

# INFRARED STUDY OF THE MUTUAL INFLUENCE OF LIGANDS IN COPPER(II) PSEUDOHALIDE COMPLEXES OF THE TYPE $\text{Cu}(\text{NCX})_2\text{L}_2$ WITH MONO- AND DIMETHYLPYRIDINES

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*Dedicated to Professor S. Škramovský on the occasion of his 75th birthday.*

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Far infrared spectra of copper(II) cyanate and thiocyanate complexes of the type *trans*- $\text{Cu}(\text{NCX})_2\text{L}_2$  with all the isomeric picolines and lutidines (L) were measured and the  $\text{Cu}-\text{N}(\text{L})^*$  and  $\text{Cu}-\text{NCX}$  stretching vibrations were assigned. From the frequency shifts of these vibrations with respect to those in the corresponding complexes with pyridine, a mutual conditioning of the  $\text{Cu}-\text{N}(\text{L})$  and  $\text{Cu}-\text{NCX}$  bonds in the equatorial plane was found, particularly if the ligands exert steric effect.

Metal halocomplexes with pyridine and its methyl derivatives have been recently extensively studied<sup>1-4</sup> by means of far infrared spectroscopy (below  $500\text{ cm}^{-1}$ ). Conspicuous relations have been found to exist between the frequencies of the central atom — donor stretching vibrations and the stereochemistry, metal atom type, ligand basicity and its steric effect. Less systematic attention has been paid<sup>3,5,6</sup> to the skeletal stretching vibrations in thiocyanate complexes with pyridine type ligands, and in the analogous cyanate complexes these vibrations have been examined<sup>7</sup> only sporadically. With regard to the correlations between the axial and the equatorial bonds found<sup>8</sup> in the coordination polyhedra of Cu(II) complexes, interesting results can be expected to follow from the far infrared spectra of a series of copper(II) thiocyanate and cyanate complexes with all the mono- and dimethylpyridines as the neutral ligands L.\*\*

These complexes of the type  $\text{Cu}(\text{NCX})_2\text{L}_2$  have — according to the data of electronic, infrared, and ESR spectra<sup>9-14</sup> — basically elongated tetragonal *trans* structures. These structures are composed of planar units, which contain short equatorial  $\text{Cu}-\text{N}(\text{L})$  and  $\text{Cu}-\text{NCX}$  bonds, mutually arranged so as to form long axial bonds of the Cu(II) atom to the donor atoms of the NCX groups of the neighbouring units (Fig. 1). The complexes treated involve thus pseudo-octahedral  $\text{CuN}_4\text{X}_2$  or  $\text{CuN}_6$  systems with various tetragonal distortion<sup>15</sup>, depending on the ligand L or on the crystal structure. In thiocyanate complexes, long axial bonds of the copper atom to the sulfur atoms of the NCS groups are assumed to occur<sup>12</sup>, similarly as<sup>16</sup> in  $\text{Cu}(\text{NCS})_2(\text{py})_2$ . For cyanate complexes with L = 3-pic and 2,3-lut, the infrared spectra indicate<sup>10,14</sup> the presence of axial bonds to the nitrogen atoms of the NCO groups, in other cases it is the oxygen atoms that can be rather assumed to occupy the axial positions, as found<sup>17</sup> in  $\text{Cu}(\text{NCO})_2(\text{py})_2$  (Fig. 2).

\* N(L) denotes the nitrogen atom of the ligand L.

\*\* Abbreviations used: py = pyridine, pic = picoline, lut = lutidine.

In this work we attempt to find correlations between the relative strengths of the equatorial Cu—N(L) and Cu—NCX bonds and to establish the factors by which they can be affected.

## EXPERIMENTAL

The complexes were prepared as described elsewhere<sup>9,12,14</sup>. The infrared spectra were measured in the range of 450—200 cm<sup>-1</sup> on a spectrophotometer Perkin-Elmer 225 by applying the technique of Nujol mulls placed between polyethylene sheets. Each spectrum was run independently at least twice. The bands of the Cu—N stretching vibrations were identified by comparing the spectra with the published spectra of the pure ligands<sup>3,18</sup> and of the corresponding chloro-complexes<sup>3,4</sup>. The positions of the band maxima, read off with the accuracy of  $\pm 2$  cm<sup>-1</sup>, are given in Table I.

## RESULTS

In pseudooctahedral Cu(II) systems, the lengths of the axial Cu—O and Cu—N bonds are<sup>8</sup> commonly about 0.25 nm, and those of the axial Cu—S bonds are<sup>19</sup> about 0.3 nm (the sum of the covalent radii<sup>20</sup> of Cu and O or N is 0.192 nm, Cu and S 0.222 nm). This warrants the first approximation, in which only the planar five-atomic CuN<sub>2</sub>N'<sub>2</sub> units with the local point symmetry  $D_{2h}$  are taken into account. The effect of the axial atoms may be regarded<sup>4</sup> as a weak perturbation of the local symmetry.

The vibrational representation  $\Gamma_{\text{vib}}$  for the CuN<sub>2</sub>N'<sub>2</sub> system possessing the point symmetry  $D_{2h}$  reduces to<sup>21</sup>

$$\Gamma_{\text{vib}} = 2A_g + B_{1g} + 2B_{1u} + 2B_{2u} + 2B_{3u}.$$

Of the infrared-active vibrations (u parity), the two  $B_{1u}$  species are out-of-plane deformations; the remaining four vibrations comprise two Cu—N stretchings with a small contribution of in-plane deformation, and two in-plane deformations with a contribution of Cu—N stretching. The two Cu—N stretchings are, naturally, coupled to an extent, dependent on the force constants of the Cu—N(L) and Cu—NCX bonds and also on the masses of L and NCX. This coupling can be anticipated to be greater for the thiocyanate complexes than for the cyanate complexes and to increase in the order of L lut < pic < py. Nevertheless it is certainly low enough to allow one of the Cu—N stretching vibrations to be considered as predominantly the stretching of the Cu—N(L) bonds and the other as the stretching of the Cu—NCX bonds. This is supported by the fact that the frequencies attributed to the Cu—N(L) stretching vibrations change only slightly on replacing the NCS group by the NCO group (*vide infra*).

The commonly strong bands occurring for the complexes of both types in the range of  $270\text{--}\sim 240\text{ cm}^{-1}$  have been assigned<sup>3,4</sup> to Cu—N(L) stretching vibrations, the strong bands in the spectra of the thiocyanate complexes lying at  $345\text{--}\sim 310\text{ cm}^{-1}$  to Cu—NCS stretching vibrations<sup>5,6</sup>. The analogous bands of the cyanate complexes,

TABLE I  
Infrared Band Maxima ( $450\text{--}200\text{ cm}^{-1}$ ) of Copper(II) Pseudohalo Complexes of the Type Cu(NCX)<sub>2</sub>L<sub>2</sub> with Mono- and Dimethylpyridines

L	$\nu(\text{Cu--NCS})$ $\text{cm}^{-1}$	$\nu(\text{Cu--N(L)})$ $\text{cm}^{-1}$	Other bands <sup>d</sup> $\text{cm}^{-1}$			
X = S						
py <sup>b</sup>	321 s	257 s	(436 s)	218 m		
2-pic	331 s	253 sh, 242 s	(434 s)	(390 ms)	(206 m)	
3-pic <sup>c</sup>	312 s	270 s	(416 s)	(362 m)	238 w	(212 ms)
4-pic <sup>d</sup>	321 s	262 s, 250 sh	417 w	363 w	(216 sh)	
2,3-lut	324 s	244 s	(437 w)	(274 w)		
2,4-lut	336 s	266 mw, 248 m	(445 s)	(432 mw)	(300 mw)	(210 w)
2,5-lut	331 s	254 ms, 237 w	(441 s)	(415 w)	(316 sh)	(206 w)
2,6-lut	345 s	248 s	(448 mw)	322 sh	(274 mw)	(208 mw)
3,4-lut	323 s	256 s	(432 mw)	(292 m)	210 m	
3,5-lut	308 s	251 s	(412 vw)	(284 ms)		
X = O						
py	378 s	358 s	(438 s)	231 w	209 s	
2-pic	388 s	278 sh, 294 s	(448 s)	(217 m)		
3-pic	378 s	263 s	(422 m)	(365 m)	238 mw	(226 w)
4-pic	374 s	266 s	415 w	358 m		
2,3-lut	373 ms	233 ms	(437 m)	(283 m)		
2,4-lut <sup>e</sup>	393 s	246 s	(447 s)	(428 m)	(299 w)	(212 m)
2,5-lut	395 s, 364 sh	256 s	(440 s)	(418 mw)	(314 mw)	
2,6-lut	394 s	242 s	(445 mw)	319 mw	(277 m)	(207 mw)
3,4-lut	374 s	267 s	(434 s)	(290 sh)	206 sh	
3,5-lut	383 s	262 s	(420 mw)	(286 m)	(222 w)	211 w

s strong, m medium, w weak, v very, sh shoulder. <sup>a</sup> The bands given in parentheses are due to the ligand L; <sup>b</sup> for Cu(NCS)<sub>2</sub>(py)<sub>2</sub> found by Frank and Rogers<sup>3</sup>: 435, 324 s ( $\nu(\text{Cu--NCS})$ ), 256 s ( $\nu(\text{Cu--N(L)})$ ), 218 m; Clark and Williams<sup>5</sup>: 431 m, 319 s ( $\nu(\text{Cu--NCS})$ ), 256 s ( $\nu(\text{Cu--N(L)})$ ), 214 m; Burgess<sup>6</sup>: 320 ( $\nu(\text{Cu--NCS})$ ), 256 ( $\nu(\text{Cu--N(L)})$ ), 215; <sup>c</sup> for Cu(NCS)<sub>2</sub>(3-pic)<sub>2</sub> found by Burgess<sup>6</sup>: 364, 315 ( $\nu(\text{Cu--NCS})$ ), 272 ( $\nu(\text{Cu--N(L)})$ ), 214 w; <sup>d</sup> for Cu(NCS)<sub>2</sub>(4-pic)<sub>2</sub> found by Burgess<sup>6</sup>: 320 ( $\nu(\text{Cu--NCS})$ ), 261 ( $\nu(\text{Cu--N(L)})$ ); <sup>e</sup> the  $\alpha$ -isomer is in question (see ref.<sup>7</sup>).

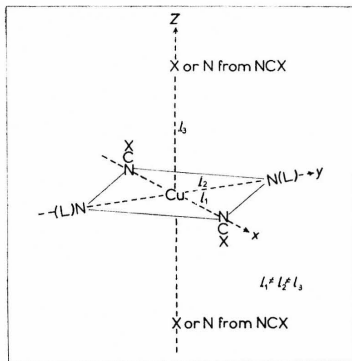


FIG. 1  
Scheme of the Surrounding of the Cu(II) Atom in the  $\text{Cu}(\text{NCX})_2\text{L}_2$  Complexes with the Coordinate System (the  $D_{2h}$  model)

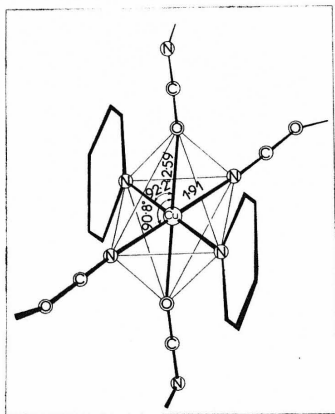


FIG. 2  
Coordination of the Cu(II) Atom in  $\text{Cu} \cdot (\text{NCO}_2)(\text{py})_2$  (according to <sup>17</sup>)  
The bond lengths are given in Ångströms.

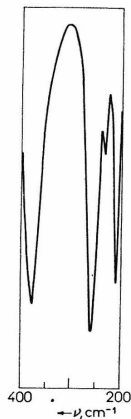


FIG. 3  
Far Infrared Spectrum of  $\text{Cu}(\text{NCO}_2)(\text{py})_2$

positioned between  $\sim 395$  and  $\sim 370$   $\text{cm}^{-1}$ , belong to the Cu—NCO stretching vibrations.

Preliminary results of X-ray structural analysis of  $\text{Cu}(\text{NCO})_2(\text{py})_2$  have been reported<sup>17</sup>. The Cu(II) atom is subject to square planar coordination by two pairs of nitrogen atoms, from two pyridine molecules and two NCO groups. This coordination is supplemented by two oxygen atoms of two different structural units to complete a deformed octahedron (Fig. 2). Although from the crystallographic view the local point symmetry of the  $\text{CuN}_4$  skeleton is  $D_{4h}$ , to the Cu—N stretching vibration of  $\text{CuN}_4$  contributes almost the total mass of the ligands involved<sup>5</sup>, and therefore the  $D_{2h}$  model has to be employed for the vibrational study. This model predicts two bands of the Cu—N stretching vibrations to appear, four bands have been, however, observed in the spectrum below 400  $\text{cm}^{-1}$  (Fig. 3). The two additional bands, a strong one at 209  $\text{cm}^{-1}$  and a weak one at 231  $\text{cm}^{-1}$ , are therefore to be elucidated. The former band belongs very likely to the Cu—N(py) in-plane bending, attributed by Goldstein and coworkers<sup>2</sup> for  $\text{CuX}_2(\text{py})_2$  ( $X=\text{Cl}, \text{Br}$ ) to bands at approximately 200  $\text{cm}^{-1}$ . The other band, regarding its essentially lower intensity as compared with the band at 257  $\text{cm}^{-1}$ , does not seem to arise from a splitting of the band of the Cu—N(py) stretching vibration. Although its relation to some of the Cu—NCO deformations is conceivable, the corresponding bands are usually not observed in this region. For the planar  $[\text{Pd}(\text{NCO})_4]^{2-}$  anion, Forster and Goodgame<sup>22</sup> assign the bands near 600  $\text{cm}^{-1}$  to the M—NCO in-plane and out-of-plane  $A$  modes and suppose that the other M—NCO deformation modes lie below 200  $\text{cm}^{-1}$ . We are therefore inclined to assign the band in question tentatively to the  $B_{1u}$  type vibration which involves<sup>4</sup> the vibration of the central atom against the  $\text{N}_4$  plane and acquires appreciably the character of a Cu—OCN stretching vibration. An analogous assignment applies obviously to the absorptions found near 210  $\text{cm}^{-1}$  in the spectra of  $\text{Cu}(\text{NCO})_2(3,4\text{-lut})_2$  and  $\text{Cu}(\text{NCO})_2(3,5\text{-lut})_2$ , as it is reasonable to expect essentially lower frequencies for the Cu—N(L) in-plane deformations in these cases.

Clark and Williams found<sup>5</sup> in the spectrum of  $\text{Cu}(\text{NCS})_2(\text{py})_2$  a medium intensity band at 214  $\text{cm}^{-1}$  and attributed it tentatively to the Cu—SCN stretching vibration (more exactly, the  $B_{1u}$  species); we found such a band at 218  $\text{cm}^{-1}$ . In the spectrum of  $\text{Cu}(\text{NCS})_2(3,4\text{-lut})_2$  a medium band can be identified at 210  $\text{cm}^{-1}$ , probably of the same origin as the band at 218  $\text{cm}^{-1}$  in the spectrum of the pyridine complex.

The other complexes display absorptions in the range of  $\sim 220 - < 200$   $\text{cm}^{-1}$ , where usually the vibrations of the ligands L appear or where the frequencies cannot be determined as they lie beyond the low-frequency measurement limit of the instrument. No conclusions can be therefore drawn from those absorptions. In some cases, however, we could observe splitting of the bands of the Cu—N stretching vibrations or occurrence of additional weak bands, which probably are not related with the Cu—N stretching. Since the crystal structures of the pertinent complexes are not

known, a detailed analysis can be hardly performed. Yet, the most probable reason of the splitting may be a lowering of the local point symmetry of the  $\text{CuN}_4$  skeleton, effected by the ligand L or the crystal structure as well as the correlation interactions between the fundamentals within the unit cell. We can also admit<sup>23</sup> that some additional absorptions may be in relation with the activation of some vibrations of the ligands L due to their coordination or with vibrations (particularly torsion ones) of the methyl groups at the pyridine ring. In all such cases, it will be the more intense band that will be considered during the following discussion.

While the values of the  $\nu(\text{Cu}-\text{N}(\text{L}))$  frequencies of the thiocyanate complexes and the corresponding cyanate complexes differ only slightly, the values of the  $\nu(\text{Cu}-\text{N}(\text{C})-\text{N}(\text{X}))$  frequencies are in average about  $60\text{ cm}^{-1}$  higher for the cyanate than for the thiocyanate complexes. This difference is obviously accounted for by the lower mass of the NCO group in comparison with the NCS group, and probably also by the shorter distance  $\text{Cu}-\text{N}(\text{C})-\text{N}(\text{X})$  for  $\text{X} = \text{O}$  (in  $\text{Cu}(\text{NCO})_2(\text{py})_2$  this distance<sup>17</sup> is  $0.191\text{ nm}$ , whereas in  $\text{Cu}(\text{NCS})_2(\text{py})_2$  it makes<sup>16</sup> about  $0.210\text{ nm}$ ).

Complexes containing ligands L with methyl groups in the  $\alpha$ -position (except for 2,3-lutidine) exhibit the  $\nu(\text{Cu}-\text{N}(\text{C})-\text{N}(\text{X}))$  frequencies in average  $\sim 15\text{ cm}^{-1}$  higher and the  $\nu(\text{Cu}-\text{N}(\text{L}))$  frequencies  $\sim 10\text{ cm}^{-1}$  lower than the corresponding pyridine complexes. These shifts indicate a stronger  $\text{Cu}-\text{N}(\text{C})-\text{N}(\text{X})$  bond and a weaker  $\text{Cu}-\text{N}(\text{L})$  bond as compared with  $\text{Cu}(\text{N}(\text{C})-\text{N}(\text{X}))_2(\text{py})_2$  with the same X. As the ligands mentioned are stronger bases than pyridine, rather stronger  $\text{Cu}-\text{N}(\text{L})$  bonds than in the pyridine complex could be expected. The fact that the reverse is true is surely a result of steric hindrance<sup>2,9,12</sup> of the ligands L involved. It makes the contact of the donor nitrogen atom with the central  $\text{Cu}(\text{II})$  atom more difficult, which leads to an elongation of the  $\text{Cu}-\text{N}(\text{L})$  bond, accompanied by a shortening of the  $\text{Cu}-\text{N}(\text{C})-\text{N}(\text{X})$  bond.

Less straightforward are the relations in the case of the complexes with the other ligands (with the unoccupied  $\alpha$ -position).  $\text{Cu}(\text{NCS})_2(4\text{-pic})_2$  and  $\text{Cu}(\text{NCS})_2(3,4\text{-lut})_2$  show the bands in question only very slightly shifted as compared with  $\text{Cu}(\text{NCS})_2(\text{py})_2$ . For  $\text{Cu}(\text{NCS})_2(3\text{-pic})_2$ , the shifts of the two bands with respect to the pyridine complex are of opposite direction in comparison with the aforementioned group of compounds. Hence in this complex the change of the strengths and lengths of the  $\text{Cu}-\text{N}(\text{C})-\text{N}(\text{X})$  and  $\text{Cu}-\text{N}(\text{L})$  bonds is opposite, probably as a consequence of a strong tetragonal distortion, as inferred<sup>12</sup> from the electronic spectrum. In the case of  $\text{Cu}(\text{NCS})_2(3,5\text{-lut})_2$  the two frequencies are surprisingly lower than in  $\text{Cu}(\text{NCS})_2(\text{py})_2$ .

The analogous cyanate complexes have the  $\nu(\text{Cu}-\text{N}(\text{L}))$  frequencies higher than  $\text{Cu}(\text{NCO})_2(\text{py})_2$ ; except for  $\text{Cu}(\text{NCO})_2(3,5\text{-lut})_2$ , the values increase – though very slightly – in the same order as the basicities<sup>3</sup> of the ligands L. Thus the effect of the ligand basicity on the strength of the  $\text{Cu}-\text{N}(\text{L})$  bond, which could not be traced at all in the case of the thiocyanate complexes, shows up very slightly in this case. The  $\nu(\text{Cu}-\text{N}(\text{C})-\text{N}(\text{O}))$  frequency is for  $\text{Cu}(\text{NCO})_2(3\text{-pic})_2$  the same as for  $\text{Cu}(\text{NCO})_2(\text{py})_2$ .

whereas in the cases of  $\text{Cu}(\text{NCO})_2(4\text{-pic})_2$  and  $\text{Cu}(\text{NCO})_2(3,4\text{-lut})_2$  it is somewhat lower. The slight strengthening of the  $\text{Cu}-\text{N}(\text{L})$  bonds in the two latter complexes is thus accompanied by a small weakening of the  $\text{Cu}-\text{NCO}$  bonds.  $\text{Cu}(\text{NCO})_2 \cdot (3,5\text{-lut})_2$  displays the  $\nu(\text{Cu}-\text{NCO})$  frequency unexpectedly somewhat higher than  $\text{Cu}(\text{NCO})_2(\text{py})_2$ .

Both  $\text{Cu}(\text{NCX})_2(2,3\text{-lut})_2$  complexes possess<sup>12,14</sup>, according to their electronic spectra, five-coordinated structures approaching square pyramid. For the thiocyanate, the  $\nu(\text{Cu}-\text{N}(\text{L}))$  frequency lies at the low-frequency limit of the pertinent range, while the  $\nu(\text{Cu}-\text{NCS})$  frequency is only little higher than that of  $\text{Cu}(\text{NCS})_2(\text{py})_2$ . In the case of the cyanate complex with 2,3-lutidine, the  $\nu(\text{Cu}-\text{N}(\text{L}))$  frequency is as low as  $\approx 10 \text{ cm}^{-1}$  below the low-frequency limit of the range established; the  $\nu(\text{Cu}-\text{NCO})$  frequency is somewhat lower than for the analogous pyridine complex. This evidences an overall weakening of the equatorial bonds in both complexes, which is in accordance with the finding<sup>15</sup> that these bonds in square pyramidal complexes are somewhat longer than in the corresponding tetragonal octahedral complexes.

## DISCUSSION

The results obtained, especially with the group of complexes containing ligands L which exert steric effect<sup>2,9,12</sup>, are remarkable in that they prove a mutual conditioning of the bonds in the equatorial plane. The steric effect of the ligands is evidently the decisive factor determining the relative strengths of the equatorial bonds in  $\text{Cu} \cdot (\text{NCX})_2\text{L}_2$  complexes. On the other hand, if the ligands do not exhibit any steric effect, the relative strengths are resultants of a complex of factors intramolecular as well as crystallostructural in character as can be expected particularly for complexes with a plastic coordination sphere<sup>8</sup>. A significant role in the mutual influencing of the bonds is certainly played by the tendency towards the highest possible effectiveness of the crystal structure packing and the possibility of its realization, given by the crystallostructural effects of the methyl groups at the pyridine rings. However, with the lack of the X-ray data it is difficult to evaluate these relations in detail. The mutual influence of the ligands, appearing explicit with ligands exerting steric hindrance, manifests itself in the case of other ligands obviously indirectly and in a more complex manner.

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