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THEORETICAL CONSIDERATION OF THE
GEOMETRICAL STRUCTURE OF THE URANIUM HALIDES

ABSTRACT

The geometrical structure of the uranium halides has been studied from a theoretical viewpoint. This theoretical consideration tends to indicate that pentavalent uranium halides are geometrically but not energetically capable of existence except as double halide compounds of hexavalent and tetravalent uranium.

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THEORETICAL CONSIDERATION OF THE GEOMETRICAL
STRUCTURE OF THE URANIUM HALIDES

INTRODUCTION

The dearth of uranium compounds in which uranium exhibits an apparent valence of +5 tends to cast suspicion upon the correctness of the views presently held concerning the structure of uranium pentachloride and pentafluoride. Although repeated attempts have been made to prepare uranium pentabromide, these endeavours have failed, thus indicating that the pentabromide does not readily exist under ordinary conditions.~Disregarding the energetics of these compounds for a moment, it would appear from a pure structural viewpoint that uranium pentabromide is as likely to exist as uranium hexachloride, but the latter compound is known, whereas the former substance apparently does not exist. Hence, the inherent energetics of the uranium atom may be the factor which prevents the formation of the pentabromide.

Since the energetics of the pentachloride should be concordant with the energetics of the pentabromide, the pentachloride itself may be incapable of existence, and the compound now known as UCl_5 may in reality be a double compound of UCl_6 and UCl_4 , and UF_5 may be a double compound of UF_6 and UF_4 . Hence, UBr_5 would then be a double compound of UBr_6 and UBr_4 , but the question now arises as to whether or not UBr_6 is a sound structural possibility. On this basis, UBr_5 can not exist unless UBr_6 exists. Calculations of the ionic radii of the atoms of these various compounds and their resulting geometry should give an indication as to whether or not UBr_6 is a sound structural possibility.

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THEORETICAL DISCUSSION

If the halides are treated as ionic spheres grouped around a central, ionic uranium sphere, the geometry of the various resulting compounds can be readily studied, providing that the radii of both the halogen and uranium spheres are known. It can be shown geometrically⁽¹⁾ that the limiting ratio of the cationic to anionic radii is 0.15, 0.22, 0.414, and 0.73 for cationic coordination numbers of 3, 4, 6 and 8 respectively. The ionic radii of the halogens and of tetravalent uranium have been established⁽²⁾ but the radii of so-called pentavalent and of hexavalent uranium do not seem to be readily obtainable. However, values for these latter radii can be estimated in the following manner.

The radius of U^{+4} is given as $1.05 \text{ \AA}$ and the removal of one electron to form U^{+5} would decrease the original ionic radius; the removal of another electron would decrease the radius even further. For example, to go from Fe^{+2} to Fe^{+3} , Co^{+2} to Co^{+3} , Ce^{+3} to Ce^{+4} , Mn^{+2} to Mn^{+4} , Tl^{+1} to Tl^{+3} , Pb^{+2} to Pb^{+4} , a decrease in the original radius occurs to the extent of 16.2, 16.6, 19.4, 37.3, 29.5 and 40.6 per cent respectively. These figures represent a 15 to 20 per cent decrease when one electron is removed and a 30 to 40 per cent decrease when two electrons are lost.

Since there is some evidence for uranium being the third member of a second rare earth series, three of its six valent electrons would exist in an inner and incomplete electron shell. Hence, the removal of one or two electrons from the U^{+4} ion should result in a minimum decrease in the ionic radius, for contraction of the resulting ionic spheres should tend

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to be held to a minimum. On this basis, an approximate 15% decrease in the radius of U^{+4} may occur when one electron is removed, and an approximate 30% decrease in the original radius may occur when two electrons are removed from U^{+4} . The radii for U^{+5} and U^{+6} would then be approximately $0.88 \text{ \AA}$ and $0.74 \text{ \AA}$.

The values given by Pauling⁽²⁾ for the ionic radii of fluorine, chlorine, bromine and iodine are 1.33, 1.80, 1.96 and $2.20 \text{ \AA}$ respectively. Hence, the respective ratios of U^{+6} radius to halide radius are, $\frac{0.74}{1.33}$, $\frac{0.74}{1.80}$, $\frac{0.74}{1.96}$, and $\frac{0.74}{2.20}$ or 0.556, 0.411, 0.377 and 0.336. Since the limiting ratio of cationic and anionic radii is 0.414 for a coordination number of six, it is readily seen that on this basis, UF_6 can exist with ease, UCl_6 can barely exist but should not be an extremely stable compound, and UBr_6 and UI_6 can not exist at all.

Since the limiting cationic to anionic ratios for coordination numbers of 3, 4, 6 and 8 are based upon the anionic spheres being arranged symmetrically around the cationic sphere, no limiting ratio of these radii can be obtained in this way for a coordination number of five since a symmetrical five planar model is physically impossible to achieve. However, an upper limit value can be assigned to the limiting ratio of cationic and anionic radii for cations with a coordination number of five; this upper limit would be the limiting ratio value for a coordination number of six. In other words, if six anions can be grouped symmetrically around a cation, it is evident geometrically that five of these same anions can be grouped unsymmetrically around the cation. The ratio value, 0.414, can thus be taken as an upper limit for a coordination number of five. Using $0.88 \text{ \AA}$

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for the radius of U^{+5} , the following ratios are obtained for UF_5 , UCl_5 , UBr_5 and UI_5 respectively, 0.661, 0.488, 0.449 and 0.363. Hence, it is seen that UF_5 , UCl_5 and UBr_5 could exist readily from this geometrical viewpoint whereas the existence of UI_5 would be problematical.

Upon superficial examination it appears that the use of ionic radii, instead of atomic radii, in these calculations is not valid, particularly in the case of UCl_5 and UF_5 . These hexavalent compounds exhibit covalent characteristics such as low melting and boiling points and hence can hardly be represented as ionic substances. However, the multivalent uranium chlorides are good examples of Fajans' statement that electrovalency and covalency should be regarded as limiting types between which it is possible to have a series of transitional forms into which many known substances can be fitted.

The U^{+3} compounds can be regarded as largely ionic in character, having high melting and boiling points whereas the transition from UCl_3 to UCl_4 makes the resulting compound relatively more covalent but not sufficiently so that the tetrachloride can be classified wholly as a covalent compound. The transition from U^{+4} to U^{+6} compounds results in an even more dramatic change and UCl_6 and UF_6 are usually regarded as being covalent compounds. These properties can be explained in the following manner, using the chlorination of uranium as a typical example.

If uranium hydride is treated with anhydrous hydrogen chloride, three chlorine atoms can each remove an electron from the uranium atom forming $U^{+3}Cl_3$. Now, the positive uranium ion will tend to attract the electron shells and repel the nuclei of the negative chloride ions which action will tend to deform the anionic structures. Although the negative chloride ions will have a similar but opposite action on the uranium cation,

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the effect will be much less pronounced since the net positive charge on the cation holds its electrons more firmly in their respective orbits than can the net negative charge of the anion. Thus, the distortion of the positive uranium ion by the chloride ions can be neglected in comparison with the much greater distortion of the anion by the cation. When $U^{+3}Cl_3$ is chlorinated to $U^{+4}Cl_4$, the uranium cation is decreased in size and increased in charge; these two factors will both tend to make the field near the cation more intense and hence will tend to increase the deformation of the anions surrounding it. The conversion of U^{+4} to U^{+6} will cause an even greater decrease in size and increase in charge of the uranium cation. Hence, the field near the U^{+6} ion will be immensely more intense than that near a U^{+4} ion, and, consequently, the deformation of the halide ions will be much more extensive.

This deformation of the anion by the uranium cation will cause a reduction in polarity since a reduction in the dipole moment of the ion-pairs will result if the electrons of both anions and cation tend to drift toward the cation. Therefore, the greater the deformation, the more the resulting bond will approximate a covalency. Thus, it is not surprising that covalent properties are exhibited by uranium compounds in the order of their increasing valence.

A good example of a transition from electrovalency to covalency is demonstrated by an analysis of the difference in properties of stannous and stannic chloride. The melting point of $SnCl_2$ is approximately 247° and the boiling point is 623° whereas the melting and boiling points of $SnCl_4$ are -30° and 114° respectively. Since the Sn^{+4} ion has a greater positive charge and a smaller ionic radius than the Sn^{+2} ion, the field surrounding the tetravalent ion is much more intense, and a more extensive deformation of

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the chloride ions will result. Hence, SnCl_4 is not only more covalent than SnCl_2 , but its covalent properties are similar in many ways to the non-polar characteristics of CCl_4 which latter substance is usually regarded as a typical covalent compound.

CONCLUSIONS

Although geometrical evidence for the existence of UR_5 can be presented, the compound itself has not been prepared, and it appears that the energetics of this compound precludes its formation. In fact, the energetics of all pentavalent uranium compounds may preclude their formation, and the compounds now known as UF_5 and UCl_5 may very well be double compounds of their respective hexavalent and tetravalent halides. The pentabromide would not be able to exist as a double bromide compound since the hexavalent bromide itself does not appear to be capable of existence geometrically although its existence is very feasible from an energetic viewpoint.

Hence, the possibility of so-called UCl_5 being a double chloride compound was investigated in this laboratory, and spectrophotometric and other evidence has been obtained, which shows that the pentachloride compound does exist in reality as a double compound of uranium hexachloride and uranium tetrachloride. This experimental evidence will be the subject of several papers soon to be issued from this laboratory.

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