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Cyanato–Copper(II) Complexes with Organic Ligands [1].
XVI. Structure Characterization of Cyanato–Copper(II) Complexes with Halogenopyridine Ligands in Comparison with Analogous Methyl-pyridine Complexes*

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Cyanato–copper(II) complexes of the type $Cu(NCO)_2L$ (L = 2-chloro- or 2-bromopyridine) and $Cu(NCO)_2L_2$ (L = 2-chloro-, 3-chloro-, 3-bromo-, 3-iodo-, 4-chloro-, or 4-bromopyridine) have been prepared. The results of various physical methods show that $Cu(NCO)_2L$ complexes have distorted five-coordinated structures with N-bridging NCO groups, while $Cu(NCO)_2L_2$ complexes, except for $Cu(NCO)_2$(2-Cl-py)$_2$, display pseudooctahedral structures, probably with axial Cu–OCN linkages. The complexes of both groups are structurally very similar to one another and the complexes of 3-halogeno-pyridines are even crystal-structurally closely related. One exception is $Cu(NCO)_2$(2-Cl-py)$_2$, being at room temperature rather unstable and displaying a square pyramidal structure with one N-bridging NCO group.

Introduction

A great deal of interest was devoted [1, 2] to cyanato–copper(II) complexes with methylsubstituted pyridines. Factors influencing the adaptation of particular stereochemistries were discussed [2] and the possibility of formation of isomeric compounds, including distortion isomers, was observed [3]. In a further work we examined the preparation of new cyanato–copper(II) complexes with halogenopyridines (abbreviations X-py). These ligands exhibit a negative inductive effect and therefore they are much weaker bases than methylpyridines [4]. They also exercise a variable steric and crystal-structure effect depending on the size and the position of the halogen atom. Finally they were expected to have a better π-acceptor capacity than pyridine or its methyl derivatives. The structure properties of the prepared complexes were studied by use of X-ray diffraction, spectrophotometric, ESR and magnetic measurements.

Experimental Section

Chemicals

2-Chloro-, 2-bromo-, 3-chloro- and 3-bromopyridine (Merck or Fluka) were purified by distillation under reduced pressure. 4-Chloro- and 4-bromopyridine were used as hydrochlorides (Fluka) without further purification. 3-Iodopyridine was synthetized by the method of Räth [5].

Preparation

The $Cu(NCO)_2L_2$ complexes, except for L = 2-Cl-py, were prepared from 25 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 30 cm^3 of water by mixing with 53 mmol of KOCN in 30 cm^3 of water and 55 mmol of ligand L in 50 cm^3 of methanol. Immediately a precipitate was formed, which was stirred for 1 hr; then the mixture was filtered and the solution was left to crystallize in a refrigerator. The light blue solids were collected by suction, washed with methanol and dried in a desiccator.

$Cu(NCO)_2$(2-Cl-py)$_2$ was prepared from 25 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 cm^3 of water by mixing with 53 mmol of KOCN in 50 cm^3 of water and 250 mmol (*ca.* fourfold excess) of 2-chloropyridine in 20 cm^3 of methanol. The solutions were cooled and the procedure was carried out under cooling in a dry ice bath. The mixture was left to crystallize in a refrigerator, and the navy-blue crystals were collected by suction and dried in a desiccator placed in a refrigerator.

The complex $Cu(NCO)_2$(2-Cl-py)$_2$ is visibly less stable than other $Cu(NCO)_2L_2$ complexes (*cf.* the decomposition temperatures, Table I) and can be maintained only in coolness.

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*Dedicated to Professor A. Okáč on the occasion of his 75th birthday.

TABLE I. Analytical Data.

Compound	Dec. T.[a] (°C)	Calcd (%)				Found (%)			
		C	H	N	Cu	C	H	N	Cu
$Cu(NCO)_2(3-Cl-py)_2$	150	38.47	2.15	14.96	16.96	37.94	2.16	14.58	16.81
$Cu(NCO)_2(3-Br-py)_2$	160	31.22	1.31	12.14	13.71	30.71	1.40	11.96	13.95
$Cu(NCO)_2(3-I-py)_2$	170	25.85	1.45	10.05	11.40	25.78	1.42	10.04	11.50
$Cu(NCO)_2(4-Cl-py)_2$	150	38.47	2.15	14.96	16.96	37.97	2.09	14.46	16.99
$Cu(NCO)_2(4-Br-py)_2$	160	31.22	1.31	12.14	13.71	30.78	1.44	11.77	13.92
$Cu(NCO)_2(2-Cl-py)_2$	40	38.47	2.15	14.96	16.96	b	b	b	16.87
$Cu(NCO)_2(2-Cl-py)$	130	32.20	1.16	16.15	24.33	32.03	1.16	16.14	24.32
$Cu(NCO)_2(2-Br-py)$	130	27.60	0.99	13.75	20.79	27.52	0.82	13.68	20.86

[a] The measurements were made with 100 mg of samples using a heating rate of 6 °C/min. [b] Not determined owing to unstability of the compound.

TABLE II. Cyanate and Copper–Ligand Vibrations (cm^{-1}).[a]

Complex	ν_{as} (NCO)	ν_s (NCO)	δ (NCO)	ν (Cu–NCO)	ν (Cu–N(L))
$Cu(NCO)_2(3-Cl-py)_2$	2233vs, 2154sh	1346mw	617ms	380s[b]	267s
$Cu(NCO)_2(3-Br-py)_2$	2229vs, 2154sh	1343mw	615ms	381s[b]	267s
$Cu(NCO)_2(3-I-py)_2$	2225vs	1343w	614mw	382s[b], 376sh	267s
$Cu(NCO)_2(4-Cl-py)_2$	2224sh, 2210vs, 2141sh	c	628m, 617ms	377s[b]	269s[b]
$Cu(NCO)_2(4-Br-py)_2$	2215vs, 2147sh	c	627mw, 614m	382s[b], 374sh	260s[b]
$Cu(NCO)_2(2-Cl-py)_2$	2228sh, 2211vs, 2164vs, 2120sh	1342mw, 1318vw	664w, 618ms, 608sh	d	d
$Cu(NCO)_2(2-Cl-py)$	2203vs, 2163vs, 2120sh	1317vw	668mw, 616s	396sh, 374s	272mw, 239mw, 210mw[e]
$Cu(NCO)_2(2-Br-py)$	2206vs, 2165vs, 2119sh	1318vw	665mw, 616s	378sh, 370s	269mw, 234mw, 207mw[e]

[a] s = strong, m = medium, w = weak, sh = shoulder, v = very. [b] A very weak splitting appears. [c] Cannot be determined for the presence of the ligand L bands. [d] Not measured owing to instability of the compound. [e] Probably a deformation band.

The $Cu(NCO)_2L$ complexes were prepared from 25 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 cm^3 of water by mixing with 55 mmol of ligand L in 50 cm^3 of methanol and 53 mmol of KOCN in 50 cm^3 of water. The mixture was allowed to stand for about 10 min, then filtered and left to crystallize in a refrigerator. The grass green crystals were collected by suction and dried in a desiccator. 2-Halogenopyridines do not get readily coordinated; therefore an excess of the ligand L is necessary.

The $Cu(NCO)_2L$ complexes decompose with time and change their colour.

Analysis

Elemental analyses were carried out on a C, H, N-analyser (Carlo Erba). Copper was determined by chelatometric titration in the $Cu(NCO)_2L_2$ complexes after destruction using concentrated H_2SO_4 and a small amount of $K_2S_2O_8$. The analytical data are summarized in Table I.

Physical Measurements

The X-ray diffraction patterns [3], infrared [1], solid state electronic [1] and ESR spectra [2c], as well as the magnetic susceptibilities [3] were obtained as described in the cited papers.

Results

X-Ray Diffraction Patterns

The X-ray diffraction patterns of the powder materials show the complexes $Cu(NCO)_2(3-Br-py)_2$ and $Cu(NCO)_2$ $(3-I-py)_2$ to be isostructural, while

$Cu(NCO)_2(3\text{-}Cl\text{-}py)_2$ exhibits a similar diffraction pattern, though not conformable with the foregoing ones. The diffraction patterns for $Cu(NCO)_2(4\text{-}Cl\text{-}py)_2$ and $Cu(NCO)_2(4\text{-}Br\text{-}py)_2$ are rather different indicating considerable differences in their crystal structures. According to their diffraction patterns, $Cu(NCO)_2(2\text{-}Cl\text{-}py)$ and $Cu(NCO)_2(2\text{-}Br\text{-}py)$ have very similar structures, however, not very close to that of $Cu(NCO)_2$(2,4-lutidine), which has been solved [6] by single crystal X-ray analysis.

Infrared Spectra

The infrared bands of the cyanate group and the copper–nitrogen modes were identified by comparison with the literature spectra [7] of the free ligands as well as with those of the $CuCl_2L_2$ complexes, partially known also from the literature [8].

I.R. spectra of the cyanate group

These spectra (Table II) for the $Cu(NCO)_2L_2$ complexes, except for L = 2-Cl-py, exhibit the ν_{as}(NCO) bands in the range of 2230–≈2210 cm^{-1} and the ν_s(NCO) bands around 1345 cm^{-1}. The $Cu(NCO)_2L$ complexes as well as $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$ have the former bands split and their maxima are at ≈2205 and ≈2165 cm^{-1}. The latter bands for these complexes appear at ≈1320 cm^{-1} and are markedly less intensive than in the foregoing case. In $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$, however, two bands may be assigned as the ν_s(NCO) mode, resembling the ν_s(NCO) bands found separately for the complexes of every other type. The frequencies of the NCO stretching vibrations evidence [2b] that the NCO groups are always bonded through the nitrogen atoms.

The δ(NCO) bands for all the complexes occur around 615 cm^{-1}. In the complexes with 4-halogenopyridines also the bands at ≈625 cm^{-1} belong to the δ(NCO) mode, so that this mode is split by ≈10 cm^{-1}. Such a small splitting is in accord [2b] with terminal bonded NCO groups, though these can form unsymmetrical bridges (pseudobridges), which contain [9] additional weaker bonds involving most likely oxygen atoms. The spectra of the 3-halogenopyridine complexes contain bands at ≈650 cm^{-1}, which can correspond not only to the δ(NCO) mode, but also to the in-plane ring deformation of the 3-halogenopyridines. This appears in the free ligands at ≈615 cm^{-1} [7]; on complex formation it may, however, move to higer frequencies; *e.g.* for $CuCl_2(3\text{-}Cl\text{-}py)_2$ it was observed [10] just at 650 cm^{-1}. Thus the δ(NCO) mode for the respective complexes is evidently unsplit and the bonding mode of the NCO groups is similar to the above said.

The $Cu(NCO)_2L$ complexes as well as $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$ show extra bands in proximity to 665 and 645 cm^{-1}. The latter bands can again belong to the in-plane ring deformation of the 2-halogenopyridines, which moves from ≈615 cm^{-1} in the free ligands to ≈640–645 cm^{-1} in Cu(II) and Co(II) complexes with these ligands [8a]. The former bands, however, must be attributed to the δ(NCO) mode, which consequently is split by ≈50 cm^{-1} and indicates a bridging function of the NCO groups by means of the bidentate nitrogen atoms. A similar splitting of the δ(NCO) mode was found [2b] for a series of the $Cu(NCO)_2L$ complexes with methylpyridines and quinoline or isoquinoline bases as ligands L. In $Cu(NCO)_2$(2,4-lutidine) the formerly mentioned bridging mode of the NCO groups was proved [6] by X-ray analysis.

Far i.r. spectra

In these spectra (Table II) for the $Cu(NCO)_2L_2$ complexes the bands around 380 cm^{-1} can be assigned [2d] to the Cu–NCO stretching mode, while those in the range of ≈270–260 cm^{-1} are ascribed [8b] to the Cu–N(L) stretching mode. Since both kinds of band are basically singlets, the given complexes apparently contain [2d] CuN_4 skeletons of effective D_{2h} symmetry (very weak splittings or shoulders on some bands could originate from secondary effects).

The Cu–N(L) stretching frequencies are with one exception by ≈10 cm^{-1} higher than for $Cu(NCO)_2(py)_2$ and similar to those for complexes of the same type with corresponding picolines [2d]. Accordingly the low basicity of halogenopyridines in the $Cu(NCO)_2L_2$ complexes has no marked influence on the strength of the Cu–N(L) bond. This makes the difference to the $CuCl_2L_2$ and $CuBr_2L_2$ complexes, where for L = 3- or 4-halogenopyridine [8b] the Cu–N(L) stretching frequencies mostly are significantly lower than for L = pyridine or the corresponding picoline [11].

In the far i.r. spectra of the $Cu(NCO)_2L$ complexes the bands at 370 cm^{-1} with higher frequency shoulders are assigned to the Cu–NCO stretching mode. Two bands around 270 and 235 cm^{-1} may be attributed to the Cu–N(L) stretching vibrations; the bands at 210 cm^{-1} are probably deformations in origin. The complex $Cu(NCO)_2$(2,4-lutidine), to which in all likelihood the $Cu(NCO)_2L$ complexes are structurally closely related, exhibits [12] similar stretching bands except that at ≈235 cm^{-1} (but has a shoulder at 253 cm^{-1}).

Electronic Spectra

The electronic spectra (Table III, Fig. 1) of the $Cu(NCO)_2L_2$ complexes, except for L = 2-Cl-py, in the solid state exhibit a ligand field band with a maximum near 1.65 μm^{-1} and (with one exception) two shoulders, namely at about 1.35 μm^{-1} and 0.80 μm^{-1}. The higher-energy shoulder is so ill resolved that it is only perceivable as an asymmetry on the main band. On the other hand, the lower-energy shoulder is very pronounced and broad. The

TABLE III. Electronic and ESR Spectral Data.

Complex	$\tilde{\nu}_{max}$ (μm^{-1})[a]				$g_\parallel$	$g_\perp$[b]	G	$k_\parallel$	$k_\perp$
$Cu(NCO)_2(3\text{-}Cl\text{-}py)_2$	≈0.80sh	≈1.36sh	1.65	≈2.38sh	2.25_8	2.06_1	4.23	0.73	0.78
$Cu(NCO)_2(3\text{-}Br\text{-}py)_2$	≈0.82sh	≈1.33sh	1.63		2.26_2	2.06_5	4.03	0.73	0.80
$Cu(NCO)_2(3\text{-}I\text{-}py)_2$	≈0.83sh		1.64		2.25_7	2.06_0	4.28	. . .	0.80
$Cu(NCO)_2(4\text{-}Cl\text{-}py)_2$	≈0.81sh	≈1.38sh	1.66	≈2.37sh	2.25_0	2.05_7	4.39	0.72	0.76
$Cu(NCO)_2(4\text{-}Br\text{-}py)_2$	≈0.81sh	≈1.35sh	1.675	≈2.37sh	2.24_3	2.05_0	4.86	0.70	0.71
$Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$			1.39		2.29_7	2.07_6	3.91	. . .	0.80
$Cu(NCO)_2(2\text{-}Cl\text{-}py)$			1.295	≈2.35sh	[c]				
$Cu(NCO)_2(2\text{-}Br\text{-}py)$			1.31	≈2.30sh	[c]				

[a] sh = shoulder. [b] Corrected for the lorentzian line shape according to J. W. Searl, R. C. Smith and S. J. Wyard, *Proc. Phys. Soc., 78,* 1174 (1961). [c] See text.

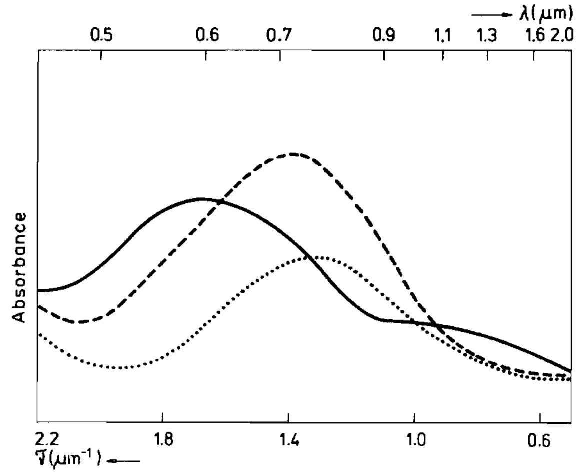

Fig. 1. Ligand field spectra of $Cu(NCO)_2(4\text{-}Br\text{-}py)_2$ (——), $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$ (-----), and $Cu(NCO)_2(2\text{-}Cl\text{-}py)$ (·····).

close similarity of these spectra to one another allows little doubt that, irrespective of possible crystallographic distinctions, the coordination geometry of all the $Cu(NCO)_2L_2$ complexes is substantially the same. This geometry is almost certainly tetragonal octahedral, four nitrogen atoms from two *trans*-positioned NCO groups, as well as L molecules occupying the equatorial sites. The planar coordination is completed to an elongated octahedron by two oxygen atoms from the NCO groups bonded in various $Cu(NCO)_2L_2$ complex units. The use of the nitrogen atoms of the NCO groups for axial ligation seems improbable with respect to the behaviour of the δ(NCO) mode (see earlier). A similar mode of association of square-planar units was evidenced [9, 13] by X-ray analysis for $Cu(NCO)_2(py)_2$. The tight polymeric structure of the $Cu(NCO)_2L_2$ complexes is supported by their slight solubility in common organic solvents.

The great energetic difference (≈0.85 μm^{-1}) between the maximum and the lower-energy shoulder indicates a relatively 'pure' separation between the lowest and the highest d ← d transitions, which should be expected [8b, 14] for comparatively little distorted pseudooctahedral systems. The peaks observed in the direction of increasing wavenumbers then involve the $^2A_{1g} \leftarrow {}^2B_{1g}$, $^2B_{2g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$ transition in a D_{4h} symmetry.

In the spectrum of $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$ only a single and fairly symmetric d ← d band appears, having its maximum appreciably shifted to lower wavenumbers with respect to other $Cu(NCO)_2L_2$ complexes. This band suggests [15] a five-coordinated, most likely square pyramidal stereochemistry for the given complex. It may be assumed that mainly for steric reasons, the 2-Cl-py molecules are rotated in the same sense out of the equatorial plane, so that on the side of the chlorine atoms they prevent a perceivable axial ligation. Most likely one NCO group of each complex unit is acting as a nitrogen bridging ligand and thus the adjacent units are linked in square pyramidal dimeric species or polymeric array. This explanation of the structure is also supported by the i.r. data. Some similarity is to be found between $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$ and $CuCl_2(2\text{-}Cl\text{-}py)_2$, since Billing and Underhill [8b], based on the electronic spectrum, ascribed to the latter complex a chlorine bridged, square pyramidal structure.

The $Cu(NCO)_2L$ complexes show a single d ← d band with the maximum at ≈1.30 μm^{-1} and a tail towards the infrared region. Such a spectrum suggest [16] a five-coordinated structure of intermediate geometry. A distorted square pyramidal configuration, formed by the nitrogen atoms from four bridging NCO groups and by one L molecule, is highly probable for these complexes. Such a configuration was established by Valach *et al.* [6] by X-ray analysis for $Cu(NCO)_2(2,4\text{-lutidine})$ having a very similar electronic spectrum.

TABLE IV. Magnetic Susceptibility Data for $Cu(NCO)_2L_2$ Complexes.

T(K)	293.4	252.8	223.1	193.4	163.7	143.9	124.1	104.3	94.4	
$Cu(NCO)_2(3\text{-}Cl\text{-}py)_2$										
$10^6\ \chi_M^{corr}$ (cgsu)	1594	1815	2054	2381	2785	3160	3644	4292	4768	C = 0.4494 cgsu
μ_{eff} (B.M.)	1.90	1.88	1.89	1.895	1.89	1.89	1.89	1.88	1.89	θ = 1.3 K
										$\mu_{eff}^{t.i.}$ = 1.90 B.M.
$Cu(NCO)_2(3\text{-}Br\text{-}py)_2$										
$10^6\ \chi_M^{corr}$ (cgsu)	1640	1880	2121	2427	2853	3196	3674	4365	4819	C = 0.4707 cgsu
μ_{eff} (B.M.)	1.92	1.92	1.92	1.91	1.91	1.90	1.89	1.895	1.90	θ = 5.4 K
										$\mu_{eff}^{t.i.}$ = 1.94 B.M.
$Cu(NCO)_2(3\text{-}I\text{-}py)_2$										
$10^6\ \chi_M^{corr}$ (cgsu)	1717	1890	2158	2509	2916	3340	3836	4500	4979	C = 0.4823 cgsu
μ_{eff} (B.M.)	1.97	1.92	1.93	1.95	1.93	1.94	1.94	1.93	1.94	θ = 4.3 K
										$\mu_{eff}^{t.i.}$ = 1.965 B.M.
$Cu(NCO)_2(4\text{-}Cl\text{-}py)_2$										
$10^6\ \chi_M^{corr}$ (cgsu)	1459	1706	1980	2167	2572	2898	3389	4003	4430	C = 0.4167 cgsu
μ_{eff} (B.M.)	1.81	1.82	1.85	1.805	1.81	1.81	1.82	1.81	1.82	θ = 1.3 K
										$\mu_{eff}^{t.i.}$ = 1.83 B.M.
$Cu(NCO)_2(4\text{-}Br\text{-}py)_2$										
$10^6\ \chi_M^{corr}$ (cgsu)	1624[a]	...	2120	2419	2827	3203	3676	4327	4741	C = 0.4730 cgsu
μ_{eff} (B.M.)	1.92[a]	...	1.92	1.91	1.90	1.90	1.895	1.89	1.88	θ = 6.7 K
										$\mu_{eff}^{t.i.}$ = 1.95 B.M.

[a] Temperature 295.5 K.

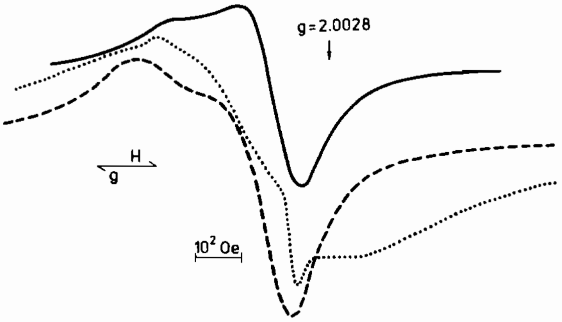

Fig. 2. ESR spectra of $Cu(NCO)_2(4\text{-}Cl\text{-}py)_2$ (———), $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$ (- - - - - -), and $Cu(NCO)_2(2\text{-}Br\text{-}py)$ (· · · · · ·).

ESR Spectra

The ESR spectra (Table III, Fig. 2) of the $Cu(NCO)_2L_2$ complexes are of the axial type. Excepting the case of L = 2-Cl-py, they yield g factor values close together: around 2.25 for $g_\parallel$ and in the range of 2.050–2.065 for $g_\perp$. The values of G, calculated as the ratio [2c, 17] of $(g_\parallel - 2)/(g_\perp - 2)$, are all greater than 4, so that the g values found adequately reflect [2c, 17] the symmetry of the copper(II) atom environment. The $g_\perp$ values are in excellent agreement with those calculated [18] and observed [2c, 17] for tetragonal CuN_4X_2 systems with a $d_{x^2-y^2}$ ground state.

Using the obtained g values and the energies of the ${}^2E_g \leftarrow {}^2B_{1g}$ and ${}^2B_{2g} \leftarrow {}^2B_{1g}$ transitions from the electronic spectra, we have calculated by means of the standard relations for a D_{4h} symmetry [2c, 17, 19], the values of the orbital reduction factors k. These are again in the range usually found [2c, 17] for tetragonal Cu(II) complexes. However, $k_\perp$ is with one exception distinctly higher than $k_\parallel$. This might be accounted for [2c, 17b, 19] by the presence of in-plane dative π-bonding, which is possible if the pyridine ring of the L molecule is perpendicular to the equatorial plane, as in $Cu(NCO)_2(py)_2$ [9, 13].

The ESR spectrum of $Cu(NCO)_2(2\text{-}Cl\text{-}py)_2$ differs from those of the other $Cu(NCO)_2L_2$ complexes by the line shape, as well as by much higher values of g. The value of G is, however, close to 4 and indicates that these values are still satisfactory [2c, 17] for an elongated tetragonal stereochemistry, including a square pyramidal one. This is further supported by the reasonable value of $k_\perp$, which was calculated [2c, 17, 19] assigning the ${}^2E \leftarrow {}^2B_1$ transition to the d ← d band maximum. Unfortunately, the $k_\parallel$ value cannot be calculated, since the ${}^2B_2 \leftarrow {}^2B_1$ transition energy cannot be evaluated, not even roughly.

The ESR spectra of the $Cu(NCO)_2L$ complexes consist of a very broad single line centered at g = 2.11 and 2.13 for L = 2-Cl-py and 2-Br-py, respectively. The overall shape of the resonance line is undoubtedly caused by an extensive exchange coupling, but the origin of some additional shoulders is obscure.

Magnetic Properties

The magnetic susceptibilities of the $Cu(NCO)_2L_2$ complexes (Table IV) obey the Curie–Weiss law $\chi_M^{corr} - N_A\alpha = C(T + \theta)^{-1}$, where $N_A\alpha = 60 \times 10^{-6}$ cgsu [20]. The Curie constants, C, and the Weiss constants, θ, were calculated by the standard linear least squares method. The greatness of the θ values (≈1–≈6.5 K) indicates only small interactions occurring between the Cu(II) atoms. The magnetic moments are therefore only slightly temperature dependent. They keep within the range expected [20] for magnetically diluted Cu(II) systems with an orbitally non-degenerate ground state. Thus the magnetic properties of the complexes under investigation are not markedly influenced by the assumed pseudobridges Cu–NCO–Cu; a similar fact was observed [2e] in the case of $Cu(NCO)_2(py)_2$. Nevertheless, certain trends can be observed in the changes of values of the temperature independent magnetic moments, $\mu_{eff}^{t.i.} = 2.83C^{1/2}$ Among the structurally similar complexes with 3-halogenopyridines these values slowly increase in the order of L = 3-Cl-py < 3-Br-py < 3-I-py. For complexes of differing crystal structure with 4-halogenopyridines the value of $\mu_{eff}^{t.i.}$ strikingly increases from L = 4-Cl-py to 4-Br-py.

The $Cu(NCO)_2L$ complexes have, at room temperature, high magnetic moments of 2.06 and 2.08 B.M. for L = 2-Cl-py and 2-Br-py, respectively. These are most likely caused by the presence of a ferromagnetic interaction between the Cu(II) atoms, being operated via the bridging nitrogen atoms from the NCO groups. This question was thoroughly discussed [6b] in order to explain the temperature dependence of the magnetic susceptibility for $Cu(NCO)_2$(2,4-lutidine).

Discussion

The results of the preparative study indicate that it is essentially more difficult to isolate complexes of the type $Cu(NCO)_2L_2$ with 2-halogenopyridines compared with those with 2-methylsubstituted pyridines. The formation of $Cu(NCO)_2(2\text{-Cl-py})_2$ is difficult and succeeds only with a considerable excess of 2-chloropyridine, while $Cu(NCO)_2(2\text{-Br-py})_2$ could not be prepared at all. This fact apparently cannot be accounted for only by the steric effect of the halogen substituent, inasmuch as the size of the chlorine atom is very close to that of the methyl group. Furthermore $CuCl_2$, $CuBr_2$ and $Cu(NO_3)_2$ produce with 2-chloro- and 2-bromopyridine complexes of the type CuX_2L_2 exhibiting tetragonal structures [8] according to their electronic spectra. It seems therefore that the cause of a preferential formation of the $Cu(NCO)_2L$ complexes with 2-halogenopyridines has to be traced to the mutual influence of ligands, steric as well as electronic. This influence makes the NCO groups to apply their N-bridging function and results in the adaptation of the highly distorted five-coordination.

The $Cu(NCO)_2L_2$ complexes, excepting $Cu(NCO)_2(2\text{-Cl-py})_2$, are structurally much more similar to one another than the complexes of the same type with L = 3- or 4-methylpyridine [2a–c] and 3- or 4-ethylpyridine [2e]. The stereochemical effect of the halogen atom in position 3 or 4 is therefore less pronounced than in the case of the alkyl group in the same position. On the other hand, divergences between $Cu(NCO)_2(2\text{-Cl-py})_2$ and the other $Cu(NCO)_2L_2$ complexes are distinctly greater than those between the corresponding methylpyridine complexes [2a–c].

The Cu–N(L) bonds in the 3- and 4-halogenopyridine complexes are fairly strong and it appears reasonable to suppose that it is the consequence of a large dative π-contribution brought about by the electron-attracting substituent on the pyridine ring. On the other hand, the NCO group itself has some π-acceptor capacity [21] which can well diminish the π-contribution in the Cu–N(L) bonds with methylpyridines, as they are not too ready π acceptors [22]. Thus, in the $Cu(NCO)_2L_2$ complexes with halogenopyridines and methylpyridines, the Cu–N(L) bonds can show a similar strength. The drift of the π-electron density from the Cu(II) atom (together with a weaker σ-donation from the halogenopyridines) probably reinforces an axial Cu–OCN interaction, which principally is made possible by the packing of the crystal structure.

The relationships between the crystal structures of the $Cu(NCO)_2L_2$ complexes suggest that the crystallostructural effect of the halogen atom makes itself felt more strongly in the position 4 than in 3. For 4-halogenopyridines apparently a considerable influence on the crystal structure is exerted by the volume of the halogen atom. On the other hand, for 3-halogenopyridines the influence of the halogen atom volume is weaker and between bromine and iodine no perceivable difference was revealed.

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