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EFFECT OF TRANSFER OF SPIN DENSITY FROM A PARAMAGNETIC COMPLEX TO SPLITTING-OFF LIGANDS

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By the method of electron paramagnetic resonance, at an oscillating magnetic-field frequency of 9320 Mc/s, we have investigated dioxane solutions of dithizonate and diphenylcarbazonate complexes of copper and, in part, dithizonate complexes of nickel and palladium. The results obtained proved to be somewhat unexpected.

Figure 1a presents the EPR spectrum from a solution of dithizonate complexes of divalent copper*. The spectrum has an asymmetric form characteristic of copper complexes and consists of four lines of hyperfine structure corresponding to interaction of the unpaired electron with the nuclei Cu^{63}, Cu^{65} ($I_{Cu} = {}^3/_2$). The g-factor of the center of the hyperfine structure is equal to 2.075, i.e., substantially greater than two. Upon slight alkalization of the solution, for example with monoethanolamine, the picture changes sharply. The spectrum from the copper complexes disappears completely and a nine-component strictly symmetrical spectrum appears from a solution of free radicals; the g-factor of this spectrum is equal to 2.0037 (Fig. 1b).

Upon slight acidification of the solution, the initial effect from the divalent copper complexes is restored.

The transition from copper complexes to free radicals and back, without noticeable loss in signal intensity (which is very large), can be repeated many times.

The acidified solutions have a red-violet color; after introduction of alkali the solutions become yellow-brown.

The smallness of the pH shifts responsible for the transitions observed is indicated by the following experiment.

Figure 2 shows EPR spectra obtained by successive dilution of a saturated dioxane solution of copper dithizonate complexes. Here dioxane as it were plays the role of an alkali. As the dilution proceeds, the number of solvent (dioxane) molecules per one complex copper particle increases. As a result, beginning

Fig. 1

Figure 1: Fig. 1

with a 3-4-fold dilution of the solution, 9 lines of the free-radical spectrum are superposed on the spectrum from the copper complexes (Fig. 2b), and with an eightfold dilution of the solution only the effect from free radicals alone is observed (Fig. 2c). The reverse transition from free radicals to copper complexes can be effected not only by lowering the pH, but also by introducing free dithizone into the solution.

Let us dwell on the nature of the effect observed. First of all it is necessary to note that the disappearance of the EPR signals from copper complexes upon alkalization of the solutions is connected with reduction of copper to the monovalent state, while the appearance of signals upon acidification of the solutions is caused by

$$^{*}\ \mathrm{Cu}^{(\mathrm{II})}\left(\begin{array}{c} \mathrm{S-C=N-N}\ \overset{\mathrm{Ph}}{\underset{\mathrm{H}}{|}} \\ \leftarrow \mathrm{N=N} \\ \backslash\mathrm{Ph} \end{array}\right)_2$$

The justification of the structure will be given elsewhere.

by the reverse transition of copper into the divalent state. This follows quite unambiguously from the fact that, in an acidic medium or upon the introduction of dithizone into the solution, diamagnetic dithizonate complexes obtained on the basis of any salt of monovalent copper become paramagnetic and give exactly the same EPR spectrum as the dithizonate complexes of divalent copper.

Fig. 1. EPR spectra from solutions of powders of dithizonate complexes of divalent copper in dioxane: **a** –weakly acidic medium ($g = 2.075$; $a_{\mathrm{Cu}} = 58.8$ Oe); **b** –weakly alkaline medium ($g = 2.0037$; $a_N = 5.6$ Oe). Here and in the remaining figures, an increase in the constant magnetic field corresponds to the direction from right to left.

As for the nine-component spectrum from free radicals, it turned out that a completely analogous spectrum can be obtained as a result of the gradual oxidation of dithizone dissolved in dioxane. As the oxidation proceeds (the process occurs spontaneously), the color of the solution changes from green to red and an EPR signal appears. Hence we conclude that the free radicals formed in solutions of copper dithizonate complexes are also a product of the oxidation of dithizone.

It is known ([1]) that dithizone (I) is readily oxidized to the diamagnetic compound diphenylthiocarbodiazone (II):

Fig. 2

Figure 2: Fig. 2

EPR spectra

Figure 3: EPR spectra

$$\mathrm{S{=}C}\left(\begin{array}{c}\mathrm{N-N-H}\\ \mathrm{N=N}\end{array}\right), \qquad \text{(I)}$$

$$\mathrm{S{=}C}\left(\begin{array}{c}\mathrm{N=N}\\ \mathrm{N=N}\end{array}\right). \qquad \text{(II)}$$

Fig. 2. EPR spectra from solutions of powders of dithizonate complexes of divalent copper in dioxane; effect of dilution with dioxane. **a** –initial (saturated) solution; **b** –the concentration of the initial solution was reduced fourfold; **c** – the concentration of the initial solution was reduced eightfold.

Our experiments show that there also exists a stable intermediate stage in the oxidation of dithizone. The structure of the radical formed is most likely conveyed by the formula:

$$\mathrm{H{-}S{-}C}^{\mathrm{N{-}N\cdot\,{-}Ph}}_{\mathrm{N{=}N{-}Ph}}. \qquad (III)$$

Here, in contrast to diphenylthiocarbodiazone (II), the oxidation process is reduced to the splitting off from the dithizone molecule not of two, but of only one hydrogen atom.

Formula (III) is in full agreement with the observed nine-component spectrum (Fig. 1). Indeed, the nine lines can evidently represent a hyperfine structure due to the interaction of the unpaired electron with the nuclei of four nitrogen atoms ($I_N = 1$). Analysis of the spectrum in Fig. 1 shows that these nitrogen atoms must be magnetically equivalent. Such are the four nitrogen atoms in the chain of conjugated bonds of the proposed structure (III).

The free radicals under consideration possess high stability. In dioxane solution, in air, they are detected for many hours and even withstand brief boiling of the solution.

Fig. 3. EPR spectra from solutions of the powder of diphenylcarbazonate complexes of divalent copper in dioxane: **a**–saturated solution ($g = 2.136$; $a_{\mathrm{Cu}} = 71.5$ Oe, narrow signal from the DPPH spectrum is indicated by the arrow); **b** –the same solution after 2-3-fold dilution with dioxane. The reverse transition to the spectrum of Fig. 3a was obtained by introducing free diphenylcarbazone into the diluted solution.

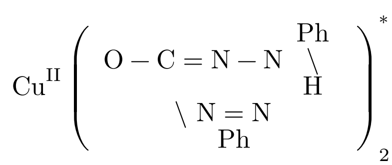
Summarizing all that has been said, we believe that the mechanism of the observed reversible transitions "solution of copper complexes—solution of free radicals" can be schematically represented by the following equation:

$$2Cu^{(II)}(HDz)_2 \rightleftarrows Cu_2^{(I)}Dz + 2(HD{\cdot}z) + H_2Dz. \quad (1)$$

Here: $Cu^{(II)}(HDz)_2$ is a dithizonate complex of divalent copper, formed in an acidic medium; $Cu_2^{(I)}Dz$ is a dinuclear dithizonate complex of monovalent copper, formed in an alkaline medium; HD·z is the molecule of the free radical (formula (III)) and H_2Dz is the dithizone molecule. The gross formulas of the dithizonate complexes entering into equation (1) are sufficiently accurately established ([1]).

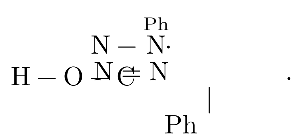
Thus, upon alkalization of the solutions, the spin density from the dithizonate complexes $Cu^{(II)}(HDz)_2$ passes to the ligands split off in the form of free radicals, and the complexes become diamagnetic; upon acidification of the solutions, the reverse transition takes place and the original picture is restored.

Analogous reversible transitions are observed in solutions of diphenylcarbazonate complexes of copper (Fig. 3).



An interesting fact is the complete identity of the nine-component spectra in Figs. 1b and 3b. At the same time, the stability of the free radicals formed in solutions of diphenylcarbazonate complexes is much lower than the stability of the free radicals in solutions of dithizonate complexes.

By analogy with structure (III), the structure of the free radicals in solutions of diphenylcarbazonate complexes probably has the form:



. (IV)

In conclusion, we note that upon dissolution in an alkaline medium of powders of dithizonate complexes of divalent nickel and palladium, we were able to observe EPR signals from dithizonate complexes of monovalent nickel ($3d^9$) and monovalent palladium ($4d^9$). The detected signals have g-factors of 2.06 and 2.02 for the nickel and palladium complexes, respectively. These results will be presented in detail in a full report on the present work.

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* The substantiation of the structure will be given elsewhere.

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