A STUDY OF NITROGEN-CONTAINING COPPER COMPLEXES
BY THE ELECTRON PARAMAGNETIC RESONANCE METHOD

N. N. Tikhomirova and K. I. Zamaraev
Chemical Physics Institute, Academy of Sciences, USSR
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A detailed analysis has been made of the electron paramagnetic resonance (EPR) spectra of complexes of copper with aliphatic amines in solution. It has been established that as the coordination sphere of the metal ion is filled with ligands there is a change in the magnitude of the hyperfine (HF) splitting and the g-factor in the EPR spectrum of the complex ion. Analysis of the EPR spectra can give information on the relative stability of complexes and on the change in stability under the influence of solvents. In the case of the copper complexes studied, it has been established that there is a correlation between the magnitude of the g-factor and the HF splitting constant: the greater the g-factor, the smaller the HF splitting constant.

Complex organic paramagnetic ions exhibit extremely interesting chemical and particularly catalytic properties [1, 2]. The chemical activity of these complexes is determined by the nature of the ligands and the bonds which they form with the central ion. The determination of the electronic structure of these complexes and its correlation with their chemical properties are of particular interest, since these complexes can be regarded as comparatively simple models of the active centers of the majority of biocatalysts. In the present work we made a study of the electronic structure of organic complexes of copper by the EPR method. We studied complexes of copper with the following ligands: ethylenediamine (EDA), diethanolamine (DEA), monoethanolamine (MEA), triethanolamine (TEA), trimethylenediamine (TMDA), isopropylamine (IPA), ammonia, and the cuprite ion [Cu(OH)]^-.

The study of the complex compounds in solution presents considerable difficulty, since various products of the step-wise dissociation of the complex, according to the general equation

\[ MA_n \rightleftharpoons M A_{n-1} + A, \]

\[ MA_{n-1} \rightleftharpoons M A_{n-2} + A \text{ etc.,} \]

may be present in equilibrium in the solution, depending on the concentration of the ligand A.

The equilibrium between these particles is determined by the corresponding equilibrium constants \( K \) which are often called the step-wise instability constants.

Complexes with either one or two molecules of EDA are known for copper in solution. The corresponding instability constants of these complexes are: \( K = 2.82 \times 10^{-11} \) and \( K = 8.92 \times 10^{-10} \) [3]. The attachment of a third EDA molecule is much more difficult, as indicated by the constant for this complex. The complexes have a chelate structure: the copper ion lies at the center of a square and the nitrogen atoms are situated at the apices of the square.

In the study of ethylenediamine complexes of copper by the EPR method (measurements carried out in the 3 cm range on a type EPR-2 spectrometer of Inst. Chem. Phys.) we established that the values of the g-factor and the HF splitting constant for the spectrum of the Cu\(^{2+}\) copper ion change with change in the ligand: copper ratio. In the complex containing two ligand molecules, which is formed in solution at \( \beta = [A^2]/[Cu^{2+}] \), the spectrum consists of four components of the HF structure (Fig. 1a;* the nuclear spin of copper is equal to \( \frac{3}{2} \)). The magnitude of the HF
splitting in this spectrum amounts to 90 Oe and the g-factor of the center of the spectrum is equal to 2.103. At low values of \( \beta \), e.g., at \( \beta = 0.58 \), a complex with one ligand molecule is formed in solution; the spectrum of this complex has a splitting of 74 Oe and a g-factor equal to 2.139 (Fig. 1b). At an intermediate value of \( \beta \) (e.g., 1.3) we observe a complex spectrum consisting of five components with different splitting between the individual components (Fig. 1c). It should be noted that the first component of this spectrum (in strong fields) coincides with the first component of the spectrum given in Fig. 1a, and the fourth component coincides with the third component of the spectrum in Fig. 1b. Figure 2 gives schemes for the spectra of the complexes with EDA at \( \beta < 1 \) (upper broken lines) and at \( \beta > 2 \) (solid lines), together with the spectrum observed at \( \beta = 1.3 \). This spectrum, consisting of five components, can evidently be regarded as the result of the superposition of two quartets. The spectra of the complexes formed at \( \beta > 2 \) are almost identical with the spectra of the complexes with two EDA molecules. This indicates that the attachment of a third molecule to the central metal ion, if it takes place at all, does not change the electronic state of the ion. This conclusion is also confirmed by the very low value for the stability constant of the complex formed by copper with three EDA molecules.

Analogous complex spectra for complexes of copper with pyridine were observed by McMillan and Smaller [4]. We are not convinced, however, by the explanation put forward by these authors for the appearance of the additional lines in the spectrum, which they attribute to splitting for the copper isotopes \( \text{Cu}^{63} \) and \( \text{Cu}^{65} \), which have identical nuclear spins of \( \frac{3}{2} \) and very similar values for the nuclear magnetic moments. In [5, 6] it was shown for the case of Tutton's copper salts and copper complexes with dithiocarbamates that the difference in the splitting for copper isotopes amounts to 7 Oe and can be observed only in the spectrum whose individual components have a maximum width of 2-4 Oe. In the case of complexes of copper with EDA and with pyridine, the magnitude of the splitting amounts to \( \sim 100 \text{ Oe} \), and for a component width of \( \sim 50 \text{ Oe} \) the splitting for copper isotopes cannot be observed. Thus the appearance of five lines in the spectra of the copper complexes is due to the superposition of two quartets given by complexes of different composition, and not to the splitting for copper isotopes.

Thus we have been able, for the case of the complexes of copper with EDA, to show that the spectrum of complexes with an incompletely filled coordination sphere exhibits parameters different from those of the spectrum of complexes with the maximum possible number of ligand molecules. The conversion of one spectrum to the other with change in the parameter \( \beta \) reflects the displacement of equilibrium (1) and is determined by the stability of the complexes formed. If the stability constant of the complex is sufficiently high, the equilibrium will be displaced to the left when \( \beta = n \) and the observed spectrum will correspond to the complex with a coordination sphere completely filled with ligands. When the stability