THE CLASSIFICATION OF COMPLEX FORMERS AND ADDENDS ON THE BASIS OF THEIR ENERGY CHARACTERISTICS

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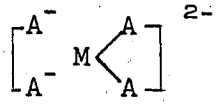
In order to judge the stability of complex ions, it is most expedient to review the process of formation of a gaseous complex ion from its constituent gas particles:

$$M^{z+}_{(g)} + nA_{(g)} = [MAn]_{(g)} + W, \qquad (1)$$

where M^{z+} is the central ion, A is the addend, and [MAn] is the complex ion. The change in energy during this process (W) we shall call "the energy of addition".

For complex ions with the predominant ionic type containing a chemical bond (aquo ions, complex fluorides, etc.), the energy of addition may be evaluated by means of the well-known equations of Kossel and Magnus. The value of W is determined in this case fundamentally by the electrostatic characteristics of the central ion and the addends (by the charges and radii of the ions, and for molecules, by the dipole moments).

In the case of complex ions with a covalent bond predominating (donor-acceptor) the energy of addition is not directly related to the electrostatic characteristics of the central ion and the addends. In order to evaluate the energy of addition in this case, we shall take as an example the formation of a complex ion with the structure:



according to the scheme above (1), we can break down the process into several steps:

$$M^{2+}_{(g)} + 2\underline{e} = M_{(g)} + I, \qquad (2)$$

$$2A_{(g)} = 2A_{(g)} + 2\underline{e} - 2E, \qquad (3)$$

$$M_{(g)} + 2A_{(g)} + 2A^-_{(g)} = \left[\begin{matrix} A^- \\ A^- \end{matrix} M \begin{matrix} A \\ A \end{matrix}\right]^{2-}_{(g)} + 2D_{M-A} + U \qquad (4)$$

Thus, for the energy of addition we obtain the following equation:

$$W\underline{c} = I - 2\underline{e} + 2D_{M-A} + U, \qquad (I)$$

where I is the total ionization potential, E is the electron affinity of the group A, D_{M-A} is the energy of the covalent bond M – A, and U is the resonance energy of the structure under consideration.

Generalizing Equation (1) for any covalent structure, we obtain:

$$Wc = I - nE + nD_{M-A} + U, \qquad (II)$$

where n is the total number of donor-acceptor bonds in the complex ion.

The overall ionization potential of the central ion and the electronic affinity of the addend are decisive and make possible the quantitative calculation of the values involved in the formation of complex ions with predominantly covalent bonds.

There is also a very broad group of complex ions in which the essential role is played by the resonance of the ionic and covalent structures. The resonance energy attains a maximum value in the case where the energies of addition for the ionic and covalent structures are equal.*

Working on this hypothesis, we can make a classification of complex ions and addends on the basis of their energy characteristics, and come close to an explanation of the phenomenon of selectivity during complex-formation. This phenomenon is pointed out by Grinberg, who payed attention to the fact that there is a definite relation between the nature of the complex-former and the addend, and that therefore it is impossible to speak about a tendency to complex-formation in general, without paying attention to the specific nature of the central atoms and the addends. Lebedinsky has indicated the possibility of dividing complex-formers into three groups, according to their tendency to form complexes with addends containing oxygen, nitrogen, and sulfur.

For the formation of a stable complex ion with a predominantly ionic bond, it is necessary not only that the central ion have a high charge and a small radius, but also that the addend have strong electrostatic characteristics (large charge and small radius, or considerable dipole moment). If at the same time the central ion is characterized by a comparatively low ionization potential, then it cannot form stable covalent complexes. Completely analogous are those addends which are characterized by a great electron affinity, and have no tendency to form stable covalent complexes. Thus, we can designate a group of central ions and of addends which we shall arbitrarily call "electrostatic". In this group we can place the ions with the outer shells of the inert gases, characterized by high charges and small radii (Be^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, etc.). The corresponding addends will be F^-, H_2O, and in some cases CO_3^{2-}.

The central ions with high ionization potentials, but a low electrostatic characteristic, form stable complexes only with addends which have low electron affinities, as it follows from equation (II) that only when both these conditions are met simultaneously can the energy of addition attain an appreciable value. In this group we must place the ions with a non-inert gas nature of the last periods of the Mendeleev system (Au^+, Hg^{2+}, Pb^{2+}, Bi^{3+}, Tl^+, etc.). The specific

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*Note. Accepting the justified criticism of the so-called "theory" of resonance given by N. D. Sokolov, (prog. chem. 18, 697, (1949)), I consider that the term "resonance energy" in my article is incorrect. In this case we are speaking of the difference between the actual value of the energy of addition and that calculated by the method of additivity. The existence of this difference results from the fact that the actual bond in the ion $[MA]_4^{2-}$ is intermediate between an ionic and a covalent bond, and it also results from the delocalization of the coordinate bonds.

The magnitude of this difference can be evaluated by means of a method of variations.

addends for this group of central ions will be $S_2O_3^{2-}$, I^-, CNS^-, Br^-, CSN_2H_4, etc. In this case, too, the well-known selectivity will be observed, as the formation of stable complex ions with central ions or addends of the first group is improbable because of the low electrostatic characteristic of the particles of the group under consideration. The central ions and the addends of this group we shall arbitrarily call "covalent".

If the central ions are characterized by high ionization potentials and at the same time by large charges and small radii, they can form stable complexes with a large number of addends of different natures, and in particular with addends of both the first and second groups. Central ions of this type may be called "universal complex-formers". Typical representatives of this group are the multiply charged ions of the middle series of the transition groups of the Periodic System (Co^{3+}, Pt^{4+}, Ir^{3+}, Rh^{3+}, Cr^{3+}, Cu^{2+}, etc.).

In a completely similar way, we can also designate a group of "universal addends" which have at the same time both a high electrostatic characteristic and, apparently, a low electron affinity, as for example $C_2O_4^{2-}$, CN^-, $C_4H_4O_6^{2-}$, etc.

Finally, it is possible to have the case where neither electrostatic interaction alone, nor the formation of a donor-acceptor bond leads to a high value of the energy of addition, but as a result of the closeness of the values of the energy of addition for the ionic and covalent structures, a very great resonance energy arises. This sort of case probably exists with the singly-charged and doubly charged central ions of the subgroups of the Periodic System (Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Ag^+, Cu^+, etc.). If the value of the ionization potential is at the same time large, complex-formation can take place with covalent addends as well (for example, for the ions Ag^+, Cu^+, Cd^{2+}, etc.). These "intermediate" addends apparently include the amines, ammonia, NO_2^-, HCO_2^-, etc. These addends can form stable complexes of ions not only with the intermediate central ions but also with the universal complex-formers. A summary of the main groups of complex-formers and addends is given in tabular form.

Name of group	Energy characteristics	Examples of complex formers	Examples of addends
1. Electrostatic complex-formers and addends	High charge, small radius, large dipole moment. Ionization potential comparatively low, electron affinity great.	Al^{3+}, Ti^{4+}, Zi^{4+}, Bi^{2+}, Hg^{2+}	F^-, H_2O, ROH, CO_3^{2-}, SO_4^{2-}
2. Covalent complex-formers and addends	High ionization potential, small electron affinity. Low electrostatic characteristics.	Au^+, Hg^{2+}, Pb^{2+}, Bi^{3+}, Tl^+	$S_2O_3^{2-}$, I^-, CNS^-, Br^-, CSN_2H_4
3. Universal complex-formers and addends	High ionization potential, small electron affinity, high charge, and small ionic radius.	Co^{3+}, Pt^{4+}, Rh^{3+}, Ir^{3+}, Cr^{3+}, Cu^{2+}	$C_2O_4^{2-}$, $C_4H_4O_6^{2-}$, CN^-
4. Intermediate complex-formers and addends.	Average values of all energy characteristics.	Ni^{2+}, Zn^{2+}, CO^{2+}, Fe^{2+}, Ag^+, Cu^+, Cd^{2+}	NH_3, $C_2H_4(NH_2)_2$, NO_2^-, HCO_2^-

This classification is to an obvious degree conditional, in the sense that the boundaries set up between the different groups of complex-formers and addends just like the actual behavior of these or other particles, is determined by the calculated values of their fundamental energy parameters.

The structures given belong to the case where there is formation of gaseous

complex ions from gaseous constituent particles. In the formation of complex ions in solution, it is necessary to take into account in addition the fact that the molecules of solvent may also act as addends, forming complex solvions.

To a first approximation, for a definite group of complex ions, we can limit ourselves to a consideration of the differences between the energies of addition of the solvent molecules and of the given addends to the central ion, as the solvation effects for a given narrow group of complexes remains approximately constant (for example, within the group of ammino compounds, complex chlorides, bromides, iodides, etc.).

In the formation of aquo-complexes, the decisive role is played by ionic dipole forces. In aqueous solutions with different energies of addition, the most stable complexes will be those with large central ions. Therefore, by no means all complex ions with high ionization potentials are capable of giving stable complexes with covalent addends in aqueous solutions. In this case, the most stable complexes will be those in which the central ion has large dimensions (Pb^{2+}, Ag^{+}, Cd^{2+}, etc.) even if the ionization potential of such a central ion is lower than that of certain ions with small radii (for example, the Be^{2+} ion).

The large dipole moment of the H_2O molecules leads to the result that pure electrostatic complexes are seldom encountered in aqueous solutions. We may assume that in solvents with small dipole moments, electrostatic complexes will be characterized by great stability.

SUMMARY

On the basis of a review of energy characteristics, a classification is proposed for complex-forming and addend ions; according to this classification, both these and other particles are divided into four groups: a) electrostatic, b) covalent, c) universal, and d) intermediate (see table). An attempt is made from this point of view to explain the phenomenon of group selectivity during complex-formation and the differences in stability of the complex ions in solutions.

LITERATURE CITED

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