

Cyanatocopper(II) complexes with organic ligands. XVII.* Preparation and physical properties of cyanatocopper(II) complexes with aliphatic and related amines

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The cyanatocopper(II) complexes of the type $\text{Cu}(\text{NCO})_2\text{L}_2$, where L = allylamine, propylamine, butylamine, benzylamine, cyclohexylamine, and diethylamine were prepared and studied using infrared, electronic, and e.s.r. spectroscopy and room temperature magnetic moments. From the results of these measurements it follows that the Cu(II) atom in the studied complexes has tetragonal stereochemistry from pseudooctahedral to practically planar. Degree of the axial interaction is influenced by basicity of the ligand L as well as by its steric and crystallostructural effects.

Были приготовлены цианатные комплексы Cu(II) типа $\text{Cu}(\text{NCO})_2\text{L}_2$ (L = аллиламин, пропиламин, бутиламин, бензиламин, циклогексиламин и диэтиламин) и изучены при помощи исследования, ИК, ЭПР и электронных спектров и магнитных моментов при комнатной температуре. Из результатов этих измерений вытекает, что в изученных соединениях атом Cu(II) обладает тетрагональной стереохимией от псевдооктаэдрической до практически планарной. Степень аксиальной дисторсии обусловлена основностью лиганда L, а также его стерическими и кристаллоструктурными эффектами.

The preparation and results of physicochemical study of the cyanatocopper(II) complexes with aromatic amines have been published in the previous papers [2—4]. The influence of these ligands on the bonding mode of the cyanate group in these complexes was examined and structural characteristics of the complexes were suggested. As aliphatic amines are much more basic than aromatic ones, we considered it interesting to study the influence of increasing basicity on stoichiometry and stereochemistry of the cyanatocopper(II) complexes with the above-mentioned amines. Moreover, the steric hindrance effects of dialkylamines are expected that could affect the possibility of preparation of the cyanatocopper(II) complexes as well as the structures of the formed compounds.

* For Part XVI see Ref. [1].

This paper deals with the preparation and physical study of the cyanatocopper(II) complexes with allylamine (ala), propylamine (pra), butylamine (bua), benzylamine (bza), cyclohexylamine (cha), and diethylamine (dea).

Experimental

Preparation of the complexes

$\text{Cu}(\text{NCO})_2\text{L}_2$ (L = ala, pra, bua, cha)

$\text{Cu}(\text{NCO})_2(2,4\text{-lutidine})$ (20 mmol), freshly prepared according to [5], several times washed with methanol and dried on glass frit, was mixed in methanol (15–20 cm³) and ligand L (50 mmol) was added to the suspension. After 2 h of stirring the mixture changes its colour from green into blue or violet hue. Crystalline precipitates were sucked off and washed with ether.

$\text{Cu}(\text{NCO})_2(\text{bza})_2$

A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (25 mmol) in water (50 cm³) was poured together with a solution of KNCO (53 mmol) in water (50 cm³). This system was added under stirring to benzylamine (55 mmol) in methanol (100 cm³). Light-blue precipitate was sucked off, washed with 1:1 water–methanol mixture and dried in a desiccator over KOH.

$\text{Cu}(\text{NCO})_2(\text{dea})_2$

Freshly prepared $\text{Cu}(\text{NCO})_2(2,4\text{-lutidine})$ was left to stand over diethylamine in a desiccator with KOH for several days. The formed product oversaturated with diethylamine was sucked off and washed with ether. The violet powder was recrystallized from the benzene–ether mixture containing diethylamine.

Analytical methods

In all prepared complexes copper was determined chelatometrically, carbon, hydrogen, and nitrogen using CHN-analyzer C. Erba, Milan.

Physical measurements

Infrared [6], solid state electronic [6], and e.s.r. spectra [4], as well as magnetic susceptibilities [6] were measured as described in the cited papers.

Results

Basic data for the studied complexes are listed in Table 1. The results of spectral and magnetic measurements are summarized in Tables 2–4.

Table 1

Basic data for cyanatocopper(II) complexes with amines

Compound	M g mol^{-1}	Colour	Calculated/found				$\text{p}K_{\text{b}}$ (25°C) of amine*
			% C	% H	% N	% Cu	
$\text{Cu}(\text{NCO})_2(\text{ala})_2$	261.78	Violetblue	36.71	5.39	21.49	24.27	4.51
			36.02	5.34	21.28	24.23	
$\text{Cu}(\text{NCO})_2(\text{pra})_2$	265.80	Violetblue	36.15	6.83	21.81	23.90	3.47
			35.85	6.69	21.50	23.84	
$\text{Cu}(\text{NCO})_2(\text{bua})_2$	293.86	Blueviolet	40.87	7.55	19.06	21.62	3.40
			40.57	7.48	18.80	21.64	
$\text{Cu}(\text{NCO})_2(\text{bza})_2$	361.88	Light-blue	53.10	5.01	15.45	17.56	4.63
			53.00	4.77	15.39	17.66	
$\text{Cu}(\text{NCO})_2(\text{cha})_2$	345.94	Light-violet	48.57	7.57	16.18	18.37	3.32
			48.38	7.28	15.98	18.53	
$\text{Cu}(\text{NCO})_2(\text{dea})_2$	293.86	Violet	40.87	7.55	19.06	21.62	3.07
			40.40	7.27	18.73	21.70	

* Landolt—Börnstein: *Zahlenwerte und Funktionen*, Vol. II, Part 7, Elektrische Eigenschaften II, Springer-Verlag, Berlin, 1960.

Table 2
Frequencies [cm^{-1}] of NCO group and Cu–N vibrations in cyanatocopper(II) complexes with amines

Compound	$\nu_{\text{as}}(\text{NCO})$	$\nu_{\text{s}}(\text{NCO})$	$\delta(\text{NCO})$	$\nu(\text{Cu}-\text{N}_{\text{amine}})$	$\nu(\text{Cu}-\text{NCO})$	$\delta(\text{N}-\text{Cu}-\text{N})$
$\text{Cu}(\text{NCO})_2(\text{ala})_2$	2218 v	1325 m	<i>a</i>	425 vw	360 ms	270 sh 228 m
$\text{Cu}(\text{NCO})_2(\text{pra})_2$	2217 vs	1325 m	<i>a</i>	456 vw ^b	357 s	263 sh 248 m 220 sh
$\text{Cu}(\text{NCO})_2(\text{bua})_2$	2218 vs	1325 m	<i>a</i>	428 vw	355 s	243 m
$\text{Cu}(\text{NCO})_2(\text{bza})_2$	2218 vs	1325 m	621 m	449 w	356 ms	248 m
$\text{Cu}(\text{NCO})_2(\text{cha})_2$	2226 vs	1328 m	604 m	424 sh 415 w	373 s	270 mw 237 m
$\text{Cu}(\text{NCO})_2(\text{dea})_2$	2206 vs	1343 m	613 m 605 m	453 m 429 w	388 s	288 mw 247 ms 208 w

s — strong, m — medium, w — weak, v — very, sh — shoulder.

a) Overlapped by the amine bands.

b) The band exhibits poorly resolved splitting (the average frequency is given).

Table 3

Frequencies [cm^{-1}] of NH_2 or NH group vibrations in cyanatocopper(II) complexes with amines

Compound	$\nu_{\text{as}}(\text{NH}_2)$	$\nu_{\text{s}}(\text{NH}_2)$	$\nu(\text{NH})$	$2\delta(\text{NH}_2)$	$\delta(\text{NH}_2)$	$10^2 \Delta\nu/\nu$
$\text{Cu}(\text{NCO})_2(\text{ala})_2$	3319 s	3265 s		3176 m	1594 m	2.13
$\text{Cu}(\text{NCO})_2(\text{pra})_2$	3316 s	3266 s		3173 m	1591 m	2.04
$\text{Cu}(\text{NCO})_2(\text{bua})_2$	3319 s	3265 s		3163 m	1598 m	1.97
$\text{Cu}(\text{NCO})_2(\text{bza})_2$	3317 m	3260 s		3162 w	1599 m	1.45
$\text{Cu}(\text{NCO})_2(\text{cha})_2$	3312 s	3263 s		3161 m	1591 m	0.80
$\text{Cu}(\text{NCO})_2(\text{dea})_2$			3260 s			2.13

Table 4

Electronic and e.s.r. spectral data and magnetic moments (20°C) for cyanatocopper(II) complexes with amines

Compound	$\tilde{\nu}_{\text{max}}$, 10^3 cm^{-1}	g_{\perp}	g_{\parallel}	g_{av}	G	μ_{eff} , B.M.
$\text{Cu}(\text{NCO})_2(\text{ala})_2$	≈ 14.8 sh	17.3		2.109 ^a		1.86
$\text{Cu}(\text{NCO})_2(\text{pra})_2$	≈ 14.8 sh	17.3		2.121 ^a		1.86
$\text{Cu}(\text{NCO})_2(\text{bua})_2$	≈ 15.1 sh	17.3		2.118 ^a		1.86
$\text{Cu}(\text{NCO})_2(\text{bza})_2$	≈ 8.1 sh	≈ 14.6 sh	17.65	2.117 ^a		1.86
$\text{Cu}(\text{NCO})_2(\text{cha})_2$		≈ 14.95 sh	17.8	2.130 ^b	4.31	1.87
$\text{Cu}(\text{NCO})_2(\text{dea})_2$	≈ 15.3 sh	≈ 18.4 sh	20.0	2.116 ^b	4.14	1.81

a) Determined from the inflection point of the pseudoisotropic e.s.r. spectrum.

b) Calculated from the relation $g_{\text{av}} = (2g_{\perp} + g_{\parallel})/3$.

Infrared spectra

Vibrations of the cyanate group

Infrared spectra of all studied complexes show the ν_{as} and ν_s stretching bands of the NCO group in the region of ≈ 2230 — ≈ 2205 and ≈ 1345 — 1325 cm^{-1} , respectively. These stretching frequencies unambiguously indicate the NCO groups to be bonded through the nitrogen atoms [7, 8]. The deformation vibration of the NCO group appears mostly as medium bands situated between ≈ 615 — ≈ 605 cm^{-1} ; they are single or weakly split into doublet, as much as by 13 cm^{-1} . From these results it follows [7—9] that the cyanate group in the complexes under consideration is bonded terminally. The NCO deformation region for $\text{Cu}(\text{NCO})_2(\text{ala})_2$, $\text{Cu}(\text{NCO})_2(\text{pra})_2$, and $\text{Cu}(\text{NCO})_2(\text{bua})_2$ is overlapped by ligand bands, but additional bands indicating bridging function of the cyanate group do not occur. However, the existence of some bonding interactions between the Cu(II) atoms and the cyanate groups of adjacent species cannot be excluded [8].

Vibrations of the molecules L

The stretching vibrations of the NH_2 or NH groups in all complexes are considerably shifted towards lower frequencies if compared with the vibrations of free amines [10—12], hence all amines are coordinated. However, the NH_2 stretching region (3300 — 3100 cm^{-1}) contains three resolved bands instead of two bands ($\nu_{as}(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$) in all complexes under study. Some authors [13] explain the presence of three bands for other amine complexes by means of the Fermi interaction between the stretching modes and overtones of the NH_2 deformation modes.

The value $\nu = (\nu_{as} + \nu_s)/2$ was used for calculation of the relative shift, $\Delta\nu/\nu$, of the NH_2 stretching vibration in the case of primary amines. This relative change in $\nu(\text{NH}_2)$ or $\nu(\text{NH})$ frequencies can be correlated with magnitude of the hydrocarbon chain. The smaller shift was found for complexes with amines sterically more hindered for interaction with the Cu(II) atom.

Vibrations of the Cu—N bonds

The absorption bands corresponding to the $\nu(\text{Cu—N}(\text{NH}_3))$ vibration in the amines occur [14] in the region of 510 — 430 cm^{-1} . Strengthening of the Cu—N bond in the alkylamine complexes is expected owing to inductive effect of the alkyl group. In view of this knowledge we consider reasonable to assign the weak to medium bands in the region of 460 — 400 cm^{-1} to the Cu—N (amine) stretching vibrations; the bands below 300 cm^{-1} correspond apparently to the deformation vibrations, $\delta(\text{N—Cu—N})$ [14].

The strong or medium bands in the region of 390 — 355 cm^{-1} can be assigned [8, 15] to the Cu—NCO stretching vibrations. The frequencies of these vibrations suggest the strongest Cu—NCO bond for the planar complex $\text{Cu}(\text{NCO})_2(\text{dea})_2$.

Solid state electronic spectra

The complexes $\text{Cu}(\text{NCO})_2(\text{ala})_2$, $\text{Cu}(\text{NCO})_2(\text{pra})_2$, $\text{Cu}(\text{NCO})_2(\text{bua})_2$, and $\text{Cu}(\text{NCO})_2(\text{cha})_2$ exhibit rather similar electronic spectra (Fig. 1) which contain main $d \leftarrow d$ bands with maxima at $17\,300\text{--}17\,800\text{ cm}^{-1}$ and more or less resolved shoulders at about $14\,800\text{--}15\,100\text{ cm}^{-1}$. Such spectra are characteristic [16] of Cu(II) complexes of pronounced tetragonal structure which can be tetragonal-bipyramidal with a strong axial distortion or essentially planar. With respect to the wavenumber values of the maxima we accept sooner the first possibility. The maxima can be assigned to the transitions ${}^2E_g, {}^2A_{1g} \leftarrow {}^2B_{1g}$ and the shoulders to the ${}^2B_{2g} \leftarrow {}^2B_{1g}$ transition.

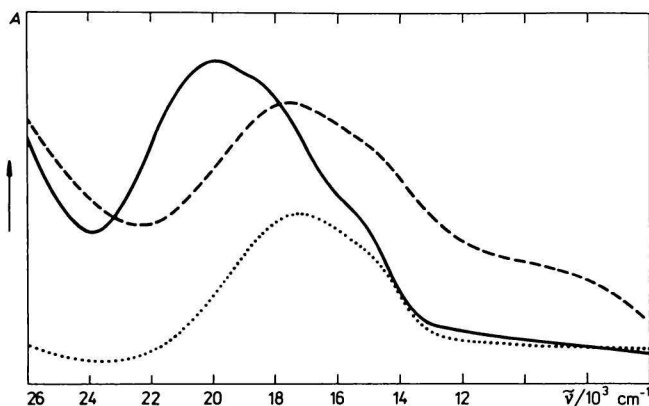


Fig. 1. Electronic spectra of complexes $\text{Cu}(\text{NCO})_2(\text{dea})_2$ (—), $\text{Cu}(\text{NCO})_2(\text{bza})_2$ (-----), and $\text{Cu}(\text{NCO})_2(\text{pra})_2$ (·····).

The electronic spectrum of $\text{Cu}(\text{NCO})_2(\text{bza})_2$ shows in the $d \leftarrow d$ region a three-component band (Fig. 1) with a maximum at $17\,650\text{ cm}^{-1}$, an inexpressive shoulder at about $14\,600\text{ cm}^{-1}$, and a broad, clear-cut shoulder at $\approx 8100\text{ cm}^{-1}$. The observed energy difference between the maximum and the low wavenumber shoulder reveals [17] a great separation of the lowest and the highest $d \leftarrow d$ transition and indicates a pseudooctahedral, weakly axially distorted configuration of the donor atoms around the Cu(II) atom. Then the maximum involves the transition ${}^2E_g \leftarrow {}^2B_{1g}$, the higher wavenumber shoulder the transition ${}^2B_{2g} \leftarrow {}^2B_{1g}$, and the lower wavenumber shoulder the transition ${}^2A_{1g} \leftarrow {}^2B_{1g}$.

The electronic spectrum of $\text{Cu}(\text{NCO})_2(\text{dea})_2$ has also a three-component $d \leftarrow d$ band (Fig. 1), with a maximum at $20\,000\text{ cm}^{-1}$ and two shoulders at about $18\,400$ and $15\,300\text{ cm}^{-1}$. The $d \leftarrow d$ band maximum is at the upper limit of wavenumbers observed for copper(II) complexes [16] and the shoulders are as well at considerably high wavenumbers. These results suggest a practically planar coordination of

donors around the Cu(II) atom, without a distinct axial interaction. In this case the higher wavenumber shoulder can be assigned to the transition ${}^2A_{1g} \leftarrow {}^2B_{1g}$ and the lower wavenumber shoulder to the transition ${}^2B_{2g} \leftarrow {}^2B_{1g}$; the maximum corresponds again to the transition ${}^2E_g \leftarrow {}^2B_{1g}$.

Magnetic moments

The effective magnetic moments, μ_{eff} , for all complexes under study were calculated from the relation

$$\mu_{\text{eff}} = 798.1[(\chi'_M - N_A\alpha)T]^{1/2}$$

For the temperature-independent paramagnetism, $N_A\alpha$, the values calculated from the approximative relation [18]

$$N_A\alpha = \frac{13.125}{\Delta} 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

were inserted, where Δ is the wavenumber of the $d \leftarrow d$ band maximum in the electronic spectrum.

The magnetic moments of the complexes (Table 4) are in agreement with those theoretically predicted [18] for magnetically diluted tetragonal systems with a nondegenerated ground state ${}^2B_{1g}$. The room temperature μ_{eff} values occur in a very small region of 1.81—1.87 B.M. and do not display any observable trend.

ESR spectra

The polycrystalline samples of $\text{Cu}(\text{NCO})_2(\text{ala})_2$, $\text{Cu}(\text{NCO})_2(\text{pra})_2$, $\text{Cu}(\text{NCO})_2(\text{bua})_2$, and $\text{Cu}(\text{NCO})_2(\text{bza})_2$ exhibit pseudoisotropic spectra with poorly resolved shoulders. The spectra of $\text{Cu}(\text{NCO})_2(\text{pra})_2$ and $\text{Cu}(\text{NCO})_2(\text{bua})_2$ are of the "reversed" type (Fig. 2), *i.e.* they have a higher intensity in the low field

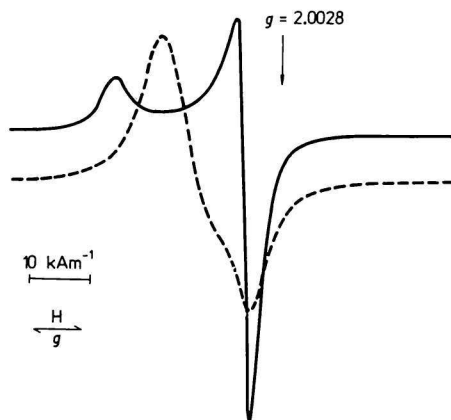


Fig. 2. ESR spectra of complexes $\text{Cu}(\text{NCO})_2(\text{cha})_2$ (—) and $\text{Cu}(\text{NCO})_2(\text{bua})_2$ (-----).

maximum than in the high field minimum. These facts are probably connected [16] with the presence of the Cu(II) atoms in crystallographically nonequivalent positions and with grossly misaligned tetragonal axes causing appreciable exchange interaction between the Cu(II) atoms. The average g factor values (Table 4) determined from the inflection points of the isotropic lines occur in a narrow region of 2.11–2.12.

$\text{Cu}(\text{NCO})_2(\text{cha})_2$ and $\text{Cu}(\text{NCO})_2(\text{dea})_2$ exhibit axial e.s.r. spectra of the normal type (Fig. 2). The g factor values (Table 4) determined by *Kneubühl's* method [19] correspond [16, 20] to the Cu(II) tetragonal systems with a $d_{x^2-y^2}$ ground state. The values of G calculated from the relation [16, 20] $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$ are higher than 4. It might be justifiably concluded from this fact [16, 20] that the Cu(II) atoms occupy approximately crystallographically equivalent positions in the crystal structures and the crystal g values represent essentially true g values of the Cu(II) atom, local environment.

Discussion

From the results of indirect physical methods we can conclude that for all studied complexes the Cu(II) atom is in a tetragonal environment with various degree of axial distortion (from pseudooctahedral to nearly planar). The N_4 environment of the Cu(II) atom in equatorial plane is formed by the nitrogen atoms of the *trans*-coordinated NCO groups and amine molecules. Through a suitable packing of the molecules in the crystal structure axial bonds of the Cu(II) atoms are formed, probably using the oxygen atoms of the NCO groups, belonging to the adjacent molecules. The existence of these axial bonds is supported especially by the e.s.r. properties of the respective complexes, because exchange interaction between the Cu(II) atoms through the NCO groups can proceed [4, 7]. The e.s.r. spectra in the case of $\text{Cu}(\text{NCO})_2(\text{cha})_2$ and $\text{Cu}(\text{NCO})_2(\text{dea})_2$ exhibit no appreciable exchange coupling and these complexes are according to the electronic spectra the most axially distorted (the last one is even planar).

A pseudooctahedral arrangement of ligands around the Cu(II) atom occurs in $\text{Cu}(\text{NCO})_2(\text{bza})_2$ with the least basic amine and a nearly planar configuration is supposed in $\text{Cu}(\text{NCO})_2(\text{dea})_2$ with the most basic amine. It might be concluded from this fact that the structures of the complexes are primarily influenced by the basicity of the coordinated ligands (Table 1). However, no dependence between the Cu–N (amine) bond strength and the basicity of amines was found. The reduction of axial interaction as well as the less strength of the Cu–N (amine) bond might be explained also by the steric effects of the organic ligands. Thus, the axial interaction as well as the Cu–N (amine) bond are stronger for $\text{Cu}(\text{NCO})_2(\text{bza})_2$ than for $\text{Cu}(\text{NCO})_2(\text{cha})_2$, because the NH_2 group is in the latter case directly linked with the sterically hindering cyclohexane ring. Likewise the planar structure

of $\text{Cu}(\text{NCO})_2(\text{dea})_2$ may be taken in connection with the steric hindrance of diethylamine, having two ethyl groups bonded on the donor nitrogen atom.

The resulting structures of the complexes under study are obviously influenced by the basicity and steric effects of the coordinated amines as well as by the conditions of the crystal structure packing. It seems that the effect of the amine basicity is primary, but in some cases it can be screened by the steric hindrance of the ligands. However, this knowledge cannot be generalized, because distinct dependence between the basicity of the nitrogen ligands and the structural characteristics of the cyanatocopper(II) complexes was not found in the other groups of these complexes [8].

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