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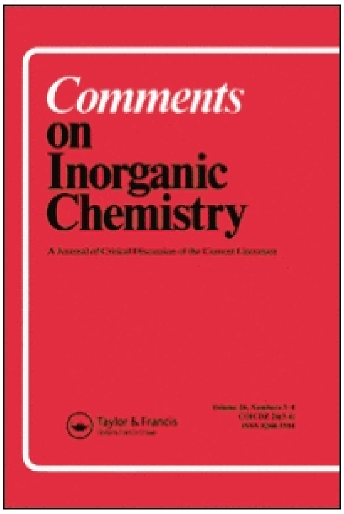

Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
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Ionic Radii: Effect of Shell Radius, Cation Charge and Lone Electron Pair

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To cite this Article Siekierski, S.(1997) 'Ionic Radii: Effect of Shell Radius, Cation Charge and Lone Electron Pair', Comments on Inorganic Chemistry, 19: 2, 121 — 131

To link to this Article: DOI: 10.1080/02603599708032731

URL: http://dx.doi.org/10.1080/02603599708032731

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Ionic Radii: Effect of Shell Radius, Cation Charge and Lone Electron Pair

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Received July 8, 1996

Radii of ions, r_i, were compared with radii of their outermost orbitals, $\langle r_{nl} \rangle$. It has been found that for *s* and *p* block elements in the oxidation state equal to the group number, r_i is a linear function of $\langle r_{nl} \rangle$ and, for a constant value of $\langle r_{nl} \rangle$, decreases with increasing formal charge of the cation. For *p* block elements in the oxidation state two less than the group number, the difference $r_i - \langle r_{nl} \rangle$ as well as the difference in orbital energies, $\epsilon_{np} - \epsilon_{ns}$, exhibit sawtooth behavior, i.e., secondary periodicity, similar to that in stability of oxidation states. The sawtooth behavior in the radii suggests that the lone pair acquires some s^2 character between the third and fourth period, and becomes mainly an s^2 pair in the sixth period ions, particularly in Tl(+1). The radii of Lr(+1), 104(+4) and 105(+5) have been estimated from linear relationships between r_i and $\langle r_{nl} \rangle$, and those of Al(+1), Ga(+1), In(+1) and Si(+2) from the sawtooth pattern.

Key Words: *ionic radii, orbital radii, lone electron pair, secondary periodicity*

INTRODUCTION

The relationship between the ionic radius, r_i, and the radius of the outermost shell in the ion appears to be of some theoretical importance. It is

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Comments Inorg. Chem.
1997, Vol. 19, No. 2, pp. 121–131
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also important for predicting ionic radii of elements in unstable oxidation states and of elements which have only short-lived nuclides. In the latter case an extrapolation of the ratio $r_i/r_{\max}$ or of the difference $r_i - r_{\max}$, where $r_{\max}$ is the radius of the maximum radial charge density, was used to estimate the ionic radius of Md(+1)[1] and the ionic radii of elements 104(+4)[2] and 105(+5).[3] In spite of its importance, it seems that the relationship between r_i and orbital radius has not been studied in detail. The main paper on this subject was published by Slater[4] who found that the ratio $r_i/r_{\max}$ was different for elements in different groups of the Periodic Table and was changing considerably across each group. That was contrary to the $r_{\text{cov}}/r_{\max}$ ratio (r_{cov} denotes the covalent radius) which was found to be constant[4] for many elements.

Correlation between ionic and orbital radii is also of importance for an inverse problem. For many *p* block elements the radii of ions in oxidation states two less than those characteristic for the group are known, but in some cases it is not evident which shell determines the ionic radius. That is because the lone electron pair can either be an s^2 pair, or occupy a hybrid orbital, or have some intermediate character. The latter case is not straightforward to recognize.

The objectives of this investigation were to study how the ionic radius depends on the shell radius, shell character (either *s*, *p* or *d*), charge of the cation and location of the lone electron pair. For that purpose ionic radii reported by Shannon[5] were compared with orbital radii calculated by Desclaux.[6]

IONS WITH FILLED *p* AND *d* OUTERMOST SHELLS

Figure 1 presents plots of the ionic radius, r_i, as a function of the radius of the outermost shell in the ion, $\langle r_{nl} \rangle$, for a number of groups of the Periodic Table. The oxidation state is equal to the (old) group number. The plots for group 3 and 4 ions also include the data points for Gd(+3), Lu(+3), Ac(+3), Cm(+3), and for Ce(+4), Th(+4), U(+4), Bk(+4), respectively. The ionic radii used are the radii in six-coordination reported by Shannon,[5] and the shell radii are the expectation orbital radii, $\langle r_{nl} \rangle$, calculated by Desclaux.[6] The *nl* subscript denotes the outermost completely filled shell in the cation. In the case of group 1–5 ions the outermost filled shell is a *p* shell, except for Li(+1) and Be(+2) which have the *s* outermost shell. In the case of group 11–16 ions the outermost

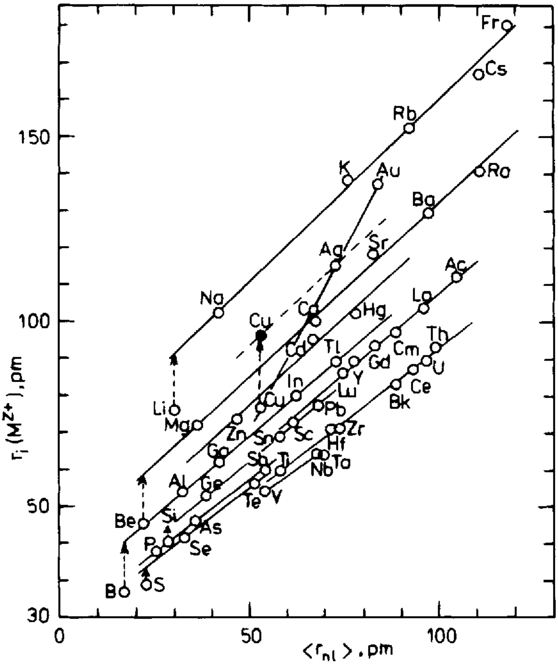

FIGURE 1 The ionic radius as a function of the radius of the outermost shell. The oxidation state is equal to the group number. The filled circle denotes the ionic radius of Cu(+1), according to Ref. 8.

shell is a *d* shell, except for B(+3) and the second row ions which have *s* and *p* outermost shells, respectively. We prefer to use the expectation value, $\langle r_{nl}\rangle$, rather than the radius of maximum radial charge density $(r_{nl})_{\max}$. The reason is that $\langle r_{nl}\rangle$ is greater than $(r_{nl})_{\max}$ and is, therefore, a more realistic estimate of the ionic radius. However, it should be noted that plots very similar to those shown in Fig. 1 can also be obtained with $(r_{nl})_{\max}$ as the shell radius. The $\langle r_{nl}\rangle$ radii reported in Ref. 6 and used in the plots are orbital radii in the atoms and not in the ions. However, according to Slater rules, the contribution to the screening constant is nil from electrons in a shell which is outer to that considered. Therefore, one can expect that the orbital radius remains the same or changes only slightly when an inner orbital in the atom becomes an outer orbital in the ion. That conclusion is corroborated by comparing the $(r_{np})_{\max}$ radii of Ti(+4), Zr(+4) and Hf(+4) ions, calculated in Ref. 2 with the $(r_{np})_{\max}$

radii of the corresponding atoms.[6] The two sets of radii are 46.9, 62.0, 62.6 pm, and 47.9, 62.5, 61.8 pm, respectively. The differences are indeed very small and may be due to differences in computing methods.

We can see in Fig. 1 that for ions of groups 1–5 and groups 12–16 the r_i vs. $\langle r_{nl} \rangle$ plots are linear to a good approximation. The slopes of the straight lines appear to decrease with increasing formal oxidation state from about 1 for alkali metal ions to about 0.7 for group 5 ions. The light elements, like Li, Be, B, Si and S, but not P, show lower ionic radii than expected from the plots. That can be explained by the effect of covalence in shortening M–O bonds.[7] A higher contribution from covalence is just expected for small ions. The observed deviations may also be caused by different outermost shells in the lighter and in the heavier members of the group. However, Al(+3) fits the straight line well, although its ionic radius depends on the $2p$ shell, while the radii of Ga(+3), In(+3) and Tl(+3) are determined by the $(n - 1)d$ shells. It should be noted that the heaviest members of group 15 and 16, i.e., Bi(+5) and Po(+6), also fall out of linear relationships. The coordinates of the data points for Bi(+5) and Po(+6), not shown in Fig. 1, are (64.9, 76) and (61.9, 67) pm. Another deviation from the general pattern is the unexpectedly high slope of the r_i vs. $\langle r_{nl} \rangle$ plot for Cu(+1), Ag(+1) and Au(+1) ions. A possible explanation is the high sensitivity of the radius of group 11 ions toward a contribution from covalence.[8] Assuming that for a perfectly ionic compound the radius of Cu(+1) is 96 pm,[8] the data points for Cu(+1) (filled circle) and Ag(+1) define a straight line with a slope of 0.9 which is similar to that for alkali metal ions. However, Au(+1) still deviates considerably from the straight line.

It can be seen from the data in Fig. 1 that for the same value of $\langle r_{nl} \rangle$ the ionic radius decreases considerably with increasing formal charge of the cation. That is because an increase in the charge of the cation favors covalent bonding and shortens the M–O bond. With the assumed constant O^{2-} radius, shortening of the M–O distance results in a smaller cationic radius. We can also see in Fig. 1 that for the oxidation states +1 and +2 the ionic radius is lower for ions with d than with p outermost shells. However, the opposite holds for oxidation states +3, +4 and +5, where the radii of ions with d shells are greater than those of their p counterparts. The latter effect can be expected if the energy required for hybridization involving $(n - 1)d$ orbitals (group 3–5 ions) is lower than that for nd orbitals (group 13–16 ions). That is because lower promotion energy results in stronger bonding and shorter metal to ligand distance. The assumption that promotion energy may be lower for $(n-1)d\ ns\ np$ than for $ns\ np\ nd$ hybridization is indirectly born out by differences in coordination numbers. Thus, for Hf(+4), which has almost the same outermost shell radius as Pb(+4), the predominant coordination number, CN, is 7 or 8, while CN for Pb(+4) is, as a rule, 6. It should be noted that eight-coordination requires four d orbitals, while six-coordination only two.

Correlations found in this work make possible an easy estimate of ionic radii of "exotic" elements. From the $\langle r_{nl}\rangle$ orbital radii[6] and from plots in Fig. 1, the ionic radii, for CN 6, of elements 104(+4) and 105(+5) are 77 and 70 pm, respectively. Our values are in good agreement with those calculated by a more elaborate methods.[2,3]

It is known that because of the relativistic effect the $7s$ electrons in the lawrencium atom are strongly bonded. That makes possible the existence of Lr(+1) which would then have the electron configuration $7s^2$, similar to that of Tl(+1), which is $6s^2$. The ionic radius and the radius of the outermost orbital in Tl(+1) (the $6s$ orbital) are 150 and 136 pm, respectively. If we assume that for 1+ ions with ns^2 configuration the slope of the r_i vs. $\langle r_{ns}\rangle$ plot is 0.95, then the radius of Lr(+1) becomes $150 + 0.95\ (190 - 136) = 201$ pm, where 190 pm is the radius of the $7s$ orbital in Lr(+1). The $7s$ orbital radius in Lr(+1) was calculated from that of the $7s^2$ nobelium atom,[6] taking into account the effect of the increased charge of the nucleus. The very large radius of Lr(+1) and, in consequence, very weak interaction with water molecules would probably make Lr(+1) unstable with respect to disproportionation to Lr(0) and Lr(+3). It should be noted that this calculation is based on the assumption that the lone electron pair in hydrated Lr^{1+} or in a Lr(+1) complex is not located on a hybrid orbital.

IONS WITH LONE ELECTRON PAIR

According to the so-called inert pair effect, p block elements show oxidation states two less than the characteristic group valence. The remaining pair of electrons can either be an s^2 pair or occupy one of the hybrid orbitals formed from the s, p and, for high coordination numbers, also d orbitals. To study the character of the lone pair in ions with a formal charge two less than the (old) group number, the ionic radius was plotted as a function of the $\langle r_{ns}\rangle$ and $\langle r_{(n-1)d}\rangle$ or $\langle r_{(n-1)p}\rangle$ orbital radius (the latter for the third period elements), Fig. 2. The ionic radii for six-coordination

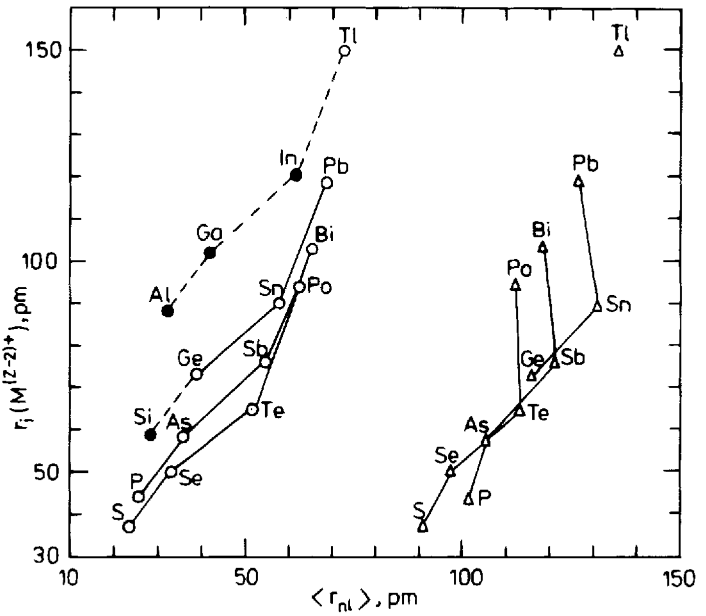

FIGURE 2 The ionic radius as a function of the radius of the outermost shell. The oxidation state is two less than the group number. Left-hand plots: the outermost orbital is the $(n-1)d$ or the $(n-1)p$ orbital. Right-hand plots: the outermost orbital is the ns orbital. Filled circles denote radii estimated from sawtooth behavior.

shown in Fig. 2 are those reported in Ref. 5, except for Sn(+2) and Te(+4), and the orbital radii (in atoms) were taken from Ref. 6. The ionic radius of six-coordinate Sn(+2) was calculated by the present author from the Sn–O distances reported in Ref. 9. Shannon's Te(+4) radius of 97 pm appears to be improbably high. From Te–F distances in TeF_5[10] and Te–O distances in α- and β-TeO_2,[11] the ionic radius of hexa-coordinate Te(+4) becomes equal to 65 pm.

In the case when the lone pair is a ns^2 pair, the ionic radius is set by the $\langle r_{ns} \rangle$ orbital radius and should, therefore, be big and increase linearly with $\langle r_{ns} \rangle$. If, however, the lone pair is on a hybrid orbital, then r_i should be small and increase linearly with $\langle r_{(n-1)d} \rangle$. From Fig. 2 we can see that r_i is neither a linear function of $\langle r_{ns} \rangle$ nor $\langle r_{(n-1)d} \rangle$. Comparison of data in Figs. 1 and 2 shows that the radius of ions with a lone pair increases with increasing orbital radius, on the average, much faster than the radius of ions without a lone pair. That suggests that with increasing atomic number the lone pair becomes more and more an s^2 pair. From the data in Fig. 2 an important feature of most p block ions with lone pair is the highly negative $r_i - \langle r_{ns} \rangle$ difference (from –30 to –50 pm.). Only for the sixth period ions is the difference either positive (for Tl(+1)) or moderately negative. That means that except for Tl(+1) and, perhaps, the remaining sixth period ions, the ionic radius is certainly not set by the *ns* subshell. That is because from the data in Fig. 1 the ionic radius is, as a rule, greater than the radius of the outermost shell in the ion. The only exceptions are heavy ions with high formal charge of 4+ and 5+. On the other hand, the data in Fig. 2 show that the difference $r_i - \langle r_{(n-1)d} \rangle$ or $r_i - \langle r_{(n-1)p} \rangle$ (the latter for the third period elements) is always positive, which suggests that the radius of ions with the lone pair is mainly set by the d or p shell. All these data lead to the following conclusions:

—The lone pair is mainly a hybrid pair, except for the sixth period elements.

—Down each group the lone pair becomes more and more an s^2 pair.

To study the change in the character of the lone pair in more detail, the difference $r_i - \langle r_{(n-1)d} \rangle$ or $r_i - \langle r_{(n-1)p} \rangle$ (the latter for the third period elements) was plotted as a function of the period number, Fig. 3. It can be

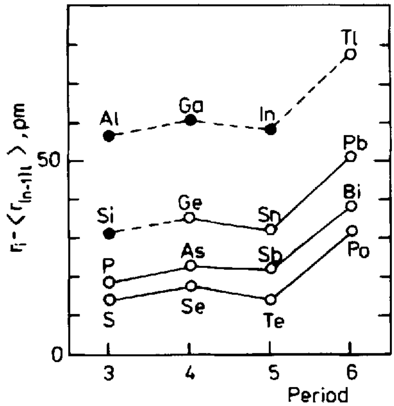

FIGURE 3 Variation in the difference $r_i - \langle r_{(n-1)l} \rangle$. The oxidation state is two less than the group number. Full circles denote values estimated from the sawtooth behavior.

seen in Fig. 3 that in each period the difference $r_i - \langle r_{(n-1)l} \rangle$ decreases with increasing atomic number, that is, with increasing formal charge of the ion. The reason is probably the same as in the case of ions without a lone pair, where the increase in the formal charge of the cation decreases the difference between the ionic radius and the radius of the outermost shell in the ion. More interesting are, however, changes in the difference $r_i - \langle r_{(n-1)l} \rangle$ across each group. Provided the character of the lone pair does not change within a given group, the difference between the ionic and orbital radius should slightly decrease with increasing period number. That is because from plots in Fig. 1 the ionic radius increases slightly more slowely than the corresponding orbital radius (the slopes of the r_i vs. $\langle r_{nl} \rangle$ plots are less than one). It can be seen in Fig. 3 that the difference $r_i - \langle r_{(n-1)l} \rangle$ decreases (slightly) only between the fourth and fifth periods, while it increases between the third and fourth and, in particular, between the fifth and sixth periods, exhibiting sawtooth behavior. Thus, plots in Fig. 3 and the left-hand plots in Fig. 2 suggest that between the fifth and sixth periods and, to some extent, between the third and fourth periods, the lone pair acquires the character of an s^2 pair, while it remains unchanged between the fourth and fifth periods. Sawtooth behavior or the so-called secondary periodicity with respect to stability of oxidation states of *p*-block elements has been known for a long time and can be exemplified by the tendency of N, As and Bi to be trivalent while P and Sb are mainly pentavalent (see Ref. 12 and references therein). Secondary periodicity in oxidation states appears to be produced by the combined effect of filling the 3*d* and 4*f* shells and by the relativistic effect.[12] Secondary periodicity in ionic radii, suggested by the data in Fig. 3, may have the same origin and can be explained by considering the difference in orbital energies, $\epsilon_{np} - \epsilon_{ns}$. The smaller this difference the smaller the promotion energy, and formation of hybrid orbitals involving *ns*, *np*, and possibly also *nd* orbitals becomes easier. Once hybrid orbitals are formed, the lone pair occupies one of them and the radius of the ion becomes smaller. That is because the ionic radius is then fixed by the small radius of the inner $(n-1)d$ orbital (the $(n-1)p$ orbital for first row elements) instead of the large radius of the outer *ns* orbital. Figure 4 shows variations in $\epsilon_{np} - \epsilon_{ns}$ for group 13–16 elements as a function of the period number. The orbital energies were taken from Ref. 6. One can see in Fig. 4 that down each group the difference $\epsilon_{np} - \epsilon_{ns}$ exhibits a well-marked sawtooth behavior. There is a similarity between plots in Figs. 4 and 3: high and low values of $\epsilon_{ns} - \epsilon_{np}$ correspond to high

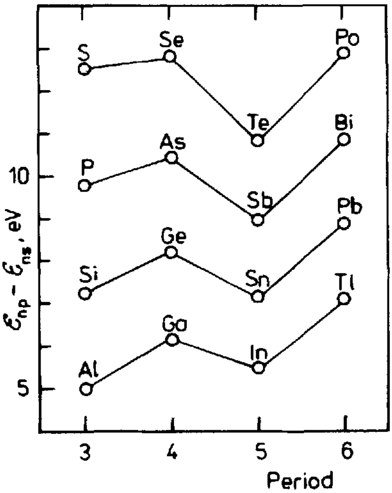

FIGURE 4 Variation in the difference $\epsilon_{np} - \epsilon_{ns}$.

and low values of $r_i - \langle r_{(n-1)d} \rangle$, although the minimum for the fifth period elements is much more distinct for the differences in energies than in radii. The reason for the sawtooth pattern in the $\epsilon_{np} - \epsilon_{ns}$ difference is that filling the $3d$ and the $4f$ shells and the relativistic effect decrease the orbital energy of the s electrons much more than the orbital energy of the more outer p electrons.

Therefore, the sawtooth changes in the difference $r_i - \langle r_{(n-1)l} \rangle$ can be explained by assuming that, except for sixth period elements, the lone pair always occupies a hybrid orbital. Changes in the difference, $\epsilon_{np} - \epsilon_{ns}$, i.e., in the promotion energy necessary for hybridization and subsequent bond formation, affect the bond energy. Weaker or stronger bonding means, in turn, longer or shorter distance between the central ion and the counter-ion, i.e., greater or smaller difference $r_i - \langle r_{(n-1)l} \rangle$.

It should be noted that changes in the character of the lone pair found in this study refer only to compounds which were used by Shannon in his estimation of the ionic radii. There is ample evidence that the character of the lone pair depends on the counter-ion in the lattice or ligand in the complex.[11,13] For example, long Pb–X distances in PbF_2 and $PbCl_2$ (255 and 298 pm, respectively[14]) suggest that in these compounds the lone pair is an s^2 pair, while in PbO where the Pb–O distance is only 230 pm and the bond arrangement is square pyramidal, the lone pair occupies the remaining bond position.[5]

Plots in Fig. 3 allow us to estimate the ionic radii in six-coordination of Al(+1), Ga(+1), In(+1), and Si(+2), provided group 13 elements and Si in lower oxidation state exhibit the sawtooth pattern. The estimate was performed by drawing lines parallel to average changes between the periods and starting from the data point for Tl (for In, Ga and Al) and from the data point for Ge (for Si). The differences $r_i - \langle r_{nl} \rangle$ and the respective ionic radii estimated from the sawtooth pattern are shown as filled circles in Fig. 3 and in the left-hand plot in Fig. 2. Except for Tl, only a few solid compounds of group 13 elements in the oxidation state +1 are known, which renders difficult comparison of predicted with experimental radii. In the recently obtained donor-stabilized AlBr,[15] there appears to be no lone pair. Instead, the two 3*s* electrons participate in two Al–Al bonds which are present in the tetrameric $(AlBrNEt_3)_4$ molecule. The Al–Br distance is short (242 pm), which means that it depends on the 2*p* and not on the 3*s* orbital radius of Al(+1). That is in qualitative agreement with the sawtooth behavior. From the Ga(I)–Cl distance in $Ga^{I}[Ga^{III}Cl_4]$[16] the Ga(+1) radius is about 135 pm, i.e., much higher than that expected from the sawtooth behavior. However, it should be noted that in this compound the Ga(+1) ion has eight nearest Cl neighbours from surrounding strongly bonded $GaCl_4^-$ groups, so that the Ga(I)–Cl interactions are probably weak. Weak interaction favors the s^2 character of the lone pair, because hybridization requires promotion energy which must be compensated by a strong metal-to-ligand bond. Therefore, in this mixed valence compound of Ga, the radius of Ga(+1) may indeed be determined by the $\langle r_{4s} \rangle$ orbital radius. Another explanation for the long Ga(I)–Cl distance is that it bears no relation to the sum of the radii, owing to the contacts of Cl with Cl.[16] From the In(I)–Cl distance in InCl[14] the ionic radius of In(+1) becomes equal to 134 pm, which suggests that the lone pair occupies the 5*s* orbital, again at variance with the sawtooth pattern. On the other hand it should be noted that the difference between the enthalpy of hydration of the In^+ and Tl^+ ions is equal to that of the Na^+ and K^+ ions.[17] That suggests that in the aqua-ions the radius of In^+ is by about 36 pm smaller than that of Tl^+. This difference is in good agreement with that estimated from the sawtooth pattern (see Fig. 2) and is evidence for the s^2 character of the lone pair in hydrated Tl^+ and mainly hybrid character in hydrated In^+.

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