Cyanatocopper(II) complexes with organic ligands. XIV.*
Physical properties and structure
of cyanatocopper(II) complexes with some diamines

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The following new cyanatocopper(II) complexes with organic diamines were prepared and studied using infrared, electronic, and e.s.r. spectroscopy and magnetic susceptibility measurements at room temperature:**$Cu(NCO)_2(o\text{-phen})\cdot H_2O$, $Cu(NCO)_2(m\text{-},$ $p\text{-phen})\cdot 0,5H_2O$, $Cu(NCO)_2(paz)$, and $Cu(NCO)_2(o\text{-tld})_2$. Structures of the complexes $Cu(NCO)_2(m\text{-}, p\text{-phen})\cdot 0.5H_2O$ and $Cu(NCO)_2(paz)$ consist of infinite chains linked by bifunctional diamine ligands. There are some indications that Cu^{2+} ion interacts axially with cyanate groups. Structure of $Cu(NCO)_2(o\text{-phen})\cdot H_2O$ exhibits some peculiarities, nevertheless the molecules of o-phenylenediamine are also bifunctional. $Cu(NCO)_2(o\text{-tld})_2$ possess a molecular structure with monofunctional o-tolidine molecules and a distorted tetrahedral arrangement of ligands.

Были получены новые комплексы цианата меди с органическими диаминами: $Cu(NCO)_2(o\text{-phen})\cdot H_2O$, $Cu(NCO)_2(m\text{-},$ $p\text{-phen})\cdot 0,5H_2O$, $Cu(NCO)_2(paz)$ и $Cu(NCO)_2(o\text{-tld})_2$, которые изучались методом инфракрасной, электронной, ЭПР спектроскопией и измерением магнитных восприимчивостей при комнатной температуре. Структуры комплексов $Cu(NCO)_2(m\text{-}, p\text{-phen})\cdot 0,5H_2O$ и $Cu(NCO)_2$ (paz) состоят из бесконечных цепей с двухфункциональными лигандами диаминов действующих как соединяющие звенья. На основании некоторых признаков можно предполагать, что существует аксиальное взаимодействие между ионом Cu^{2+} и группами цианата. Структура $Cu(NCO)_2(o\text{-phen})\cdot H_2O$ обладает некоторыми особенностями, но однако имеет двухфункциональные молекулы o-фенилендиамина. Комплекс $Cu(NCO)_2(o\text{-tld})_2$ имеет молекулярную структуру характеризованную с однофункциональными молекулами o-толидина и деформированным тетраэдрическим расположением лигандов.

Recently several papers concerning the new cyanatocopper(II) complexes with monofunctional nitrogen ligands like pyridine, quinoline or isoquinoline [1—3] as well as aniline [4, 5] have been published. In particular, the influence of these ligands on stereochemistry of

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* Part of this work was presented at the Meeting of Czechoslovak Chemists, Section 8 (Inorganic Chemistry), Brno, 1974.

** *Abbreviations:*

phen   phenylenediamine.
paz   piperazine.
tld   tolidine.

Table 1

Characteristics of the prepared complexes

Complex	Colour	M	Solubility[a]			Calculated/found			
			++	+	O	% Cu	% N	% C	% H
$Cu(NCO)_2(o\text{-phen})\cdot H_2O$	Greyblack	273.72		DMF, M	A, E	23.21	20.47	35.07	3.68
					CH, D	b	20.33	34.86	3.59
$Cu(NCO)_2(m\text{-phen})\cdot 0.5H_2O$	Greenbrown	264.72		DMF, M	A, E	24.00	21.16	36.29	3.43
					CH, D	23.82	21.31	36.45	3.47
$Cu(NCO)_2(p\text{-phen})\cdot 0.5H_2O$	Brown	264.72		DMF	M, A, E	24.00	21.16	36.29	3.43
					CH, D	24.09	21.26	35.93	3.34
$Cu(NCO)_2(paz)$	Light violetblue	233.72			DMF, M, A	27.19	24.08	30.97	4.31
					E, CH, D	27.02	23.86	30.47	4.32
$Cu(NCO)_2(o\text{-tld})_2$	Chocolate brown	572.14	DMF, M[c] A	E[c], CH[c] D[c]		11.14	14.68	62.96	5.64
						10.99	14.73	62.21	5.42

a) ++ well soluble, + poorly soluble, O practically insoluble, DMF — N,N-dimethylformamide, M — methanol, A — acetone, E — ethanol, CH — chloroform, D — dioxan.

b) See text.

c) The solution was turbid.

the prepared complexes and on the type of bonding of the cyanate group in these complexes and their structural peculiarities were examined. From this aspect we thought it interesting to prepare and study the cyanatocopper(II) complexes containing some potentially bifunctional ligands, which would differ in coordination ability due to their stereochemistry and basicity.

In this paper the preparation of the cyanatocopper(II) complexes with various diamines and a study of these complexes using infrared, electronic, and e.s.r. spectroscopy and magnetic moments measurement at the room temperature are described.

Experimental

Preparation of the complexes

$Cu(NCO)_2L \cdot nH_2O$, where $L = o$-, m-, p-phen, paz (for n see Table 1) — Aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ is mixed with aqueous solution of KNCO. The methanol solution of freshly prepared compound L is added under a continuous stirring. The corresponding complex precipitates immediately in the form of a fine crystalline precipitate, which is collected, washed by the water—methanol mixture, and dried in a desiccator with KOH.

$Cu(NCO)_2(o$-tld$)_2$ — Aqueous solution of copper(II) nitrate is mixed with aqueous solution of KNCO and is added to the methanol solution of o-tolidine under a continuous stirring. The rest is the same as in the previous case.

Solutions used: 1. 6.04 g $Cu(NO_3)_2 \cdot 3H_2O$ (25 mmoles) in 75 cm³ of water, 4.3 g KNCO (53 mmoles) in 75 cm³ of water, and 3 g o-, m-, or p-phenylenediamine (28 mmoles) in 100 cm³ of methanol; 2. 6.04 g $Cu(NO_3)_2 \cdot 3H_2O$ (25 mmoles) in 20 cm³ of water, 4.3 g KNCO (53 mmoles) in 30 cm³ of water, and 2.3 g piperazine (30 mmoles) in 50 cm³ of methanol; 3. 6.04 g $Cu(NO_3)_2 \cdot 3H_2O$ (25 mmoles) in 100 cm³ of water, 4.3 g KNCO (53 mmoles) in 150 cm³ of water, and 10.8 g o-tolidine (51 mmoles) in 250 cm³ of methanol.

In order to prevent the formation of various oxidation products at the preparation of complexes with o- and p-phenylenediamine, the preparation started from dihydrochloride of o- and p-phenylenediamine, which neutralized by NaOH gives the pure base. All operations were carried out in nitrogen. m-Phenylenediamine was recrystallized in ethanol, collected, and dried in nitrogen.

Analytical methods

Copper in the m-, p-phen, and paz complexes was determined chelatometrically after a decomposition of compounds by diluted H_2SO_4 and a oxidation of organic parts by $K_2S_2O_8$ [6]. Copper in $Cu(NCO)_2(o$-tld$)_2$ was determined by electroanalysis after total decomposition by calcination and heating with conc. H_2SO_4 in a quartz vessel. We did not succeed in determining of copper in $Cu(NCO)_2(o$-phen$) \cdot H_2O$ by any of the known method.

The elemental organic analysis was carried out using a CHN analyzer Carlo Erba.

Physical measurements

Electronic spectra of solid samples were recorded using the Nujol technique [4] with a Specord UV VIS (Zeiss, Jena) and Perkin—Elmer 450 spectrophotometers in the range 9100—30 000 cm⁻¹

Electronic absorption spectra of N,N-dimethylformamide (DMF) solutions were determined using an SF-8 (Leningrad Opto-mechanical Association) and Specord UV VIS (Zeiss, Jena) spectrophotometers

in the region 8300—30 000 cm^{-1}. Position of the absorption maxima did not change with time, however, the absorbance increased sharply; therefore the solutions were measured immediately after preparation.

Magnetic susceptibilities were measured by Gouy method using an instrument of our own design at 293 K with a field intensity in the region 280—520 kA m^{-1}. Effective magnetic moments (in Bohr magnetons) μ_{eff} were calculated from the relation $\mu_{eff} = 798.1 \ (\chi'_M \ T)^{1/2}$, where χ'_M is the molar susceptibility (in SI units) corrected by the Pascal's constants [7].

Thermal data were recorded with a Derivatograph OD-102 (MOM Budapest) at the heating rate 6°C/min in air; temperature was measured by Pt—Pt,Rh thermocouples. Sample (100 mg) was placed into a platinum crucible which is a standard accessory of the instrument.

The e.s.r. and infrared (550—3600 cm^{-1}) spectra were measured as previously described [1, 4]. Infrared spectra in the region 250—550 cm^{-1} were recorded using a Perkin—Elmer spectrophotometer. The sample was in Nujol suspension in a polyethylene capsule.

Results and discussion

Analytical and some other data of the studied complexes are presented in Table 1. The results of spectral and magnetic measurements are collected in Tables 2—4.

Thermal decompositions

Cu(NCO)$_2$(o-phen)·H$_2$O begins to lose water at 60°C and at 205°C the anhydrous compound decomposes explosively. In both other compounds of phenylenediamines the first release of water is observed at 60°C. In the case of Cu(NCO)$_2$(m-phen)·0.5H$_2$O the slow thermal decomposition of anhydrous compound starts at 127°C and even at 600°C the compound is not completely decomposed. Cu(NCO)$_2$(p-phen)·0.5H$_2$O loses slowly water up to 165°C. From the decrease of weight at 595°C one can deduce that the residue of thermal decomposition is CuO. With Cu(NCO)$_2$(paz) the total destruction occurs at 180°C. The slow thermal decomposition of Cu(NCO)$_2$(o-tld)$_2$ starts at *ca.* 130°C.

Infrared spectra

Region 550—3600 cm^{-1}

In this region primarily the vibrations of cyanate group, NH$_2$ group or NH diamine group and water molecules were studied. These vibrations were assigned by comparing the cyanate complexes spectra with those of free diamines known from literature and with the measured spectra of chloro complexes CuCl$_2$(o-phen) [8], CuCl$_2$(m-phen)·2H$_2$O [9], CuCl$_2$(p-phen)·C$_2$H$_5$OH [10], and CuCl$_2$(o-tld)$_2$ [11]*.

With the exception of Cu(NCO)$_2$(o-phen)·H$_2$O the vibrations of NCO group were observed in the usual regions [4, 12] *i.e.* $\bar{\nu}_{as}$ at 2230—2270 cm^{-1}, $\bar{\nu}_s$ at 1340—1360 cm^{-1}, and δ which is a doublet (splitting 12—23 cm^{-1}) at 600—640 cm^{-1}. From these results it follows [4, 12] that NCO groups in these complexes are bonded through the terminal nitrogen atom. Naturally they can participate also in weaker additional bonds [3, 4]. $\bar{\nu}_{as}$ in Cu(NCO)$_2$(o-tld)$_2$ is split appreciably (≈ 40 cm^{-1}) which is a certain indication for a non-centrosymmetric environment of the Cu^{2+} ion [12].

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* Only the chloro complex of an undefined composition was prepared with piperazine.

Table 2

Infrared data, cm^{-1}*

Complex	$\bar{\nu}_{as}(NCO)$[a]	$\bar{\nu}_s(NCO)$	$\delta(NCO)$	$\bar{\nu}_{as}(NH_2)$	$\bar{\nu}_s(NH_2)$	$\bar{\nu}(NH)$	$\delta(NH_2)$	$\bar{\nu}(OH)$	$\delta(OH)$
$Cu(NCO)_2(o\text{-phen})\cdot H_2O$	b	b	b	3302 s	3209 s, br[c]	3122 s[e]	1625 ms	3455 s, vbr[c]	1642 ms[c]
$Cu(NCO)_2(m\text{-phen})\cdot 0.5H_2O$	2247 vs, br[c]	1338 ms	614 ms 627 ms	3332 s	3247 s	3179 s[e]	1613 s 1628 s	3440 ms, vbr[c, d] 3529 ms	1643 sh
$Cu(NCO)_2(p\text{-phen})\cdot 0.5H_2O$	2241 sh 2253 vs, br[c]	1357 m	614 ms 637 m		3278 s		1606 ms 1621 ms	3390 sh, br 3475 m, vbr[c, d] 3537 m	
$Cu(NCO)_2(paz)$	2234 sh 2253 vs, br[c]	1347 m	608 ms 620 ms			3265 s	1618 vw[f]		
$Cu(NCO)_2(o\text{-tld})_2$	2225 vs, br 2252 sh 2266 vs	1341 mw	g	3313 ms 3399 ms 3463 sh, br	3269 ms 3329 ms	3189 m[e]	1616 ms 1633 ms		

* Relative intensities: s — strong, m — medium, w — weak, v — very; br — broad; sh — shoulder.
a) The band exhibits also side peaks at ≈2170 to ≈2180 cm^{-1}.
b) See text.
c) The band exhibits not well resolved splitting and number corresponds to the mean frequency.
d) The band exhibits complicated fine structure.
e) The band of not coupled $\bar{\nu}(NH)$ vibration.
f) The $\delta(NH)$ band.
g) Overlapped by the diamine band.

Table 3

Magnetic, e.s.r., electronic, and infrared (250—550 cm⁻¹) data

Complex	$\chi'_M \cdot 10^8$ m³mol⁻¹ at 293 K	μ_{eff} B.M.	$g_\perp$ or g_1	g_2	$g_\parallel$ or g_3	$\tilde{\nu}_{max}$ [10³ cm⁻¹]				$\tilde{\nu}$(Cu—NCO)		$\tilde{\nu}$(Cu—N$_{amine}$)
Cu(NCO)₂ (o-phen)·H₂O	1.199	1.50	1.99		2.235	≈14.3[a]			≈21.8[a]	b		
Cu(NCO)₂ (m-phen)·0.5H₂O	1.707	1.79	2.053	2.081	2.218	13.9	17.4		≈25.0[a]	·378 vs	404 sh	486 w
Cu(NCO)₂ (p-phen)·0.5H₂O	1.317	1.57	2.044		2.262	≈14.1[a]			≈23.1[a]	256 s[c]	356 s	492 s
Cu(NCO)₂(paz)	1.642	1.75	2.040		2.245	≈14.3 sh	17.7		29.4[d]	280 m[c]	356 s	417 m
Cu(NCO)₂(o-tld)₂	2.159	2.01	2.180		2.044	9.25	≈15.0 sh	21.1	≈27.8 sh	376 s		b

a) The maximum is extraordinary broad.

b) See text.

c) The bands not assigned.

d) Wavenumber gives only the border of maximum.

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Table 4

Spectral data for the complexes in DMF solutions

Complex	$\bar{\nu}_{max}$ $(\varepsilon_{max})^a$		
Cu(NCO)$_2$(*o*-phen)·H$_2$O	10.55 (3170)	15.1 (4010)	≈19.2 sh
	21.7 (3780)	≈28.9 sh	
Cu(NCO)$_2$(*m*-phen)·0.5H$_2$O	10.1 (25)	16.9 (310)^b	22.25 (740)^b
	27.55 (1450)		
Cu(NCO)$_2$(*p*-phen)·0.5H$_2$O	10.2 (23)	15.2 (130)^b	20.75 (430)
	24.2 (610)		
Cu(NCO)$_2$(*o*-tld)$_2$	9.4 (165)	≈11.2 sh	≈12.8 sh
	14.6 (1100)	≈19.8 sh	21.95 (5480)

a) $\bar{\nu}_{max}$ are given in 10^3 cm^{-1}, ε_{max} in cm^2 mmol^{-1}.
b) The maximum is very shallow.

The vibrational behaviour of the NCO group in Cu(NCO)$_2$(*o*-phen)·H$_2$O are quite anomalous. Only the weak split band with a centre at ≈2245 cm^{-1} is observed in the 2200 cm^{-1} region, while in the region 1315—1455 cm^{-1} the strong split band with maxima at 1368 and 1398 cm^{-1} and a contour very similar to that of $\bar{\nu}_{as}$(NCO) band appears. This band is in no way interchangeable with the bands of $\bar{\nu}$(CN) *o*-phenylenediamine which appear at 1255 cm^{-1} and as a shoulder at 1310 cm^{-1}. Furthermore, it was not possible to identify the bands corresponding to $\bar{\nu}_s$ and δ with a certainty. These rather surprising changes suggest a drastic rearrangement of the *II*-electronic system of the NCO groups, caused apparently by their bonding state in this complex (the above-listed frequencies nearly correspond to a simple C—N bond).

In order to assess the effect of crystal structure we have measured also the infrared spectra of Cu(NCO)$_2$(*o*-phen)·H$_2$O in the DMF and pyridine solutions (c ≈0.5 mol dm^{-3}). In analogy with the solid state spectra we have observed in both cases a band at ≈1350 cm^{-1}, which however, is not split (in pyridine with a shoulder at low frequency side), but no other bands that could be assigned to the NCO vibrations at 2200 and 600 cm^{-1}. This means that in measured solutions (at least at concentrations used) the NCO groups are virtually in the same state as in the solid complex.

It is obvious that without the knowledge of crystal structural data one cannot attempt to explain the nature of this effect. On the other hand it should be noted that similar anomalies were observed in the infrared spectra of other cyanatocopper(II) complexes [13]; the X-ray structure analysis of the α-modification of Cu(NCO)$_2$(3,5-dimethylpyrazole)$_2$ monocrystal which belongs to this class is already under way in our laboratory.

The stretching vibrations of the NH$_2$ or NH groups in the phenylenediamine and piperazine complexes are appreciably shifted toward lower frequencies if compared with the vibrations of free diamines [14—16], hence all these groups are coordinated [17—19]. However, Cu(NCO)$_2$(*o*-tld)$_2$ is different. In the spectrum of pure *o*-tolidine [13] appear four bands at 3461, 3401, 3366, and 3331 cm^{-1} in the region of NH$_2$ stretching vibrations. There are five $\bar{\nu}$(NH)$_2$ bands in the spectrum of Cu(NCO)$_2$(*o*-tld)$_2$, the three of them having frequencies close to those of pure *o*-tolidine while the other two are shifted toward lower

frequencies. From this it follows that the first three bands correspond to free amino groups while the other two to coordinated amino groups. o-Tolidine ligands are therefore in this complex apparently monofunctional.

In the spectra of the hydrated compounds the $\bar{v}(OH)$ vibrations at ≈ 3390 to ≈ 3540 cm^{-1} appear as broad bands with complex structure suggesting the bonding of water by hydrogen bonds [20].

Region 250—550 cm^{-1}

In this region we tried to assign the bands to stretching vibrations Cu—NCO and Cu—N$_{amine}$ by comparing the spectra of cyanate complexes with the measured spectra of free diamines. The spectrum of Cu(NCO)$_2$(o-phen)·H$_2$O was measured several times, however, its quality was always so poor that this spectrum could not be evaluated; the absorption of o-tolidine prevented the determination of Cu—N$_{amine}$ vibration in the spectrum of Cu(NCO)$_2$(o-tld)$_2$.

The stretching vibrations Cu—NCO were identified as strong bands at 355—380 cm^{-1} observed also in the spectra of other cyanatocopper(II) complexes [3, 13]. These vibrations suggest that the Cu—NCO bonds are weaker in Cu(NCO)$_2$(p-phen)·0.5H$_2$O and Cu(NCO)$_2$(paz) than in Cu(NCO)$_2$(m-phen)·0.5H$_2$O.

The bands with variable intensity in the 415—490 cm^{-1} region were tentatively assigned to the stretching vibration Cu—N$_{amine}$. *Clark* and *Williams* [21] found the vibrations M—NH$_3$ of diammonium metal compounds of the first transition period in the same region, for Cu(II) compounds shifted to the upper limit. *Lever* and *Mantovani* [22, 23] assigned to the stretching vibrations Cu—N$_{amine}$ in Cu(II) complexes with ethylenediamines mostly the bands in the vicinity of 400 cm^{-1} contrary to previous assignments. In view of this data our assignments seem to be correct; the unidentified bands below 300 cm^{-1} apparently cannot correspond to Cu—N$_{amine}$ vibrations.

Electronic spectra

Spectra in solid state

The spectra of Cu(NCO)$_2$(m-phen)·0.5H$_2$O and Cu(NCO)$_2$(paz) show in the ligand field region a broad band at about 17 500 cm^{-1} and a prominent shoulder at about 14 000 cm^{-1}. Such spectra are characteristic [23, 24] for tetragonal configuration with N$_4$-surrounding in the plane which can be supplemented by weak axial bonds. Under D_{4h} symmetry, the broad band can be assigned [25] to the transitions ^2E_g, $^2A_{1g} \leftarrow ^2B_{1g}$ and the shoulder to the $^2B_{2g} \leftarrow ^2B_{1g}$ transition. Using the relationship reported by *Billing* and *Underhill* [24], we get for 10 Dq parameters the values 7700 and 7500 cm^{-1} similar to those of tetragonal complexes of Cu(II) with the nitrogen donors [24, 26]. In the spectra of the complexes with o- and p-phenylenediamine the absorption in the region of $d \leftarrow d$ transitions decreases almost continuously and only very weak maxima can be observed at about 14 000 cm^{-1}.

The spectrum of Cu(NCO)$_2$(o-tld)$_2$ shows only a relatively narrow band at 9250 cm^{-1}, a broad shoulder at $\approx 15\ 000$ cm^{-1}, and a broad band at 21 100 cm^{-1} (Fig. 1). The wavenumbers of the first two maxima are too low for a predominantly planar N$_4$-coordination but they agree well [27—29] with the distorted tetrahedral stereochemistry. In that case the maxima apparently involve all $d \leftarrow d$ transitions of a Cu^{2+} ion; this is indicated by solution spectrum in which appear four peaks at similar wavenumbers (see below). The band near to 21 000 cm^{-1} which is also often observed [27] in the spectra of the pseudotetrahedral complexes of Cu(II) corresponds most probably to some low-lying charge-transfer transition (or transitions).
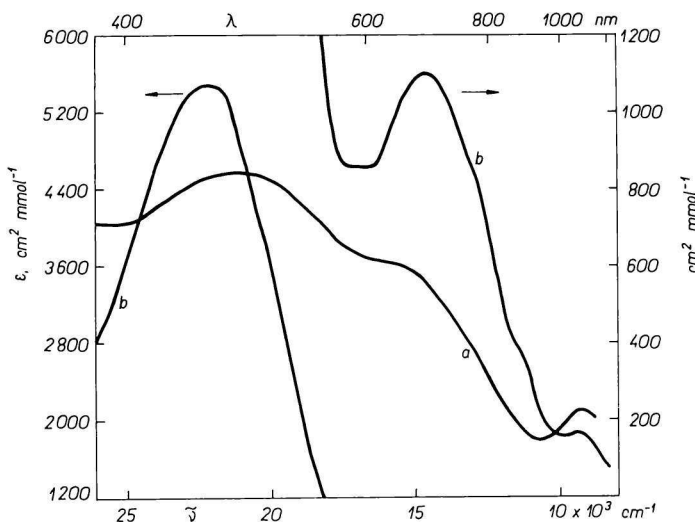
28

Fig. 1. Electronic spectra of $Cu(NCO)_2(o\text{-tld})_2$ in solid state (*a*) and in the DMF solution (*b*).

The spectra of phenylenediamine complexes exhibit broad maxima between 22 000—25 000 cm^{-1} which can be assigned [30] to the transfer of σ electrons from easily oxidable organic ligands to Cu^{2+} ion.

Solution spectra

The absorption spectrum of $Cu(NCO)_2(p\text{-phen}) \cdot H_2O$ shows in the ligand-field region two very strong bands at 10 550 and 15 100 cm^{-1}. The position of these bands is typical [31—33] of distorted *cis*-octahedral stereochemistry which apparently arises by supplementing the *cis* formations $Cu(NCO)_2(p\text{-phen})$ with the chelate-bonded *o*-phenylenediamine ligands by the DMF molecules. However, the ε_{max} values of both bands confirmed by repeated measure-
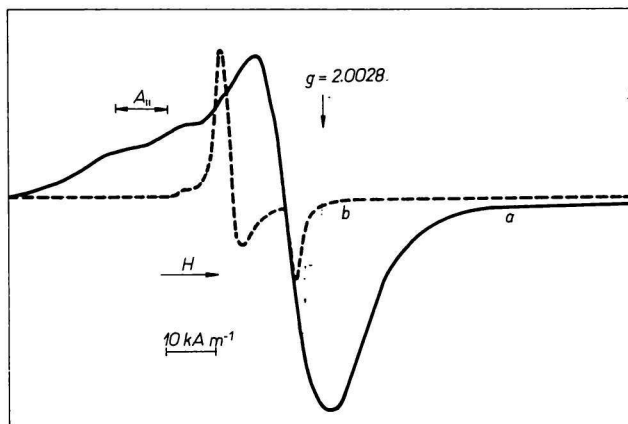

Fig. 2. The e.s.r. spectra of $Cu(NCO)_2(o\text{-phen}) \cdot H_2O$ (*a*) and $Cu(NCO)_2(o\text{-tld})_2$ (*b*).

ments are too high, even for $d \leftarrow d$ transitions of non-centrosymmetric configurations and we are not able to explain them satisfactorily. The charge-transfer band at 21 700 cm^{-1} has nearly the same energy as the similar band in a solid state compound.

Absorption spectra of the complexes with m- and p-phenylenediamine are rather similar. They exhibit the $d \leftarrow d$ bands at about 10 000 and 15 000 or 17 000 cm^{-1} and charge-transfer bands in the region 20 800—27 600 cm^{-1}. These spectra seem to be an intermediate type between the spectra typical of planar and pseudotetrahedral configuration [27]. We believe that the solutions contain the tetrahedrally distorted planar formations arising from the breakdown of solid polymer complexes (see Structures of the complexes) and by supplementing the Cu(NCO)$_2$(m-, p-phen) fragments with one solvent molecule.

The absorption spectrum of Cu(NCO)$_2$(o-tld)$_2$ is very similar to the solid state spectrum, the difference being made by two shoulders between the bands at ≈ 9000 and $\approx 15\,000$ cm^{-1} (Fig. 1). Hence the same pseudotetrahedral formations which form the solid complex are present also in the solution, probably due to the o-tolidine molecules which represent a steric hindrance for the change of configuration connected with coordination of solvent molecules. The mentioned four maxima then correspond [34] to four $d \leftarrow d$ transitions of the Cu^{2+} ion which are allowed in the ligand field of D_2 or C_{2v} symmetry.

The absorption spectra of the methanol solutions of complexes with o- and m-phenylenediamine and o-tolidine as well as the acetone, chloroform, and dioxan solutions of Cu(NCO)$_2$(o-tld)$_2$ were also measured, however, we shall not discuss them as they do not contain any new information with respect to the spectra of DMF solutions.

The solution spectrum of Cu(NCO)$_2$(paz) could not be recorded for the inadequate solubility of this compound in DMF (and other appropriate solvents).

The e.s.r. spectra

The e.s.r. spectra of Cu(NCO)$_2$(paz) and Cu(NCO)$_2$(p-phen)$\cdot 0.5$H$_2$O are of a normal axial type. While the lines in the first spectrum are very sharp, the other spectrum is flattened and indicates [35—37] that the exchange coupling takes place in the given complex. Since in both cases $g_\perp \geqslant 2.04$ the ground state of the Cu^{2+} ion in ligand surrounding is approximately $d_{x^2-y^2}$ [35—37].

The spectrum of Cu(NCO)$_2$(o-phen)$\cdot$H$_2$O (Fig. 2) is also normal axial, however it is considerably broadened and exhibits a hyperfine splitting in the parallel part, from which the value $A_\parallel \approx 10.203$ kA m^{-1} (≈ 135 Oe) is obtained [38, 39]. It cannot be decided whether the shoulder below maximum of the line in the perpendicular part of spectrum corresponds to the unresolved third g value or to hyperfine splitting. At $-140°$C the hyperfine splitting almost ceases to be observable and spectrum becomes "pseudoisotropic" [40], undoubtedly due to an exchange interaction between the nonequivalent Cu^{2+} ions. Using a Kneubühl's analysis [41] we obtain from the both spectra for $g_\perp$ the value 1.99. The lowest g value near to 2 indicates [42] existence of the ground state with considerable participation of orbital hybridization which takes place in low symmetry Cu(II) systems though it is also possible [40] that the $g_\perp$ value is influenced by unresolved hyperfine splitting.

Cu(NCO)$_2$(m-phen)$\cdot 0.5$H$_2$O exhibits a normal orthorhombic spectrum with sharp lines, and g values satisfying the relation $(g_2 - g_1)/(g_3 - g_2) \ll 1$, therefore the ground state is unambiguously $d_{x^2-y^2}$ [43, 44]. The orthorhombic component is weak ($\Delta g_\perp = 0.028$) and the complex can be considered to be essentially tetragonal as we assumed when interpreting its electronic spectrum.

An inspection of the g values for Cu(NCO)$_2$(m-phen)$\cdot 0.5$H$_2$O, Cu(NCO)$_2$(paz), and Cu(NCO)$_2$(p-phen)$\cdot 0.5$H$_2$O shows that while the $g_\perp$ values are very close to each other, the

$g_\parallel$ values increase considerably in the given order. This can be caused [45, 46] by an elongation of the equatorial bonds of the Cu^{2+} ion which occurs at an increase of its axial interaction with the NCO groups manifested also by magnetic moments of the corresponding complexes (see below).

The spectrum of $Cu(NCO)_2(o\text{-tld})_2$ (Fig. 2) is essentially axial, however, the line at lower field is considerably more intense than the line at higher field so that it must be considered to be "reversed" [37] $(g_\parallel < g_\perp)$. However, the determined g values clearly do not correspond to the true g values of the Cu^{2+} ion since they do not comply with the symmetry of ligand field indicated by other methods. This is probably connected [37] with the mutual positions of individual molecules in the elementary cell causing an exchange coupling. The origin of the small shoulder appearing reproducibly on the lower field side is not clear.

Magnetic moments

The complexes with o- and p-phenylenediamine show magnetic moments considerably lower than is the pure spin value for the Cu^{2+} ion. Hence, in agreement with the e.s.r. spectra it is to be assumed that these are magnetically condensed systems where an exchange interaction between Cu^{2+} ions takes place causing a partial pairing of their spins. The subnormal magnetic moments could be possibly caused also by the presence of copper(I) arisen by a partial reduction of copper(II) by phenylenediamine. However, the results of analysis were fairly good and besides, the measurements of independently prepared samples gave the same μ_{eff} values.

Magnetic moments of $Cu(NCO)_2(m\text{-phen})\cdot 0.5H_2O$ and $Cu(NCO)_2(paz)$ are "normal" for one unpaired electron of the Cu^{2+} ion. In spite of it the values are surprisingly low especially when it is realized that they were calculated without considering the temperature independent paramagnetism. Therefore, it is necessary to admit the possibility of some exchange connection which, however, could be proved only by a measurement of the temperature dependence of magnetic susceptibilities.

$Cu(NCO)_2(o\text{-tld})_2$ has a high magnetic moment which supports the assumption of a pseudotetrahedral coordination of Cu^{2+} ion. Magnetic moments of the Cu(II) complexes with a configuration between a planar and a tetrahedral one have usually values in the range 1.9—2.0 B.M. [47] and their values increase with an increasing content of the tetrahedral component [48]. The determined μ_{eff} value is by 0.01 B.M. lower than that for $[(C_2H_5)_4N]_2CuCl_4$ [49] where anion $CuCl_4^{2-}$ shows the slight flattening of tetrahedral geometry (less than in Cs_2CuCl_4, $\mu_{eff} = 1.99$ B.M. [49]).

Structures of the complexes

On the basis of results obtained by the used physical methods we can make following assumptions concerning structures of the studied complexes.

The complexes with m- and p-phenylenediamine and piperazine have polymer structures with the Cu^{2+} ions bonded in *trans* positions with the NCO groups and bifunctional nitrogen ligands that link them into infinite chains; a part of such chain is illustrated for $Cu(NCO)_2$ $(m\text{-phen})\cdot 0.5H_2O$ in Scheme 1. These polymer structures are confirmed also by the low solubility of all three compounds in common organic solvents. On the basis of physical data *Duff* [50] also deduced for the complexes of cobalt(II) and nickel(II) with m- and p-phenylenediamine polymer structures with phenylenediamine molecules functioning as bridge ligands.
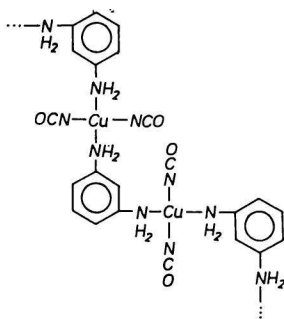
Scheme 1
Section of the assumed structure of $Cu(NCO)_2(m\text{-phen}) \cdot 0.5H_2O$.

As mentioned, according to e.s.r. results the axial interaction in the discussed complexes increases in the order (only diamines are presented) m-phen—paz—p-phen. The μ_{eff} values decrease in the same order, this being probably connected with increasing exchange coupling between the Cu^{2+} ions realized through the NCO groups. Thus, it can be assumed that by a suitable arrangement of the described chains in crystal structure weaker axial bonds of Cu^{2+} ions with NCO groups of a neighbour chain are formed. Remarkably low value of μ_{eff} for $Cu(NCO)_2(p\text{-phen}) \cdot 0.5H_2O$, which thus far has never been observed for cyanatocopper(II) complexes [51], together with the e.s.r. spectrum suggest a strong exchange interaction in this complex. This could be better mediated through N-bridging function of the NCO groups than by their bridging at both ends [5]. Splitting of NCO bonding is not too large, but still larger than in the complexes with m-phenylenediamine and piperazine.

The structure of $Cu(NCO)_2(o\text{-phen}) \cdot H_2O$ is not quite clear in spite of all obtained results. From the infrared data it follows that o-phenylenediamine should be bifunctional. According to *Duff* [8], this ligand can be either chelate or bridging; the latter type is assumed in $NiCl_2(o\text{-phen})$ and $CuCl_2(o\text{-phen})$. In the DMF solution ($c = 2.5 \times 10^{-4}$ mol dm^{-3}) according to absorption spectra $Cu(NCO)_2(o\text{-phen}) \cdot H_2O$ is present in the form of distorted *cis*-octahedral molecules. This does not mean, however, that a similar structure necessarily exists also in solid state, where a breakdown or a rearrangement of the structure can occur on dissolving with participation of solvent molecules. This possibility was indicated by the change of colour during dissolving. In any case the structure of this complex is very stable, which is manifested by its chemical properties, in particular by its resistance towards decomposition by common analytical methods. Anomalies in vibrations of the NCO groups and the e.s.r. spectra together with the low μ_{eff} value, which is still lower than the one for $Cu(NCO)_2(p\text{-phen}) \cdot 0.5H_2O$, indicate such peculiarities in its structure that any attempt at their clarifying could be only speculative. For these reasons only the X-ray structure analysis can bring a decisive information on the structure of this interesting compound.

$Cu(NCO)_2(o\text{-tld})_2$ exhibits molecular structure consisting of distorted tetrahedral molecules, the o-tolidine molecules being monofunctional. This compound is a rare case of nonchelate complex of Cu(II) with a pseudotetrahedral structure. The structure is probably enforced by a compromise between repulsive forces caused by the large o-tolidine molecules with steric hindrance and the requirements of stability in the ligand field.

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