A. K. Piskunov, D. N. Shigorin, V. I. Smirnova, and B. I. Stepanov

1960

SovietRxiv

Abstract

Full Text

Physical Chemistry

A. K. Piskunov, D. N. Shigorin, V. I. Smirnova, and B. I. Stepanov

Electron Paramagnetic Resonance Spectra of Certain Inner-Complex Copper Compounds

(Presented by Academician V. A. Kargin on 18 VIII 1959)

In the present work we studied the spectra of electron paramagnetic resonance (E.P.R.) of inner-complex copper compounds, which it forms with various azo compounds ([1]), as well as with the enol forms of acetylacetone and ethyl acetoacetate ([2]).

Measurement of the magnetic moments of these compounds shows that the copper atom forms chemical bonds with the participation of two valence electrons. If the initial valence state of the copper atom is d^9sp, then in the compound it must possess one unpaired electron. It is known that the metal atom simultaneously forms in the molecule of an inner-complex compound more bonds than the number of valence electrons participating in their formation. Thus, for example, the copper atom participates in the formation of bonds by two valence electrons, but forms four equivalent bonds in the acetylacetonate molecule. This can be explained only by the fact that the metal atom of inner-complex compounds participates directly in the π-electron interaction of the system. The mechanism of this interaction may be different. It may be assumed that one of the electrons of the metal atom, using its p-orbital, simultaneously interacts with the π-electrons of neighboring atoms and, through the latter, with the π-electrons of the entire system. It is also possible for the free p-orbital of the metal atom to be included in π-electron interaction with neighboring atoms. Solving the question of the "behavior" of the unpaired electron of the metal (as in the case of copper acetylacetonate) represents an important theoretical problem. In particular, the question must be resolved whether the unpaired electron is localized on the copper atom or whether it is "delocalized" (redistributed) in the molecule. In the event that electron delocalization takes place, it is important to determine how structural changes in the molecule affect the character of this phenomenon. Problems of this kind can to some extent be solved by studying E.P.R. absorption spectra. In the case where hyperfine structure (h.f.s.) is observed, definite conclusions about the behavior of the unpaired electron in the molecule can be drawn from the number of h.f.s. lines and their intensity. However, because of the presence of strong exchange interaction in condensed systems of paramagnetic substances, h.f.s. is observed only rarely. With appropriate dilution it is often possible to remove the exchange interaction and thus obtain the necessary information. For many substances it is very difficult to select solvents that would effectively remove the exchange interaction. Moreover, for some molecules even under conditions of h.f.s. resolution it is not always possible to analyze the spectrum. An example is the spectrum observed by Jarrett and Sloan (^{3}) for a 0.001 M solution of triphenylmethyl in benzene, consisting of no fewer than 72 components.

It seems to us that in certain cases, in particular in the case of the inner-complex copper compounds we have investigated, a number of qualitative conclusions about the influence of the nature and structure of the groups surrounding the copper atom can be drawn by comparing the E.P.R. spectra of condensed systems,

since delocalization of the unpaired electron, which depends strongly on the nature of the surrounding atoms and on the number of π-electrons in the system, must affect the exchange interaction and, consequently, the width of the absorption line.

Table 1

No.	Compounds	Line width, gauss	g-factor	Magnetic moment, μ_B
I	Structural formula shown: bis-chelate copper complex with two acetylacetonate-type ligands, bearing H_3C, CH_3, and H substituents around the C=O, C=C, O−Cu−O chelate rings.	458 ± 10	$2,105 \pm 0,01$	$1,75 \pm 0,05$

No.	Compounds	Line width, gauss	g-factor	Magnetic moment, μ_B
II	Structural formula shown: bis-chelate copper complex with substituted acetoacetic-ester-type ligands; visible groups include H_3C, CH_3, CH_2, C_2H_5, carbonyl oxygens, and O—Cu—O chelate coordination.	75 ± 5	$2,079 \pm 0,01$	$1,87 \pm 0,05$

No.	Compounds	Line width, gauss	g-factor	Magnetic moment, μ_B
III	Structural formula shown: bis-chelate copper complex with chlorinated acetylacetonate-type ligands; visible groups include H_3C, CH_3, Cl, carbonyl oxygens, and O—Cu—O chelate coordination.	56 ± 3	$2,072 \pm 0,01$	$1,83 \pm 0,05$
IV	Structural formula shown: copper complex of two azo ligands with benzene and naphthalene rings, N=N groups, and O—Cu—O coordination.	117 ± 6	$2,087 \pm 0,01$	–

No.	Compounds	Line width, gauss	g-factor	Magnetic moment, μ_B
V	Structural formula shown: copper complex of two azo ligands with benzene and naphthalene rings, N=N groups, O—Cu—O coordination, and two visible Cl substituents.	48 ± 3	$2,051 \pm 0,01$	–
VI	Structural formula shown: copper complex of two azo ligands with benzene and naphthalene rings, N=N groups, O—Cu—O coordination, and four visible Cl substituents.	38 ± 3	$2,055 \pm 0,01$	–

No.	Compounds	Line width, gauss	g-factor	Magnetic moment, μ_B
VII	Structural formula shown: copper complex of two azo ligands with naphthalene rings, N=N groups, O–Cu–O coordination, and two visible Cl substituents.	29 ± 2	$2,051 \pm 0,01$	–

Table 1 (continued)

No.	Compounds	Line width, Oe	g-factor	Magnetic moment, μ_B
VIII	[[chemical structure diagram of a copper azo complex with Cl substituents]]	79 ± 5	2.080 ± 0.01	1.80 ± 0.05
IX	[[chemical structure diagram of a copper azo complex with OCH_3 substituents]]	85 ± 5	2.075 ± 0.01	2.06 ± 0.05

Table 1 gives the intracomplex copper compounds studied by us and the values obtained for them for the line widths ΔH (between the points of maximum slope) at a frequency of 9370 MHz, the g-factors, and the magnetic moments. If for copper acetylacetonate (I) $\Delta H = 158 \pm 10$ Oe, then upon introduction into the molecule of the substituents $O = C—OR$ (II) and (Cl) (III), the absorption lines become noticeably narrower (respectively 75 ± 5 and 56 ± 3 Oe). The group $O = C—OR$ must participate more actively in the π-electron interaction than hydrogen. An even greater activity should be exhibited by the chlorine atom, which participates in the π-electron interaction by means of an unshared electron pair. Apparently this interaction promotes delocalization of the unpaired electron, which substantially affects the exchange interaction leading to narrowing of the absorption line.

In the EPR spectra of intracomplex copper azo compounds (^{4}), containing the azo group $—N = N—$ and groups richer in π-electrons, the value of ΔH becomes still smaller. Thus, for compound IV the value of ΔH is 40 Oe smaller than for copper acetylacetonate. Introduction of a chlorine atom into the azo compound, especially in the ortho position relative to the azo group, just as in the case of copper acetylacetonate, leads to strong narrowing of the EPR line. From Table 1 it is seen that compound V has a line 2.5 times narrower than IV. In the presence of two chlorine atoms in the molecule of azo compound VI, an even greater narrowing of the line (38 Oe) is observed in comparison with V. If the chlorine atom in the azo compound is located not in the ortho position relative to the azo group, but in a position more distant from it (as, for example, in VIII), then in this case a broadening of the line is observed (in VIII, 79 Oe, whereas in VII, 29 Oe).

An increase in the number of π-electrons in the molecule is accompanied by narrowing of the absorption line. This is seen from a comparison of the results obtained for compounds V and VII. It should also be noted that a chlorine atom located in the ortho position affects the line width much more strongly than the introduction of an OR group (IX).

The facts considered indicate that the unpaired electron of the copper atom interacts effectively with the π-electrons of the azo group and, through the latter, with the π-electrons of the entire system. This interaction apparently substantially affects the exchange interaction of the electrons of the copper atoms, leading to narrowing of the absorption line. Introduction of substituents into the molecule will lead to a change in the crystal lattice, which should affect both the exchange interaction and the internal crystalline field, which influences the shape and width of the lines as a result—

···the effect of anisotropy of the g-factor. It should be noted that all the lines had a strong asymmetry toward lower fields. The observed facts can in no way be explained solely by a change in the exchange interaction for the reason mentioned above. Thus, on going from acetylacetonate to its derivatives II and III, the distance between the molecules increases, and consequently the Cu—Cu exchange interaction should decrease. Nevertheless, a sharp narrowing of the

Fig. 1. Derivatives of e.p.r. absorption lines at a frequency of 9370 Mc; 0.01 M solutions of compounds VIII and VI in benzene

Figure 1: Fig. 1. Derivatives of e.p.r. absorption lines at a frequency of 9370 Mc; 0.01 M solutions of compounds VIII and VI in benzene

line is observed.

As can be seen from Table 1, for copper acetylacetonate and its derivatives, on passing from one substance to another with broadening of the line, the value of the *g*-factor changes noticeably. However, the observed regularities also cannot be explained by anisotropic broadening alone. A detailed analysis of the spectra obtained for azo compounds gives no grounds for explaining the change in line width solely by anisotropic broadening.

Fig. 1. Derivatives of e.p.r. absorption lines at a frequency of 9370 Mc; $0.01M$ solutions of compounds VIII and VI in benzene.

More definite conclusions can be drawn by investigating solutions of the indicated compounds.

We have obtained recordings of the spectra of solutions of some compounds in benzene, chloroform, dioxane, and other solvents. For solutions of copper acetylacetonate (spin $S_{\mathrm{O}^{16}} = 0$, $S_{\mathrm{Cu}} = 3/2$) the spectrum is analogous to the spectrum obtained by McGarvey (5); however, a number of azo compounds give a more complex spectrum (see, for example, Fig. 1). The appearance of additional hyperfine splitting (of the most intense line), consisting of five components, is due to the interaction of the electron of the copper atom with the nitrogen nuclei ($S_{\mathrm{N}^{14}} = 1$) of the azo groups. The presence and character of the additional splitting depend on the state of the nitrogen atoms of the azo group (valences and their coplanar arrangement) in the compound.

Thus, the experimental data obtained indicate the presence of an indirect participation of the unpaired electron of the copper atom of inner-complex compounds in interaction with the π-electrons of the system, and that this participation depends on the nature and structure of the surrounding groups.

Scientific Research Physico-Chemical Institute
named after L. Ya. Karpov

Moscow Chemical-Technological Institute
named after D. I. Mendeleev

Received
15 VIII 1959

REFERENCES

1. D. N. Shigorin, ZhFKh, 554 (1953); *Problems of Physical Chemistry*, 1, 173 (1958).

2. D. N. Shigorin, *Spectrochim. Acta*, **14**, 198 (1959).

3. H. S. Jarrett, G. J. Sloan, *J. Chem. Phys.*, **22**, 1783 (1954).

4. B. I. Stepanov, M. A. Salivani et al., ZhOKh, **28** (1958); M. A. Andreeva, B. I. Stepanov, ZhOKh, **28**, 2966 (1958); B. I. Stepanov, V. A. Savel' eva, ZhOKh, **28**, 2968 (1958); B. I. Stepanov, M. A. Andreeva, *Scientific Reports of Higher Schools*, Chemistry, 141 (1959).

5. B. R. McGarvey, *J. Phys. Chem.*, **60**, 71 (1956).

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