DOI: 10.1002/ejic.200600975

Thallium Halides – New Aspects of the Stereochemical Activity of Electron Lone Pairs of Heavier Main-Group Elements

Anja-Verena Mudring*[a]

Dedicated to Prof. Dr. Josef Hahn on the occasion of his 65th birthday

Keywords: Halides / Thallium / Electron lone pairs

Density functional theory studies in the linear muffin tin approximation on thallium halides (TlX; X = F, Cl, Br, I) show that structural distortions due to a stereochemically active lone pair of electrons depend crucially on cation–anion interactions. Such distortions do not originate from a 6s–6p hybridisation on the heavy metal as the Tl 6s and 6p states are energetically too far apart to mix directly. In the case of TlF, the Tl 6s and the F 2p states are located in the same energy region, which leads to an efficient interaction that produces strongly antibonding Tl–F states directly below the Fermi level that would destabilize the solid. Minimisation of these unfavourable covalent antibonding interactions is the driving force for structural distortion. In the case of the heavier thallium halides, the growing energetic mismatch between Tl 6s states and X *n*p states leads to weaker covalent interactions. Thus, the compounds become more ionic and high symmetry structures are adopted as covalent interactions play only a minor role. The low symmetry structure of TlI observed at low temperatures is stabilized by attractive metal–metal bonding.

Introduction

Thallium shows a strong preference for the oxidation state +1, which has been attributed to the effect of the "inert electron pair", a term introduced by Sidgwick[1] to describe the tendency of the heavier main-group elements to adopt oxidation numbers that are two less than the respective group number.[2] Traditional considerations assume that this inert electron pair is generated by mixing of the 6s and 6p orbitals on the heavy metal cation. The hybrid orbital is therefore often considered to behave like an additional ligand in the coordination sphere.[3] The corresponding pair of electrons is thought to be chemically inert but stereochemically active. However, this would imply that the lone pair is stereochemically active in any environment, which is obviously not the case. Many thallium compounds are known where the lone pair is not stereochemically active, many of which even show interesting phase transitions between structures where the lone pair is active or not. So far, no comprehensive studies on the origin and nature of the lone pair in thallium compounds have appeared that can explain or even predict the stereochemistry of the $6s^2$ lone pair.

Thallium halides (TlX; X = F–I) offer a unique possibility to study the stereochemistry of the (chemically) inert electron pair since a large variety of TlX phases are known even though these compounds are simple 1:1 salts. Much work has been done over the years on the study of phase transitions of these simple compounds, mainly to investigate the temperature- and pressure-dependent behaviour of the $6s^2$ lone pair on the thallium atom.

Thallium(I) fluoride adopts an orthorhombic structure in the space group *Pbcm*, which can be regarded as a distorted rock-salt-type structure (Figure 1), under ambient conditions where both thallium and fluorine are coordinated by six counterions. However, the coordination polyhedron around the thallium cation deviates strongly from ideal octahedral symmetry. This fact has been ascribed to the presence of a stereochemically active lone pair. Although the orthorhombic structure of TlF is stable up to 3.5 GPa,[4] a structural phase transition apparently takes place at temperatures above 355 K to a higher symmetrical tetragonal structure, which still can be derived from a rock-salt-type structure.[5] The space group *I*4/*mmm* has been proposed for this structure. ^{205}Tl and ^{19}F NMR studies question this assumption, however, as they indicate different coordination polyhedra around Tl and F.[6] In contrast to TlF, the thallium halides with heavier halogens (TlCl and TlBr) adopt highly symmetrical cubic structures. Both compounds crystallise in the CsCl structure type under ambient conditions,[7] whereas at low temperatures a

---

[a] Anorganische Chemie I der Ruhr-Universität Bochum
Universitätsstraße 150, 44801 Köln, Germany
http://www.anjamudring.de

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

transition to the NaCl structure takes place.[8] TlI also crystallises in a CsCl-type structure under ambient conditions.[9] Interestingly it undergoes a phase transition, at low temperatures to a structure type in the space group *Cmcm*[10] (Figure 2) that is also found for indium monohalides.[11] Reliable crystallographic structure determinations are a requirement for further studies as wrong crystallographic studies, for example for TlF, have led to wrong interpretations of the lone pair effect[6] and even speculations about Tl–Tl interactions.[12]

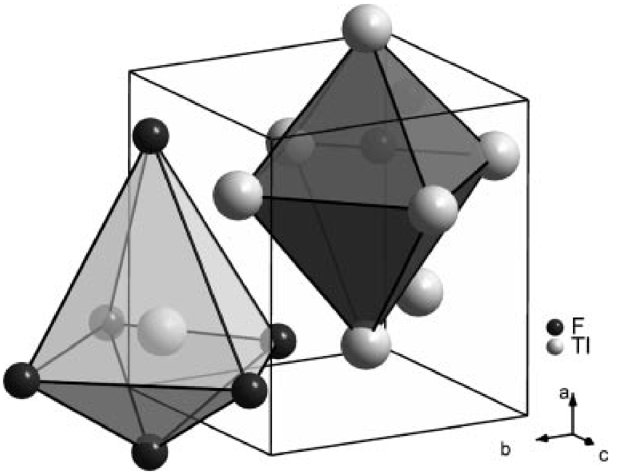

Figure 1. Crystal structure of TlF (*Pbcm*). The coordination polyhedra surrounding thallium and fluorine are shaded.

Recent studies on thallium(I) coordination compounds[13] show that s–p mixing on the heavy atom is neither the origin nor a necessity for a structural distortion that might otherwise be associated with a stereochemically active lone pair. Instead, antibonding Tl 6s/ligand-p interactions are the origin of these structural distortions. In order to investigate the lone pair effect in extended solid materials, calculations have been carried out on the different modifications of the thallium halides using density functional theory.[14]

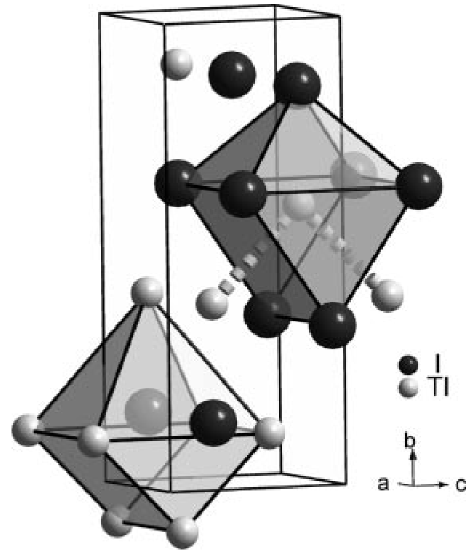

Figure 2. Crystal structure of TlI (*Cmcm*). The coordination polyhedra surrounding thallium and iodine are shaded. Closest Tl–Tl contacts indicated by broken bonds.

Results and Discussion

The density of states for TlX (X = F, Cl, I) in the NaCl and CsCl structure types as well as for TlF and TlI in their own structure types are shown in Figures 3, 6 and 9, respec-

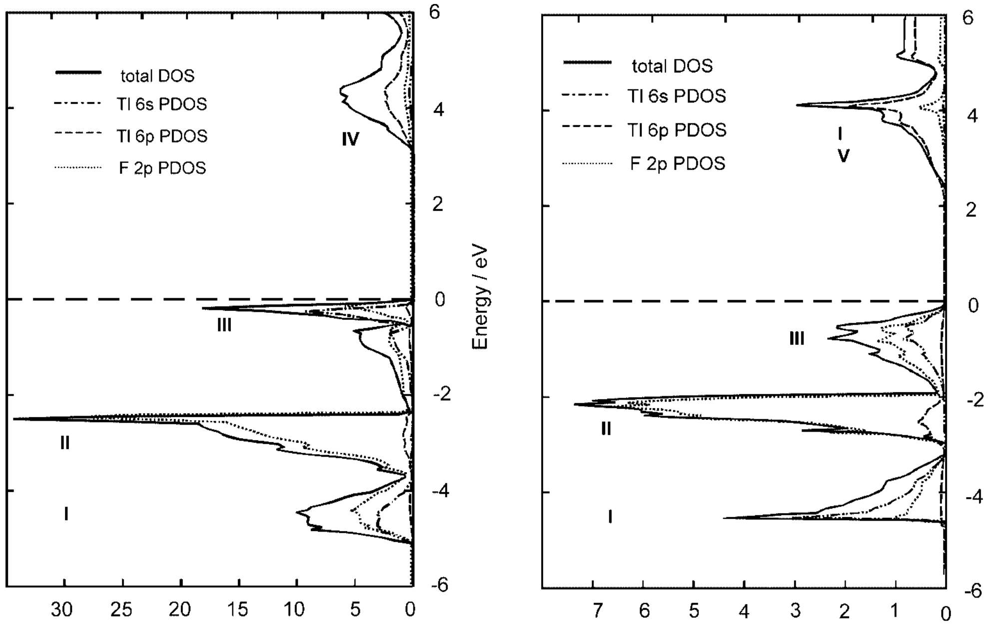

Figure 3. Total and partial densities of states for TlF (left: *Pbcm*; right: $Fm\bar{3}m$).

tively, between –6 and +6 eV (with respect to the highest occupied state). As both the halogen *n*s states and the Tl 5d states are located at energies significantly lower than –6 eV and have no impact on the chemical bonding, they are not shown.

Thallium Fluoride (TlF)

The density of states (DOS) for TlF (Figure 3) in its room-temperature structure (space group *Pbcm*) and in the hypothetically idealised NaCl-type of structure (space group $Fm\bar{3}m$) can be partitioned into four significant sections, a region above the Fermi level which is mainly of Tl 6p character (IV) and a complex area below the Fermi level. This latter area shows three different segments (I–III). A region at lower energies around –4/–5 eV, which is of Tl 6s and F 2p character (I), is followed by a region of high DOS mainly made up by F 2p with small Tl 6p contributions (II). Then, up to the highest occupied states, a region is observed which again shows Tl 6s as well as F 2p contributions (III). The crystal orbital Hamiltonian population (COHP) curves for the Tl–F interactions (Figure 4) reveal that regions I and II are Tl–F bonding and region III right below the Fermi level is Tl–F antibonding. This clearly shows the ambivalent bonding situation in thallium halides: on the one hand there is a strong Coulombic attraction between cations and anions in the solid, whereas on the other unfavourable covalent antibonding Tl 6s/F 2p interactions take place right at the Fermi level. If these are reduced, the whole solid is energetically stabilized. A more thorough study of the DOS for TlF in both structures reveals some rather significant differences between the different structures (Table 1). The integrated DOSs show a higher F p and lower Tl s contribution for region I in the distorted NaCl structure compared to the undistorted (hypothetical) NaCl structure, whereas for region III the opposite is found. Furthermore, a significantly larger Tl p contribution is found for region II in the idealised NaCl structure. These observations can best be explained by a simple interaction

Table 1. Integrated projected density of states (IPDOS) and crystal orbital Hamiltonian populations (ICOHP) for TlX (X = F, Cl, I) in the different structure types.

Compound	TlF		TlCl		TlI	
Space group	*Pbcm*	$Fm\bar{3}m$	$Fm\bar{3}m$	$Pm\bar{3}m$	*Cmcm*	$Pm\bar{3}m$
I[a]						
IPDOS Tl s	9.6%	15.1%	17.9%	17.5%	21.0%	20.2%
IPDOS Tl p	0.7%	0.8%	0.3%	1.1%	0.4%	0.5%
IPDOS X p	14.8%	8.7%	7.3%	5.3%	4.4%	4.5%
ICOHP (Tl–X)	1.58	1.38	1.83	1.79	1.17	1.61
II						
IPDOS Tl s	0.7%	0.4%	0.7%	2.6%	1.5%	2.6%
IPDOS Tl p	0.1%	3.6%	4.8%	5.0%	5.6%	6.4%
IPDOS X p	49.2%	46.2%	45.7%	38.1%	35.1%	36.5%
ICOHP (Tl–X)	0.54	0.65	1.39	1.29	1.04	1.36
III						
IPDOS Tl s	12.4%	8.7%	7.2%	4.2%	3.1%	2.1%
IPDOS Tl p	1.2%	0.7%	1.1%	5.1%	1.5%	1.2%
IPDOS X p	11.4%	15.7%	16.0%	21.1%	27.4%	26.1%
ICOPH (Tl–X)	–1.13	–1.18	–1.63	–1.20	–0.58	–0.62
Total ICOHP (Tl–X)	0.99	0.85	1.59	1.88	1.63	2.36

[a] The Roman numbers refer to the different segments of the DOS and COHP curves (see Figure 3).

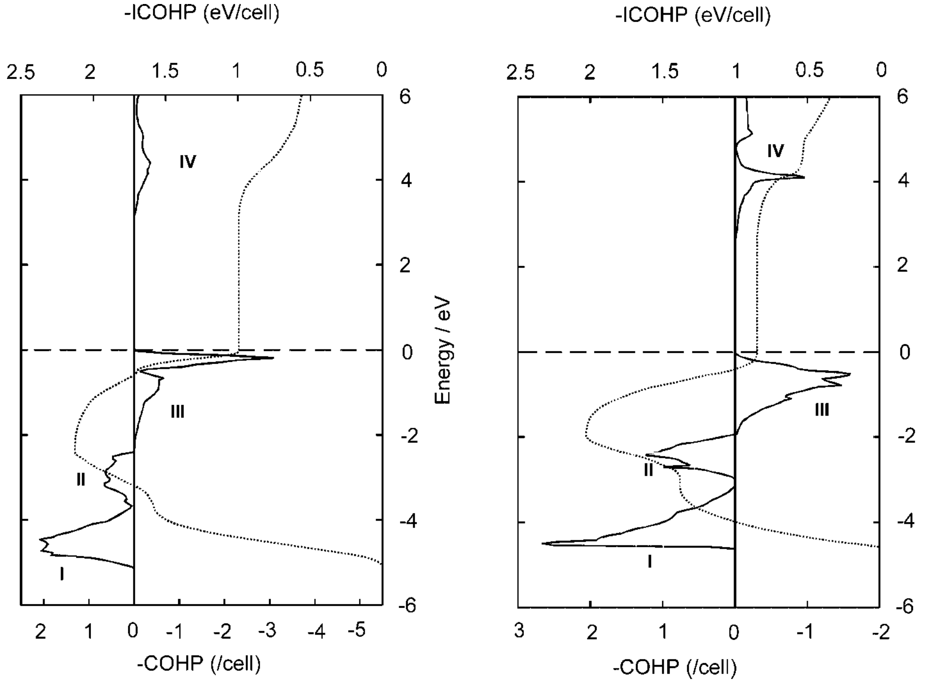

Figure 4. COHP and ICOHP of the Tl–F interaction (left: *Pbcm*; right: $Fm\bar{3}m$).

scheme (Figure 5). The Tl 6s and F 2p levels are found in a similar energy region and thus are able to interact efficiently which, however, leads to both strong bonding Tl 6s/F 2p combinations (region I) and antibonding Tl 6s/F 2p states right at the Fermi level (region III).

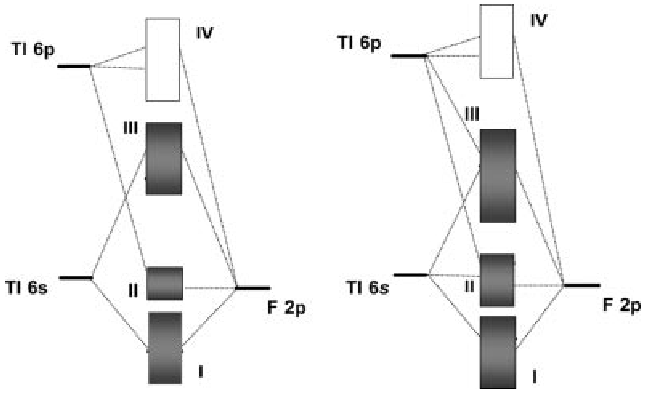

Figure 5. Schematic orbital interaction diagrams for TlF (a) in its actual distorted structure (*Pbcm*) and (b) in a hypothetical symmetrical structure ($Fm\bar{3}m$). Shaded blocks symbolize occupied levels, open blocks correspond to empty levels.

If the antibonding Tl 6s/F 2p interactions were reduced, an energetic stabilisation of the whole solid would be achieved. This can indeed be accomplished by a structural distortion [Figure 5(b)]. A comparison of the total energies per formula unit shows the distorted structure to be more stable than the undistorted NaCl type of structure. Upon distortion, the low-lying region I loses some of its Tl 6s character to region III right below the Fermi level. In exchange, region I gains F 2p character and region III loses F 2p character. Note also the high integrated crystal orbital Hamiltonian population (ICOHP) for region I (Table 1). Accordingly, the high lying antibonding Tl 6s/F 2p states in particular come closer in energy to the Tl 6p states, which now can mix into the antibonding region III. This introduces some additional Tl 6p/F 2p bonding, as noted earlier,[15] and, more importantly, moves the antibonding states partially above the Fermi level so that a net gain in bonding is achieved. Indeed, the ICOHP value for the Tl–F bond is higher for the distorted structure than for the symmetric structure (Table 1). In the distorted structure, the Tl–F contacts are unevenly distributed. Four shorter contacts at 243, 255 and 271 pm (2×) and two rather long Tl–F distances of 312 and 370 pm are observed. Closer inspection of the COHP curves (see Supporting Information) shows that the four shorter Tl–F distances essentially determine the whole Tl–F interaction, whereas the interactions at the two larger distances become essentially non-bonding.

It has been realized previously that the crystal orbital Hamiltonian population can be used as an indicator in trends of lone pair stereochemical activity.[16] This mixing cannot occur in highly symmetric (cubic) structures like the rock-salt-type structure, however, as it would be symmetry-forbidden. Note that for this gedankenexperiment the mean Tl–F distance is the same in all cases.

Thallium Chloride and Bromide (TlCl and TlBr)

In contrast to TlF, no distortions associated with the stereochemistry of a lone pair have been observed so far for TlCl and TlBr. This becomes obvious by comparing the density of states and COHP curves for the thallium–halogen bond for hypothetically cubic TlF (Figures 3 and 4) with that for TlCl (Figures 6 and 7). As for TlF in the rock-salt structure, the density of states and COHP curves for

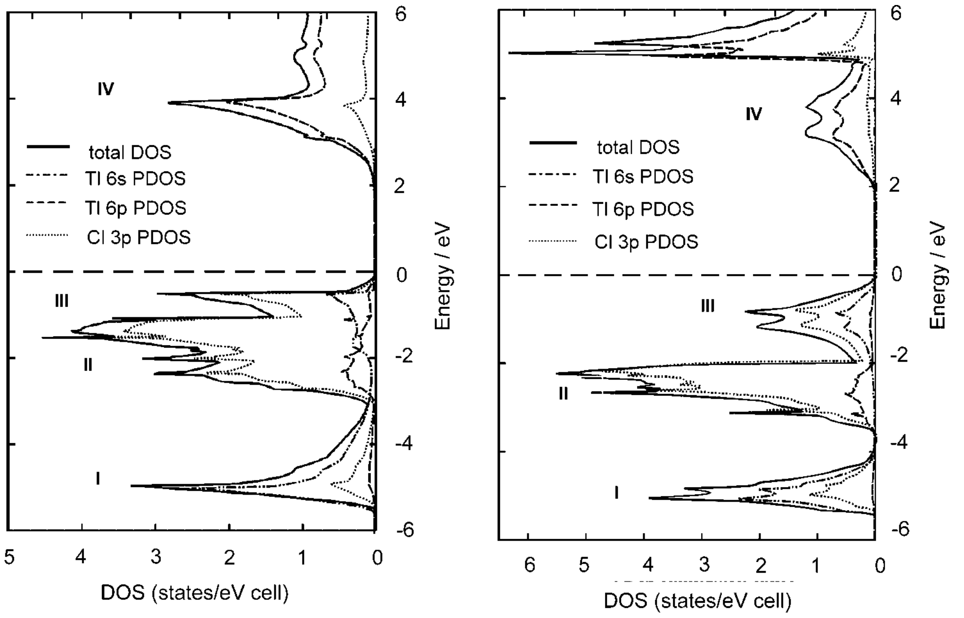

Figure 6. Total and partial densities of states for TlCl (left: *Pbcm*; right: $Fm\bar{3}m$).

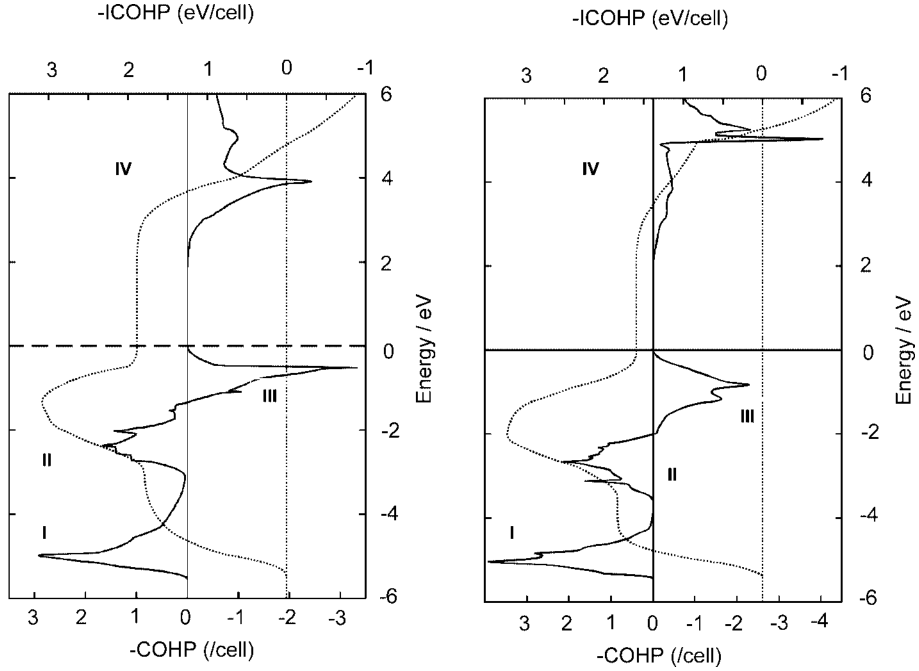

Figure 7. COHP and ICOHP of the Tl–Cl interaction (left: *Pbcm*; right: *Fm*$\bar{3}$*m*).

TlCl can be separated into four distinct regions. In the case of the CsCl-type structure, regions II and III have grown together when compared with the situation for TlF. However, it becomes clear that the principal features are still present, particularly when looking at the partial density of states and COHP curves. In the low energy region the states have predominantly Tl 6s/Cl 3p bonding character whereas the highest occupied states are Tl 6s/Cl 3p antibonding. the low lying states have substantially more Tl 6s character compared to TlF, and the states right below the Fermi level more Cl 3p character (Table 1). This can, again, be illustrated by a simple interaction scheme (Figure 8). As the Cl 3p states are located at higher energies than the F 2p states, they are farther apart from the Tl 6s states and thus the Tl 6s/Cl 3p interaction is less strong. This becomes particularly obvious when the band structures of TlF and TlCl in the CsCl-type structure are compared. The effects described for TlCl are even more pronounced for TlBr. The heavier the halogen atom, the larger the energy separation between Tl 6s and X-*n*p states and the weaker the covalent and the stronger the ionic interaction between Tl^+ and X^-. The energy separations between distorted and undistorted structures are reduced. Thus, in compounds with heavier halogens the necessity for a structural distortion from a highly symmetric structure with a large lattice energy (Madelung factor) to minimize unfavourable (antibonding) covalent interactions gradually vanishes.

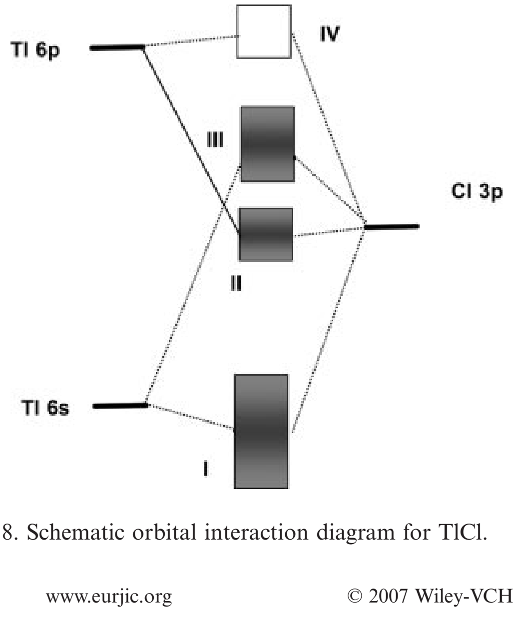

Figure 8. Schematic orbital interaction diagram for TlCl.

Thallium Iodide (TlI)

The total and partial DOS diagrams for TlCl and TlI in the CsCl-type structure show similar features. The more ionic character of TlI becomes obvious by the fact that a pseudo gap opens up around about –3 eV due to the increasing ionic nature of the compound, this is in agreement with the trend observed for TlCl and TlBr (see above). However, the question remains as to why TlI adopts a comparatively low symmetry structure at low temperatures (Figure 2), which is also seen for the red monohalides of indium(I) (InX; X = Cl, Br, I).[17] This TlI type of structure (Figure 9) has the special property that the contraction of one sublattice (the cations) can be coupled with the dilatation of the other sublattice (the anions).[18] In the case of the low-temperature modification of TlI, the anions move apart from each other and the cations come closer. At the same time the mean cation–anion distance remains almost the same. Most importantly, short metal–metal contacts are created (two of about 371 pm and two of 457 pm). The

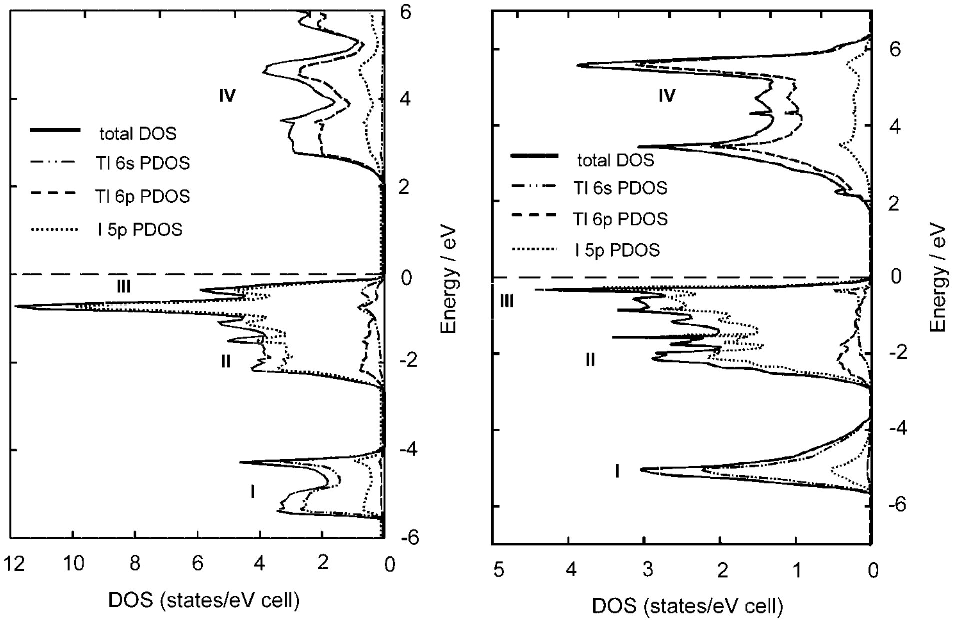

Figure 9. Total and partial densities of states for TlI (left: *Cmcm*; right: *Pm*$\bar{3}$*m*).

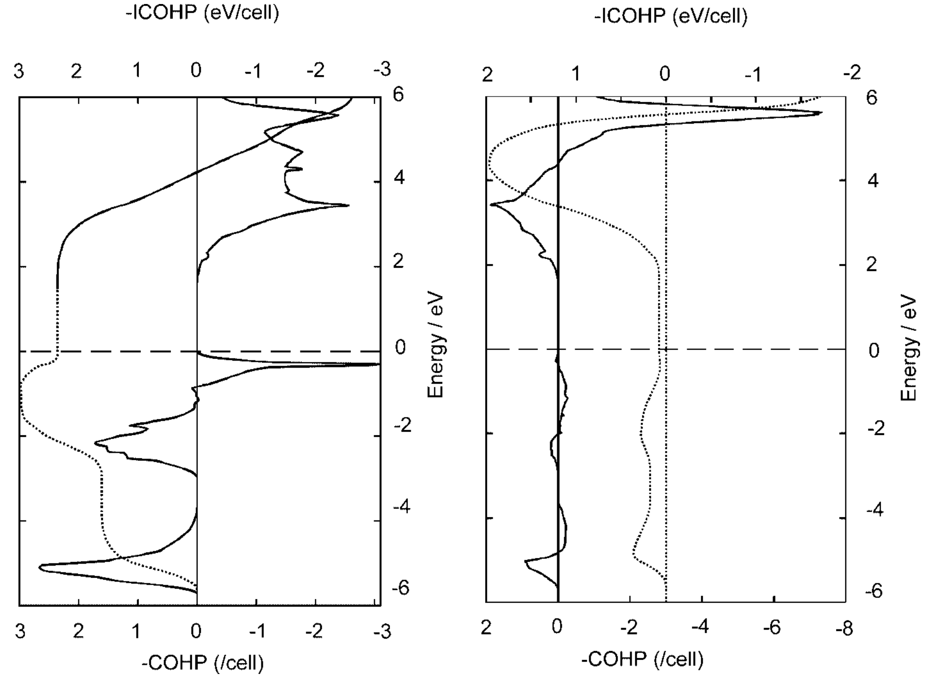

Figure 10. TlI (*Pm*$\bar{3}$*m*): COHP and ICOHP of the Tl–I (left) and Tl–Tl interactions.

COHP curves for the Tl–Tl interactions in TlI in the CsCl (P*m*$\bar{3}$*m*; Figure 10, right) and InX (*Cmcm*; Figure 11, right) types of structure make it clear that Tl–Tl bonding becomes important in the case of the low-temperature (InX) structure whereas it is negligible for the room temperature structure (CsCl). Accordingly, the ICOPH values (Table 2) for the Tl–Tl interaction up to the Fermi level are higher for TlI in the InX type of structure than in the CsCl type of structure, which accounts for a stabilisation of the distorted structure at low temperatures through Tl–Tl bonding. Inter-

Table 2. ICOHP values of Tl–Tl interactions for TlI in the InX (*Cmcm*) and CsCl (*Pm*$\bar{3}$*m*) structure types.

Region	Space group	
	Cmcm	*Pm*$\bar{3}$*m*
I	0.29	0.36
II	–0.14	–0.18
III	0.05	0.10
IV	–0.08	–0.21
V	0.05	0.01
Total ICOHP	0.17	0.07

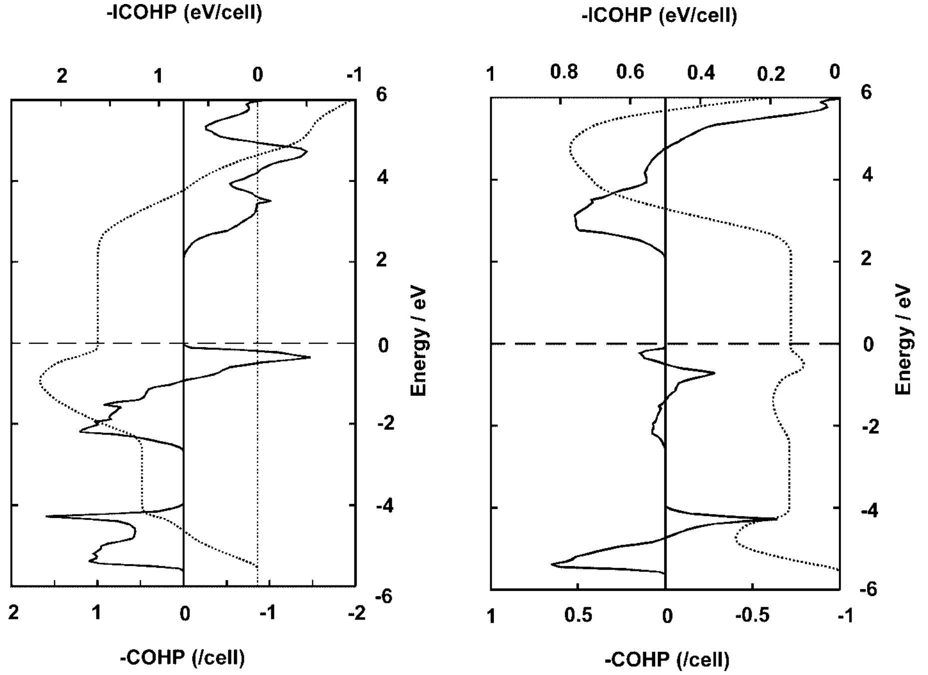

Figure 11. TlI (*Cmcm*): COHP and ICOHP of the Tl–I (left) and Tl–Tl interactions.

estingly, the shortest observed Tl–Tl distance of 371 pm in TlI is comparable to that found in pentabenzylcyclopentadienidothallium(I) (363 pm).[19]

Conclusions

In summary, the calculations on thallium halides show, just like previous theoretical work on Tl^I coordination compounds,[20] that structural distortions in Tl^I compounds do not originate from a stereochemically active lone pair in the sense that Tl 6s and Tl 6p mix directly (or hybridize) to give the electron pair on thallium a directional character. The Tl 6s and Tl 6p states are energetically too far apart from each other to mix efficiently.[21,22] Instead, the minimisation of unfavourable covalent antibonding states, which originate from the interaction of the Tl 6s lone pair with lone pairs of the bonding partner, is the driving force for structural distortions. A comparison of TlF with the heavier thallium halides TlX (X = Cl, Br, I) shows that such lone pair distortions depend crucially on the relative energy levels of the valence states of the constituting elements and, in turn, on the number of occupied antibonding states within the crystal.

In the case of TlF, the Tl 6s and the F 2p states are located in the same energy region, which leads to a strong covalent interaction between both bonding partners that produces strongly antibonding Tl–F states just below the Fermi level that destabilize the solid. Due to the strong splitting, the highest states move closer in energy to the Tl 6p states. The admixture of empty Tl 6p states at the top of the valence band becomes allowed through a structural distortion (symmetry reduction). This leads to a decrease in energy of the antibonding states and thereby a net stabilisation of the structure. The large dispersion in the case of fluorine thus minimizes the energy gap between the Tl 6s and Tl 6p states such that the latter can participate in chemical bonding.

The heavier the anion the larger the energy mismatch between Tl 6s states and X *n*p states. This leads to weaker covalent interactions. The highest occupied valence states gain increasingly higher X p character while the lower valence states are mainly Tl 6s like. Thus, the compounds become more ionic and the gain of Coulombic energy outweighs the (decreasing) covalent antibonding forces at the Fermi level (note that this observation is in contrast to what would have been expected judging from relative electronegativities). Consequently, typical ionic structures like the rock-salt or cesium chloride types of structure are adopted. Similar observations have been made recently for lead chalcogenides.[23] That covalent forces may, under certain conditions, lead to unsymmetrical structures even in the case of heavier anions is exhibited by the example of TlI, which gains stability at low temperatures by attractive metal–metal bonding.

Computational Details

Calculations of the electronic structure of the thallium halides were carried out using the tight-binding linear-muffin-tin orbital (LMTO) method in the local density (LDA) and atomic sphere (ASA) approximation within the framework of the density functional theory (DFT) method.[24,25] All major relativistic effects except spin-orbit coupling were taken into account using the scalar relativistic approximation. The calculations include corrections for the neglect of the interstitial regions and the partial waves of higher order. To reduce the overlap of atomic spheres (AS), empty interstitial spheres were added to the crystal potential and the basis set. The construction of the atomic sphere radii was performed according to an automatic procedure of the program package until the empty space was sufficiently filled.[26] Reciprocal space integrations were carried out using the tetrahedron method.[27] The basis set of short-range, atom-centred TB-LMTOs contained 6s, 6p, 6d and 5f wave functions for Tl (n = 5). The 6d and 5f partial waves were included only in the tails of the LMTOs according to the Löwdin downfolding procedure.[28] For fluorine, 3s and 2p were taken into account as valence orbitals and the 3s orbital was treated by the downfolding technique; for chlorine (n = 4) and bromine (n = 5), ns, (n – 1)p and (n – 1)d functions were treated as valence orbitals, with ns and (n – 1)d being downfolded. For iodine, 6s, 5p, 5d and 4f orbitals were considered as valence orbitals and 6s and 5d were downfolded. The partial (l and m quantum number decomposed) electronic DOSs were calculated to examine the effect of the anion on the electronic density of states in detail. These were calculated by projecting the wave functions onto spherical harmonics centred on each atom. For bond analysis, the crystal orbital Hamiltonian population (COHP) method was used together with its integration, the ICOHP.[29] COHP gives the energy contributions for all electronic states for selected bonds by partitioning the band structure energy in terms of the respective orbital pair contributions. Note, however, that the values are negative for bonding and positive for antibonding interactions. Thus, the sign is inverted with respect to the crystal orbital overlap population (COOP) diagrams originally used in semi-empirical extended-Hückel calculations.[30]

For TlF[31] in space group *Pbnm*, TlCl[32] and TlBr[32] in the CsCl (*Pm*$\bar{3}$*m*) and NaCl (*Fm*$\bar{3}$*m*) structures as well as for TlI in the CsCl[8] structure and its low-temperature modification,[33] the structural data were employed as reported in the literature. Lattice constants for a hypothetical TlF in the rock-salt structure were estimated from the molar volume of room temperature TlF in space group *Pbcm*.

Supporting Information (see footnote on the first page of this article) contains COHP and ICOHP curves for the Tl–F interaction in TlF (*Pbcm*).

Acknowledgments

A.-V. M. thanks the Bundesministerium für Bildung und Forschung (BMBF) and Fonds der Chemischen Industrie for support through a Liebig fellowship and the Deutsche Forschungsgemeinschaft for generous financial support. Prof. Dr. G. Meyer is acknowledged for his interest in this research, helpful discussions and for providing the infrastructure necessary to conduct this research.

---

[1] a) N. V. Sidgwick, *Some Physical Properties of the Covalent Link in Chemistry*, Cornell University Press, Ithaca, New York, **1933**; b) N. V. Sidgwick, *Annu. Rep.* **1933**, *30*, 120; c) N. V. Sidgwick, H. M. Powell, *Proc. R. Soc., London Ser. A* **1940**, *176*, 153; d) N. V. Sidgwick, *The Chemical Elements and their Compounds*, vol. 1, Clarendon Press, Oxford, **1950**.

[2] a) N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, **1997**; b) J. G. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, Pearson Education, New York, **1997**; c) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**.

[3] a) L. E. Orgel, *J. Chem. Soc.* **1959**, 3815; b) J. D. Dunitz, L. E. Orgel, *Adv. Inorg. Chem. Radiochem.* **1960**, *2*, 42.

[4] P. Berastegui, S. Hull, *J. Solid State Chem.* **2000**, *150*, 266. High-pressure DTA measurements indicate that a phase transition takes place at pressures of 1.3 GPa but no structural data are available (see ref.[5a]).

[5] a) C. W. F. T. Pistorius, J. B. Clark, *Phys. Rev.* **1968**, *173*, 692; b) M. Barlow, C. Meredith, *Z. Kristallogr.* **1968**, *130*, 304; c) D. Cubicciotti, H. Eding, *J. Chem. Eng. Data* **1965**, *10*, 343.

[6] S. P. Gabuda, S. G. Koziova, *J. Struct. Chem.* **1997**, *38*, 140.

[7] a) W. P. Davey, F. G. Wick, *Phys. Rev.* **1921**, *17*, 403; b) W. P. Davey, F. G. Wick, *Z. Phys. Chem.* **1925**, *117*, 51; c) A. E. van Arkel, *Physica* **1924**, *4*, 33; d) A. E. van Arkel, *Norsk Geologisk Tidsskrift* **1925**, *8*, 217.

[8] M. Blackman, I. H. Khan, *Proc. Phys. Soc.* **1961**, *77*, 471.

[9] T. Barth, G. Lunde, *Norsk Geologisk Tidsskrift* **1925**, *8*, 293.

[10] L. Helmholtz, *Z. Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie* **1936**, *95*, 129.

[11] a) R. E. Jones, D. H. Templeton, *Acta Crystallogr.* **1955**, *8*, 847; b) C. P. J. M. van der Vorst, G. C. Verschoor, W. J. A. Maaskant, *Acta Crystallogr., Sect. B* **1978**, *34*, 3333c) G. Meyer, T. Staffel, *Z. Anorg. Allg. Chem.* **1989**, *574*, 114.

[12] S. P. Gabuda, S. G. Kozlova, R. L. Davidovich, *Chem. Phys. Lett.* **1996**, *263*, 253.

[13] F. Rieger, A.-V. Mudring, *Inorg. Chem.* **2005**, *44*, 6240.

[14] Comprehensive and state-of-the art calculations on thallium halides are available: a) P. Schwerdtfeger, G. A. Heath, M. Dolg, M. A. Bennett, *J. Am. Chem. Soc.* **1992**, *114*, 7518; b) P. Schwerdtfeger, J. Ischtwan, *J. Comput. Chem.* **1993**, *14*, 913.

[15] U. Häussermann, P. Berastegui, S. Carlson, J. Haines, J.-M. Léger, *Angew. Chem. Int. Ed.* **2001**, *40*, 4624.

[16] R. Seshadri, N. A. Hill, *Chem. Mater.* **2001**, *13*, 2892.

[17] G. Meyer, T. Staffel, *Z. Anorg. Allg. Chem.* **1989**, *574*, 114.

[18] D. Becker, H. P. Beck, *Z. Kristallogr.* **2004**, *219*, 348.

[19] a) H. Schumann, Ch. Janiak, J. Pickhardt, U. Börner, *Angew. Chem.* **1987**, *99*, 788; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 115. For theoretical calculations see: b) C. Janiak, R. Hoffmann, *Angew. Chem.* **1989**, *101*, 1706; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1688; c) C. Janiak, R. Hoffmann, *J. Am. Chem. Soc.* **1990**, *112*, 5924; d) P. Schwerdtfeger, *Inorg. Chem.* **1991**, *30*, 1660.

[20] F. Rieger, A.-V. Mudring, *Inorg. Chem.* **2005**, *44*, 6240.

[21] If the Tl$^+$ cation lies on a centre of symmetry, mixing between occupied 6s and empty 6p states is forbidden. Lowering the internal energy by mixing can only be achieved by a second order Jahn–Teller effect that destroys the symmetry.

[22] R. Dronskowski, *Computational Chemistry of Solid State Materials*, Wiley-VCH, Weinheim, **2005**, Table 2.1 In the case of InBr a similar strong In s/p energy separation has been observed: R. Dronskowski, *Inorg. Chem.* **1994**, *33*, 6201.

[23] a) G. W. Watson, *J. Chem. Phys.* **2001**, *114*, 758; b) A. Walsh, G. W. Watson, *Phys. Rev. B* **2004**, *70*, 2535114; c) A. Walsh, W. Graeme, *J. Phys. Chem. B* **2005**, *109*, 18868; d) A. Walsh, G. W. Watson, *J. Solid State Chem.* **2005**, *178*, 1422.

[24] a) H. L. Shriver, *The LMTO Method*, Springer, Berlin, **1984**; b) O. Jepsen, M. Snob, O. K. Andersen, *Linearized Band-Structure Methods*, in *Electronic Band-Structure and its Applications*, Springer Lecture Note, Springer, Berlin, **1987**; c) O. K. Andersen, O. Jepsen, *Phys. Rev. Lett.* **1984**, *53*, 2571.

[25] R. W. Tank, O. Jepsen, A. Burckhardt, O. K. Andersen, *TB-LMTO-ASA Program*, ver. 4.7, Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany, **1998**.

[26] O. Jepsen, O. K. Andersen, *Z. Phys. B* **1995**, *97*, 35.

[27] a) O. K. Andersen, O. Jespen, *Solid State Commun.* **1971**, *9*, 1763; b) P. Blöchl, O. Jepsen, O. K. Andersen, *Phys. Rev. B* **1994**, *34*, 16223.

[28] a) W. R. L. Lambrecht, O. K. Andersen, *Phys. Rev. B* **1986**, *34*, 2439; b) O. Jensen, O. K. Andersen, *Z. Phys. B* **1995**, *97*, 35;

c) G. Krier, O. Jepsen, O. K. Andersen, Max-Planck-Institute fur Festkörperforschung, Stuttgart, Germany, unpublished results.
[29] R. Dronskowski, P. E. Blöchl, *J. Phys. Chem.* **1993**, *97*, 8617.
[30] S. Wijeyesekera, R. Hoffmann, *Organometallics* **1984**, *3*, 949.
[31] P. Berastegui, S. Hull, *J. Solid State Chem.* **2000**, *150*, 266.
[32] See ref. [8] and M. A. Popova, T. J. Darvojd, M. A. Gurevich, *Zh. Neorg Khim.* **1966**, *11*, 1236.
[33] L. Helmholtz, *Z. Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie* **1936**, *95*, 129.

Received: July 13, 2006