ESR-SPECTRA OF CYANATO-COPPER(II) COMPLEXES
WITH HETEROCYCLIC NITROGEN LIGANDS*

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Dedicated to Professor A. Okáč on the occasion of his 70th birthday.

The ESR-spectra of cyanato-copper(II) complexes of the $Cu(NCO)_2L_2$ type, where L is a methyl derivative of pyridine or a ligand of the quinoline or isoquinoline type, were measured in the polycrystalline state at the X-band frequency. The spectra obtained are of the axial type, the $g_\perp$-values lying between c. 2·04—2·06 and $g_\parallel$-values between c. 2·21—2·27; the spectrum of the complex $Cu(NCO)_2$ (2,4,6-collidine)$_2$ has an unresolved $g_\parallel$-value. The g-values obtained are in agreement with elongated tetragonal microsymmetry involving the donor nitrogen atoms. Approximate values of $k_\perp$ and $k_\parallel$ were calculated; they serve for qualitative evaluation of the participation of out-of-plane or in-plane π-bonds in the bonding system of individual complexes.

In our previous papers[1] we have studied a number of cyanato-copper(II) complexes of the Cu. .(NCO)$_2$L$_2$ type (where L = picoline = pic, lutidine = lut, collidine = coll, quinoline = qin, methylquinoline = mqin, isoquinoline = i-qin, methylisoquinoline = mi-qin) based on measurements of magnetic susceptibilities[1], and electronic[1,2] and infrared spectra[3]. In order to find further structural parameters, we studied these complexes by the method of electron spin resonance (ESR). The results of this investigation are dealt with in the present paper.

Rein and coworkers[4] have already measured the ESR spectra of $Cu(NCO)_2L_2$ complexes, where L = α-, β-, or γ-pic, 2,6-lut, and 2,4,6-coll. However, their results do not quite agree with ours and since the above complexes are included in our broader research field[1] we consider publication of our ESR data for these complexes to be justified.

EXPERIMENTAL

The ESR-spectra were obtained using the Varian E-3 instrument, operating in the X-band with 100 kHz modulation. The measurement was performed with compounds prepared earlier[1,5] in a polycrystalline powder state; the spectra obtained were evaluated by the Kneubühl method[6]. The g-factor values were determined relative to "Varian pitch" as a calibration standard[7] ($g_0 = 2·0028$; $\Delta H_{pp} = 1·4$ Oe). The modulation of the magnetic field was calibrated using Mn^{2+} ions ($\Delta H_s = 96$ Oe). The maximum error amounts to ±0·008 and ±0·015 for the determination

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of $g_\perp$ and $g_\parallel$, respectively. For control purposes, the ESR-spectrum of a $CuSO_4 . 5 H_2O$ poly-crystalline sample was recorded, yielding $g_1 = 2.077$ and $g_2 = 2.265$; the literature[8] values are $g_1 = 2.08$ and $g_2 = 2.27$ both for a single crystal and for polycrystalline material. The values of the g-factors found are given in Table I; selected spectra are depicted in Fig. 1.

RESULTS AND DISCUSSION

Except for L = 2,4,6-coll, the ESR-spectra of $Cu(NCO)_2L_2$ complexes are of the axial type without developed hyperfine structure at $g_\parallel$. The $g_\perp$ values lie between c. $2.04 - 2.06$ and the $g_\parallel$ values between c. $2.21 - 2.27$. This is in agreement with the data calculated[9] and found[8] for Cu(II) complexes with elongated tetragonal micro-symmetry (the $d_{x^2-y^2}$ ground state) with nitrogen donor atoms.

The g-factor values, published[4] earlier for $Cu(NCO)_2L_2$ complexes (L = α-, β-, or γ-pic, 2,6-lut, and 2,4,6-coll), are higher by $0.013 - 0.046$ for $g_\perp$ and by 0.01 to 0.02 for $g_\parallel$ (except for a single case) than our values, obtained by repeated measurements on samples with well-defined analytical composition. The reason for these differences, which are especially conspicuous with the more accurately determinable $g_\perp$-values, cannot be unambiguously explained, since the authors[4] did not specify the preparation method and results of analyses of the measured samples, so that the sample quality cannot be evaluated. Certain deviations between the $g_\perp$-values in the given direction may be caused by the different techniques used for their determination (the techniques employed for obtaining the more consistent $g_\parallel$ values

TABLE I

The Electronic Parameters of the $Cu(NCO)_2L_2$ Complexes

L	$g_\perp$	$g_\parallel$	g_0^a	G	$k_\perp$	$k_\parallel$
α-pic	2.048	2.251	2.116	5.23	0.72	0.75
β-pic	2.053	2.249	2.118	4.70	0.70	0.76
γ-pic	2.039	2.242	2.107	6.21	0.62	0.77
2,4-lut	2.053	2.240	2.115	4.53	0.74	0.70
2,6-lut	2.050	2.216	2.105	4.41	0.76	0.68
2,4,6-coll	2.051	—	—	—	—	—
qin	2.061	2.244	2.122	4.00	0.76	0.76
2-mqin	2.040	2.214	2.098	5.35	0.62	0.66
4-mqin	2.038	2.224	2.100	5.90	0.62	0.75
i-qin	2.039	2.216	2.098	5.54	0.63	0.67
3-mi-qin	2.060	2.270	2.130	4.50	0.77	0.72

[a] Calculated from relation $g_0 = (1/3) (2g_\perp + g_\parallel)$.

are identical). However it must be emphasized that the $g_\perp$-values given in paper[4] are generally considerably higher than the upper limit acceptable[8,9] for Cu(II)—N systems.

Cu(NCO)$_2$(2,4,6-coll)$_2$ also exhibits an asymmetrical ESR-spectrum, but with a single broad line (about 1050 Oe), without a resolved $g_\parallel$-value. This behaviour is most probably caused[8] by considerable misalignment of the molecular or magnetic axes in the crystal structure, leading to an efficient exchange interaction between non-equivalent Cu^{2+} ions. Such a misalignment may be caused by the tendency of the Cu(NCO)$_2$(2,4,6-coll)$_2$ species, containing 2,4,6-collidine molecules with protruding methyl groups, to form as smooth and spatially efficient arrangement in the crystal as possible.

For the g-factors of Cu^{2+} ion in the tetragonal ligand field ($\mathbf{D_{4h}}$) with the $d_{x^2-y^2}$ ground state, the simplified equations

$$g_\perp = 2.0023 - 2k_\perp^2 \lambda / \Delta(^2\mathbf{E_g}), \qquad (1)$$

$$g_\parallel = 2.0023 - 8k_\parallel^2 \lambda / \Delta(^2\mathbf{B_{2g}}), \qquad (2)$$

hold[8,10,11] where λ is the spin-orbit coupling constant for free Cu^{2+} ions ($-0.829\,\mathrm{kK}$), $\Delta(^2\mathbf{E_g})$ and $\Delta(^2\mathbf{B_{2g}})$ denote the energies of $^2\mathbf{E_g} \leftarrow {}^2\mathbf{B_{1g}}$ and $^2\mathbf{B_{2g}} \leftarrow {}^2\mathbf{B_{1g}}$ electron transitions, respectively, which can be found from the electronic spectra, and the parameters $k_\perp$ and $k_\parallel$ represent the so-called orbital reduction factors. These parameters account for[8,12,13] delocalization of the unpaired electron in the Cu^{2+} ion, which is caused by formation of molecular orbitals and leads to a decrease in the orbital angular momentum operator, L, as well as for the spin-orbital reduction, resulting in a decrease in constant λ.
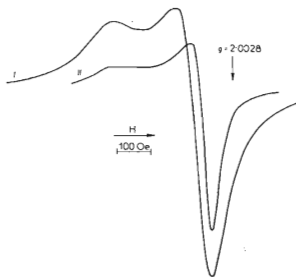

FIG. 1

The ESR-Spectra of the Complexes I — Cu(NCO)$_2$(γ-pic)$_2$ and II — Cu(NCO)$_2$ (4-mqin)$_2$

For prolonged tetragonal Cu(II) complexes, Procter and coworkers introduced[14] the factor G, derived from equations (1) and (2)

$$G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4k_{\parallel}^2 \varDelta(^2\mathbf{E}_g)/k_{\perp}^2 \varDelta(^2\mathbf{B}_{2g}). \tag{3}$$

Since it generally holds for these complexes that $k_{\parallel}^2 \geqq k_{\perp}^2$ and $\varDelta(^2\mathbf{E}_g) \geqq \varDelta(^2\mathbf{B}_{2g})$, the G value should vary from 4·0 to 4·5. If the G value is lower than 4, Procter and co-workers conclude[14] that exchange interaction between crystallographically non-equivalent Cu^{2+} ions takes place, with consequent drawing of the crystal g-values together, so that these values no longer reflect the microsymmetry of the Cu(II) complexes present.

Using the obtained g-values, we calculated the G values according to relation (3) for the complexes investigated; they are given in Table I. These values are betwen 4·0 — 6·21, i.e. higher than 4. Hence we can conclude that the Cu^{2+} ions occupy at least approximately crystallographically equivalent positions in the crystal structures, the directional properties of the g-tensor thus remaining practically unchanged. Therefore we considered it useful to calculate the values of parameters $k_{\perp}$ and $k_{\parallel}$, using equations (1) and (2), from the g-factors and the energy values of the corresponding transitions obtained from the electronic spectra[1,2]; they are given in Table I.

Parameters k were interpreted[10] on the basis of the molecular orbital theory. Relations correlating them with α, β_1, and β coefficients, which express the contribution from the $d_{x^2-y^2}$, d_{xz} or d_{yz}, and d_{xy} orbitals of the Cu^{2+} ion to the molecular orbitals, and with the Cu-ligand overlap integrals, were derived[15,16]. Billing and coworkers[17] neglect these integrals and employ the approximate relations

$$k_{\perp} \approx \alpha\beta_1, \tag{4}$$

$$k_{\parallel} \approx \alpha\beta. \tag{5}$$

The coefficient α is a criterion of the σ-bond strength and coefficients β_1 and β of the out-of-plane and in-plane π-bond strength, respectively.

It is impossible to find all three molecular orbital coefficients from relations (4) and (5), using $k_{\perp}$ and $k_{\parallel}$, nonetheless a qualitative evaluation is possible.

The calculated k-parameter values indicate a significant contribution of covalence to the Cu—N bonds. The group of complexes with methyl derivatives of pyridine exhibits fairly regular behaviour. For L = α-, β-, and γ-pic, $k_{\parallel}$ is greater than $k_{\perp}$, $k_{\parallel}$ being approximately constant and $k_{\perp}$ remarkably decreasing in the above L order. On this basis we conclude that, with very similar σ-bond strengths, the participation of out-of-plane π-bonds in the complex bonding system increases along the above L order. With $Cu(NCO)_2 (\alpha\text{-pic})_2$, the unimportant contribution from out-of-plane π-bonding may be connected with steric hindrance, which prevents the α-pic mole-

cule from remaining in the xy plane and forces it out of this plane[1], thus reducing the possibility of Cu → L out-of-plane π interaction. The strengthening of the out-of-plane π-bonding going from L = β-pic to L = γ-pic (a decrease of $k_\perp$) is in agreement with the greater π-acceptor ability of γ-picoline compared to β-picoline[18].

For complexes with the lutidines it holds, on the other hand, that $k_\perp > k_\parallel$; $k_\perp$ is very close to the $k_\parallel$ value for the picoline complexes, while $k_\parallel$ decreases from L = = 2,4-lut to L = 2,6-lut. This can be considered as an indication of existence of in-plane π-bonding, the participation of which increases by the above L. The 2,4- and 2,6-lut molecules again exhibit a steric effect and if they deviate from the xy plane by roughly the right angle, the steric interaction is decreased and a Cu → L in-plane π-interaction is simultaneously rendered possible. This process seems to be especially significant with $Cu(NCO)_2(2,6\text{-lut})_2$, where $k_\perp$ is higher than $k_\parallel$ by 0·08. This agrees with the presence of two methyl groups in the sterically hindered α-positions.

If the complexes discussed are ordered according to the increasing Cu → L π-interaction, be it out-of-plane or in-plane, the following rough order is obtained (only ligands L are given) α-pic < 2,4-lut < β-pic < 2,6-lut < γ-pic. It is interesting that the thermal stability of the $Cu(NCO)_2L_2$ complexes increases in the same order[1], the first two, with which the participation of π-bonding seems to be very small, showing a tendency for conversion into $Cu(NCO)_2L$ complexes on dissociation of one L molecule[1].

A less clear situation exists with complexes having ligands of the quinoline or iso-quinoline type. For the $Cu(NCO)_2(qin)_2$ complex it holds that $k_\perp = k_\parallel$, which, according to equations (4) and (5), would indicate the complete absence of π-bonds. However, Hathaway and coworkers[19] have pointed out that this approach neglects the effect of purely orbital and spin-orbital reduction on the k-values. Both these effects may be significant in some cases[20]. For $Cu(NCO)_2(2\text{-mqin})_2$, $Cu(NCO)_2(i\text{-qin})_2$ and $Cu(NCO)_2(4\text{-mqin})_2$ the $k_\perp$ and $k_\parallel$ values indicate that with the former two complexes is the out-of-plane π-interaction Cu → L approximately the same, but with the latter one is considerably stronger. With $Cu(NCO)_2$ (3-mi-qin)$_2$, however, the relation $k_\perp > k_\parallel$ shows the in-plane rather than out-of-plane π-interaction. It should be noted that the $k_\parallel$-values may be subject to a rather high error with these complexes, since $^2B_{2g} \leftarrow {}^2B_{1g}$ transitions are included in main bands in the electronic spectra or are manifested as poorly resolved shoulders, and thus their energies cannot be determined with sufficient accuracy. In any case, we do not consider a more detailed analysis of the electronic parameters of these complexes to be useful under the present circumstances.

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