Contribution from the Institute of Organic Chemistry,
Bulgarian Academy of Sciences, Sofia 13, Bulgaria

EPR Studies of Dithiophosphate and Dithiocarbamate Complexes. III. Influence of Axial Ligands on the Structure of Copper(II) Complexes*

N.D. Yordanov[1] and D. Shopov

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The influence of pyridine on the EPR spectra of some copper(II) dithiocarbamate and dithiophosphate complexes has been studied, and it is found that two pyridine molecules coordinate around the complex. The changes in the EPR spectra are due to the influence of the pyridine molecules along the z axis of the complex. The unpaired electron moves onto a MO, which is a linear combination of the orbitals $|z^2-y^2>$ *and* $|3z^2-r^2>$. *A possibility of opening of the chelate arises.*

Introduction

In part I and II of the present series[2,3] some dithiophosphate and dithiocarbamate copper(II) complexes in nonpolar solvents were studied. An interaction between the molecules of coordinating solvents and copper(II) complexes is observed[4-12] causing sensible alteration in the shape of the EPR spectra and in the molecular orbital parameters. Two assumptions about these changes were made, based on the Jahn-Teller effect[4] and on the representations of interaction between the solvent molecules and the functional groups of the ligands.[12] The large excess of coordinating solvent in all previous studies prevented a distinction of the solvent influence along the z axis from that in the xy plane.

In the present paper we report results on the influence of pyridine on the structure of some dithiocarbamate and dithiophosphate copper(II) complexes. In order to clarify the mechanism of complex-solvent interaction all the experiments were carried out using a solvent mixture of pyridine and toluene, the concentration of the former in the mixture being proportional to the complex concentration as follows: 1:1, 1:2, 1:4, 1:8, 1:16, 1:32, 1:80, 1:160, and 1:320.

The EPR and absorption spectra of copper(II) diethyldibenzyl-, and piperidinedithiocarbamate and diisopropyldicyclohexyl, and diorthocresyldithiophosphate complexes were studied using the solvent mixture mentioned above, and also in pure toluene, heptane, and pyridine.

Results and Discussion

I. *Dithiocarbamate Complexes.* Figure 1 shows the EPR spectra typical of copper(II) dithiocarbamate complexes at room temperature and at 77°K in non-

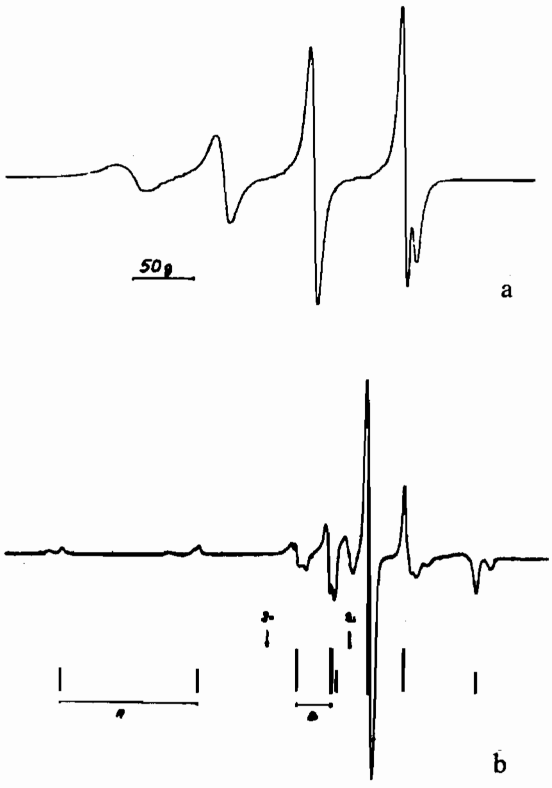

Figure 1. Epr spectrum typical for copper(II) dithiocarbamate complexes in noncoordinating solvent (toluene): a—T=300°K,b—T=77°K.

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[1] To whom correspondence should be addressed.

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coordinating solvents (heptane or toluene). Figure 2 shows the low temperature EPR spectrum of the same complexes in the presence of pyridine with complex to pyridine ratio 1:2. Figure 3 shows the variation in the parameters $g_{\parallel}$, $g_{\perp}$, A and B with the complex to pyridine ratio. These data are calculated from the low temperature EPR spectra, each point being obtained by averaging the results of at least three EPR spectra. It can be seen from Figure 3 that sharp alterations in all EPR parameters for the vitreous state are observed at complex to pyridine ratio 1:2. The EPR parameters measured at this complex: pyridine ratio are equal to the parameters measured in pure pyridine ($g_{\parallel} = 2.111 \pm 0.002$; $g_{\perp} = 2.033 \pm 0.002$; $A = 145 \pm 2G$, and $B = 24 \pm 2G$). As the EPR parameters do not change further when the relative pyridine concentration increases above 1:2 the conclusion is that no influence of radial interaction exists. The variation of the EPR parameters is probably caused by changes in the electronic structure of the central ion.

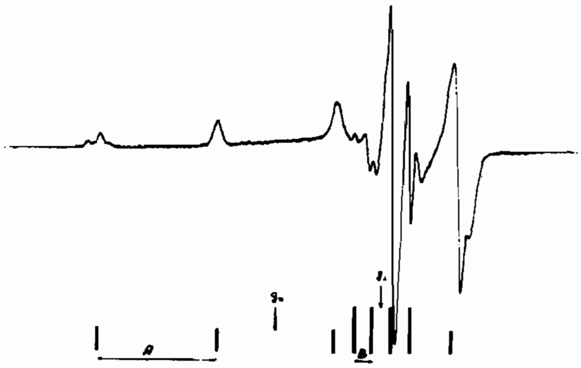

Figure 2. EPR spectrum typical for copper(II) dithiocarbamate complexes at 77°K in a solvent mixture of toluene and pyridine. Concentrations: complex $5\times10^{-3}M$; pyridine—$1\times10^{-2}M$.

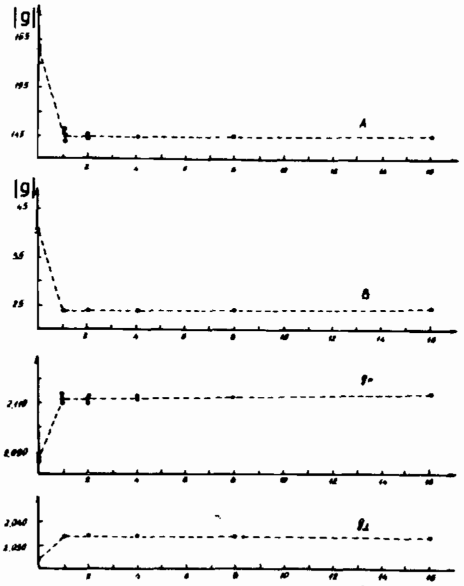

Figure 3. Variations in the anisotropic spin-Hamiltonian parameters of copper(II) dithiocarbamate compleexs in a solvent mixture of toluene and pyridine with the complex: pyridine ratio. Concentration of the complex $5\times10^{-3}M$.

When the complex: pyridine ratio is 1:1 two complexes 1:0 and 1:2 with approximately equal intensities are detected from the EPR spectra (Figure 4) with respectively planar and octahedral structures.

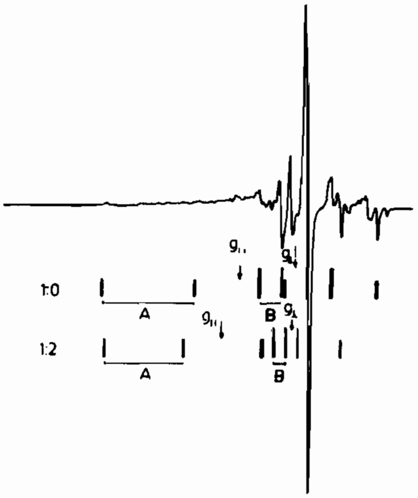

Figure 4. EPR spectrum typical for copper(II) dithiocarbamate complexes at 77°K and complex: pyridine ratio 1:1. The stick spectrum shows that a superposition of the EPR spectra of two complexes 1:0 and 1:2 takes place.

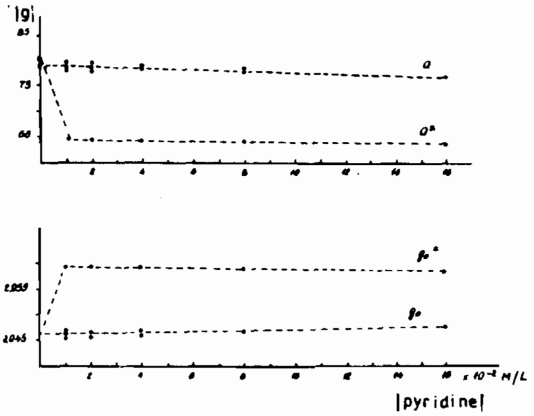

Figure 5. Variation in the isotropic spin-Hamiltonian parameters of copper(II) dithiocarbamate complexes in a solvent mixture of toluene and pyridine with the complex: pyridine ratio. Concentration of the complex $5\times10^{-3}M$.

The EPR data show an equilibrium between the upper two complexes taking place up to complex: pyridine ratio 1:2. The 1:1 complex was not detected.

Figure 5 shows the variations in the isotropic spin-Hamiltonian parameters with the complex: pyridine ratio. The values of g_0' and a' calculated from the anisotropic parameters[13] of the EPR spectra are also

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[13] H.M. McConnell, *J. Chem. Phys.*, *25*, 709 (1956).

shown. It can be seen from Figure 5 that until the experimental values of g_o and a, up to complex: pyridine ratio 1:16, are equal to those observed in noncoordinating solvent, the calculated values a' and g_o' correspond to those observed in pure pyridine. This fact can be explained by the unstability of the six-coordinated complex at room temperature and low pyridine concentration.

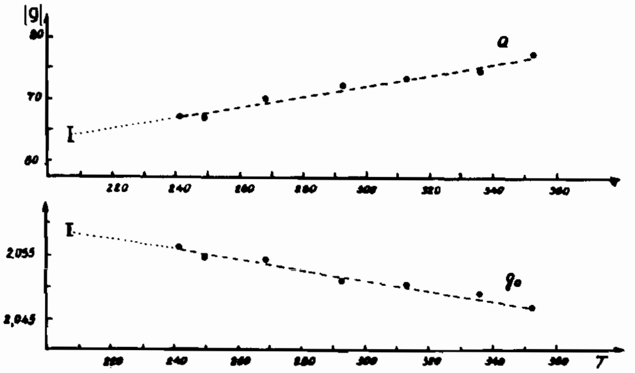

Figure 6. Variations in the isotropic spin-Hamiltonian parameters of copper(II) dithiocarbamate complexes in a solvent mixture of toluene and pyridine with the temperature. Concentration of the complex $5\times10^{-3}M$; complex: pyridine ratio—1:80.

We have studied the variations in the parameters g_o and a with temperature and pyridine concentration. Figure 6 shows the temperature dependance of the parameters g_o and a. (The measurements are carried out in the temperature interval 240°K-350°K on samples with complex: pyridine ratio 1:80.) No measurements were carried out under 240°K owing to the toluene vescosity rise. The temperature dependance of the parameters g_o and a is affected by the pyridine concentration in the sample. When the complex: pyridine ratio is 1:80 (Figure 6) the realisation of two extreme states: no pyridine molecules along the z axis (at high temperature) and two pyridine molecules along it (at low temperature) is possible.

Two absorption bands are observed in the electronic spectra of copper(II) dithiocarbamate complexes in noncoordinating solvent (toluene, heptane) corresponding to the transitions

$$d_{x^2-y^2}\rightarrow d_{xy}(23.000\ \mathrm{cm}^{-1})\ \text{and}\ d_{x^2-y^2}\rightarrow d_{xz,yz}(33.000\ \mathrm{cm}^{-1})^{2,3}$$

The molecular orbital coefficients were calculated according to the method of Maki and McGarvey[14] and Kivelson and Neiman[15] with the use of the anisotropic spin-Hamiltonian parameters shown in Figure 3 and the above optical spectral data. In pure noncoordinating solvents (toluene, heptane) $\alpha^2=0.57$, $\beta_1^2=0.52$, $\beta^2=0.85$, and at complex: pyridine ratio 1:2 $\alpha^2=0.55$, $\beta_1^2=0.70$, $\beta^2=1.0$ are equal to the corresponding values observed in pure pyridine.

The values of the molecular orbital parameters show that greatest alterations are observed in the xz and yz planes where the π bonds become ionic ($\beta^2=1.0$). The changes taking place in the xy plane are smaller, the orbital xy being the most affected. The behavior of the orbital $|x^2-y^2>$ seems interesting. The value of α^2 does not increase, as might have been expected owing to the lowering of the metal-ligand bond covalent character, but decreases. This fact is discussed below.

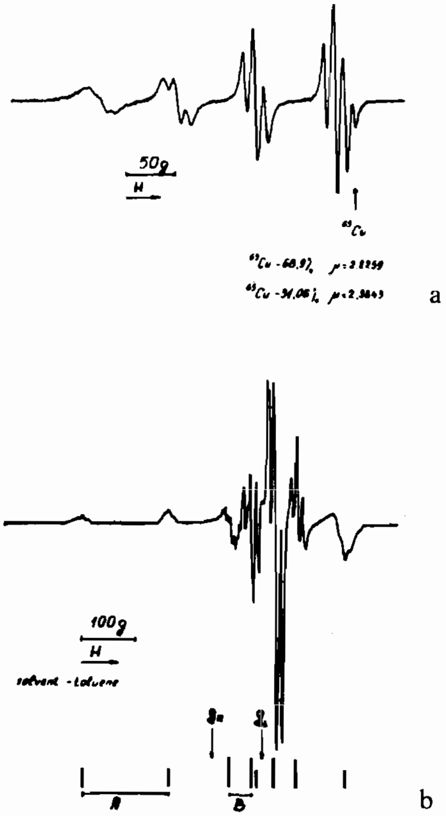

Figure 7. EPR spectrum typical for copper(II) dithiophosphate complexes in noncoordinating solvent (toluene): a—T =300°K,b— T=77°K.

II. *Dithiophosphate Complexes.* Figure 7 shows EPR spectra typical for copper(II) dithiophosphate complexes in toluene at room temperature and at 77°K. The EPR parameters of these complexes are: $g_o = 2.046\pm0.001$, $a = 72\pm2$G, $a^{31P} = 9.9\pm1$G, $g_\parallel = 2.083\pm0.002$, $g_\perp = 2.023\pm0.002$, A = 164±3G, B = 41±2G, $A^{31P} = 11.1\pm1$G.

The absorption spectra of this type of copper(II) complexes contain two bands corresponding to the transitions $d_{x^2-y^2}\rightarrow d_{xy}$ (23.700 cm^{-1}) and $d_{x^2-y^2}\rightarrow d_{xz}$, d_{yz} (31.000 cm^{-1}).[2,3]

$$d_{y^2-y^2}\rightarrow d_{xy}\ (23.700\ \mathrm{cm}^{-1})\ \text{and}\ d_{x^2-y^2}\rightarrow d_{xz},d_{yz}(31.000\ \mathrm{cm}^{-1})^{2,3}.$$

The corresponding molecular orbital coefficients are:[2,3] $\alpha^2=0.56$, $\beta_1^2=0.53$, and $\beta^2=0.70$.

In 0.08% pyridine solution (complex: pyridine ratio 1:2) the upper parameters aquire the following values: $g_o = 2.046\pm0.001$, $a = 74\pm2$G, $a^{31P} = 9.6\pm1$G, g = 2.032±0.002, A = 140±3G, B = 20±2G, and $A^{31P} = 8.7\pm1$G.

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Figure 8 shows the typical EPR spectrum of these complexes at 77°K. At room temperature it has the shape shown on Figure 7. The absorption spectra contain the bands at 23.700 cm^{-1} and at 31.000 cm^{-1}. The molecular orbital coefficients are $\alpha^2=0.53$, $\beta_1^2=0.74$, $\beta^2=1.0$.

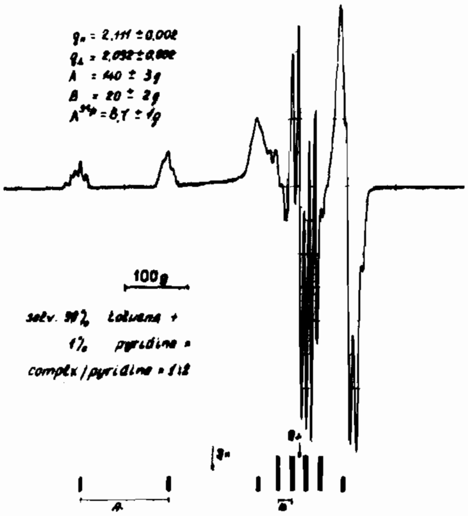

Figure 8. EPR spectrum typical for copper(II) dithiophosphate complexes in a solvent mixture of toluene and pyridine. Concentrations: complex $5\times10^{-3}M$; pyridine— $1\times10^{-2}M$; T=77°K.

Some conclusions about the changes in the electronic structure of these complexes could be reached using variations in the ehfs values of their EPR spectra with complex: pyridine ratio. The following equation is written[14] for the direct interaction of copper(II) orbitals with the ligand atom orbitals giving ehfs in the EPR spectrum of the complex:

$$A^{shf} = - -\alpha\beta_o\beta_N\alpha'^2\delta(r) \qquad (1)$$

Applyng correlations (1) and (2)[15]

$$\alpha^2+\alpha'^2-2\alpha\alpha' S=1 \qquad (2)$$

and the value 0.2[16] for the overlap integral S in noncoordinating solvent to our data for dithiophosphate complexes we obtain the value 0.07 for the overlap integral in pyridine as a solvent.

The following conclusions arise from our studies: 1) The variations of the EPR parameters and MO coefficients with the complex: to pyridine ratio are due to the interaction between the pyridine molecules and copper(II) ion along the z axis of the complex. 2) Two pyridine molecules are coordinated around the copper(II) dithiophosphate and dithiocarbamate complexes. 3) There is no interaction between the pyridine molecules and the ligand functional groups in these complexes. 4) The unpaired electron is standin on an orbital given by the following expression:

$$\Psi=c_1|x^2-y^2>-c_2|3z^2-r^2>$$

When the complex is unperturbed by the solvent molecules (in noncoordinating solvent) $c_2=0$. When the complex is perturbed by the solvent molecules $c_2\neq0$. A hybridization between the orbitals $|x^2-y^2>$ and $|3z^2-r^2>$ is available in this case.[17]* For that reason it is probable that some possibility of opening of the chelate will arise owing to the changes in the electronic structure of the copper(II) ion. 5) It is probable that the hybridization of the orbitals $|x^2-y^2>$ and $|3z^2-r^2>$ causes a partial screening of the copper(II) nuclei and thus decreases the positive charge in the xy plane, *i.e.* the complex extends in it.

Experimental Section

The preparation of dithiocarbamate and dithiophosphate complexes was described.[2,3] In all experiments $CuCl_2$ with a natural mixture of two copper isotopes (^{63}Cu-68.9% and ^{65}Cu-31.1%) was used. The lines of these isotopes are observed in all EPR spectra, but they are not marked, in the stick spectra in order to simplify the latter.

The complex concentration in all experiments was 5.10^{-3} *M*.

The EPR spectra were obtained with a JEOL EPR spectrometer Model JES-3BS-X using 100-kc modulation. A quarz dewar vessel was used in the experiments carried out at 77°K where the spectrometer resonator was placed. The investigations at different temperatures were carried out with a standard attachment to the spectrometer. The oxygen influence on the line widths was eliminated by evacuation of all investigated samples to 1.10^{-4} mm Hg.

The optical spectra were obtained with Unicam SP 800 spectrophotometer.

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* The symmetry D_{2h} was supposed for these complexes[2,3].

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