A. K. PISKUNOV, D. N. SHIGORIN, B. I. STEPANOV, and E. R. KLINSHPRONT

1961

SovietRxiv

Abstract

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PHYSICAL CHEMISTRY

A. K. PISKUNOV, D. N. SHIGORIN, B. I. STEPANOV, and E. R. KLINSH-PRONT

STUDY OF THE PARAMAGNETIC RESONANCE OF SOLUTIONS OF CERTAIN COPPER OXYAZO COMPOUNDS

(Presented by Academician V. A. Kargin, June 20, 1960)

At a frequency of 9375 Mc/s, the spectra of electron paramagnetic resonance (EPR) were investigated for solutions in chloroform of copper complexes of 2-chlorobenzol-(1-azo-1′)-naphthol-2′ (I), 2-methoxybenzol-(1-azo-1′)-naphthol-2′ (II), 2-nitrobenzol-(1-azo-1)-naphthol-2′ (III), 2-butoxybenzol-(1-azo-1′)-naphthol-2′ (IV), 2,6-dichlorobenzol-(1-azo-1′)-naphthol-2′ (V), 2-oxy-1,1′-azonaphthalene (VI), 2-chloro-2′-oxy-1,1′-azonaphthalene (VII), and 8-chloro-2′-oxy-1,1′-azonaphthalene (VIII).

In addition to the four lines of the hyperfine structure (h.f.s.) caused by the interaction of the unpaired electron with the copper nucleus ($I = {}^3/_2$), an additional hyperfine splitting was detected. The form of the spectrum consisting of the four principal h.f.s. lines is analogous to that observed by McGarvey (^{1}) in solutions of copper acetylacetonate and its substituted derivatives, and is interpreted qualitatively with the aid of the relaxation theory developed by McConnell (^{2}), which explains the asymmetry of the spectrum by the dependence of the contribution of the anisotropic hyperfine interaction to paramagnetic relaxation on the nuclear spin quantum number I_z. Such a dependence leads to the result that the h.f.s. lines for different values of I_z differ in width. The magnitudes of the splittings between the four h.f.s. components for different compounds vary within the range from 60 to 70 Oe.

With the exception of the solution of compound VIII, the additional h.f.s. of five lines is clearly resolved on the most intense line ($I_z = -{}^3/_2$) of the main h.f.s. spectrum, whereas already on the second line ($I_z = -{}^1/_2$) it is barely noticeable. This is in full agreement with the McConnell relaxation mechanism, since broadening of the components of the principal h.f.s. spectrum with increasing I_z should lead to a decrease in the resolution of the additional h.f.s. The additional hyperfine splitting indicates that the unpaired electron is not localized on the copper atom, but is also located in the field of two nuclei of the nitrogen atoms of two azo groups. The interaction of the electron only with two nitrogen atoms (one from each azo group) can apparently be explained by the fact that the π-electrons of the azo groups do not take part in the formation

Fig. 1

Figure 1: Fig. 1

of chemical bonds with the copper atom, since additional energy is required for their excitation. It is known that the energy of the π-bond in an azo group is almost twice as large as the energy of a σ-bond (^{3}). The copper atom, using two valence electrons (s and p), forms two chemical bonds with oxygen atoms. The copper forms the two other bonds with the aid of two of its free orbitals (p and d) and the unshared electron pairs of the nitrogen atoms of the azo groups. Thus, if our assumption is correct, the free electron density should be distributed only over the two nitrogen atoms participating in the formation of bonds with the copper atom. More distant atoms affect the widths of the h.f.s. lines and the magnitudes of the g-factors, as well as the resolution of the spectra of the additional h.f.s. The position and resolution of the spectra depend substantially on the solvents. The strongest changes in the spectra were observed in the study of compounds dissolved in dioxane.

Figure 1 shows recordings of the EPR spectra of centimolar solutions I, V, and VIII (spectra II and III differ little from spectrum I, and spectrum VII from spectrum V; spectra IV and VI have better resolution than I). Table 1 gives the measured values of the g-factors and the widths of the fully resolved lines of the principal h.f.s. spectrum (between the points of maximum slope). The resolution of the additional h.f.s. depends on the nature of the substituents, their number, and their positions in the aromatic rings. A similar character of the influence of substituents on the resolution of h.f.s. spectra was observed in chromocenes (^{4}).

From the spectra shown in Fig. 1 it is evident that, for compound V, containing two chlorine atoms in the ortho position with respect to the azo group, the resolution of the spectrum increases in comparison with I.

Fig. 1

It is not possible to explain the observed changes in the spectra solely by means of the line-broadening mechanisms considered by McGarvey (^{5}). From studies of luminescence spectra it is known that complex molecules with a large number of π-electrons, and especially those having unpaired electrons, can form associates with one another even in very dilute solutions. The formation of such associates in the solutions we studied will promote magnetic dipole-dipole and exchange interaction between molecules; on the other hand, the reorientation times for associates will be greater than for individual molecules. For the copper complex of benzolazonaphthol-2, which contains no substituents in the aromatic rings, the ability to associate is apparently so great that it cannot be dissolved in chloroform or in other solvents (benzene, dioxane, tetrahydrofuran, pyridine, toluene).

The introduction of substituents Cl and OR, possessing large van der Waals radii, will decrease the possibility of associate formation. The better resolution of the additional h.f.s. in solution V than in I is probably due to the greater ability of I to associate. Thus, in analyzing the observed changes in the EPR spectra, it is necessary, along with other mechanisms, also to take into account the influence on the form of the spectrum of the ability of the compounds to form associates in solutions.

Attention is drawn to the dependence of the resolution of the additional h.f.s. on the magnitude of the *g*-factor of the most intense h.f.s. line, caused by interaction of the electron with the copper nucleus.

For all the compounds studied, except IV, the smaller the value of the *g*-factor, the better the resolution.

The fact that in spectrum VIII the additional h.f.s. is not observed can probably be explained by steric hindrance preventing interaction of the unpaired electron with the nitrogen nuclei. The proximity of the nitrogen and chlorine atoms in VIII may lead to a disturbance of the coplanarity of the molecule. This should sharply weaken the interaction of the electron with the nuclei of the nitrogen atoms.

In frozen solutions the h.f.s. completely disappears and broad asymmetric lines of the order of 200–250 G are observed. The investigated so-

Table 1

Values of the *g*-factors and widths of hyperfine-structure lines of centimolar solutions of copper complexes in chloroform

No.	Compounds	g_1	g_2	g_3	ΔH_1 (G)	ΔH_2 (G)	ΔH_3 (G)
I	Structural formula of the copper complex as shown; substituents: Cl, Cl	2.042	2.079	2.117	5 lines of additional h.f.s. with splitting 11 G	29	33

No.	Compounds	g_1	g_2	g_3	ΔH_1 (G)	ΔH_2 (G)	ΔH_3 (G)
II	Structural formula of the copper complex as shown; substituents: OCH_3, OCH_3	2.041	2.086	2.124	Same	35	38
III	Structural formula of the copper complex as shown; substituents: NO_2, NO_2	2.030	2.072	2.116	″ ″	38	42
IV	Structural formula of the copper complex as shown; substituents: OC_4H_9, OC_4H_9	2.043	2.082	2.117	″ ″	34	39

No.	Compounds	g_1	g_2	g_3	ΔH_1 (G)	ΔH_2 (G)	ΔH_3 (G)
V	Structural formula of the copper complex as shown; substituents: Cl, Cl, Cl, Cl	2.021	2.067	2.110	″ ″	32	36
VI	Structural formula of the copper complex as shown	2.036	2.072	2.111	″ ″	32	35

Table (continued)

No.	Compounds	g_1	g_2	g_3	ΔH_1 (Gs)	ΔH_2 (Gs)	ΔH_3 (Gs)
VII	[[chemical structural formula shown in the original]]	2.024	2.068	2.113	Same	36	38

No.	Compounds	g_1	g_2	g_3	ΔH_1 (Gs)	ΔH_2 (Gs)	ΔH_3 (Gs)
VIII	[[chemical structural formula shown in the original]]	2.050	2.090	2.126	27	30	35

···thane (6), the polycrystalline samples of these compounds had line widths of 30–50 Gs. Consequently, exchange interactions have a substantial effect on the line widths of polycrystalline samples.

All the compounds investigated dissolve well in acetylacetone and give one and the same spectrum of four lines with $g_1 = 2.052$, $g_2 = 2.097$, $g_3 = 2.141$, $g_4 = 2.175$ and $\Delta H_1 = 26$, $\Delta H_2 = 24$, $\Delta H_3 = 28$, $\Delta H_4 = 37$ Gs.

Apparently, on dissolution the azo-compound molecules are displaced from the complexes by acetylacetone molecules.

In studying EPR in magnetically diluted single crystals of copper bis-salicylaldehydeimine, Maki and McGarvey (7) observed an additional h.f.s. consisting of 11 lines, owing to interaction of the unpaired electron with nitrogen nuclei and with the protons of the hydrogen of CH groups. The solutions that we investigated of this compound and of a number of its derivatives in pyridine, dioxane, and tetrahydrofuran do not give an additional h.f.s.

Physicochemical Institute
named after L. Ya. Karpov

Moscow Institute of Chemical Technology
named after D. I. Mendeleev

Received
1 VI 1960

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