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Lone Pair Effect in Thallium(I) Macrocyclic Compounds

Anja-Verena Mudring* and Franziska Rieger

Institut für Anorganische Chemie, Universität zu Köln, Greinstrasse 6, D-50939 Köln, Germany

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The role of the inert (lone) pair of electrons in thallium(I) salts is studied by comparison of the compounds $[Tl@18\text{-crown-6}]^+X^-$ ($X = TlI_4$, ClO_4) and $[K@18\text{-crown-6}]^+ClO_4^-$. In contrast to common introductory chemistry textbook opinions, the paradigm that s–p hybridization is a prerequisite for an inert electron pair to become stereochemically active in compounds of the heavier main group elements has to be revised. Instead, an inert pair of electrons is expected to become stereochemically involved whenever it is forced to participate in antibonding orbital interactions with its surroundings, and there is the possibility for a structural distortion that minimizes these repulsive forces. The structural distortion will occur to such an extent that repulsive orbital interactions and attractive electrostatic interactions counterbalance. Our results also provide an explanatory background for many of the rules of thumb that are found in the literature about why and when an inert electron pair is expected to become stereochemically active in a certain compound.

Introduction

Thallium, when compared with the remainder of the group 13 elements, shows a pronounced preference for the oxidation state +I. This has been attributed to the effect of the "inert electron pair" introduced by Sidgwick[1] and since then generally used in introductory textbooks to explain the tendency of the heavier main-group elements to adopt oxidation numbers that are 2 less than the respective group number.[2] This phenomenon originates from a combination of shell structure effects and relativity.[3] Owing to the relativistic downshift in energy of the 6s orbital, Tl does indeed favor the oxidation state +I over +III.[4] Moreover, Tl might be regarded as "a relativistic alkali metal" because Tl chemistry parallels that of the alkali metals (and silver) in many ways. The solubility of the hydroxides, MOH, and its tendency to absorb CO_2 may serve as examples. Many Tl and alkali-metal compounds crystallize isotypically, e.g., Tl_2SO_4 and K_2SO_4.[5] Tl is able to replace K ions in biological systems,[6] where it has an affinity of about 10 times that of potassium.[7] Therefore, it appears of fundamental interest to study the interaction of Tl with organic macrocycles such as crown ethers, which are well-known to mimic biological systems. The question of whether alkali-metal and Tl compounds behave similar is, however, crucially determined whether the $6s^2$ lone pair of Tl(I) is stereochemically active or not.

During comparative studies of the host−guest chemistry of potassium (K^+) and thallium (Tl^+) cations, we have observed that thallium and potassium salts in this class of compounds seldom crystallize isotypically. Rather, Tl^+ is included by the host in such a way that a stereochemically active electron pair may be assumed. This observation is made for all possible combinations of Tl(I) salts with

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* To whom correspondence should be addressed. E-mail: a.mudring@uni-koeln.de. Fax: (49)221 470 5083. Web site: www.anjamudring.de.

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macrocyclic polyethers such as podands, crown ethers, or cryptands, as an evaluation of structural data in the CCDC database clearly shows. To elucidate this behavior, we have not only investigated the crystal structures of thallium coronates with weakly coordinating counterions such as ClO_4^- and TlI_4^- but also, even more importantly, undertaken theoretical investigations to establish the nature of the stereochemically active $6s^2$ lone pair.

Experimental Section

[Tl(18-crown-6)ClO$_4$]. A total of 0.030 g (10^{-4} mol) of $TlClO_4$ and 0.026 g of crown ether, 18-crown-6, were dissolved in 20 mL of ethanol p.a., and the resulting mixture was stirred for 1 h. The solution was allowed to stand at room temperature for 4 days. After evaporation of the solvent, colorless transparent needle-shaped crystals were obtained.

[Tl(18-crown-6)TlI$_4$]. A total of 0.33 g (10^{-3} mol) of TlI and 0.53 g (2×10^{-3} mol) of crown ether, 18-crown-6, were heated in 20 mL of dichloromethane, and after the addition of 0.25 g (10^{-3} mol) of iodine, TlI dissolved. A total of 100 mL of ethanol were added, and the boiling mixture was stirred for 1 h. The hot mixture was slowly cooled by placing the reaction vessel in a Dewar containing hot water. After 1 day, bright orange crystal blocks were obtained.

Suitable single crystals of [Tl@18-crown-6][ClO_4][8] (0.5 × 0.1 × 0.1 mm) and [Tl@18-crown-6][TlI_4][9] (0.3 × 0.3 × 0.3 mm) were mounted in a glass capillary. Intensity data were collected on an IPDS diffractometer (Stoe, Darmstadt, Germany). The data were processed with the program system SHELX-97,[10] scattering factors were taken from *International Tables for Crystallography*, Vol. C,[11] and numerical absorption correction after crystal shape optimization was performed using the programs XRED and XSHAPE.[12]

Computational Details

Ab initio calculations were carried out at the MP2 as well as DFT level of theory with the B3LYP functional with the aid of the program GAMESS[13] using a 6-31G basis set for H, C, and O. For K as well as Tl, the SBKJC VDZ relativistic effective core potentials with the accompanying valence basis sets were used.[14] To investigate the Tl-centered orbitals, the Edminston−Ruedenberg localization scheme was applied.[15]

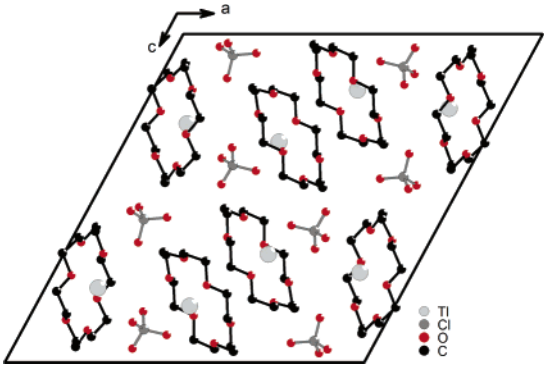

Figure 1. Crystal structure of {Tl@18-crown-6}ClO_4.

Results and Discussion

An asymmetric surrounding of Tl(I) in a crown ether is especially surprising because these polyethers generally provide a highly symmetric surrounding for the coordinated cation. Alkali-metal cations such as sodium, potassium, and even rubidium [with the latter cation being larger than Tl(I)] show a strong preference for a symmetric complexation by 18-crown-6, although strong interactions with better ligands might pull them out of the crown ether plane. To minimize these influences in our studies, we have concentrated on coordination compounds with weakly coordinating anions such as ClO_4^- or TlI_4^-. Common to all these structures is a relatively large cation−anion separation, although the individual arrangement of the M(18-crown-6) and the tetrahedral building units is determined by packing effects such as the relative size. In [Tl@18-crown-6][ClO_4] (Figure 1), the Tl(I) cation resides 75 pm above the plane defined by the oxygen atoms of the crown ether and 66 pm in [Tl@18-crown-6][TlI_4] (Figure 2), whereas, for example, in the analogous potassium compound [K@18-crown-6]-[ClO_4],[15] the cation is found right in the middle of the crown ether (Figure 3; the crystal structure of [K@18-crown-6][TlI_4] is so far unkown).

The distance of Tl^+ to the mean plane of oxygen atoms in 18-crown-6 has been observed to become as large as 113.4(2) pm in the dimethyl-*N*-(trichloroacetyl)amidophosphate salt, Tl@(18-K-6){$Cl_3CC(O)NP(O)(OCH_3)_2$}.[17] The ionic radius of Tl^+ lies between those of K^+ and Rb^+. The Shannon radii for 6-fold coordinates are $r(K^+) = 152$ pm, $r(Rb^+) = 166$ pm, and $r(Tl^+) = 164$ pm.[18] Because they are

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(8) Monoclinic, space group $P2_1/c$; $a = 2147.8(2)$ pm, $b = 866.88(4)$ pm, $c = 2234.3(2)$ pm, $\beta = 118.507(7)°$, $V = 3.650(2)$ nm^3; $Z = 8$; $\rho_{calc} = 2.068$ g·cm^{-3}; 1, 9° < 2θ < 54.3°; IPDS II, Mo Kα radiation ($\lambda = 71.073$ pm); $T = 170(2)$ K; $F(000) = 2192.0$; $\mu = 9.04$ mm^{-1}; 37 536 reflections were measured, of which 8090 are unique and 6418 are considered as observed. R1 = 0.0258 for 6418 $F_o > 4\sigma(F_o)$ and 0.0399 for all 8090 data, wR2 = 0.0538, GOF = S = 1.002. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk) upon quoting the depository number 244858.

(9) Monoclinic, space group $P2_1/n$; $a = 840.90(7)$ pm, $b = 2110.4(2)$ pm, $c = 1464.4(1)$ pm, $\beta = 101.97(1)°$, $V = 2.542(4)$ nm^3; $Z = 4$; $\rho_{calc} = 3.021$ g·cm^{-3}; 1, 9° < 2θ < 54.3; IPDS II, Mo Kα radiation ($\lambda = 71.073$ pm); $T = 170$ (2) K; $F(000) = 326.0$; $\mu = 3.77$ mm^{-1}; 27 992 reflections were measured, of which 5660 are unique and 4466 are considered as observed. R1 = 0.0399 for 4466 $F_o > 4\sigma(F_o)$ and 0.0536 for all 5660 data, wR2 = 0.1041, GOF = S = 1.068. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk) upon quoting the depository number 244860.

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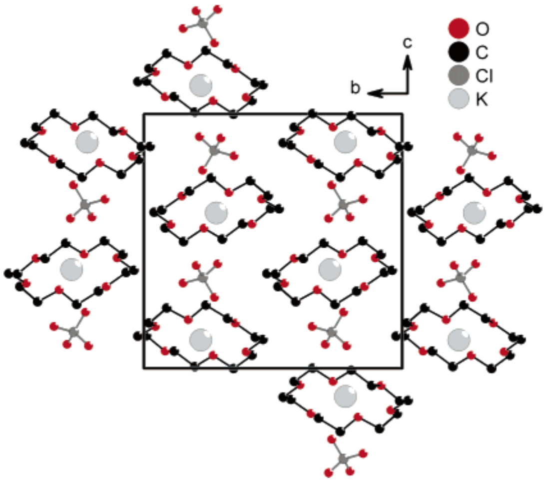

Figure 2. Crystal structure of {K@18-crown-6}ClO_4 according to Luger et al.[16]

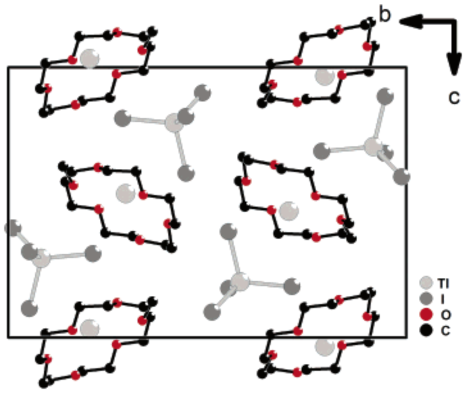

Figure 3. Crystal structure of {Tl@18-crown-6}TlI_4.

determined with either O^{2-} or F^- as counterions (both strongly polarizing anions), a comparison of the lattice constants of compounds with a less coordinating counteranion might be more suitable to illustrate the ionic radii, e.g., M_2PtCl_6 [$a(K_2PtCl_6) = 974.5$ pm, $a(Rb_2PtCl_6) = 990.4$ pm, and $a(Tl_2PtCl_6) = 977.5$ pm].[19] Thus, from purely geometric considerations, the Tl(I) cation should well fit into the crown ether cavity. Even the larger rubidium cation is known to fit into 18-crown-6.[20] Hence, a "stereochemical active lone pair" on Tl may be held responsible for the structural behavior of thallium−18-crown-6 compounds.

General explanations for the stereochemical behavior of lone pairs are usually given in general chemistry textbooks.[21] It is said that the stereochemical activity of the lone pair of a central atom decreases both down the groups of the periodic table and with increasing coordination number. High site symmetry for the central atom is also held responsible for the suppression of the stereochemical influence of a free electron pair. Geometric requirements of a lone pair versus available space around the central atom[22] as well as the basicity of the counterion[23] are also discussed. All of these rules of thumb lack any deeper explanation or quantification, and their predicting power is generally low.

Valence bond theory attributes the stereochemical activity of a lone pair to s−p hybridization. For example, the distortion of the CsCl type of structure by the Tl(I) lone pair has been explained for TlF and TlI in terms of s−p mixing on Tl.[23] It is widely believed that s−p mixing is a prerequisite for a lone pair to become stereochemically active.[24,25] On the other hand, it was early noted that the first excited state of Tl^+ (in the gas phase), s^1p^1, lies 7.4 eV above the s^2 ground state.[26] The high energy separation and the strongly different spatial distribution of the 6s/6p wave functions, which get strongly enhanced by relativity, stand against an efficient s−p hybridization.

To investigate the true origin of the structural distortion in the above-mentioned thallium−18-crown-6 complex compounds, we have optimized the geometries of metal−crown ether complexes at the MP2 as well as DFT/B3LYP level of theory. The optimized geometries clearly show that Tl^+ favors a position above the crown ether (the MP2 level of theory gives a distance of 66 pm, as was found experimentally for [Tl@18-crown-6][TlI_4]; at the DFT/B3LYP level, a distance of 77 pm is calculated). In contrast, similar calculations show that K^+ (and even Rb^+, which is larger than Tl^+ [18,19]) prefers a symmetrical coordination within the cavity of the crown ether, as is commonly observed in potassium−crown ether complexes. Data for all equilibrium geometries are available as Supporting Information.

Inspection of the molecular orbitals of both complexes reveals a bonding (Figure 4a) and an antibonding (Figure 4b) interaction of the Tl 6s electron pair with the oxygen atoms of the crown ether. The unfavorable antibonding interaction is obviously missing in the analogous potassium compound because the K 4s orbital is basically empty and, thus, no significant antibonding orbital interactions arise from the K 4s/O 2p interaction. From this, we conclude that it is this antibonding interaction that drives the Tl(I) cation out of the crown ether guest cavity (as far as the counteracting attractive electrostatic forces allow). An extensive study on Pb(II) complexes also shows higher total energies for undistorted compared to distorted structures.[27] A comparison of the total energies for a hypothetical complex with Tl in the middle of the crown ether with the total energies for the optimized geometries with Tl above the crown ether shows

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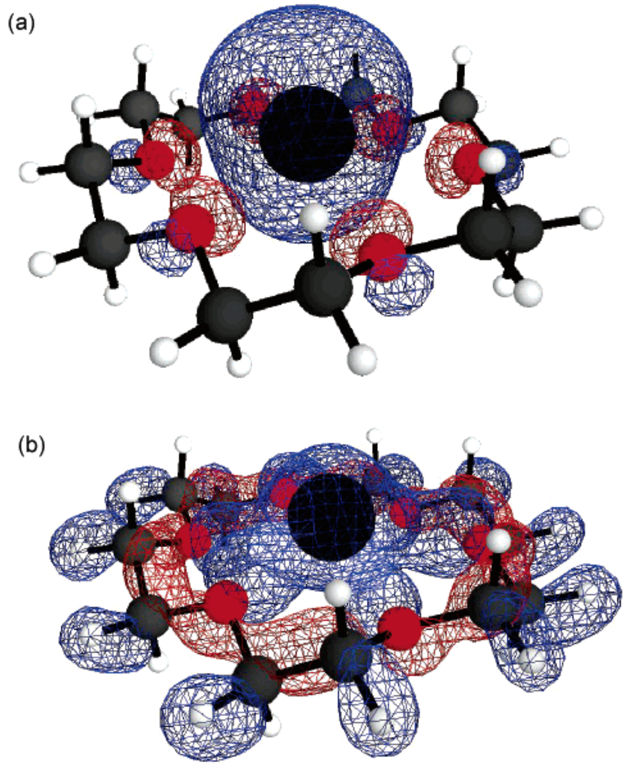

Figure 4. (a) Tl s/O p bonding orbital. (b) Tl s/O p antibonding orbital.

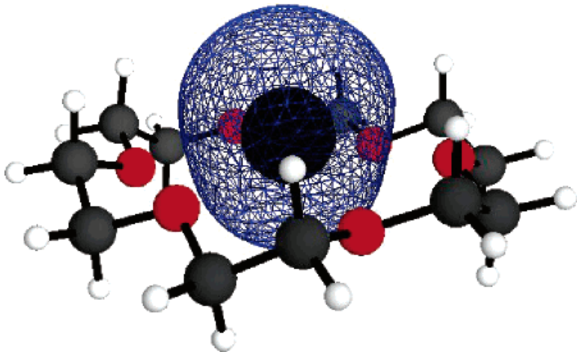

Figure 5. Tl s orbital obtained by the Edminston–Ruedenberg localization.

the latter geometry to be more stable by approximately 1.6 kcal/mol (MP2)/4.1 kcal/mol (B3LYP).

Consequently, this repulsion leads to a distortion of the Tl 6s lone pair, which is no longer totally spherical, as one should expect for an s orbital according to freshmen chemistry textbooks. Atomic orbital Mulliken population analysis for the respective O p/Tl s antibonding orbital reveals an overall composition of 81% Tl, 14.3% O, and 4.7% H; on Tl, 97.7% s, 1.8% p, and 0.5% d character is found. For further proof of our view, the Edminston–Ruedenberg localization method was used to gain information about the Tl-centered orbitals. This procedure shows the expected distortion for the Tl $6s^2$ pair of electrons (Figure 5).

Indeed, we do not observe any substantial p contributions on Tl. This clearly shows that p orbital contribution or "s–p hybridization" is not essential for a lone pair to become stereochemically active. To summarize, a so-called s^2 inert pair of electrons becomes stereochemically active if involved in antibonding orbital interactions with its surroundings, and the possibility for a structural distortion arises that minimizes these repulsive forces.

Basically, the equivalent observations apply to typical solid-state compounds such as thallium halides and lead chalcogenides when analyzing the reported band structure calculations. It is reported that in the structures of SbI_3, Sb_2Te_3, SbTeI, TlSbS, and Tl_3SbS_3 a stereochemically active electron pair on Sb is observed when the 5s levels rise from the bottom to the top of the valence band.[28] This can only be achieved by (antibonding!) interaction of the Sb 5 s with the "ligand S p" levels. The importance of anionic p states for the structure of lead chalcogenides was also realized.[29] In studies on the origin of distortion of α-PbO, it was found that "the classical theory of hybridization of the lead 6s and 6p orbitals is incorrect and that the 'lone pair' is the result of the lead–oxygen interaction."[30] In this case, the antibonding lead–oxygen interactions get minimized by a structural distortion that allows more efficient mixing of O 2p and unoccupied Pb 6p (because of symmetry, this is not possible at the Γ point, which would represent the "molecular orbital scheme"!).

Conclusion

In summary, one can state that s–p hybridization on the heavier main-group metals is not responsible for the stereochemical activity of a lone pair but instead can draw the general conclusion that antibonding metal *n* s/ligand *n* p interactions lead to structural distortion that minimize these unfavorable interactions, either in the solid state by O 2p/Pb 6p mixing or in the molecular case through enlargement of the metal–ligand.

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Supporting Information Available: Structural data (CIF format) for {Tl@18-crown-6}TlI_4 and {Tl@18-crown-6}ClO_4 and the equilibrium geometries for Tl^+@18-crown-6 and K^+@18-crown-6 at the different levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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