

## ESR STUDY OF THE STRUCTURE AND BONDING SITUATION IN THIOCYANATOCOPPER(II) COMPLEXES WITH IMIDAZOLE DERIVATIVES

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ESR spectra of thiocyanatocopper(II) complexes with imidazole derivatives were studied in ethanolic solutions at 295 and 123 K. Axiallysymmetric spectra, attributed to the monomeric complex units, were obtained for the frozen solutions. The bonding parameters were interpreted by using calculated  $g$ , Cu-hyperfine, and  $^{14}\text{N}$ -ligand hyperfine splitting values. The Cu—N bond parameters indicate a considerable delocalization of the unpaired electron. The values of the isotropic Cu-hyperfine splitting suggest that the deviations from the planar symmetry of the  $\text{CuN}_4$  units are due to tetrahedral perturbation of the ligand field.

Thiocyanatocopper(II) complexes with imidazole type ligands (L) have been studied recently<sup>1</sup>. Their physical data indicate that all of the complexes studied have tetragonal stereochemistry, formed by *trans*-planar  $[\text{Cu}(\text{NCS})_2\text{L}_2]$  units between which bilateral axial interaction via the sulphur atoms of the NCS groups takes place. The thiocyanatocopper(II) complexes have been studied for comparing their structure properties with those of the analogous cyanato complexes<sup>2,3</sup>. ESR data of the cyanatocopper(II) complexes with imidazole ligands have given evidence that in complexes containing bulky ligands that pose steric hindrance (2-methyl- and 2-ethylbenzimidazole), the planar arrangement of Cu(II) is distorted.

The present ESR study was undertaken with a view to gaining insight into the bonding situation in thiocyanatocopper(II) complexes of  $[\text{Cu}(\text{NCS})_2\text{L}_2]$  type where L is imidazole (iz), 1- and 2-methylimidazole (1-meiz and 2-meiz, respectively), 1,2-dimethylimidazole (1,2-dimeiz), benzimidazole (bz), and 2-ethylbenzimidazole (2-etbz) in solutions.

### EXPERIMENTAL

The complex compounds were prepared as described in ref.<sup>1</sup>. Fresh solutions in ethanol,  $c = 10^{-4} \text{ mol dm}^{-3}$ , were used for ESR measurements. The frozen solutions were in a glassy state.

The ESR spectra were measured at 295 and 123 K on a Varian E-112 spectrometer (U.S.A.) in the X-band (100 kHz modulation). The magnetic field was calibrated by using the polycrystalline  $\alpha, \alpha'$ -diphenyl- $\beta$ -picrylhydrazyl radical (DPPH) as standard.

The electronic spectrum of  $[\text{Cu}(\text{NCS})_2(\text{iz})_2]$  in ethanol ( $c = 10^{-3} \text{ mol dm}^{-3}$ ) was scanned on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena, G.D.R.).

## RESULTS AND DISCUSSION

The  $[\text{Cu}(\text{NCS})_2\text{L}_2]$  complexes in ethanolic solutions at room temperature exhibit intense, poorly resolved ESR spectra with large line widths. The spectral parameters determined from these spectra involve large errors. The spectrum of  $[\text{Cu}(\text{NCS})_2(\text{iz})_2]$  is well-resolved and the high intensity line of the Cu-hyperfine structure displays hyperfine splitting from the nitrogen ligands, arising from the effect of the unpaired electron with the  $^{14}\text{N}$  nuclei of the coordinated ligands.

The ESR spectrum of  $[\text{Cu}(\text{NCS})_2(\text{iz})_2]$  in solution can be described by the spin Hamiltonian

$$\mathbf{H}_{\text{sp}} = g_0 \beta_e B \mathbf{S} + a_0 \mathbf{S} \mathbf{I} + \sum_{\text{N}} a_0^{\text{N}} \mathbf{S} \mathbf{I}^{\text{N}}, \quad (1)$$

where  $g_0$  is the isotropic value of the  $g$  factor,  $\beta_e$  is Bohr magneton,  $B$  is the magnetic field induction,  $\mathbf{S}$  is the electron spin operator,  $a_0$  is the isotropic constant of the hyperfine structure arising from the interaction of the electron spin and the Cu nuclear spin,  $\mathbf{I}$  is the nuclear spin operator,  $a_0^{\text{N}}$  is the isotropic constant of the hyperfine structure arising from the interaction of the electron spin and the  $^{14}\text{N}$  nuclear spin and  $\mathbf{I}^{\text{N}}$  is the  $^{14}\text{N}$  nuclear spin operator. For  $[\text{Cu}(\text{NCS})_2(\text{iz})_2]$  the values of  $g_0 = 2.138 \pm 0.003$ ,  $a_0 = (60 \pm 3) \cdot 10^{-4} \text{ cm}^{-1}$  and  $a_0^{\text{N}} = (13.58 \pm 0.5) \cdot 10^{-4} \text{ cm}^{-1}$  were obtained.

The ESR spectra of all the complexes in frozen solutions at 123 K exhibit well-resolved Cu-hyperfine splitting in the parallel spectral region; in the perpendicular region the Cu hyperfine splitting approaches zero. Such axial spectra give evidence of the occurrence of monomeric units in the solution. Apparently, the axial ligation formed by the sulphur atoms of the NCS groups<sup>1</sup> is disturbed in solution, whereupon the monomeric species are formed from the polymeric structures of the complexes. A weak coordination of solvent, however, is conceivable.

The ESR spectra of the  $[\text{Cu}(\text{NCS})_2(\text{iz})_2]$ ,  $[\text{Cu}(\text{NCS})_2(2\text{-meiz})_2]$ ,  $[\text{Cu}(\text{NCS})_2(1,2\text{-dimeiz})_2]$ , and  $[\text{Cu}(\text{NCS})_2(\text{bz})_2]$  complexes exhibit hyperfine splitting of the  $^{14}\text{N}$  ligands both in the parallel and perpendicular regions (Fig. 1), whereas in the spectrum of the  $[\text{Cu}(\text{NCS})_2(1\text{-meiz})_2]$  complex this splitting is observed in the parallel region only. The number of lines (9) as well as their nearly identical spacing gives evidence that the four nitrogens are equally strongly bonded. The spectra of the frozen solutions can be described by the spin Hamiltonian of axial symmetry

$$\begin{aligned} \mathbf{H}_{\text{sp}} = & \beta_e [g_{\parallel} B_z \mathbf{S}_z + g_{\perp} (B_x \mathbf{S}_x + B_y \mathbf{S}_y)] + A_{\parallel} \mathbf{S}_z \mathbf{I}_z + \\ & + A_{\perp} (\mathbf{S}_x \mathbf{I}_x + \mathbf{S}_y \mathbf{I}_y) + \sum_{\text{N}} \mathbf{S} A^{\text{N}} \mathbf{I}^{\text{N}}, \end{aligned} \quad (2)$$

where  $g_{\parallel}$ -,  $A_{\parallel}$ -components and  $g_{\perp}$ -,  $A_{\perp}$ -components refer to the  $\mathbf{g}$ -,  $\mathbf{a}$ -tensor parallel with and perpendicular to the  $z$ -axis, respectively, and the subscripts  $x$ ,  $y$ ,  $z$  refer to the respective components of the quantities; the other symbols have the same meaning as before. By means of the isotropic value  $a_0$  of hyperfine splitting Cu and  $A_{\parallel}$ , calculated value  $A_{\perp} = 5.5 \cdot 10^{-4} \text{ cm}^{-1}$  is in agreement with the assumption that the value of hyperfine splitting in perpendicular region is small. The experimentally obtained parameters are given in Table I.

If the primary coordination sphere of  $[\text{Cu}(\text{NCS})_2\text{L}_2]$  is assumed to possess the  $D_{4h}$  symmetry, the following antibonding molecular orbitals are obtained in order of increasing energy<sup>4,5</sup> (for the N donors located on the  $x$ ,  $y$  axes):

$$\begin{aligned} |B_{1g}\rangle &= \alpha |d_{x^2-y^2}\rangle - (\alpha'/2) [\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)}] \\ |B_{2g}\rangle &= \beta |d_{xy}\rangle - (\beta'/2) [p_y^{(1)} + p_x^{(2)} - p_y^{(3)} - p_x^{(4)}] \\ |E_g\rangle &= \begin{cases} \varepsilon |d_{xz}\rangle - (1/2)^{1/2} \varepsilon' [p_z^{(1)} - p_z^{(3)}] \\ \varepsilon |d_{yz}\rangle - (1/2)^{1/2} \varepsilon' [p_z^{(2)} - p_z^{(4)}] \end{cases} \end{aligned} \quad (3)$$

The equation

$$\sigma^{(i)} = n p^{(i)} \pm (1 - n^2)^{1/2} s^{(i)}, \quad (4)$$

where  $n^2$  is the degree of hybridization between the  $2s$  and  $2p$  orbitals at the nitrogen atom, holds true.

The parameters of the spin Hamiltonian calculated within the MO model allow some conclusions concerning the bonding situation in the complexes to be drawn.

The unpaired electron is predominantly localized at the Cu—N  $\sigma$ -bond which is

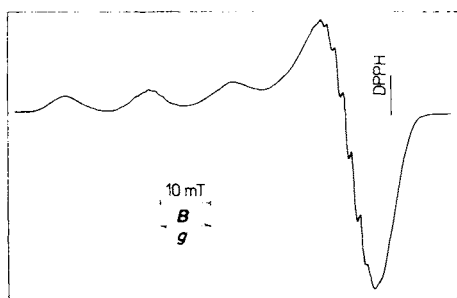


FIG. 1  
X-band ESR spectrum of  $[\text{Cu}(\text{NCS})_2 \cdot (2\text{-meiz})_2]$  in ethanol at 123 K

described by the  $B_{1g}$  molecular orbital, and the  $\alpha$  coefficient is a measure of ionic nature of this bond. The  $B_{2g}$  and  $E_g$  molecular orbitals characterize the in-plane and out-of-plane  $\pi$ -bonds, respectively.

The  $\alpha^2$ ,  $(\alpha')^2$ , and  $n^2$  coefficients for the molecular orbital of the unpaired electron, calculated conventionally<sup>6,7</sup> from the experimentally obtained parameters of the spin Hamiltonian are given in Table I. The following values were used<sup>4</sup>: spin-orbital coupling constant for the free  $\text{Cu}^{2+}$  ion,  $\lambda_0(\text{Cu}) = -829 \text{ cm}^{-1}$  and probability of occurrence of the  $2s$ -electron at the N-nucleus,  $|\Psi_{2s}(0)|^2 = 33.4 \cdot 10^{24} \text{ cm}^{-3}$  for  $\langle r^{-3} \rangle_{2p}(\text{N}) = 21.1 \cdot 10^{24} \text{ cm}^{-3}$  and for the overlap integral of the group orbitals of  $B_{1g}$  symmetry  $S = 0.1$ .

The degrees of hybridization of the nitrogen atoms of the thiocyanate group and the imidazole ligand are different: for the former,  $sp$  hybridization is most probable<sup>8</sup> whereas for the latter,  $sp^2$  hybridization will occur<sup>9</sup>. Since the isotropic part of the  $^{14}\text{N}$ -hyperfine tensor prevails over the anisotropic part, the nitrogen atoms cannot be discriminated in the ESR spectra of the frozen or liquid solutions.

The hybridization degree  $n^2$  calculated from the observed  $A_{\parallel}^{\text{N}}$  and  $A_{\perp}^{\text{N}}$  values lies within the region of 0.68–0.72, the  $\alpha^2$  and  $(\alpha')^2$  values lie within the regions of 0.78–0.82 and 0.28–0.32, respectively, indicating a high degree of delocalization of the unpaired electron in the  $B_{1g}$  molecular orbital. The degree of covalency of the

TABLE I

ESR parameters and bonding coefficients of  $[\text{Cu}(\text{NCS})_2\text{L}_2]$  type thiocyanatocopper(II) complexes

Parameter <sup>a</sup>	L					
	iz	1-meiz	2-meiz	1,2-dimeiz	bz	2-etbz
$g_{\parallel}$	2.279	2.274	2.281	2.284	2.284	2.311
$g_{\perp}$	2.051	2.064	2.033	2.053	2.053	2.048
$A_{\parallel}(\text{Cu})$	170.9	175.8	175.7	176.3	176.0	159.2
$A_{\perp}^{\text{N}}$	12.8	12.9	12.8	12.1	12.4	—
$A_{\parallel}^{\text{N}}$	15.9	—	15.6	15.0	15.0	—
$a^{\text{N}b}$	13.83	—	13.73	13.0	13.3	—
$\alpha^2$	0.78	0.82	0.81	0.80	0.81	0.81
$(\alpha')^2$	0.32	0.28	0.32	0.32	0.30	0.29
$n^2$	0.72	—	0.69	0.71	0.68	—

<sup>a</sup> Exchange constants in  $10^{-4} \text{ cm}^{-1}$ ; accuracy:  $g_{\parallel} \pm 0.002$ ,  $g_{\perp} \pm 0.005$ ,  $A_{\parallel}(\text{Cu}) \pm 1.0$ ,  $A_{\perp}^{\text{N}} \pm 0.2$ ,  $A_{\parallel}^{\text{N}} \pm 0.3$ ; <sup>b</sup> calculated as  $a^{\text{N}} = (2A_{\perp}^{\text{N}} + A_{\parallel}^{\text{N}})/3$ .

Cu—N  $\sigma$ -bond, however, is lower than in other neutral  $\text{CuN}_4$  complexes with poly-functional ligands<sup>7,10</sup>, for which the  $\alpha^2$  values have been found within the 0.7–0.75 range.

The knowledge of the energy corresponding to the  $d-d$  transitions in the ligand field is prerequisite for the calculation of the  $\beta^2$  and  $\varepsilon^2$  bonding parameters characterizing the in-plane and out-of-plane  $\pi$ -bonds, respectively. The electronic spectrum of  $[\text{Cu}(\text{NCS})_2(\text{iz})_2]$  in ethanol displays an asymmetrical ligand field band at  $14\,400\text{ cm}^{-1}$ . The band at  $27\,000\text{ cm}^{-1}$  is a CT band, so that the band at  $14\,400\text{ cm}^{-1}$  can be attributed to the two transitions  $B_{1g} \rightarrow B_{2g}$  and  $B_{1g} \rightarrow E_g$ . Calculations<sup>7</sup> based on the  $g$ -tensor give values of  $\beta^2 = 0.86$  and  $\varepsilon^2 = 0.60$ , which, however, are subject to large errors due to the unresolved  $d-d$  transitions. Still, the  $\varepsilon^2$  value indicates an appreciable covalency of the out-of-plane  $\pi$ -bonds. The in-plane  $\pi$ -bonds in the thiocyanatocopper(II) complexes have a more ionic character than in the analogous cyanatocopper(II) complexes<sup>3</sup>.

The calculated isotropic  $a_0$  values of the Cu hyperfine splitting in the spectra of frozen solutions over the region of  $(53-60) \cdot 10^{-4}\text{ cm}^{-1}$  indicate some distortion of the planar arrangement toward the tetrahedral arrangement. The reason for this is probably in the steric hindrance of the imidazole ligands, the distortion being most pronounced in the complex with 2-ethylbenzimidazole.

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