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The Stereochemical Character of s^2 Lone Pair in Bi^{3+} Aqua Cation

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The inert pair effect is characteristic for the *p* block elements. Lone electron pair can either be an s^2 pair or occupy one of the hybrid orbitals. In the case, when the lone pair is a ns^2 pair, the ionic radius is large since it is determined by outermost n*s* orbital. Down each group of the periodic table the lone pair becomes more and more an s^2 pair [1]. The ionic radius strongly decreases, when the pair enters a hybrid orbital and becomes stereochemically active. There is ample evidence, that the character of the lone pair depends on the ligand in the complex. In the case of Bi^{3+} in fluorides and oxides, the lone pair is inactive [2], while in other complexes, *e.g.* chlorides, bromides [3] or tropolonates [4], $6s^2$ pair occupies the hybrid orbital. Stereochemical character of $6s^2$ pair depends on the stability of the complexes formed. In chlorides, bromides and tropolonates, high promotion energy for hybridization is compensated by formation of strong complexes and $6s^2$ pair occupies one of the hybrid orbitals. The complexes with fluorides and oxides are weaker and the $6s^2$ pair remains on unhybridized orbital.

Due to high tendency for polymerization in perchlorate aqueous solutions, such species as $Bi_6O_6^{6+}$, $Bi_6(OH)_{12}^{6+}$, $Bi_6O_6(OH)_3^{3+}$ and $Bi_6O_4(OH)_4^{6+}$ are formed as a result of association and hydrolysis [5,6]. The mean Bi–O bond distances in $Bi_6O_4(OH)_4^{6+}$ were determined to be 215.4 pm (bridging oxide) and 240.2 pm (hydroxide group) [6]. From these data it is difficult to conclude about stereochemical character of the lone $6s^2$ pair in the hydrated cation. Short distance would indicate that it is active, while long distance – nonactive. Because the simple mononuclear aqua cation $Bi(H_2O)_m^{3+}$ exists only in diluted bismuth solutions, determination of Bi–O bond distance in $Bi(H_2O)_m^{3+}$ by X-ray structural methods is very difficult. However, Suganuma, Ono and Hataye [7] using ^{210}Bi radiotracer found only mononuclear complexes: $Bi(H_2O)_m^{3+}$, $Bi(OH)_n(H_2O)_{m-n}^{(3-n)+}$ in $(Na,H)ClO_4$ aqueous solutions for ultratrace concentrations of Bi^{3+}. Radioisotope methods with ^{212}Bi, which have been applied in our studies, permit to study extremely diluted Bi^{3+} aqueous solutions in concentrations

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down to 10^{-15}–10^{-16} mol dm^{-3}. Under these conditions, the probability of collisions between Bi^{3+} ions is negligible and, therefore, they do not exist in any polynuclear forms. The aim of our studies was to explain the character of 6s^2 lone pair in the mononuclear aqua complexes of Bi^{3+} using the radiotracer technique. The ^{212}Bi ($T_{1/2}$ = 60 min) was obtained from ^{232}U as one of the decay products. Separation of ^{212}Bi from ^{232}U and other decay products was performed in a two-step procedure. In the first step ^{224}Ra was eluted by 0.1 mol dm^{-3} HNO$_3$ from HDEHP-teflon column loaded by ^{232}U. In the second step ^{212}Bi was separated from ^{224}Ra on a cation exchange resin by elution with 0.1 mol dm^{-3} HCl solution. The eluted BiCl$_4^-$ complex has been decomposed with a small volume of concentrated HClO$_4$, evaporated and dissolved in 2 mol dm^{-3} HClO$_4$. The ion exchange method with strong acidic cation exchange resin was used for the estimation of the ionic radius of Bi^{3+} in Bi(H$_2$O)$_m^{3+}$. For cations of the same charge, it has been found that distribution coefficients (K$_d$) are inversely proportional to the radius of hydrated cations [8]. By this method ionic radii of elements, which exist only in trace level (Fr$^+$, Md^{2+}, No^{2+}), were determined [9,10]. Using batch technique, K$_d$ of Bi^{3+} and other trivalent cations like Nd^{3+}, Ho^{3+}, La^{3+}, Lu^{3+} and Y^{3+} have been determined in 2 mol dm^{-3} HClO$_4$ solution. Fig. 1 presents plots of the K$_d$ as a function of the outermost shell radii in the M^{3+} cation. The shell radii are the expected orbital radii $< r_{nl} >$ calculated by Desclaux [11]. The nl subscript denotes the outermost completely filled shell in the cation. Two hypothetical cases have been considered, when 6s^2 lone pair of Bi^{3+} is stereochemically inactive (6s^2 outermost shell) or

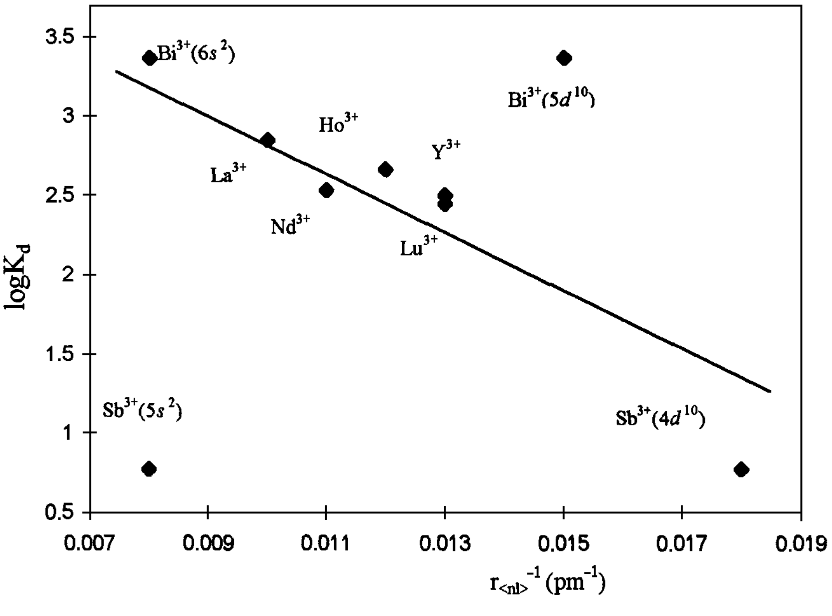

Figure 1. The distribution coefficient of 3+ cations on strong acidic resin Dowex 50×4 as a function of the radius of the outermost shell. In the case of Bi^{3+} and Sb^{3+} ns^2 and (n-1)d^{10} outermost orbital are taken into account. K$_d$ values are determined in 2 mol dm^{-3} HClO$_4$ solution.

occupies the hybrid orbital and is stereochemically active ($5d^{10}$ outermost shell). For comparison, the distribution coefficient of Sb^{3+} (using ^{125}Sb radiotracer), which is a Bi^{3+} homologue in the group 15, was determined.

As shown in Fig. 1 the K_d value for Bi^{3+} fits well the straight line observed for trivalent cations only when $6s^2$ shell radius is considered. In the case of Sb^{3+}, K_d value is much smaller and fits the line only when $4d^{10}$ not $5s^2$ is considered. The studies have shown that the lone pair in Bi^{3+} aqua ions is stereochemically inactive and ionic radius is large. In the case of Sb^{3+} aqua ion, lone s^2 pair occupies the hybrid orbital and is stereochemically active. Our conclusions have recently been confirmed by large angle X-ray scattering (LAXS) determination of Bi–O distances in a high concentrated solution of $HClO_4$ [12]. According to this information, such a solution consists mainly of unhydrolyzed Bi(III) cations.

The lone s^2 electron pair in group 15 behaves similarly to that in groups 13 and 14. It is easy to deduce from crystallographic data and enthalpy hydration values, that in Tl^+ and Pb^{2+} aqua ions $6s^2$ pair is stereochemically inactive and for their homologues in 5th period – In^+ and Sn^{2+} lone $5s^2$ pair is active and occupies the hybrid orbital.

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