ACTA CHEMICA SCANDINAVICA 10 (1956) 723—726

The Stability of Metal Halide Complexes in Aqueous Solution

I. The Stability of Metal Halide Complexes in Relation to the Position of the Metal in the Periodic System

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With respect to the strength of their halide complexes central ions may be divided into two groups. The first group shows decreasing stability in the order $F^- \gg Cl^- > Br^- > I^-$, the second one in the reversed order $F^- \ll Cl^- < Br^- < I^-$. The extension of the two groups within the Periodic System is discussed.

As pointed out previously by Ahrland and Larsson [1] central ions may be divided into two distinct groups with respect to their ability to form halide complexes. The ions of the first group form fluoride complexes which are much stronger than the complexes formed with the heavier halide ions. The strength of these decreases in the order $Cl^- > Br^- > I^-$. On the contrary, the ions of the second group form fluoride complexes which are much weaker than the complexes formed with the heavier halide ions. Moreover the strength of these always increases in the order $Cl^- < Br^- < I^-$.

The strength of the halide complexes is thus completely reversed between the two groups. In both cases however, the complexity varies monotonicly with the atomic number of the halogen and there is moreover always a difference in the order of magnitude between the complexity of the fluoride and that of the other halide ions.

The first group is the more numerous one. It certainly contains * H^+, Ce^{3+}, U^{4+}, UO_2^{2+}, Zr^{4+}, Fe^{3+}, and In^{3+}, most probably also Be^{2+}, Th^{4+}, Pu^{4+}, Cu^{2+}, Zn^{2+}, Al^{3+}, and Sn^{2+}. In the latter cases many desirable data are admittedly still lacking but the trend nevertheless seems obvious. In the case of Be^{2+} and Al^{3+} where only the fluoride systems have been quantitatively measured supplementary evidence is provided by the fact that the chlorides [9, 10, p. 573] are typical strong electrolytes, quite unlike the fluorides. This is also the case for aluminium bromide [11].

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* A very comprehensive list of references has been compiled by Carleson and Irving [2]. Further references: U^{4+}, see [3]; Be^{2+}, see[4]; Pu^{4+}, see [5,6]; Hg^{2+}, see [7]; Pb^{2+}, see [8].

The less numerous second group certainly contains Pt(II), Cu^+, Ag^+, Cd^{2+}, Hg^{2+} and Pb^{2+}. The complexes of Pt(II) are as a rule inert and their equilibria therefore difficult to measure. In the olefin complexes however, the bond *trans* to the olefin position becomes labilised [12] and measurements of equilibria involving this ligand are therefore feasible, as shown by Leden and Chatt [13]. These measurements prove definitely that Pt(II) belongs to the second group and this could also be expected from preparative data known previously. Thus Pt(II) forms very stable chloro and bromo salts while the corresponding fluoro compounds do not even seem to exist [14]. For Pb^{2+}, the order $Cl^- < Br^-$ has recently also been confirmed by ion exchange measurements [15].

Most probably Pd(II), Pd(IV), Pt(IV), Au(III), and Tl^{3+} also belong to the second group. For Pd(II), Pd(IV) and Au(III) this conclusion is based on preparative data similar to those quoted for Pt(II) above (*cf.*[16,17] and references quoted therein). For Pt(IV), semi-quantitative measurements of Schlesinger and Palmateer [18] unequivocally indicate the second group order $Cl^- < Br^- < I^-$ of complex stability.

Now the striking fact is that all the central ions of the second group are derived from neighbouring elements around the end of the transition series. Moreover these elements seem to form a roughly triangular figure with the apex at Cu and the base stretching from somewhere to the left of Pt to the right of Pb.

The right borderline of the triangle seems fairly well established. It certainly runs between the pairs Cu—Zn, Zn—Cd, Cd—In, In—Tl, and Sn—Pb; only the last part of its course is still unknown.

On the other hand the left borderline is only roughly known at present. Fe is definitely outside the triangle and there is no doubt that the border runs between Cu and Ni, as the heavy halides of Ni^{2+} are typical strong electrolytes. Thus the activity coefficients of nickel chloride resemble those of barium and calcium chlorides [10, p. 423] and the absorption spectrum of the solution is practically identical with that of nickel perchlorate [19], both solutions evidently containing the same absorbing species, Ni^{2+}. Thus Cu^+ is the only central ion of the 4th period belonging to the second group, and the triangular area has an apex at copper. Unlike Cu^+, Cu^{2+} belongs to the first group. Copper is the only element where different valency states have been found to belong to different groups. It would be interesting if a method of investigating halide complexes of Ag(II) could be found, to see whether silver behaved analogous to copper in this respect. As to the further course of the left borderline, it may be supposed that the remaining platinum metals are also inside the triangle on account of their resemblance to Pd and Pt. However, it is not known at present if there is a further extension to the left of the second group area. The known facts are that Zr^{4+} and Ce^{3+} (and certainly the other lanthanides as well) are outside it, as are also the actinides of the 7th period.

The relative strength of the halide complexes of central ions belonging to the first group, outside the triangle, is just the one which would be expected if the complex formation is due to essentially electrostatic forces. In such a case strong bonds should be formed by ligands combining slight polarizability with small ionic radius. These quantities both decrease monotonicly from

I^- to F^-, but F^- occupies a unique position as the differences between F^- and Cl^- are much greater than those between the heavy halides. Therefore the sequence of halide complexity should be $F^- \gg Cl^- > Br^- > I^-$ as is also found for the first group.

The strength of the complex formation will also depend upon the central ion, and strong electrostatic bonds should be formed by central ions of high ionic charge and small radius. As pointed out by Connick and Tsao[20] the strength of the fluoride complexes just follow this pattern thus indicating their essentially electrostatic character.

The reversal of the relative strength of the halide complexes for the central ions within the triangle has been explained by Leden and Chatt[13] as being due to a formation of partial double bonds of an essentially covalent character between the metal ion and the heavy halide donor. In their penultimate shells, the elements at the end of the transition series have filled d-orbitals of an energy close to that of the ordinary valency hybrids. These orbitals might therefore be incorporated in the bond system of the complex provided the ligand is able to accomodate the extra bonding electrons thus offered. The three heavier halides have vacant d-orbitals in their outer shells and are therefore able to participate in a double bond while the fluoride ions has no such orbitals and thus cannot form any double bond. If the strength of the complexes is determined by a covalent double bond formation, the fluoride complexes should therefore be much weaker than those of the heavier halide ions. The order between these will be determined by their donating properties, which show a smooth increase from Cl^- to I^-. The expected order will therefore be $F^- \ll Cl^- < Br^- < I^-$, or just the one found within the second group.

Leden and Chatt[13] also point out that those metals which show a strong complexity of the chloride relative to the fluoride are also characterized by the much greater stability of thio-ether complexes relative to ether complexes, and trialkylphosphine complexes relative to trialkylamine complexes. In these cases too the formation of strong complexes might be attributed to the formation of double bonds with those ligands which possess vacant d-orbitals in their outer shells.

The existence of multiple metal to ligand bonds involving d-orbitals of the metal was first postulated by Pauling[21] in order to account for the remarkable stability of carbonyl, nitrosyl and cyano complexes of the later transition metals. In these cases it was assumed that the additional bonding electrons are accommodated in the ligand by means of an electronic rearrangement leading to a decrease in bond order of the internal ligand bond. Later Dewar[22] and Chatt[23, 24] have explained the formation of olefin complexes along similar lines. In all those cases there is also strong physical evidence (from measurements of bond lengths and infrared stretching frequencies) that the bonds of the complexes are really of the orders postulated by the multiple bond theory. Evidence of that kind is admittedly still lacking for the halide complexes.

Measurements on further halide systems are now in progress in order to see whether they all fit into the above scheme. In the first hand systems on the supposed borderlines are being investigated as they will give the information required about the exact extension of the triangular area. Such systems will possibly also show some interesting transitional properties.

This work is part of an investigation supported by *Statens naturvetenskapliga forskningsråd (Swedish Natural Science Research Council)*. My thanks are due to Dr. J. Chatt, Dr. Sture Fronæus, Dr. Ido Leden and Dr. F. J. C. Rossotti for interesting discussions and useful comments.

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Received February 13, 1956.