

PREPARATION AND STRUCTURAL CHARACTERIZATION OF CYANATOCOPPER(II) COMPLEXES WITH SUBSTITUTED PIPERIDINES*

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Dedicated to M. Zikmund, corresponding member of the Slovak Academy of Sciences, on the occasion of his 70th anniversary.

Coordination geometry of the newly prepared complex compounds of $[\text{Cu}(\text{NCO})_2\text{L}_2]$ type (L is piperidine, 2-methylpiperidine, 4-methylpiperidine and 2,6-dimethylpiperidine) was investigated at room temperature utilizing the results of infrared, electronic and ESR spectra and magnetic moments. All complexes show a tetragonal arrangement with small axial interaction depending on steric properties of the piperidine ligand given.

The cyanatocopper(II) complexes with pyridine and its methyl derivatives were recently examined in detail by vibration and electronic spectroscopies¹. The coordination geometry of these complexes depends to a great extent on steric requirements of the pyridine ligands. Piperidine derivatives are bulkier than the corresponding pyridines and therefore, they can influence the conditions for formation of cyanatocopper(II) complexes with these ligands. The influence of an anionic ligand need not be neglected, as well, because the cyanato group is preferentially terminally linked through the nitrogen atom. Eggli and Ludwig² prepared complexes $[\text{Ni}(\text{NCO})_2(\text{piperidine})_2]$ and $[\text{Ni}(\text{NCS})_2(\text{piperidine})_2]$; the coordination number of Ni(II) of the former is 5, that of the latter 6. Substitution in positions 2,6 of piperidine led to formation of square-planar compounds $[\text{Ni}(\text{NCX})_2(\text{dimethylpiperidine})_2]$. It seemed interesting to prepare cyanatocopper(II) complexes with piperidines (pip, piperidine; 2-mepip, 2-methylpiperidine; 4-mepip, 4-methylpiperidine; 2,6-dimepip, 2,6-dimethylpiperidine) and investigate the

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influence of piperidine ligands and the cyanato group on the steric arrangement of compounds prepared.

EXPERIMENTAL

Preparation of Complexes

$[Cu(NCO)_2(pip)_2]$. A mixture of potassium cyanate (53 mmol) in water (10 ml) and piperidine (65 mmol) in methanol (150 ml) was poured into a stirred solution of $Cu(NO_3)_2 \cdot 3 H_2O$ (25 mmol) in methanol (50 ml). After the fine light green precipitate had been filtered off, dark violet crystals began to separate from the filtrate allowed to stand; they were filtered off and washed with a small amount of methanol. This crystalline powder was dried over KOH.

$[Cu(NCO)_2L_2]$ (L is 2-mepip, 4-mepip, 2,6-dimepip). Ligand L (50 mmol) was added to a methanolic suspension (100 ml) of fresh dried $[Cu(NCO)_2(pyridine)_2]$ prepared according to ref.³ and several times washed with methanol. The mixture was stirred for 1 h and the solid was filtered off. The crystalline precipitate separating from the filtrate was filtered off, washed with a small amount of methanol and dried over KOH.

Analytical Methods and Physical Measurements

The copper content in all complexes under investigation was determined chelatometrically after a precedent decomposition of the complex with H_2SO_4 in the presence of $K_2S_2O_8$. The respective carbon, hydrogen and nitrogen content was determined with a CHN analyser (Carlo Erba). Results of analyses are listed in Table I. The ESR spectra were measured at an ambient temperature in the same way as in our precedent paper⁴, instruments and conditions for other physical measurements were already published⁵.

TABLE I
Characteristic data

Compound (M. w.)	Colour	Calculated/Found			
		% C	% H	% Cu	% N
$[Cu(NCO)_2(pip)_2]$ (317.9)	violet	45.34	6.98	19.99	17.63
		45.10	6.95	20.07	17.56
$[Cu(NCO)_2(2-mepip)_2]$ (345.9)	violet	48.61	7.58	18.37	16.20
		47.68	7.56	18.30	16.08
$[Cu(NCO)_2(4-mepip)_2]$ (345.9)	violet	48.61	7.58	18.37	16.20
		47.90	7.64	18.37	16.09
$[Cu(NCO)_2(2,6-dimepip)_2]$ (374.0)	rose-	51.39	8.09	16.99	14.98
	violet	51.55	8.26	17.01	14.78

RESULTS AND DISCUSSION

Infrared Spectra

All complexes under examination (Tables II and III) reveal a single very strong band at $2\,232 - 2\,240\text{ cm}^{-1}$ ($\nu(\text{CN})$) and medium bands at $1\,340 - 1\,365\text{ cm}^{-1}$ ($\nu(\text{CO})$). The $\nu(\text{CO})$ stretching vibration wavenumber values indicate the presence of cyanato groups bonded through nitrogen¹. The bending $\delta(\text{NCO})$ vibration bands, positioned at $600 - 640\text{ cm}^{-1}$ are splitted into a doublet up to 15 cm^{-1} . These results indicate the terminally bonded NCO groups, although formation of asymmetric pseudobridges involving their oxygen atom could not be excluded.

Stretching vibration of the NH groups of all complexes are considerably shifted towards lower frequencies when compared with those of free piperidines⁶. The main NH band of piperidine lies at $3\,343\text{ cm}^{-1}$ with a shoulder at $3\,315\text{ cm}^{-1}$. The high-frequency component of the band was assigned as NH equatorial conformation, the low-frequency one as NH axial form (ref.⁶). The $\nu(\text{NH})$ bands maintain their character also in coordination with the complexes prepared.

TABLE II
Medium-region infrared spectral data (cm^{-1})

Compound	$\nu(\text{NH})$	$\nu(\text{CN})$	$\nu(\text{CO})$	$\delta(\text{NCO})$
$[\text{Cu}(\text{NCO})_2(\text{pip})_2]$	3 248 s, 3 175 sh	2 232 vs	1 341 m	604 m, 617 m
$[\text{Cu}(\text{NCO})_2(2\text{-mepip})_2]$	3 240 s, 3 170 sh	2 240 vs	1 360 sh	600 m, 613 m
$[\text{Cu}(\text{NCO})_2(4\text{-mepip})_2]$	3 270 s, 3 250 sh	2 240 vs	1 350 m	610 m, 620 sh, 625 m
$[\text{Cu}(\text{NCO})_2(2,6\text{-dimepip})_2]$	3 250 s, 3 180 sh	2 240 vs	1 365 m	605 sh, 615 m

TABLE III
Far-infrared spectral data (cm^{-1})

Compound	ν (Cu-N(L))	ν (Cu-NCO)	δ (Cu-N-C)	Other bands	$\nu(\text{Cu-OCN})$
$[\text{Cu}(\text{NCO})_2(\text{pip})_2]$	457 mw	376 vs	260 m	217 m 168 - 148 w, sp	95 w
$[\text{Cu}(\text{NCO})_2(2\text{-mepip})_2]$	435 mw	384 s	258 s	208 m 142 - 111 w, sp	75 w
$[\text{Cu}(\text{NCO})_2(4\text{-mepip})_2]$	437 mw	364 s	266 m	215 m 146 - 130 m, sp	93 m
$[\text{Cu}(\text{NCO})_2(2,6\text{-dimepip})_2]$	440 mw	384 s	250 s	205 m 133 m, 117 w	75 w, 65 w

Stretching vibrations of the Cu–N and Cu–O bonds were ascertained in the 500 – 50 cm^{-1} region. Strong bands varying between 364 and 384 cm^{-1} were assigned to $\nu(\text{Cu-NCO})$ stretching vibration¹. Wavelengths of these vibrations indicated a stronger Cu–NCO bond in complexes $[\text{Cu}(\text{NCO})_2(2\text{-mepip})_2]$ and $[\text{Cu}(\text{NCO})_2(2,6\text{-dimepip})_2]$. Weak bands in the 435 – 457 cm^{-1} region were ascribed to $\nu(\text{Cu-N(pip)})$ stretching vibrations. Bands in the 300 – 100 cm^{-1} range belong evidently to various bending vibrations, the splitted weak bands at 150 cm^{-1} are probably associated with $\delta(\text{N-Cu-N})$ vibration^{7,8}. Bands of weak intensity below 100 cm^{-1} can be attributed to the stretching $\nu(\text{Cu-OCN})$ vibrations⁹, but also to lattice vibrations. Should these belong to the stretching $\nu(\text{Cu-OCN})$ vibrations, then their positions indicate a very weak Cu–O bond in complexes $[\text{Cu}(\text{NCO})_2(2\text{-mepip})_2]$ and $[\text{Cu}(\text{NCO})_2(2,6\text{-dimepip})_2]$.

Electronic Spectra

Electronic spectra of all complexes are quite similar (Table IV); the main d–d bands and the more or less pronounced shoulders are observed at 17 900 – 20 150 and 14 700 – 15 300 cm^{-1} , respectively. Compounds $[\text{Cu}(\text{NCO})_2(\text{pip})_2]$ and $[\text{Cu}(\text{NCO})_2(4\text{-mepip})_2]$ display the main band at about 18 000 cm^{-1} and therefore, a tetragonal bipyramidal structures with a strong axial distortion¹⁰ are assumed. This structure consists of units having two cyanate groups and two piperidine ligands coordinated by nitrogen atoms to the Cu(II) atom in equatorial plane in trans positions. This square configuration could be completed to tetragonal bipyramidal one by an axial interaction of the NCO group oxygen with Cu(II) atoms at the adjacent units. The d–d maxima of $[\text{Cu}(\text{NCO})_2(2\text{-mepip})_2]$ and $[\text{Cu}(\text{NCO})_2(2,6\text{-dimepip})_2]$ bands are observed at higher wavenumbers (Table IV). This type of spectrum is characteristic of an almost planar coordination of ligands around the Cu(II) atom without an evident axial interaction⁹ probably due to a steric hindrance of α -methyl groups. Considering the wavenumbers of Cu–O stretching

TABLE IV
The electronic and ESR spectral values and magnetic moments at room temperature

Compound	$\tilde{\nu}_{\text{max}} (10^3 \text{ cm}^{-1})$		g_{\perp}	g_{\parallel}	G	$\mu_{\text{eff}} (\text{B.M.})$
$[\text{Cu}(\text{NCO})_2(\text{pip})_2]$	c. 14.8 sh	18.1	2.063	2.216	3.43	1.87
$[\text{Cu}(\text{NCO})_2(2\text{-mepip})_2]$	c. 15.3 sh	19.05	2.044	^a		1.82
$[\text{Cu}(\text{NCO})_2(4\text{-mepip})_2]$	c. 14.7 sh	17.9	2.053	2.253	4.77	1.89
$[\text{Cu}(\text{NCO})_2(2,6\text{-dimepip})_2]$	c. 15.2 sh	20.15	2.048	2.218	4.54	1.82

^a The g_{\parallel} value is unresolved.

vibrations we presume a tetragonal bipyramidal arrangement also in these complexes, but with a substantially stronger axial distortion than in the first two complexes.

ESR Spectra

The ESR spectra of cyanatocopper(II) complexes are of a normal axial type, the g_{\parallel} value for the $[\text{Cu}(\text{NCO})_2(2\text{-mepip})_2]$ complex is not well resolved (Table IV). The g_{\parallel} and g_{\perp} values are in accord with the calculated¹⁰ and observed¹ ones for a tetragonal symmetry around the Cu(II) atom with nitrogen donor atoms having the ground state $d_{x^2-y^2}$. The line for the complex $[\text{Cu}(\text{NCO})_2(\text{pip})_2]$ is clearly flattened and the G value calculated from the relation

$$G = (g_{\parallel} - 2) / (g_{\perp} - 2)$$

making 3.43 indicates¹¹ that molecular axes of the ground units are misaligned to some extent and consequently, the crystal g -values are deviated from the g -factors of molecular configuration. The G values for complexes $[\text{Cu}(\text{NCO})_2(4\text{-mepip})_2]$ and $[\text{Cu}(\text{NCO})_2(2,6\text{-dimepip})_2]$ are higher than 4. This fact entitled us to conclude that the crystal g -values represent the true values of local Cu(II) environment.

Magnetic Measurements

The magnetic moment values varied at room temperature within a very close range (1.82 – 1.89 B.M.) and agreed with the non-degenerated state $^2B_{1g}$ (ref.¹⁰) without a visible exchange interaction.

CONCLUSIONS

All complexes under investigation display tetragonal structures formed by $\text{Cu}(\text{NCO})_2\text{L}_2$ units in which the Cu(II) atom has a square-planar coordination produced by two pairs of nitrogen atoms from two piperidine molecules and two NCO groups. This coordination is completed in axial positions by oxygen atoms of the NCO groups belonging to the adjacent molecules. Steric hindrance of 2-mepip and 2,6-dimepip caused the axial donors to be more remote this resulting in a very strong axial distortion.

Complexes under study display on comparison with complexes $\text{Cu}(\text{NCO})_2\text{L}_2$ containing methylpyridines¹ as ligands an approximate parallel concerning the effect of neutral ligands on the tetragonal distortion of complexes. Nevertheless, complexes with piperidine ligands are, in general, more distorted especially those with a steric hindrance what can be due to the bulkier ligand.

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