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Abstract

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ON SOME QUESTIONS IN THE THEORY OF EXTRACTION OF INNER-COMPLEX COMPOUNDS

Consideration of a large number of data from the literature and of experimental data obtained in our laboratory makes it possible to put forward a number of considerations on the connection between the extraction of inner-complex compounds (i.c.c.) and the coordination number of the central atom; these considerations concern, in particular, the influence of the nature of the solvent. In the present article the indicated considerations are set forth briefly and, of necessity, schematically; they are treated in greater detail elsewhere*. The extraction of i.c.c. is considered from the standpoint of the coordinative saturation or unsaturation of the central atom.

The formation of an i.c.c. involves the appearance, between the metal ion and each molecule of the organic reagent, of one ionic and one coordination bond. If the coordination number (c.n.) of the metal ion does not exceed its doubled valence, then after formation of the i.c.c. the metal will have no free coordination positions left; if, however, the c.n. is greater than the doubled valence, part of the coordination positions of the central atom will remain free. In this connection all i.c.c. may be divided into two groups: 1) i.c.c. with a coordinatively unsaturated central atom (we shall call them coordinatively unsaturated) and 2) i.c.c. with a coordinatively saturated central atom (coordinatively saturated).

Coordinatively unsaturated i.c.c. If a coordinatively unsaturated i.c.c. is formed in aqueous solution, the free coordination positions of the metal are, in the general case, occupied by water molecules. Thus, for example, Mg forms with 8-hydroxyquinoline a complex in which two water molecules complete the c.n. of magnesium to six. However large and hydrophobic the organic part of the complex may be, compounds of the type under consideration are usually not extracted. They can apparently be made capable of extraction in two ways. The first way is the displacement of water molecules. In our view, water may be displaced by molecules of the organic solvent; by molecules of the organic reagent itself, taken in excess; by molecules of another substance present in the system and capable of coordination; by mutual satisfaction of the coordinative unsaturation by two molecules of the complex (dimerization); and by satisfaction of the coordinative unsaturation at the expense of donor atoms present in the complex molecule (in addition to those already bound to the metal in the formation of the i.c.c.). The second way is the "blocking" of water molecules by molecules of the organic solvent, reagent, etc., through the formation of hydrogen bonds. In the present work we consider only the first way. It should be emphasized at once that the possible mechanisms of water displacement listed above and discussed in greater detail below may be superimposed on one another.

Let there be present in an aqueous solution a coordinatively unsaturated i.c.c., for example calcium oxinate, Ca $(C_9H_6NO)_2 \cdot 2H_2O$. If in the sys–

* Yu. A. Zolotov, I. P. Alimarin, *Collection of Works on Extraction*, Moscow, 1961 (in press).

system there is, in addition, an organic oxygen-containing solvent, then conditions are created for competition between the molecules of this solvent and water molecules for a place in the hydrate-solvate layer around calcium. The competition proceeds the more successfully for the organic solvent, the higher its donor capacity (or the more polar the solvent). A necessary condition for the displacement of water is a sufficiently suitable structure of the solvent molecule, since otherwise steric hindrance makes coordination of the solvent impossible.

If, owing to its high donor capacity (high polarity) and suitable structure, the solvent replaces the water molecules, the compound that is formed, now provided with a still more enlarged organic part and deprived of hydrophilicity, may become capable of dissolving in an excess of the solvent. If, however, the solvent used for dissolution (extraction) of the inner-complex compound, for example C_6H_6 or CCl_4, is nonpolar and its ability to compete with water molecules is very small, there is a very slight probability that the solvent molecules will be able to free the coordination layer of calcium from water molecules, and the hydrated molecule of the inner-complex compound may prove unable to pass into the organic phase*. In this connection one may expect that the distribution coefficients when using low-polar solvents will be lower than for more polar oxygen-containing solvents with a clearly expressed donor capacity. Numerous examples may be cited showing that inner-complex compounds of coordinatively unsaturated ions are, in general, extracted better by oxygen-containing polar solvents than by oxygen-free low-polarity extractants.

In a number of cases the coordinative unsaturation of the central atom may be satisfied by addition of additional neutral molecules of the reagent, with formation, for example, of a compound $Me^{II}R_2 \cdot 2HR$. In this case the excess reagent molecules play the same role as the organic solvent. In this case extraction may take place also when a low-polar, noncoordinating solvent is used. Which molecules exactly—of the solvent (if a coordinating solvent is used) or of the reagent—will occupy a place in the coordination sphere depends, as may be expected, on the ratio of their donor capacities, their structure, and concentration. In a number of cases anionic complexes of the type, for example, $Me^{II}R_3^-$, are formed, which will become capable of being extracted if their charge is compensated by the charge of the extracting cation.

Extraction of coordinatively unsaturated inner-complex compounds may be promoted by additions of foreign substances capable of coordination. Such substances may be, for example, certain coordinating solvents, added in small amounts to an inert solvent in order to improve extraction. They may also be certain other polar substances, for example aliphatic amines (^{1}). Apparently the first to point out this possibility of improving extraction was Dziomko, who, however, attributed to these substances another mechanism of action (^{2}). Systematic work in this direction is being carried out by Umland and co-workers ($^{1,3-8}$). The action of these additives may be twofold. On the one hand, this is the coordination discussed above; on the other hand, in some cases the molecules of the added substances are capable of giving cations, which form extractable salts with the anionic metal complexes. For example, in the presence of *n*-butylamine and an excess of oxine, calcium is extracted in the form $C_4H_9NH_3Ca\,(C_9H_6NO)_3$ (^{4}). At the same time Zn and Cd form simply addition products of *n*-butylamine to a complex of the type $Zn\,(C_9H_6NO)_2 \cdot C_4H_9NH_2$ (coordination) (^{5}).

* It is assumed that the reagent molecule does not contain isolated hydrophilic groupings that hinder its dissolution in organic solvents.

Furthermore, cases are not excluded in which the nonpolar solvent is unable to replace the water molecules at the central atom, other polar substances capable of coordination are absent from the system, and the reagent used cannot be coordinated either for steric reasons or because its concentration is insufficiently high. In this case, the only possibility for satisfying the coordinative unsaturation of the metal remains the formation of bonds between neighboring molecules of the complex, i.e., dimerization of the molecule in the organic phase. The role of "displacers" of water molecules is thus played by the molecules of the inner-complex compound themselves. The bond is then formed between the central atoms and some donor atoms that are part of the neighboring molecule of the complex. In this connection, the possibility of dimerization will be determined to a considerable extent by the structure of the organic reagent.

Finally, a phenomenon often occurs whereby the free coordination sites of the central atom in an inner-complex compound are occupied by donor atoms located in the very molecule of the complex (polydentate reagents). In this case, inner-complex compounds of coordinatively unsaturated ions can also be extracted by noncoordinating, slightly polar solvents, for example CCl_4, C_6H_6, etc., in the absence of an excess of reagent and of foreign coordinating additives. Thus, dithizonates of a number of coordinatively unsaturated ions are extracted by CCl_4. Umland (9) synthesized a tridentate derivative of 8-hydroxyquinoline in order to avoid the addition of amines, which promote the extraction of oxinates of a number of divalent metals. The use of polydentate reagents whose structure permits the formation of several rings is, in our opinion, very promising, especially since the presence of several rings in a complex increases its stability.

Coordinatively saturated inner-complex compounds. Examples of such compounds include aluminum 8-hydroxyquinolinate, gallium pyrocatecholate, the U^{IV} complex with acetylacetone, and Pu^{IV}—with thenoyltrifluoroacetone. The metal ions in these compounds have no free coordination sites and are well shielded by organic ligands. For inner-complex compounds belonging to this group, the nature of the solvent has only a weak effect on extraction. Nevertheless, some influence is present even in this case. We shall point out two circumstances that are important here.

The determining criterion for choosing a solvent in this case is apparently the old rule: "like dissolves like." Since the ligand molecules of the extracted inner-complex compounds usually do not contain hydrophilic groups but are ordinarily simply a hydrocarbon chain or ring, slightly polar hydrocarbons and their halogen-substituted derivatives may prove to be more convenient extractants for the compounds under consideration. Conversely, more hydrophilic and polar solvents containing oxygen will be less suitable. Consideration of intermolecular interactions in the solvent itself leads to the same conclusion. Duyssen (10) noted that well-shielded inner-complex compounds of the type considered are extracted better by nonassociating solvents, between whose molecules only weak van der Waals forces act, as, for example, in benzene or CCl_4. If the interaction between molecules is strengthened by the introduction of a carbonyl or hydroxyl group, extraction deteriorates.

It may be assumed that the extraction of compounds of the type under consideration depends only weakly on an excess of reagent and on additions of other substances, and also that these compounds have little tendency toward dimerization.

For the use of the ideas set forth above for practical purposes, it is necessary to know exactly which ions are capable of exhibiting coordinative unsaturation in inner-complex compounds. In discussing this question, one cannot fail to take into account that the coordination number of an ion in its various compounds does not remain constant. It is possible that the nature of the donor atoms, with

with which the ion combines, and the type of compound formed, exert an influence on the coordination number. Coordination unsaturation may apparently be exhibited by intracomplex compounds of Li^+, Tl^+, NpO^+ and its analogues, of the alkaline-earth elements, Mn^{2+}, Zn^{2+}, Cd^{2+}, UO_2^{2+} and its analogues. Intracomplex compounds of tetravalent elements are coordination-saturated, and apparently also those of trivalent elements, although with regard to the latter this cannot be asserted definitely.

The approach set out above for describing the extraction of intracomplex compounds can apparently be used both for interpreting previously obtained experimental data and for guidance in choosing the solvent and extraction conditions for those intracomplex compounds whose extraction has not been studied. For this it is necessary to estimate *a priori* the properties: 1) of the metal cation—valence and coordination number, sometimes radius, affinity for ordinary donor atoms; 2) of the organic reagent—spatial structure, number and arrangement of donor atoms, presence or absence of hydrophilic groups; 3) of the organic solvent

—presence of donor atoms (oxygen), polarity. On the basis of these data, taking into account the scheme set out in the article, it is possible to make certain predictions about the behavior of the elements.

It seems to us desirable to reconsider, with allowance for the properties of the metal ion, many recommendations made earlier by a number of authors on the use of solvents for extraction of intracomplex compounds of elements. These recommendations were based on the assumption that the nature of the extractant is of no great importance. For example, chloroform was recommended for the extraction of all oxinates without exception. It should be said that chloroform was in general sometimes regarded as a universal solvent for extraction of intracomplex compounds.

The ability of a solvent, displacing water, to coordinate to the central atom should preferably be assessed by some parameter convenient for measurement or easily calculated. For oxygen-containing solvents, the property that is probably of substantial importance for extraction is donor ability. To express it one may use, for example, the "electronegativity" of the oxygen atom. A similar approach for complex-forming solvents was used by Berger ([11]). However, a quantitative expression of the "electronegativity" of oxygen is difficult; it is hard even to compile a corresponding series. It is possible that, as a first approximation, it is better to use another property—the polarity of the solvent. This property is all the more convenient because it makes it possible to consider both oxygen-containing and oxygen-free solvents from a unified standpoint. Parameters suitable in principle for comparing solvents in this case may be the dipole moment, polarizability, dielectric constant, and molar polarization. The last two parameters are apparently the most acceptable, although they too, of course, are not universal.

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CITED LITERATURE

1. F. Umland, W. Hoffmann, *Angew. Chem.*, **68**, 704 (1956).
2. V. Dzíomko, Collection of articles, All-Union Correspondence Polytechnic Institute, issue 4, 1953, p. 44.
3. F. Umland, W. Hoffmann, *Angew. Chem.*, **69**, 396 (1957).
4. F. Umland, K.-U. Meckenstock, *Zs. anal. Chem.*, **165**, 161 (1959).

5. F. Umland, W. Hoffmann, *Zs. anal. Chem.*, **168**, 268 (1959).

6. F. Umland, H. Puchelt, *Anal. chim. acta*, **16**, 334 (1957).

7. F. Umland, W. Hoffman, *Anal. chim. acta*, **17**, 234 (1957).

8. F. Umland, W. Hoffmann, K.-U. Meckenstock, *Zs. anal. Chem.*, **173**, 211 (1960).

9. F. Umland, K.-U. Meckenstock, *Angew. Chem.*, **71**, 373 (1959).

10. D. Dyrssen, *Svensk Kem. Tidskr.*, **68**, 212 (1956).

11. L. L. Burger, *J. Phys. Chem.*, **62**, 590 (1958).

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