoms were frozen. For type IV basis sets the C core is frozen up to 1s, Ga up to 2p, O to 1s, S up to 2p, Se up to 3p and Te and I up to 4p. For type II basis sets double-zeta Slater type orbitals were used with no polarisation function, and the gallium core was frozen up to 3d and I up to 4d. First order relativistic corrections were made to the cores of the atoms using the Pauli formalisation. Dirac relativistic corrections were included. The generalised gradient approximation (GGA non-local) method was used, using Vosko, Wilk and Nusair's local exchange correlation,[15] with non-local exchange corrections by Becke,[16] non-local correlation corrections by Perdew.[17] On all structures, geometry optimisation was employed with a type IV basis set, except for geometry optimisation on the $Ga_2[Tp]I_3$ structure where both type II and IV basis sets were employed.

Fragment analysis was carried out on these compounds. The molecular orbitals were first calculated for the bonding of the Tp ligand and the Ga basis atom. For the terminal chalcogen complexes Ga[Tp]E, Ga[Tp] and the E basis atom were the fragments. The bonding for the $Ga_2[Tp]I_3$ adduct was calculated using Ga[Tp] and GaI_3 fragments. In all cases the structure of the fragment was taken as that in the optimised structure of the complex. The basis atoms were spin restricted with equal populations of degenerate orbitals, *i.e.* not necessarily the atomic ground state. Orbitals for the molecules were then calculated in terms of linear combination of basis set of fragment orbitals, rather than the constituent atoms. Mulliken populations were also calculated and used to estimate charges on each atom.

To evaluate bond energies for Ga[Tp]E (E = O, S, Se or Te) the energies found for binding of the fragments described above were adjusted for the energies of forming the basis E atoms from their ^3P ground states, and of forming the appropriate Ga[Tp] fragment from its ground state structure.

Results and discussion

It is believed the six bulky *tert*-butyl groups in the tris(3,5-di-*tert*-butylpyrazolyl)hydroborato ligand play a passive role in these compounds, by protecting the reactive monovalent gallium centre or Ga–E bonds. Hence for computational purposes it is assumed that it is acceptable to replace these butyl groups with H atoms, thereby using a tris(pyrazolyl)hydroborato (Tp) ligand instead.

Geometry optimisations were carried out on the monovalent gallium complex Ga[Tp] **I**, terminal chalcogen complexes Ga[Tp]E **II** (E = O **a**, S **b**, Se **c** or Te **d**) and the GaI_3 adduct $Ga_2[Tp]I_3$ **III** under C_{3v} symmetry. Such a symmetry assumption is an approximation as Ga[$\mathrm{Tp^{Bu^t_2}}$] has C_3 symmetry for the gallium pyrazolylborato core in the solid state, the ligand being slightly twisted from C_{3v} symmetry, and complexes **2b**–**2d** and adduct **3** are of lower symmetry. However, it was considered a small approximation, and was computationally advantageous. The input geometries used were experimentally determined average parameters from the $\mathrm{Tp^{Bu^t_2}}$ ligand (**1**, **2b–2d**, **3**). Selected optimised structural parameters are presented in Table 1 and compared with experimental values.

The agreement between the calculated optimised structure without the *tert*-butyl substituent and the values from the X-ray diffraction of the compounds with the substituents is reasonably good. Most results are within 3% of each other. There are several discrepancies. The largest discrepancy in the Ga[Tp] complex was the Ga–N bond distances (2.18 Å), which were significantly shorter than in the experimental structure (2.24 Å). However, this is only 3% shorter. Geometry optimisation on Ga[$\mathrm{Tp^{Me_2}}$] and Ga[$\mathrm{Tp^{F_2}}$], with Me and F groups substituted in the 3,5 ring positions, gave Ga–N distances of 2.16 and 2.23 Å, *i.e.* shorter for the electron donating Me substituent but longer for the electron withdrawing F substituent. This suggests that the *electronic* effect of $\mathrm{Bu^t}$ substituents would be to shorten the predicted Ga–N distance.

For the Ga[Tp]E series the Ga–E distances are all slightly shorter in the calculated structures. The general trends are the same; the length of the Ga–E bond increases from E = S to Te and the differences between E = S and Se and E = Se and Te are about the same in the calculated structure as in the experimental products Ga[$\mathrm{To^{Bu^t_2}}$]E.

For $Ga_2[Tp]I_3$ the Ga–Ga bond is significantly shorter in the calculated optimised structure (2.36 calculated, 2.506(3) Å experimental). To test whether the results are sensitive to choice of basis set, geometry optimisation was run using a type II basis set, with the gallium core frozen up to 3d without any polarisation function. This *less extensive* basis set gave a longer Ga–Ga distance (2.48 Å) although still shorter than the experimental value. It should be noted that throughout the calculations give somewhat shorter distances from Ga to other atoms than are found experimentally. A more extensive basis set might improve the calculations. However, the relatively large discrepancy found for the GaI_3 complex may be due to using model ligands in the calculations. The close contacts between the bulky *tert*-butyl groups and the iodine on the GaI_3 group may cause repulsive steric effects, leading to a longer Ga–Ga distance.

Bonding

Ga[Tp]. The molecular orbital diagram of Ga[Tp] (Fig. 1) is generated using fragment analysis. It represents selected one electron energies of the molecule with respect to those of the Ga and Tp fragments. Table 2(a) gives percentage fragment contributions to the molecular orbitals of the molecule to which the Ga makes a significant contribution.

The highest occupied molecular orbital (HOMO), the Ga "lone pair", is of a_1 symmetry and is 61% Ga 4s in character

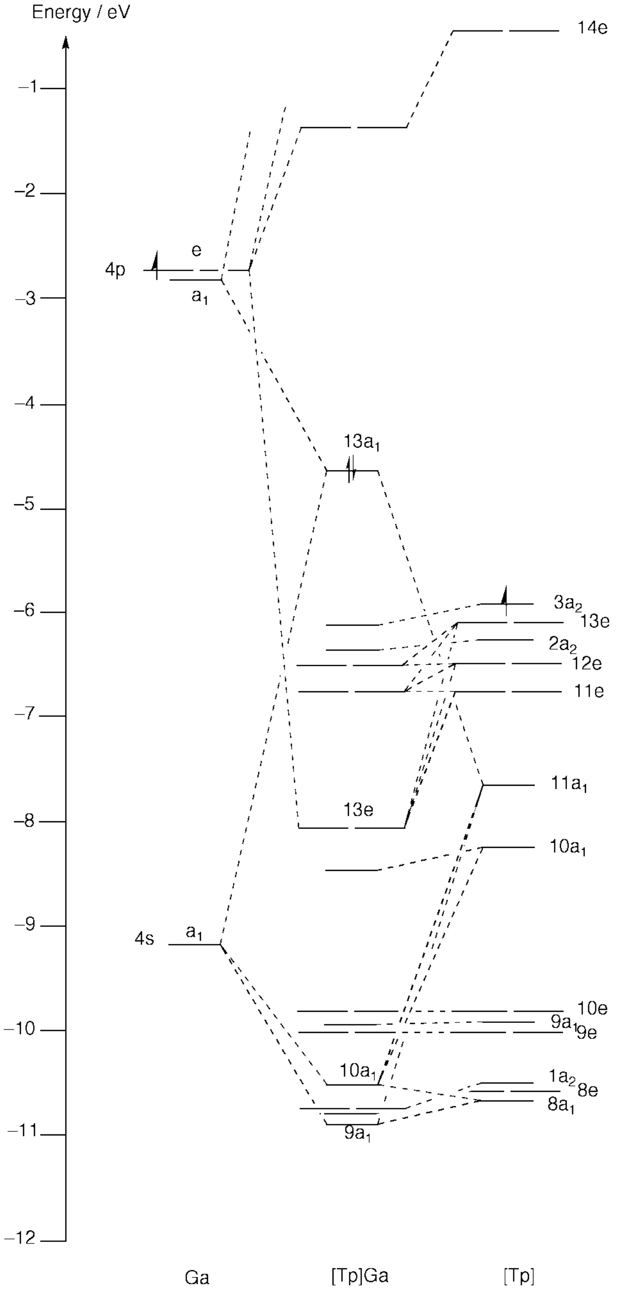


Fig. 1 The MO scheme showing the interaction of a Ga atom with the Tp ligand to form Ga[Tp].

together with a 21% contribution from the $4p_z$ orbital. Isosurface representations of the HOMO (Fig. 2A) show this orbital to be primarily Ga localised, as the proportion of mixing between the Tp and gallium fragments is small (only 17% from Tp). Such mixing gives the HOMO partial antibonding character, as is also evident from the raised energy indicated in Fig. 1. The $9a_1$ and $10a_1$ orbitals encompass bonding in phase combinations of the nitrogen lone pairs and the Ga 4s orbital. An interaction involving an e_1 combination of nitrogen lone pairs and the $4p(x,y)$ orbitals on Ga combines to give the bonding orbital $13e_1$. The Tp ligand can therefore stabilise the monovalent gallium complex by having orbitals of the appropriate symmetry and energy to provide an overall bonding effect. The fragment contributions show that covalent mixing is moderate. Gallium has a partial positive charge while each of the binding nitrogens has a similar negative charge as shown in the Mulliken populations given in Table 3. Also the electron density assigned to Ga is polarised away from the negatively charged N atoms. This suggests a significant electrostatic component to the bonding.

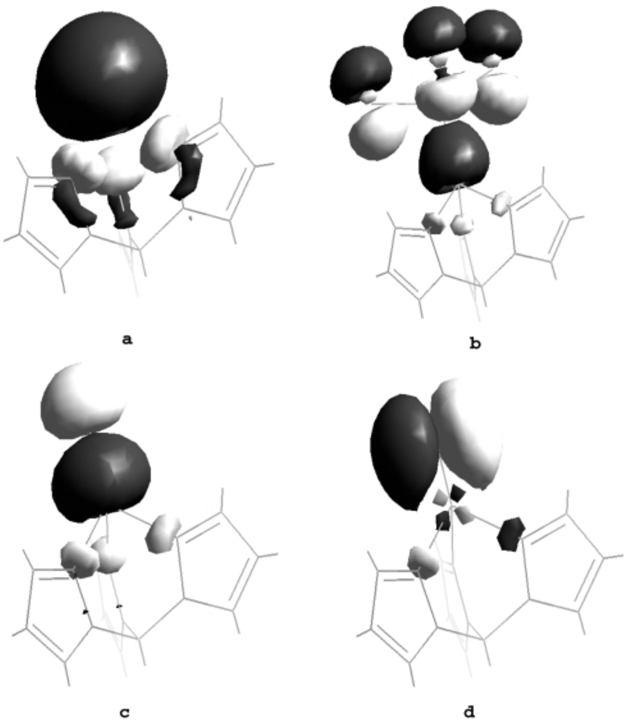


Fig. 2 Isosurface representations of selected MOs: (A) $13a_1$ HOMO of Ga[Tp]; (B) $20a_1$ HOMO of $Ga_2[Tp]I_3$; (C) $14a_1$ σ bond of Ga[Tp]E; (D) 16e π HOMO of Ga[Tp]E.

Ga[Tp]E. The bonding of the terminal chalcogen complexes of gallium Ga[Tp]E **II** (E = O **a**, S **b**, Se **c** or Te **d**) could be imagined to be composed of a σ bond between Ga and E with two π bonds between E and acceptor orbitals on Ga, which are antibonding between ligands and Ga. The degree of this π interaction determines which of the resonance structures M^+–E^-, M=E, M^-≡E^+ is most dominant. A similar bonding scheme has been proposed for tertiary phosphine oxides, R_3PO.[18]

An MO diagram for Ga[Tp]Ga **IIb** which is generally representative of Ga[Tp]E, is shown in Fig. 3. Table 2(b) gives the results of the fragment analysis for all four compounds. The MO diagram in Fig. 3 shows that the Ga[Tp] and S form one σ bond between $3p_z$ and 3s on sulfur and the $13a_1$ HOMO of the Ga[Tp] fragment. Table 2(b) indicates a π interaction between the $3p_{x,y}$ on sulfur and 18e on Ga[Tp]. The 18e fragment orbital has 5% Ga 5p character and acts as a polarisation function for the S atom. In Ga[Tp]S the σ bonding is reasonably substantial: 23% of the MO is from the Ga[Tp] fragment, indicating significant mixing (see Fig. 2C). However, π bonding is quite small, only about 5% of the bonding π orbital comes from the Ga[Tp] fragment (Table 2b). These fragment contributions together with the Mulliken populations (Table 3) indicate that for all four chalcogen gallium complexes the dominant resonance structure is M^+–E^-, *i.e.* a semipolar covalent bond as described by Pauling.[18,19] However, there is a trend in properties as E changes descending the chalcogen elements. The most striking is the decrease in σ donation, while the p polarisation barely changes. The small amount of mixing (5%) suggests that the electrons in the π bond are located on the chalcogen element as lone pairs (see Fig. 2D). The short Ga–E bond distances had been taken to imply multiple bond interaction.[6]

Populations also show that the charge on the chalcogen element decreases as E descends Group 16 (Table 3), *e.g.* −0.84 for E = S, −0.35 for E = Te. This is to be expected with the higher electronegativity of oxygen and sulfur polarising the charge distribution. This should produce a large ionic contribution to the energy of the Ga–E bond.

We thought it of interest to calculate the energy of combination of Ga[Tp] with a ground state chalcogen atom, eqn. (1).

Table 2 Fragment analyses

(a) Ga[Tp], expressed as a percentage of mixing from fragment orbitals (FOs). Only occupied where significant Tp–Ga mixing is present are given

MO	Contributing FOs from ligand	AOs from Ga	Energy/eV
13a$_1$ (HOMO)	17% 11a$_1$	61% 4s, 21% 4p	−4.66
13e$_1$	49% 11e$_1$, 16% 12e$_1$, 25% 13e$_1$	6% 4p	−8.04
10a$_1$	40% 8a$_1$, 15% 10a$_1$, 26% 11a$_1$	10% 4s	−10.57
9a$_1$	59% 8a$_1$, 19% 11a$_1$	9% 4s	−11.55

(b) Ga[Tp]E (C_{3v} symmetry) illustrating the relative composition of the HOMO (π bonding orbital; e$_1$ symmetry) and HOMO − 1 orbital (σ bonding orbital, a$_1$ symmetry)

	a$_1$ (HOMO − 1)									e$_1$ (HOMO)			
E	O		S		Se		Te		E	O	S	Se	Te
% Chalcogen	2p	2s	3p	3s	4p	4s	5p	5s	% Chalcogen	2p	3p	4p	5p
	67	6	61	7	54	7	44	10		85	86	86	86
% Ga[Tp] (13a$_1$)	16		23		33		43		% Ga[Tp] (18e$_1$)	5	5	5	5
Energy/eV	−6.04		−6.55		−6.53		−6.53		Energy/eV	−4.18	−4.17	−4.11	−4.00

(c) Ga$_2$[Tp]I$_3$

MO	Contributing FOs from Ga[Tp]	Contributing FOs from GaI$_3$	Energy/eV
19a$_1$	21% 13a$_1$	57% 7a$_1$, 10% 8a$_1$, 6% 6a$_1$	−7.30
20a$_1$ (HOMO)	17% 13a$_1$	41% 7a$_1$, 34% 8a$_1$	−5.42
21a$_1$	17% 13a$_1$	37% 8a$_1$, 46% 9a$_1$	−1.91

Table 3 Mulliken populations

	Charge					
Atom	Ga[Tp]	Ga[Tp]O	Ga[Tp]S	Ga[Tp]Se	Ga[Tp]Te	Ga$_2$[Tp]I$_3$
N^1	−0.14	−0.15	−0.15	−0.15	−0.15	−0.15
N^2	−0.24	−0.23	−0.24	−0.25	−0.25	−0.26
C^1	0.27	0.27	0.27	0.27	0.25	0.28
C^2	0.07	0.07	0.08	0.08	0.08	0.10
C^3	0.27	0.28	0.28	0.28	0.28	0.29
B	0.70	0.69	0.68	0.68	0.68	0.69
H(B)	−0.25	−0.23	−0.23	−0.23	−0.23	−0.22
E		−0.92	−0.84	−0.66	−0.36	
Ga^1	0.29	1.04	0.97	0.80	0.50	0.79
Ga^2						−0.15
I						−0.20

Table 4 Calculated bond energies (eV) of Ga[Tp]E

Energy	Ga[Tp]O	Ga[Tp]S	Ga[Tp]Se	Ga[Tp]Te
Of forming E basis atom from ^{3}P E ground state	1.55	0.85	0.75	0.63
Of forming Ga[Tp] fragment from Ga[Tp] ground state	0.48	0.56	0.57	0.58
Of binding fragments together	−6.57	−4.99	−4.46	−3.79
Total bonding energy	−4.54	−3.57	−3.14	−2.57

$$\mathrm{Ga[Tp]} + \mathrm{E} \longrightarrow \mathrm{Ga[Tp]E} \qquad (1)$$

This involved adjustment of the binding energy found in the fragment calculation by the formation of the basis atom and the preorganised Ga[Tp] from their respective ground states. Data are given in Table 4. These calculations predict a gradual decrease in bond strength on descending the chalcogen group.

The calculations indicate a shortening of the Ga–N bond between Ga[Tp] (2.18 Å) and Ga[Tp]E (2.03–2.01 Å) as is found experimentally for the related Tp$^{\mathrm{Bu^t_2}}$ complexes (Table 1). This can be explained by considering the HOMO of the Ga[Tp] fragment, the 13a$_1$ orbital shown in Fig. 2A. The bond between the gallium and E centres reduces the electron density in this orbital and, as this orbital has Ga–N antibonding character, the bond gets shorter. In the fragment analysis the 13a$_1$ orbital is only fractionally occupied, so the antibonding interaction between the Ga and Tp ligand is lessened and consequently the bond shortens.

Ga$_2$[Tp]I$_3$. The calculations indicate a shortening of the Ga–N bond between Ga[Tp] (2.18 Å) and Ga$_2$[Tp]I$_3$ (1.99 Å) as is found experimentally for the related Tp$^{\mathrm{Bu^t_2}}$ complexes (Table 1). As with the chalcogen adducts, this shortening can be associated with reduced occupancy of the Ga[Tp] fragment 13a$_1$ orbital.

From the MO diagram of Ga$_2$[Tp]I$_3$ (Fig. 4) the σ bonding interaction can be seen as slightly more complex than with the chalcogen adducts. In this case significant mixing takes place between four fragment orbitals, the HOMO of the Ga[Tp]

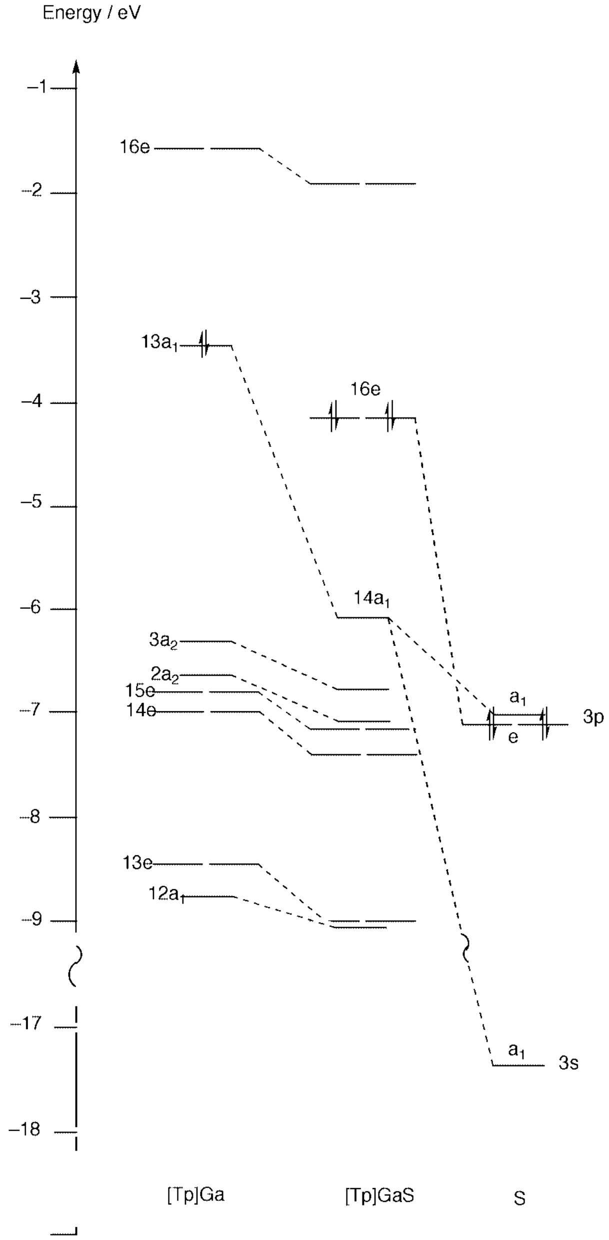


Fig. 3 The MO scheme showing the interaction of Ga[Tp] with a chalcogen atom E to form Ga[Tp]E.

fragment, the LUMO of GaI_3, and two lower orbitals ($7a_1$ and $6a_1$) of the same symmetry on the GaI_3 fragment, giving rise to molecular orbitals ($21a_1$, $20a_1$, $19a_1$). The HOMO of compound **3**, $20a_1$, which is Ga–Ga bonding, is shown in Fig. 2B. No significant mixing is found among the e set of orbitals. The charge on the Ga co-ordinated by Tp is again positive (+0.79), that on the Ga co-ordinated by iodine is negative (−0.15). Thus the bond can also be viewed as having an ionic component. With a total charge of −0.74 on GaI_3, the charge distribution most resembles that between Ga and Se of the chalcogen series. In a similar fashion the bond is best described as a semipolar covalent bond, *i.e.* $[Tp]Ga^+–Ga^-I_3$.

As expected, there is no evidence of Ga–Ga multiple bonding in $Ga_2[Tp]I_3$.

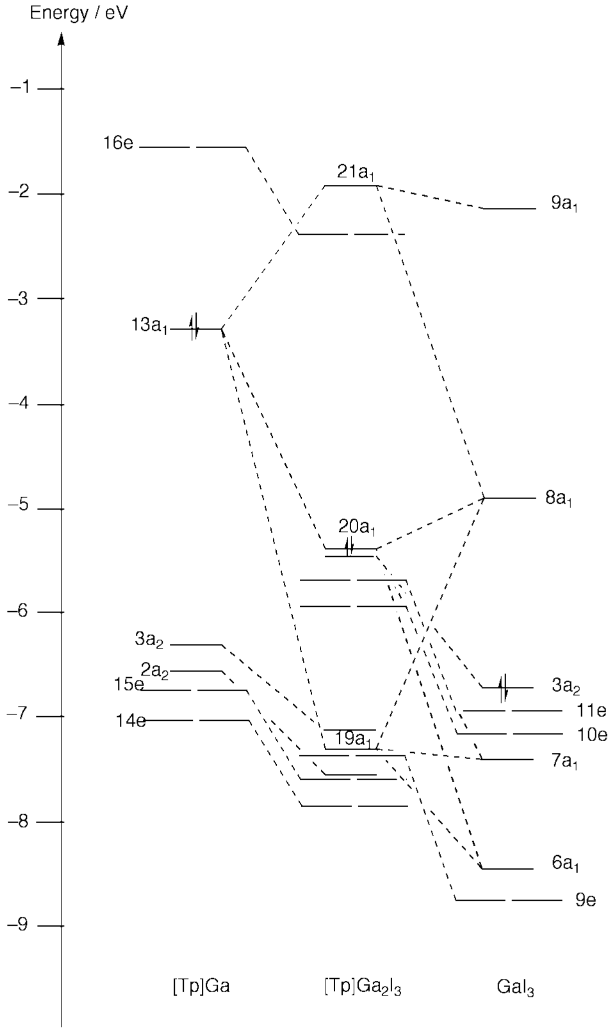


Fig. 4 The MO scheme showing the interaction of Ga[Tp] with GaI_3 to form $Ga_2[Tp]I_3$.

Conclusion

Good agreement has been obtained between calculated and observed structures for Ga[Tp] and its adducts. The HOMO "lone pair" in the monovalent gallium complex, $Ga[Tp^{But_2}]$, is primarily Ga 4s in character with some mixing from the Ga 4p orbital and has partial gallium–ligand antibonding character. The lengths of the Ga–N bonds are shorter in the chalcogen and GaI_3 adducts as a consequence of this the gallium lone pair orbital is only partially occupied in the adducts. The distance change is also in agreement with predictions using the ionic model, *i.e.* Ga^{III} is smaller than Ga^{I}. The bonding in the terminal chalcogen complexes $Ga[Tp^{But_2}]E$ (E = O, S, Se or Te) shows no significant π character and has been determined as a semipolar covalent bond with the most representative resonance structure being $M^+–E^-$. The polarisation of charge is greatest for oxygen and sulfur, due to their higher electronegativity and hence higher ionic contribution to bond energy. The Ga–Ga bonding in $Ga_2[Tp^{But_2}]I_3$ is also best described as semipolar covalent and represented by the resonance structure $[Tp]Ga^+–Ga^-I_3$. Calculations suggest that the bond polarity is similar to that of the selenium complex.

Acknowledgements

We thank Gerard Parkin, Matthew C. Kuchta and Christian N. Jardine for valuable discussion.

References

1 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th edn., Wiley, New York, 1988.
2 A. J. Downs, *Chemistry of Aluminium, Gallium, Indium and Thallium*, Blackie, Glasgow, 1993.
3 M. C. Kuchta, J. Bonanno and G. Parkin, *J. Am. Chem. Soc.*, 1996, **118**, 10914.
4 D. Tuck, *Polyhedron*, 1990, **9**, 377.
5 G. Garton and H. Powell, *J. Inorg. Nucl. Chem.*, 1957, **4**, 84.

6 M. C. Kutcha and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 1998, 2279; G. Parkin, personal communication.

7 M. C. Kutcha and G. Parkin, *Main Group Chem.*, 1996, **1**, 291.

8 M. C. Kutcha and G. Parkin, *Inorg. Chem.*, 1997, **36**, 2492.

9 H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase and M. Goto, *J. Am. Chem. Soc.*, 1998, **120**, 11096.

10 P. Schleyer and D. Kost, *J. Am. Chem. Soc.*, 1988, **110**, 2105.

11 H. Robinson, J. Su, X. Li and R. Crittendon, *J. Am. Chem. Soc.*, 1997, **119**, 5471.

12 R. Schleyer, H. Schaefer III, G. Robinson, Y. Xie, R. Grev and J. Su, *J. Am. Chem. Soc.*, 1998, **120**, 3773.

13 F. A. Cotton, A. Cowley and X. Feng, *J. Am. Chem. Soc.*, 1998, **120**, 1795.

14 B. te Velde and E. J. Baerends, *J. Comput. Phys.*, 1992, **99**, 84.

15 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1990, **58**, 1200.

16 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 2398.

17 J. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

18 D. G. Gilheany, *Chem. Rev.*, 1994, **94**, 1339.

19 L. Pauling, *The Nature Of The Chemical Bond*, 3rd edn., Cornell University Press, Ithaca, 1960.

Paper 9/05441C