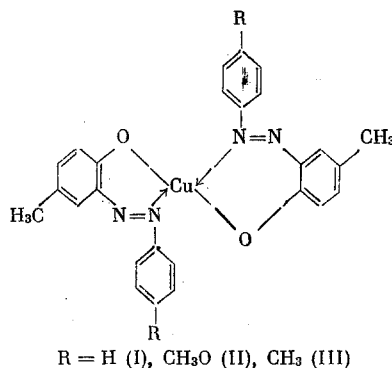


DELOCALIZATION OF UNPAIRED ELECTRON IN  
COPPER(II) COMPLEXES WITH AZO COMPOUNDS

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In [1] we reported the results of studying the magnetically diluted monocrystal of copper(II) bis-[2,6-dichlorobenzene-(1-azo-1')-2'-naphthol], which is a member of a broad class of chelate complexes of copper(II) with azo compounds. In this compound the additional hyperfine structure (AHFS) in the EPR spectra is caused by the interaction of the unpaired electron of the copper atom with the two equivalent nitrogen atoms, which are attached directly to the copper atom. The question arises of whether this interaction is characteristic only for the complexes of copper(II) with benzene-azo- $\beta$ -naphthol derivatives, or whether it is more general and inherent to the complexes of copper(II) with other azo compounds. In order to answer this question we used the EPR method to study the complexes of copper(II) with benzeneazo-p-cresol derivatives: copper(II) bis(benzeneazo-p-cresol) (I), copper(II) bis(4-methoxybenzeneazo-p-cresol) (II) and copper(II) bis(4-methylbenzeneazo-p-cresol) (III).



## EXPERIMENTAL METHOD

The study was made on magnetically diluted powders, since in the case of compounds (I)-(III) we were unable to grow sufficiently large magnetically diluted monocrystals. The magnetically diluted powders were prepared by the coprecipitation of the Cu(II) complexes with the analogous Ni(II) complexes and a slow evaporation of the solvent, which in every case was benzene. The ratio of the copper and nickel complexes was 1:300. The EPR spectra were taken on a JES-ZBX radiospectrometer with a klystron operating frequency of 9.4 Hz.

TABLE 1

Compound	$g_{\parallel} (\pm 0,003)$	$g_{\perp} (\pm 0,005)$	$A (\pm 2), \text{Oe}$	$B (\pm 2), \text{Oe}$	$A_N (\pm 0,3), \text{Oe}$	$B_N (\pm 0,3), \text{Oe}$
(I)	2,208	2,056	165	37	12,7	16,4
(II)	2,203	2,056	167	35	12,7	16,4
(III)	2,208	2,058	165	35	12,7	16,4
(IV)	2,195	2,033	189	30	12,7	16,4

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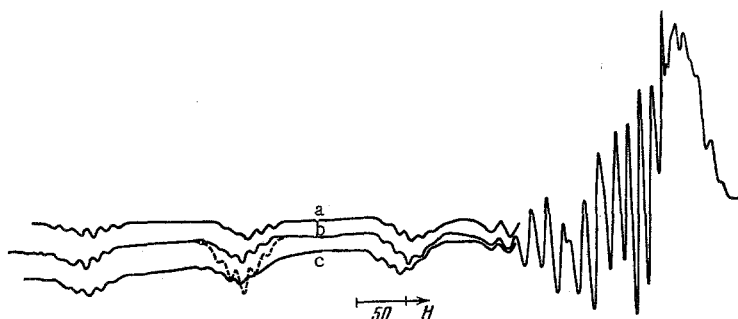


Fig. 1. EPR spectra of polycrystalline compounds: a) (II), b) (I), and c) (III), magnetically diluted with the corresponding nickel complexes.

## DISCUSSION OF RESULTS

Previously [2] we had reported the results of using the EPR method to study compound (I) and it was indicated that the probability of finding the unpaired electron of the copper atom on all four nitrogen atoms was different from zero. The argument in support of this conclusion was the satisfactory agreement of the experimental and theoretical spectra, which corresponded to the hyperfine interaction of the unpaired electron with the four nitrogen atoms. However, the theoretical spectra were constructed without taking into account the two copper isotopes,  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , with the same spins of the nuclei and close values of the nuclear magnetic moments (respectively 2.221 and 2.380 nuclear magnetons), while the studies themselves were carried out in solutions and low-temperature glasses, the interpretation of the results of which cannot be completely reliable and unequivocal. A study of the magnetically diluted polycrystals makes it possible to obtain more complete information from the EPR spectra.

The EPR spectra of the magnetically diluted polycrystalline compounds (I)-(III) are given in Fig. 1, in which connection only the  $g_{\parallel}$  region is shown for compounds (II) and (III), since the EPR spectra in the  $g_{\perp}$  region and the peak of the additional absorption are practically the same for all three compounds. The AHFS is resolved from five components on each component of the HFS from the nucleus of the copper atom ( $I = 3/2$ ) in the parallel orientation, which can be seen most distinctly on the HFS peak that corresponds to  $M_I = -1/2$ . On the HFS peak, corresponding to  $M_I = -3/2$ , the number of AHFS components is equal to six, which is associated with the presence of the two  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  isotopes. Five components of the AHFS, with an intensity ratio of 1:2:3:2:1, can arise if the unpaired electron of the copper atom accomplishes contact interaction only with the two equivalent nitrogen atoms that are directly attached to the copper atom.

We also took the EPR spectrum of the magnetically diluted copper(II) [2,6-dichlorobenzene-(1-azo-1')-2'-naphthol] (IV) powder. An analysis of this spectrum hardly differs from that given above. The presence of five components of the AHFS is also due to the interaction of the unpaired electron with the two equivalent nitrogen atoms, which is in agreement with the results of studying this compound as the magnetically diluted monocrystal [1].

The EPR spectra of compounds (I)-(IV) are described by an axial-symmetric Hamiltonian spin of the type:

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A I_z S_z + B (I_x S_x + I_y S_y) + \sum_i A_N I_{iz}^N S_z + \sum_i B_N (I_x^N S_x + I_y^N S_y)$$

where  $S = 1/2$ ,  $I = 3/2$ ,  $I^N = 1$ , and  $i = 2$ .

The parameters of the Hamiltonian spin are given in Table 1.

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## CONCLUSIONS

Contact interaction of the unpaired electron of the copper atom with the two equivalent nitrogen atoms, attached directly to the copper atom, is accomplished in the inner complexes of copper(II) with bis(benzeneazo-p-cresol) derivatives.

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