

## INFLUENCE OF THE NITRILE GROUP ON STRUCTURE PROPERTIES OF PSEUDOHALOGENO-COPPER(II) AND NICKEL(II) COMPLEXES WITH 3- AND 4-CYANOPYRIDINES

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*Dedicated to Professor J. Gažo on the occasion of his unlied 60th birthday.*

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Pseudohalogenocomplexes of the types  $[\text{CuX}_2\text{L}_2]$  ( $\text{X} = \text{NCO}, \text{C}(\text{CN})_3, \text{N}(\text{CN})_2$ ;  $\text{L} = 3\text{- or }4\text{-CN-py}$ ) and  $[\text{NiX}_2\text{L}_2]$  ( $\text{X} = \text{C}(\text{CN})_3, \text{N}(\text{CN})_2$ ;  $\text{L}$  as before) have been prepared and investigated by spectroscopic methods. As the results show the  $[\text{CuX}_2\text{L}_2]$  complexes have pseudo-octahedral structures with variable degree of tetragonal distortion and contain bridging pseudohalide ligands. The NCO groups bridge on the end-to-end fashion, forming by their oxygens long axial bondings. The  $\text{N}(\text{CN})_2$  groups very likely bridge asymmetrically by means of their amide and cyanide nitrogens, the former ones being used for strong equatorial bonds. The  $[\text{NiX}_2\text{L}_2]$  complexes are octahedral and also exhibit the pseudohalides in bridging function which, however, is realized with dicyanamide symmetrically through both cyanide nitrogens.

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In recent period, considerable attention has been devoted to study copper(II) and nickel(II) complexes with cyanates as with non linear pseudohalides, tricyanmethanides and dicyanamides, containing a variety of pyridine (py) derivatives as neutral ligands<sup>1-6</sup>. It has been ascertained that in cyanatocomplexes the electronic and especially the steric effect of the pyridine ring substituent exert a distinct influence upon the stereochemical properties of the relevant systems, on their tetragonal distortion (in the case of Cu(II)), etc. On the other hand, the structural influence of various alkylpyridines in tricyanmethanide or dicyanamide complexes is manifested in much smaller extent, the stereochemistry remains practically unchanged, and only subtle changes in some parameters were observed.

Continuing this research, we examined ten pseudohalogeno-copper(II) and nickel(II) complexes of 3- and 4-cyanopyridine. These ligands, in contrast to the alkylpyridines, exhibit negative inductive effect from the cyano group, are relatively

weak bases (measured in the order 4-CN-py > 3-CN-py)<sup>7</sup> but fairly good  $\pi$ -acceptors. Furthermore, cyanopyridines have two chemically different nitrogens of the pyridine and nitrile type which can be applied as donors and thus, they are potentially bidentate ligands. Various spectroscopic techniques were applied to assign adequate structures to these compounds. Cyanato-nickel(II) complexes of cyanopyridines were not included in this work, since they were exhaustively studied by Nelson<sup>8</sup>. For  $[\text{Cu}(\text{NCO})_2(4\text{-CN-py})_2]$  the infrared spectrum in the range 4 000–400  $\text{cm}^{-1}$  and solution electronic spectrum were already measured<sup>9</sup>.

## EXPERIMENTAL

### Preparation of Compounds

$[\text{CuX}_2\text{L}_2]$ , where X = NCO, C(CN)<sub>3</sub>, N(CN)<sub>2</sub>; L = 3-CN-py, 4-CN-py and  $[\text{NiX}_2\text{L}_2]$ , where X = C(CN)<sub>3</sub>, N(CN)<sub>2</sub>; L as before. Aqueous solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  or  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  is mixed with aqueous solution of KX and a methanol solution of the compound L is added under continuous stirring. The respective complex precipitates immediately in the form of a fine crystalline material which is collected, washed by a water-methanol mixture and dried in a desiccator over KOH.

Solutions used: 5 mmol of  $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$  or  $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$  in 6  $\text{cm}^3$  of water, 11 mmol of KNCO in 6  $\text{cm}^3$  of water, 11 mmol of  $\text{KC}(\text{CN})_3$  or  $\text{KN}(\text{CN})_2$  in 8  $\text{cm}^3$  of water, 12 mmol of 3-CN-py in 12  $\text{cm}^3$  of methanol, 12 mmol of 4-CN-py in 10  $\text{cm}^3$  of methanol.

Attempts were made to prepare also pseudohalide complexes of 2-cyanopyridine, but only products of undefined composition were obtained.

### Analyses and Other Properties

Copper and nickel were determined chelatometrically after decomposition of the compounds by diluted  $\text{H}_2\text{SO}_4$  and oxidation of the organic component by  $\text{K}_2\text{S}_2\text{O}_8$ . The elemental analysis was carried out using a C,H,N-analyser Carlo-Erba. The analytical results for the complexes are shown in Table I, together with some other characteristic data.

The compounds under study are well soluble in dimethylformamide, less in water and methanol and slightly soluble in ethanol and acetone.

As it follows from the powder diffraction patterns, both tricyanmethanido-copper(II) complexes have considerably similar crystal structures but they are not isostructural.

### Physical Measurements

The infrared spectra were measured in the region 4 000–200  $\text{cm}^{-1}$  on a Specord M80 spectrophotometer (Carl Zeiss, Jena); the spectra were obtained as Nujol mulls. The ESR spectra were recorded on a Bruker ER 200E-FRC apparatus operating at X-band frequency (9.416 GHz) with 100 kHz modulation. Polycrystalline powder samples were taken for measurements. The electronic spectra were measured as described previously.<sup>6</sup>

## RESULTS AND DISCUSSION

*Infrared Spectra*

The infrared bands of the pseudohalide ligands and of the M—N stretches were assigned by comparing the spectra recorded with the already published spectra of the free cyanopyridines as well as of the metal complexes with these ligands<sup>8,10,11</sup>. The infrared frequencies, characteristic for the complexes under study, are listed in Table II.

TABLE I  
Analytical and other characteristic data for  $[MX_2L_2]$  complexes

Compound	Colour	Calculated/Found				Dec. t. <sup>a</sup> , °C
		% C	% H	% N	% M	
$[Cu(NCO)_2(3-CN-py)_2]$	blue	47·26	2·27	23·62	17·86	140
		46·82	2·30	23·23	17·68	
$[Cu(NCO)_2(4-CN-py)_2]$	light blue	47·26	2·27	23·62	17·86	130
		46·63	2·34	23·14	17·71	
$[Cu\{C(CN)_3\}_2(3-CN-py)_2]$	ochre	53·16	1·78	31·00	14·06	165
		52·73	1·81	30·46	13·97	
$[Cu\{C(CN)_3\}_2(4-CN-py)_2]$	brown	53·16	1·78	31·00	14·06	135
		52·65	1·82	30·66	13·92	
$[Cu\{N(CN)_2\}_2(3-CN-py)_2]$	blue	47·59	2·00	34·68	15·73	150
		47·42	2·08	34·70	15·64	
$[Cu\{N(CN)_2\}_2(4-CN-py)_2]$	green blue	47·59	2·00	34·68	15·73	135
		47·14	2·03	34·38	15·66	
$[Ni\{C(CN)_3\}_2(3-CN-py)_2]$	light blue	53·73	1·80	31·33	13·13	310
		53·20	1·88	31·04	13·01	
$[Ni\{C(CN)_3\}_2(4-CN-py)_2]$	grey blue	53·73	1·80	31·33	13·13	200
		52·81	1·80	30·88	13·00	
$[Ni\{N(CN)_2\}_2(3-CN-py)_2]$	light blue	48·16	2·02	35·10	14·71	178
		47·67	2·09	34·73	14·64	
$[Ni\{N(CN)_2\}_2(4-CN-py)_2]$	blue	48·16	2·02	35·11	14·71	186
		47·58	2·06	34·83	14·58	

<sup>a</sup> Decomposition temperature; the measurements were made with 100 mg samples at a heating rate of 6°C/min.

TABLE II  
Characteristic infrared frequencies,  $\text{cm}^{-1}$ , for  $[\text{MX}_2\text{L}_2]$  complexes<sup>a</sup>

[Cu(NCO) <sub>2</sub> L <sub>2</sub> ]		[Cu{C(CN) <sub>3</sub> } <sub>2</sub> L <sub>2</sub> ]		[Cu{N(CN) <sub>2</sub> } <sub>2</sub> L <sub>2</sub> ]		[Ni{C(CN) <sub>3</sub> } <sub>2</sub> L <sub>2</sub> ]		[Ni{N(CN) <sub>2</sub> } <sub>2</sub> L <sub>2</sub> ]		Assignment
3-CN-py	4-CN-py	3-CN-py	4-CN-py	3-CN-py	4-CN-py	3-CN-py	4-CN-py	3-CN-py	4-CN-py	
2 243 m <sup>b</sup>		2 238 s <sup>d</sup>	2 246 sh <sup>b</sup>	2 242 s	2 238 s <sup>d</sup>	2 246 ms	2 243 ms <sup>d</sup>	2 294 vs	2 290 vs	$\nu_s +$ $\nu_{\text{as}}(\text{C-N})$ $\nu(\text{C}\equiv\text{N})$
		2 190 vs	2 238 mw	2 232 sh <sup>b</sup>	2 208 sh	2 232 mw <sup>b</sup>	2 202 vs	2 249 vs	2 256 vs	
		2 166 vs	2 200 vs	2 166 vs	2 166 vs	2 197 sh	2 185 vs	2 232 m <sup>b</sup>	2 238 sh <sup>b</sup>	
			2 166 vs			2 183 vs		2 185 vs	2 187 vs	
2 209 vs	2 212 vs									$\nu_{\text{as}}(\text{NCO})$
1 348 m <sup>c</sup>	1 347 ms			1 352 s <sup>c</sup>	1 329 ms			1 340 vs	1 365 sh	$\nu_{\text{s}}(\text{NCO})$ $\nu_{\text{as}}(\text{C-N})$ $\nu(\text{C-C})$
		1 260 ms	1 257 ms			1 258 m	1 259 sh			
		1 249 m	1 248 s			1 253 m	1 251 ms			
635 ms	634 sh			947 w	943 w			960 w <sup>c</sup>	915 vw	$\nu_s(\text{C-N})$
613 s	629 ms			665 sh	682 w			671 mw	683 w	$\delta(\text{CNC})$ $\delta(\text{NCO})$
	612 s									
		610 vw	626 vw			614 sh	617 vw			$\delta(\text{C-C}\equiv\text{N})$
		605 vw	616 vw			608 vw	600 vw			
		567 vs	<sup>e</sup>			565 s	<sup>e</sup>	533 ms	537 ms	$\nu(\text{C-C}\equiv\text{N})$ $\delta(\text{NCN})$
				525 m	535 m					
				499 m	529 m					
384 vs	380 vs	288 w	292 w		503 m	276 s	276 s	500 m	503 m	$\nu(\text{NCN})$
268 vs	264 s	268 mw	252 mw	316 s	304 ms	268 s	256 s	276 vs	272 vs	$\nu(\text{M-N})$
		248 w	232 mw	260 s	252 s	260 s	248 s	260 s	252 vs	
						244 vs		224 s	236 s	

<sup>a</sup> s = strong, m = medium, w = weak, v = very, sh = shoulder; <sup>b</sup> the  $\nu(\text{CN})$  vibration of cyanopyridine; <sup>c</sup> the band can contain also a cyanopyridine vibration; <sup>d</sup> the band contains also the  $\nu(\text{CN})$  vibration of cyanopyridine; <sup>e</sup> overlapped by an intense band of 4-cyanopyridine.

In the cyanate complexes, the NCO asymmetric and symmetric stretching vibrations at ca.  $2\,210\text{ cm}^{-1}$  and fairly above  $1\,300\text{ cm}^{-1}$ , respectively, are consistent with the nitrogen bonding of the cyanate groups<sup>1</sup>. The NCO deformation modes, occurring not too high above  $600\text{ cm}^{-1}$ , are split to a relatively small extent of  $\approx 20\text{ cm}^{-1}$ . From the latter it may be concluded that the end-on nitrogen fashion of cyanate bridging can be excluded, however, the alternative, end-to-end bridging fashion is well possible in the given systems. As for cyanato-copper(II) complexes it is usual case, each NCO ligand forms a tight nitrogen bond with one Cu(II) atom and simultaneously it is coordinated by oxygen to other Cu(II) atom being at a distinctly greater distance<sup>1</sup>. It is noteworthy that according to the NCO deformation splitting the analogous Ni(II) complexes exhibit the end-on nitrogen bridge NCO groups<sup>8</sup>. These different NCO bridging modes are very likely conditioned by expressive distinctions in electronic properties of Cu(II) and Ni(II) and consequently, by unlike conditions for metal-ligand interactions in both cases.

The most conclusive information about the bonding mode of tricyanmethanide or dicyanamido ligands in the respective complexes can be obtained from the values of their  $\text{C}\equiv\text{N}$  stretching frequencies<sup>5,12,13</sup>. In the tricyanmethanido- and dicyanamido-complexes, one band around  $2\,245\text{ cm}^{-1}$  and one or two bands between ca.  $2\,200\text{--}2\,165\text{ cm}^{-1}$  were found for the pseudohalide  $\text{C}\equiv\text{N}$  stretches which obviously indicate the bidentate bridging nitrogen function of the pseudohalide ligands. Other vibrational modes of the pseudohalides are relatively slightly altered on coordination.

The  $\text{C}\equiv\text{N}$  stretching mode of the cyanopyridine ligands appears somewhere as a weak to medium band or shoulder between ca.  $2\,245\text{--}2\,230\text{ cm}^{-1}$ ; elsewhere it interferes in the more intense  $\nu(\text{C}\equiv\text{N})$  mode of the pseudohalide and in one case it is entirely obscured. Nevertheless, even from these data it is clear that shifts in the cyanopyridine  $\nu(\text{C}\equiv\text{N})$  frequency in regard to the free ligands are minimal and in substance exclude the use of their nitrile function for coordination<sup>8,10,11</sup>. Thus, in all complexes it is the pyridine nitrogen which is coordinated to the central atom.

In the far infrared region, the skeletal M—N stretching frequencies were identified as two to four bands spreading in the range  $380\text{--}\approx 225\text{ cm}^{-1}$ . In the case of the cyanate complexes, the bands about  $380\text{ cm}^{-1}$  can be assigned predominantly to the Cu—NCO stretches and those about  $265\text{ cm}^{-1}$  are assignable mainly to the Cu—N(L) stretches<sup>1,14</sup>. The latter frequencies are very similar to those for analogous complexes of corresponding picolines<sup>14</sup>, in spite of considerably lower basicity of cyanopyridines<sup>7</sup> and thus their weaker ability to  $\sigma$ -bond formation. This is the same ascertainment as made for the  $[\text{Cu}(\text{NCO})_2\text{L}_2]$  complexes of 3- and 4-halogenopyridines<sup>2</sup> and may be similarly explained in terms of rather strong dative  $\pi$ -bonding which contributes to the Cu—N(L) bond system enhancing thus its total strength.

For the tricyanmethanido- and dicyanamidocomplexes, the  $\nu(\text{M}-\text{N})$  vibrations are in energy much closer to each other than in the cyanate case and therefore, an

appreciable mixing of these vibrations can take place. An important statement, however, is unquestioned here. In the case of  $[\text{Cu}\{\text{N}(\text{CN})_2\}_2(3\text{-CN-py})_2]$  the highest  $\nu(\text{Cu-N})$  value is fairly above  $300\text{ cm}^{-1}$  and in all likelihood it may be assigned to the  $\text{Cu-N}(\text{amide})$  stretch<sup>6,15</sup>. Thus, the dicyanamide ligands in this compound form asymmetric bridges using their amide and cyanide nitrogens:  $\text{Cu-N}(\text{CN})\text{CN}-\text{Cu}$ , the amide nitrogens being employed for short strong bonds while the cyanide ones for long bonds. With  $[\text{Cu}\{\text{N}(\text{CN})_2\}_2(4\text{-CN-py})_2]$  the situation is less clear, since the upper  $\nu(\text{Cu-N})$  value is only slightly higher than  $300\text{ cm}^{-1}$ , but compared with the corresponding value for the  $\text{Ni}(\text{II})$  analogue, the foregoing dicyanamide bridging mode can be anticipated, too.

It may be reasonably suggested that the electron withdrawing effect of the cyanopyridine ligands is transferred through the central atom electron shell and as a consequence, the dicyanamide ligand is forced to prefer its amide nitrogen for equatorial  $\sigma$ -bonding. Plasticity of the  $\text{Cu}(\text{II})$  coordination sphere seems to be of a particular importance, facilitating the manifestation of stereochemical consequences of the mutual influence of ligands, as it was proved by Gažo and coworkers<sup>16</sup> for many cases of  $\text{Cu}(\text{II})$  complexes.

In the  $[\text{Ni}\{\text{N}(\text{CN})_2\}_2\text{L}_2]$  complexes the  $\nu(\text{Ni-N})$  frequencies well below  $300\text{ cm}^{-1}$  clearly indicate the symmetric bridging mode of the dicyanamides, viz. through both cyanide nitrogens:  $\text{Ni-NCNCN-Ni}$  (refs<sup>6,15</sup>).

### Electronic Spectra

Each pair of copper(II) complexes of the same pseudohalide ligands shows comparable electronic spectra (Table III, Fig. 1) which are, however, different from those of the remaining two pairs of complexes.

The ligand field band of the cyanate complexes shows two absorption maxima, one close above  $1.6\ \mu\text{m}^{-1}$  and the second about  $1.4\ \mu\text{m}^{-1}$ , which for  $[\text{Cu}(\text{NCO})_2 \cdot (3\text{-CN-py})_2]$  is deformed into a broad shoulder. These  $d \leftarrow d$  spectral features

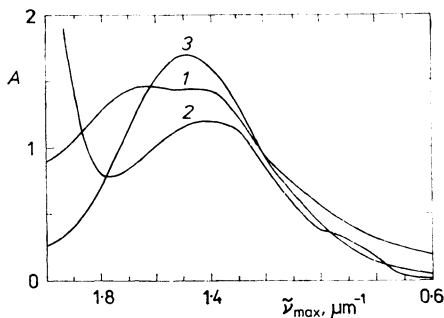


FIG. 1

Ligand field spectra of the complexes: 1  $[\text{Cu}(\text{NCO})_2(4\text{-CN-py})_2]$ , 2  $[\text{Cu}\{\text{C}(\text{CN})_3\}_2 \cdot (3\text{-CN-py})_2]$ , 3  $[\text{Cu}\{\text{N}(\text{CN})_2\}_2(3\text{-CN-py})_2]$ . The absorbance is given in arbitrary units

TABLE III  
Electronic and ESR spectral data for  $[\text{MX}_2\text{L}_2]$  complexes

Compound	$\tilde{\nu}_{\text{max}}, \mu\text{m}^{-1}$	$g_{\perp}$ or $g_{\perp}$	$g_2$ or $g_0$	$g_3$ or $g_{\parallel}$	$\bar{g}^a$	$G^b$
$[\text{Cu}(\text{NCO})_2(3\text{-CN-py})_2]$	$\approx 1.39$ sh, br	1.61		2.301	2.141	5.28
$[\text{Cu}(\text{NCO})_2(4\text{-CN-py})_2]$	1.44	1.62		2.265	2.124	5.30
$[\text{Cu}\{\text{C}(\text{CN})_3\}_2(3\text{-CN-py})_2]$	$\approx 0.86$ sh, br	$\approx 1.28$ sh	1.41	2.29	2.133	4.48
$[\text{Cu}\{\text{C}(\text{CN})_3\}_2(4\text{-CN-py})_2]$	$\approx 0.88$ sh, br	$\approx 1.29$ sh	1.44	2.21	2.138	3.90
$[\text{Cu}\{\text{N}(\text{CN})_2\}_2(3\text{-CN-py})_2]$	1.49	2.87 br		2.069	2.140	3.67
$[\text{Cu}\{\text{N}(\text{CN})_2\}_2(4\text{-CN-py})_2]$	1.46	$\approx 2.93$ br		2.073	2.140	3.67
$[\text{Ni}\{\text{C}(\text{CN})_3\}_2(3\text{-CN-py})_2]$	1.07	$\approx 1.34$ sh	1.74			
$[\text{Ni}\{\text{C}(\text{CN})_3\}_2(4\text{-CN-py})_2]$	1.08	$\approx 1.34$ sh	1.73			
$[\text{Ni}\{\text{N}(\text{CN})_2\}_2(3\text{-CN-py})_2]$	1.03	$\approx 1.34$ sh	1.63			
$[\text{Ni}\{\text{N}(\text{CN})_2\}_2(4\text{-CN-py})_2]$	1.02	$\approx 1.35$ sh	1.69	2.12		

<sup>a</sup> Calculated from the relation  $\bar{g} = [(1/3)(2g_{\perp}^2 + g_{\parallel}^2)]^{1/2}$ ; <sup>b</sup> calculated from the relation  $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$  or  $G = (g_3 - 2)/[(1/2) \cdot (g_1 + g_2) - 2]$ .

indicate elongated tetragonal configurations<sup>17-19</sup>, formed in equatorial planes by four nitrogens from the cyanate and cyanopyridine ligands and completed in longer axial distances by two oxygens belonging to the cyanates already coordinated in adjacent moieties (see Fig. 11 from ref.<sup>1</sup>). The lower and higher energy absorption can be assigned to the transitions of  ${}^2A_{1g} \leftarrow {}^2B_{1g}$  and  ${}^2E_g, {}^2B_{2g} \leftarrow {}^2B_{1g}$  or  ${}^2A_{1g}, {}^2B_{2g} \leftarrow {}^2B_{1g}$  and  ${}^2E_g \leftarrow {}^2B_{1g}$ , respectively, in  $D_{4h}$  symmetry (effect of a possible small lower symmetry component on the ligand field states is neglected). From the mutual position of the lower energy peaks it may be concluded that in the 4-CN-py complex the tetragonal distortion is somewhat stronger.

Both tricyanmethanide complexes exhibit maxima and low energy shoulders of the  $d \leftarrow d$  bands shifted, in comparison with the foregoing spectra by ca.  $0.2$  and  $0.55 \mu\text{m}^{-1}$ , respectively, to lower energies; additional, ill resolved shoulders appear close below  $1.3 \mu\text{m}^{-1}$ . Such spectral changes can be interpreted in terms of the pseudooctahedral, relatively weak tetragonally distorted Cu(II) atom environment<sup>17,19,20</sup>. This is formed in a similar way as in cyanate complexes, the tricyanmethanide nitrogens taking the places of the cyanate nitrogens (in-plane) and oxygens (out-of-plane). The three  $d \leftarrow d$  absorptions in the increasing energy order correspond to the  $D_{4h}$  transitions of  ${}^2A_{1g} \leftarrow {}^2B_{1g}$ ,  ${}^2B_{2g} \leftarrow {}^2B_{1g}$ , and  ${}^2E_g \leftarrow {}^2B_{1g}$ . The ligand field parameter,  $10Dq$ , can be calculated according to the relation<sup>19</sup>  $10Dq = \delta_3 - (1/2)\delta_1 - (1/3)(\delta_3 - \delta_2)$ , where  $\delta_1$ ,  $\delta_2$  and  $\delta_3$ , respectively, are energies of the foregoing transitions. The values of  $0.94$  and  $0.95 \mu\text{m}^{-1}$  are obtained for the 3-CN-py and 4-CN-py complex, respectively, and are higher than the  $10Dq$  values for the cyanate complexes ( $0.84 \mu\text{m}^{-1}$  for both assigning the  ${}^2B_{2g} \leftarrow {}^2B_{1g}$  transition to the lower energy peaks). This is in agreement with the mutual position of the  $\text{C}(\text{CN})_3$  and  $\text{NCO}$  ligands in the spectrochemical series<sup>5</sup>.

The electronic spectra of the dicyanamide complexes consist of single  $d \leftarrow d$  bands, having their maxima shifted, compared with the bands of the tricyanmethanide complexes, by ca.  $0.05 \mu\text{m}^{-1}$  to higher energies. These shifts can be rationalized if we admit that the pseudooctahedral arrangement with the dicyanamide  $\text{N}(\text{amide})_{eq} \text{N}(\text{cyanide})_{ax}$  bridges in place of the tricyanmethanide ones is submitted to a stronger tetragonal distortion.

All nickel(II) complexes have similar  $d \leftarrow d$  spectra consisting of two spin allowed bands and a spin forbidden absorption between them. These spectra are characteristic of octahedral structures<sup>21</sup> formed by bridging  $\text{C}(\text{CN})_3$  or  $\text{N}(\text{CN})_2$  groups and the cyanopyridine molecules. The spin allowed bands in the increasing energy order are assigned to the  ${}^3T_{2g} \leftarrow {}^3A_{2g}$  and  ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$  transitions; the highest energy transition  ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$  is mostly not observable because of overlapping by other, very intense UV absorption. Octahedral structures were also attributed on the basis of the similar  $d \leftarrow d$  spectra to the cyanato-nickel(II) complexes of 3- and 4-cyanopyridine<sup>8</sup>.



## ESR Spectra

ESR spectra were measured only in the case of Cu(II) complexes as polycrystalline samples; the calculated  $g$  and  $G$  values are listed in Table III.

These ESR spectra are of orthorhombic (three  $g$  values), axial (two  $g$  values) or nearly isotropic type<sup>17</sup>. The spectrum of  $[\text{Cu}\{\text{C}(\text{CN})_3\}_2(3\text{-CN-py})_2]$  shows in its low field portion a distinct feature of hyperfine splitting (Fig. 2, curve 1); such shaping was not observed in any other case. The  $g_{\parallel}$  values lie in the range 2.265 to  $\approx 2.30$  and the  $g_{\perp}$  or  $(1/2)(g_1 + g_2)$  ones in the range 2.05– $\approx 2.07$ , and agree with an elongated tetragonal  $\text{CuN}_6$  chromophore having a  $d_{x^2-y^2}$  ground state<sup>17</sup>. Nevertheless, the value of the  $G$  parameter allow us to make further considerations<sup>17,22,23</sup>.

The compound  $[\text{Cu}\{\text{C}(\text{CN})_3\}_2(3\text{-CN-py})_2]$  shows its  $G$  value very close to 4.5 indicating that the observed orthorhombic  $g$  values are true molecular ones. The orbital reduction factors,  $k_{\parallel}$  and  $k_{\perp}$ , evaluated by means of the approximative equations for  $g_{\parallel}$  and  $g_{\perp}$ , as given e.g. in ref.<sup>23</sup>, are 0.72 and 0.70, respectively, and correspond with the values usually found for Cu(II) complexes with nitrogen ligands<sup>17</sup>. Moreover, the proximity of both  $k$  values to each other reveals that participation of  $\pi$ -bonding in Cu–N bonds is only slight.

The  $G$  values of  $[\text{Cu}\{\text{C}(\text{CN})_3\}_2(4\text{-CN-py})_2]$  and  $[\text{Cu}\{\text{N}(\text{CN})_2\}_2(3\text{-CN-py})_2]$  are between 3.5 and 4.0, thus pointing to a slight affection of the  $g$  values by exchange coupling between the Cu(II)-atoms whose molecular axes are somewhat misaligned. In the case of the first complex, the  $k_{\parallel}$  and  $k_{\perp}$  parameters calculated from the corresponding  $g$  values are 0.72 and 0.76, respectively. Considering the structural similarity of  $[\text{Cu}\{\text{C}(\text{CN})_3\}_2(4\text{-CN-py})_2]$  and  $[\text{Cu}\{\text{C}(\text{CN})_3\}_2(3\text{-CN-py})_2]$ , an appreciable increase of  $k_{\perp}$  (and a reverse relation between  $k_{\parallel}$  and  $k_{\perp}$ , i.e.  $k_{\perp} > k_{\parallel}$ ) seems to be not well justifiable. It can be assumed that exchange coupling obliterates the orthorhombic character of the ESR spectrum and modifies a new, exchange coupled  $g_{\perp}$  values. For  $[\text{Cu}\{\text{N}(\text{CN})_2\}_2(3\text{-CN-py})_2]$  the  $k_{\perp}$  value obtained from the  $g_{\perp}$  com-

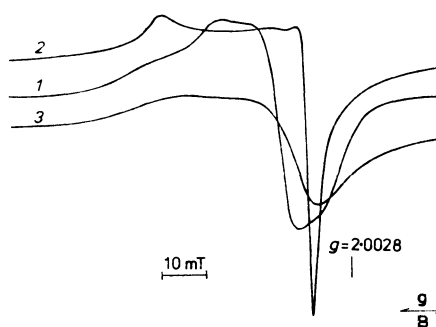


FIG. 2

ESR spectra of the complexes 1  $[\text{Cu}\{\text{C}(\text{CN})_3\}_2(3\text{-CN-py})_2]$ , 2  $[\text{Cu}(\text{NCO})_2(3\text{-CN-py})_2]$ , 3  $[\text{Cu}(\text{NCO})_2(4\text{-CN-py})_2]$

ponent should be as high as 0.80, and apparently the situation in this instance is analogous to that in the foregoing complex.

The nearly isotropic ESR spectrum of  $[\text{Cu}\{\text{N}(\text{CN})_2\}_2(4\text{-CN-py})_2]$  is<sup>1</sup> apparently caused by extensive exchange coupling between the Cu(II) atoms occupying crystallographically nonequivalent positions in the unit cells<sup>17,18</sup>. It should be pointed out that the bridging  $\text{N}(\text{CN})_2$  or  $\text{C}(\text{CN})_3$  ligands represent a suitable medium for exchange coupling which was for several related Cu(II) complexes proved by temperature-variable measurements of magnetic susceptibility<sup>24</sup>.

The ESR spectrum of  $[\text{Cu}(\text{NCO})_2(3\text{-CN-py})_2]$  is exchange-narrowed but that of  $[\text{Cu}(\text{NCO})_2(4\text{-CN-py})_2]$  has its signal considerably broadened (Fig. 2, curves 2, 3). For both compounds the  $G$  parameters are little above 5 and do not assure the strict molecular  $g$  factors<sup>17,18</sup>. However, the  $g_{\parallel}$  and in a smaller degree also the  $g_{\perp}$  values are increasing towards a weakening of tetragonal distortion<sup>25</sup> ascertained from the electronic spectra. The calculated orbital reduction factors,  $k_{\parallel}$  and  $k_{\perp}$ , are about 0.78 and 0.71, respectively, also similar to those found for some cyanato-copper(II) complexes with methylpyridines<sup>23</sup> and indicate a distinct participation of the out-of-plane  $\pi$ -bonds in the bonding systems present.

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