PHYSICAL CHEMISTRY

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1965

SovietRxiv

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PHYSICAL CHEMISTRY

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THE INFLUENCE OF THE NATURE OF THE CATION AND ANION OF A SALT ON THE STATE OF A COORDINATED AMINO GROUP*

(Presented by Academician I. V. Tananaev, September 23, 1964)

In papers (1,2), the formation by the nitrogen atom of a coordination bond with the copper cation was considered. In the present work we examine the results of measurements of the infrared absorption spectra of aniline compounds with sulfates and halides of Co, Ni, and Zn of the compositions $MSO_4 \cdot 2An$ and $MG_2 \cdot 2An$, where $An = C_6H_5NH_2$, G is a halogen. The preparation of these compounds has been described in the literature (3). The results of the analysis confirmed the composition corresponding to the formulas given above (carbon and hydrogen were determined by the micromethod; the metal content in the complexes was determined by the trilonometrical method). The absorption spectra were measured on an IKS-14u instrument with LiF and NaCl prisms. The samples were prepared as suspensions in fluorinated oil, vaseline oil, and hexachlorobutadiene. For the sulfates and halides of copper, spectral measurements were repeated in connection with the use of more advanced apparatus.

Figure 1 presents the change in the force constant (Δf_{NH}) and the overlap integrals (ΔS_{NH}) of the valence orbitals in the nitrogen—hydrogen bond, calculated from the values of the stretching vibrations with the aid of equations given in the literature (1,2,4), for sulfate complexes as a function of the atomic number of the metal. The curves in Fig. 1 show the influence of the nature of the cation on the displacement of the frequencies of the NH stretching vibrations in the spectra of aniline complexes with sulfates and chlorides, $\nu_{\text{cp}} - \nu'_{\text{cp}}$ as a function of the atomic number of the metal $\left(\nu_{\text{cp}} = \frac{\nu_a+\nu_s}{2}\right.$ in the spectrum of free aniline; ν'_{cp} is the corresponding quantity for the complex compound). The plots presented in Figs. 1 and 2 (curves for sulfate complexes) are similar to those representing the change in the stability constants of complex compounds of the metals of the first transition decade with different ligands (the Irving—Williams series).

A correlation between spectroscopic characteristics (the displacement of the ligand absorption bands) and thermodynamic characteristics (the isobaric formation potential) of complex compounds has been established in a number of works (5), in which compounds with a variety of ligands were investigated: ethylenediamine, hydrazine, benzimidazole, ammonia, etc. (the displacements of the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

absorption bands can be compared more rigorously not with the isobaric potentials, but with the enthalpies of formation. The entropy effects of formation of these complexes are apparently close). The existence of such a dependence is not accidental. The degree of perturbations caused by the complex-forming cation in the electronic structure (and consequently also in the vibrational frequencies) of the coordinated group is determined primarily by the electron-acceptor capacity of the cation, on which the strength of the metal—ligand bond also depends.

The influence of the nature of the anion on the vibrational frequencies of the coordinated amino group is considerably more complex. Here only preliminary considerations can be expressed. It is known that a lowering of the frequencies stretching vibrations of NH in amine molecules is caused both by the formation of coordination bonds metal—nitrogen (bond through nitrogen) and as a result of the formation of hydrogen bonds N—H . . . A with anions (bond through hydrogen). The amino groups in the complex compounds under consideration may participate in bonds of both types. There are data (6) that make it possible to assume that in sulfate complexes of aniline the hydrogen bonds are less strong than in halide complexes. In cases where the cation M^{2+} forms comparatively weak covalent bonds with halogen anions, both factors lowering the frequencies ν_{NH} (the bond through nitrogen and the bond through hydrogen) act to a considerable degree independently and lead to the maximum lowering of the frequencies. The more strongly the covalent character of the metal—halogen

Fig. 1

Fig. 2

Fig. 1. Change in the magnitude of the overlap integrals (1) and the force constant (2) for sulfate complexes as a function of the atomic number of the metal.
Fig. 2. Shift of the NH stretching-vibration bands in the spectra of aniline compounds with sulfates (1) and halides (2) of Co, Ni, Cu, Zn as a function of the atomic number of the metal $\left(\nu_{\mathrm{av}} = \dfrac{\nu_a + \nu_s}{2}\right.$ in the spectrum of free aniline; ν'_{av} is the corresponding value for the complex compound).

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* Yu. S. Varshavskii took part in the work and in the discussion of the results.

bond is expressed, the more both the electron-acceptor capabilities of the cation and the ability of the anion to form hydrogen bonds are mutually neutralized, and the less significant should be the shift of the NH bands in the spectrum of the halide complex. The comparatively high degree of covalency, which can be judged from the "polarization energy" of the crystal lattices (7), is apparently the reason why, in compounds with copper halides, the amino group experiences the least strong perturbing action in both of the senses indicated above; this also accounts for the inversion of the Irving–Williams series on going from sulfates to halides. It is possible that their geometrical configuration also plays a substantial role in changing the character of the dependence of the ν_{NH} frequencies of the complexes investigated.

Received
15 IX 1964

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Note: Figure translations are in progress. See original paper for figures.