CHEMISTRY

1963

SovietRxiv

Abstract

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CHEMISTRY

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ON THE STABILITY OF COMPLEX COMPOUNDS OF TRANSITION METALS

(Presented by Academician I. V. Tananaev on July 11, 1962)

Various attempts are known in the literature to establish regularities linking the stability of complex compounds both with the nature of the metal atom and with the nature of the ligand. For complexes of transition metals there is the Irving—Williams regularity (^{1}) in the variation of instability constants with the atomic number of the element. An explanation of the Irving—Williams regularity in terms of ligand-field theory was given by Yatsimirskii (^{2}). Orgel' s stabilization idea, likewise based on ligand-field theory, makes it possible to explain the variation with atomic number of certain other thermodynamic characteristics of complex compounds: heats of hydration (^{3}), energies of crystal lattices of the coordination type (^{4}), etc. The values of these characteristics depend linearly on the atomic number of the elements for compounds of Ca, Mn(II), and Zn, since the stabilization in a cubic field for these elements is equal to 0 (the numbers of *d*-electrons are respectively 0, 5, and 10). Deviations from linearity are a measure of field stabilization.

The influence of stabilization on instability constants was considered briefly in (^{5}). In the present work we attempt to examine in more detail the question of the relation between the instability constants of complex compounds and the nature of the metal atom among transition metals of the fourth period.

To verify whether the linear dependence of instability constants on the atomic number of the elements for Ca, Mn, and Zn is preserved, we used the tables of Bjerrum and Schwarzenbach (^{6}) and of Yatsimirskii (^{7}). Unfortunately, only for a small number of ligands (about 30) are there sufficiently complete data for many cations, including Ca, Mn(II), and Zn. Analysis of these data showed that, although the indicated linear dependence occurs in many cases (Fig. 1), deviations from it are observed for a large number of ligands, sometimes quite considerable ones (see Fig. 2). The number of these deviations is too large to regard them as accidental. It is also hardly possible to explain them by experimental errors, since the determinations of the instability constants were for the most part carried out by one and the same method, many of them by the same authors, under the same conditions.

Below we give examples of ligands for which the indicated linear dependence was

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

found and for which this dependence is absent, with their numbers according to the tables (^{6}). Of the ligands considered, 13 obey the linear dependence for Ca, Mn, Zn: oxalic acid No. 5, aminoacetic acid No. 20, ethylenediaminetetraacetic acid No. 362, 2-ethoxycarbonylaminoethyliminodiacetic acid No. 325, 2,2′-bis-(dicarboxymethyl)amino-diethyl sulfide No. 998, as well as Nos. 25, 45, 92, 142, 143, 217, 364, 365. In 14 cases deviations from the linear dependence were found. Among them are: 2,2-bis-(dicarboxymethyl)-aminodiethyl ether No. 396, nitrilotriacetic acid No. 209, *N*-2-hydroxyethyliminodiacetic acid No. 215, 8-hydroxyquinoline-5-sulfonic acid No. 328, dibenzoylmethane No. 433, and Nos. 96, 206, 212, 230, 269, 327, 379, 420, 440. It is possible that this difference in the behavior of the ligands is connected with certain features of complex formation, but they are difficult to identify. It is unclear, for example, how one can explain deviations from linearity for one complexone, whereas for another complexone of analogous composition and structure they are not observed. The detection of any regularity for these deviations is further complicated by the fact that they may be both positive and

positive and negative, as is evident from Fig. 1b. From the examples we have given it can be seen that both the preservation of linearity and deviations from it are observed for ligands of related type and for complexes of varying stability, i.e., they do not depend on the ligand field strength. The possible features of complex formation in these cases are characterized by neither very small nor very high values of $\lg K$. At the same time, examples of cobalt(III) ammine or iron(II) *o*-phenanthrolinate show that features of complex formation associated with strengthening of the ligand interaction with metals, leading to the formation of low-spin complexes, are accompanied by a sharp increase in the instability constant of the complex and by a violation of the Irving-Williams regularity. In the examples we have considered, the Irving-Williams regularity is preserved in all cases, regardless of the nature of the ligand. Proceeding from these considerations, it may be assumed that the deviations we have found from the linear course of change of the instability constants with changing atomic number of the elements Ca, Mn(II), Zn indicate the limited applicability of the idea of crystal-field stabilization to instability constants.

Fig. 1. Linear dependence of the instability constants of complexes of Ca, Mn(II), Zn on the atomic number of the elements. **1** –complexes with cyanomethyliminodiacetic acid; **2** –the same with 1,2-diaminocyclohexanetetraacetic acid

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 2. Deviations from the linear dependence of the instability constants of complexes of Ca, Mn(II), Zn on the atomic number of the elements. **1** –complexes with ethylenediaminetetraacetic acid; **2** –the same with methyliminodiacetic acid

It seems to us that the explanation available in the literature of the Irving-Williams regularity from the standpoint of level splitting and their gradual filling by shielding electrons, although in general it agrees with experiment, is not sufficiently rigorous, since it proceeds from the notion of a purely electrostatic interaction between the metal and the ligand, which apparently occurs only in a limited number of cases. On the other hand, it is very interesting that the dependence of the instability constants of complexes on the change in atomic number of the metal for a given ligand in the series of transition elements corresponds to the dependence, on atomic number, of the second ionization potentials of atoms in the gaseous state.

state (in the absence of a ligand field). From Fig. 3 it is seen that the potential curve has two maxima–at the chromium atom and at the copper atom. The second ionization potential of the zinc atom is less than the second ionization potential of the nickel atom. There are not enough systematic data on instability constants for titanium and vanadium, but for chromium it has been shown that its complexes are more stable than the complexes of manganese ([9]). The special stability of copper complexes is well known; zinc complexes are usually less stable than nickel complexes.

Fig. 3. Dependence of the ionization potentials of atoms on atomic number. **1** –sum of the first and second ionization potentials; **2** –second ionization potential.

An analogous correspondence between the instability constants of complexes ([6]) and the values of the sums of three ionization potentials ([10]) may be noted in the series of rare-earth elements. These data are presented in Fig. 4. The straight lines in this figure correspond to a linear interpolation, which suggests itself here, since the deviations from linearity are small. Nevertheless, these deviations are apparently not accidental, since they have the same character on all curves of the instability constants and on the curve of ionization potentials.

Fig. 4. Dependence of the instability constants of complexes and the ionization potentials of atoms on the atomic number of the rare-earth elements. **1** –total ionization potential, **2** –instability constants of complexes with nitrilotriacetic

acid, **3** —the same for complexes of ethylenediaminetetraacetic acid, **4** —the same for complexes of diaminocyclohexanetetraacetic acid.

All-Union Scientific Research Institute
of Chemical Reagents and Especially Pure Chemical Substances

Received
9 VI 1962

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