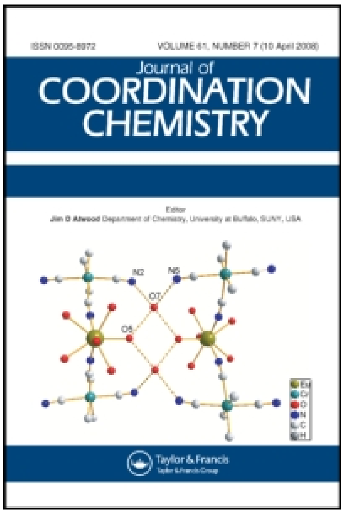

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PROPERTIES AND CHARACTERIZATION OF VARIOUS SPECIES AND ISOMERIC FORMS ISOLATED FROM THE Cu(II)-NCO^--3,4,5-TRIMETHYLPYRAZOLE SYSTEM[†]

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From the Cu(II)-NCO^--3,4,5-trimethylpyrazole (tmpz) system three isomeric compounds of the composition $Cu(NCO)_2$.2tmpz and one compound of the composition $Cu(NCO)_2$.tmpz were isolated. According to the infrared data two of the 1 : 1 compounds consist of $Cu(tmpz.NCO)_2$ complexes, comprising 3,4,5-trimethyl-1-carbamoylpyrazolate anions as chelate ligands, while the third represents the cyanato complex $Cu(NCO)_2(tmpz)_2$. This type of isomerism might be designated as coligand isomerism. The 1 : 1 compound exhibits terminally bonded as well as bridging NCO ligands. The ligand field spectra indicate that one of the compounds $Cu(tmpz.NCO)_2$ shows a square-planar configuration while the second differs by axial interactions between the basic structure units. $Cu(NCO)_2(tmpz)_2$ shows a molecular pseudotetrahedral structure and $Cu(NCO)_2(tmpz)$ has also a pseudotetrahedral but polymeric structure. The g values from the ESR spectra strongly support the above structure conclusions.

INTRODUCTION

As recent investigations[1,2] showed, a reaction of NCO^- with 3,5-dimethylpyrazole (dmpz) in the Cu(II) atom coordination sphere led to the formation of the compound Cu(dmpz.-$NCO)_2$. In it two 3,5-dimethyl-1-carbamoylpyrazolate anions are chelate coordinated on the Cu(II) atom coordination sphere led to the formation of the compound Cu(dmpz.-$NCO)_2$. In it two 3,5-dimethyl-1-carbamoylpyrazolate anions are chelate coordinated on the cyanato complex $Cu(NCO)_2(pz)_2$. In this paper the results obtained by study of the system Cu(II)-NCO^--3,4,5-trimethylpyrazole (tmpz) are presented.

EXPERIMENTAL

Preparation of α-$Cu(tmpz.NCO)_2$ A suspension of 8 mmol of freshly obtained $Cu(NCO)_2$(2,4-lutidine)[4] and of 20 mmol of 3,4,5-trimethylpyrazole in 18 ml of methanol was stirred for 1 h at room temperature. The formed solution was left to stand. The *violet crystals* precipitated from the solution were collected by suction, washed with methanol and dried in a desiccator over KOH.

Preparation of β-$Cu(tmpz.NCO)_2$ This compound was prepared in the same way as the α-form, only the suspension of $Cu(NCO)_2$(2,4-lutidine) with 3,4,5-trimethylpyrazole in methanol was heated for some minutes to ca. 60°C. The solution was left to stand for 2–3 h at room temperature. Dark *green crystals* precipitated from the solution were treated as in the case of the α-form.

[†] Dedicated to Professor J. Klikorka on the occasion of his 60th birthday.

Preparation of $Cu(NCO)_2(tmpz)_2$ A warm solution (≈40°C) of 4 mmol of $Cu(NO_3)_2.3H_2O$ in 10 ml of water was treated with a warm solution (≈40°C) of 8,5 mmol of KNCO in 10 ml of water. Under continual stirring this mixture was added to a solution of 8,5 mmol of 3,4,5-trimethylpyrazole in 15 ml of methanol. The precipitated *green crystals* were collected by suction, washed with a small amount of 1:1 methanol – water mixture and dried in a desiccator over KOH.

Preparation of $Cu(NCO)_2(tmpz)$ After separation of α-$Cu(tempz.NCO)_2$, the filtrate was left to stand during the night in a refrigerator. A light *brown powder* was collected by suction and dried.

Analyses

Elementary analyses were carried out on a C,H,N-analyzer (Carlo Erba); copper was determined chelatometrically. The analytical data are summarized in Table I.

Physical Measurements

The infrared spectra were recorded in nujol mulls on polyethylene with Perkin-Elmer spectrophotometers, *viz.* model 457 (4000–400 cm^{-1}) and 180 (500–50 cm^{-1}). Other physical measurements were made as noted previously.[5]

RESULTS

Generalities

The solubility of the isomeric pairs $Cu(NCO)_2(tmpz)_2$ and $Cu(tmpz.NCO)_2$ in organic solvents – methanol, acetone, dioxane and chloroform appear to be considerably different, the compounds $Cu(tmpz.NCO)_2$ being essentially less soluble.

By recrystallization of $Cu(NCO)_2(tmpz)_2$ from hot methanol solution, complex β-$Cu(tmpz.NCO)_2$ is formed. Heating the compound α-$Cu(tmpz.NCO)_2$ with methanol for some hours, converts it into the β-form, which seems to be more stable.

Decomposition temperatures (Table I) of the isomers are rather different and are in agreement with the assumed stabilities.

The X-ray powder diffraction patterns (Figure 1) of the α- and β-isomers exhibit some obvious differences.

TABLE I
Analytical data and other basic properties

Compound	Dec.t.[a] (°C)	Calcd. %	Found % C	% H	% N	% Cu	μ_{eff} (B.M.)
α-$Cu(tmpz.NCO)_2$	125	[b]	45.59	5.49	22.66	17.17	1.95
β-$Cu(tmpz.NCO)_2$	150	[b]	45.42	5.51	22.48	17.14	1.89
$Cu(NCO)_2(tmpz)_2$	70	[b]	45.47	5.48	22.69	17.21	1.985
$Cu(NCO)_2(tmpz)$	—	[c]	37.02	3.88	21.58	24.49	—

[a] The measurements were made with 100 mg of samples at a heating rate of 6°C/min.
[b] C, 45.70; H, 5.48; N, 22.84; Cu, 17.27.
[c] C, 37.28; H, 3.91; N, 21.83; Cu, 24.65.

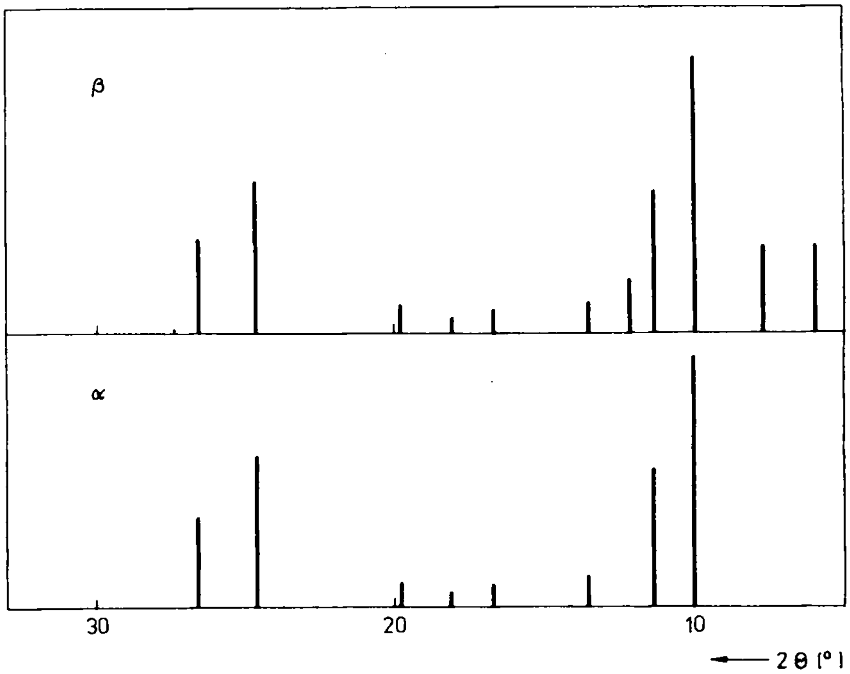


FIGURE 1 X-ray diffraction patterns of α- and β-Cu(tmpz.NCO)$_2$.

Infrared Spectral Characteristics

The infrared spectra (Table II) allow us to determine the fundamental difference between the pair of compounds Cu(tmpz.NCO)$_2$ and the compound Cu(NCO)$_2$(tmpz)$_2$. The bands observed at *ca.* 1690, 1345 and 505 cm^{-1} for Cu(tmpz.NCO)$_2$ belong[1-3] to the vibrations of the bent NCO group as a constituent of 3,4,5-trimethyl-1-carbamoylpyrazolate ligand. This was formed by a nucleophilic addition tmpz-CNO in the Cu(II) atom coordination sphere. The intensive absorption at *ca.* 1250 cm^{-1} is apparently connected with the N(ring)—C(chain) stretching vibration of this ligand. On the other hand, for Cu(NCO)$_2$(tmpz)$_2$ the bands at 2224, 1353 and 613 cm^{-1} indicate[6,7] the terminal, nitrogen coordinate NCO ligand.

Similarly as for the analogous pz compounds,[3] the very weak bands, occurring in the spectra of Cu(tmpz.NCO)$_2$ at ≈2250 cm^{-1}, may be ascribed to a small amount of the Cu(NCO)$_2$(tmpz)$_2$ species. The likewise very weak band in the spectrum of Cu(NCO)$_2$(tmpz)$_2$ at ≈1700 cm^{-1} is connected with small contents of the Cu(tmpz.NCO)$_2$ species.

The spectrum of Cu(NCO)$_2$(tmpz) is rather complex, containing many more bands than the spectra of the former compounds. An interesting feature is the presence of two very strong bands at 2245 and 2165 cm^{-1}, which show split patterns at 2275 (as shoulder), 2179 and 2114 cm^{-1}. These bands belonging to the ν_{as}(NCO) vibration indicate,[8,9] that in the given compounds two kinds of unequivalently coordinated NCO ligands occur. The strong band at 1688 cm^{-1} can correspond only to the ν(CO) vibration of the bent NCO group and thus reveals a considerable admixture of the Cu(II) species with tmpz.NCO ligands. In the range of 700–600 cm^{-1} six weak to medium bands appear, at least four of which must be assigned to the δ(NCO) vibration. This fact is consistent[8,9] with the occurrence of terminal bonded, as well as one-end N-bridging NCO groups, those latter exhibiting a considerably split deformation mode.

TABLE II

Most important infrared absorptions (cm^{-1})[a]

Compound	ν_{as}(NCO)	ν(C$\cdots$O)	ν_{s}(NCO)	ν(C$\cdots$N)	ν(C—N) + ring	δ(NCO)	γ(NCO)	ν(Cu—N)	δ(NCuN)
α-Cu(tmpz.NCO)$_2$		1691vs 1680sh		1351vs 1342sh	1252ms		506s	352s 226s	209m
β-Cu(tmpz.NCO)$_2$		1692vs 1677vs		1343vs	1248s		509s	348s 227m	207m
Cu(NCO)$_2$(tmpz)$_2$	2224vs 2173sh		1353m			613s		374s[b] 244ms	207m

[a] Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder, ν = stretching vibration, δ = in-plane bending vibration, γ = out-of-plane bending vibration, as = asymmetric, s = symmetric.

[b] A weak unresolved splitting occurs.

The band assigned to the NH stretching vibration appears[10] in the free 3,4,5-trimethylpyrazole at 3145 cm^{-1}, with side peaks at 3190 and 3090 cm^{-1}. In Cu(NCO)$_2$-(tmpz)$_2$ and Cu(NCO)$_2$(tmpz) the relevant band is shifted to 3332 and $\approx$3290 cm^{-1}, respectively. This can, however, quite be expected[11] on transition from the solid ligand to its coordinated state. In α- and β-Cu(tmpz.NCO)$_2$ a band occurs at 3366 and 3360 cm^{-1}, respectively; these frequencies seem to be too high for the coordinated NH group, which is supposed in Cu(dmpz. NCO)$_2$[2] and Cu(pz.NCO)$_2$.[3] Thus, on the basis of the infrared data, it is difficult to estimate the position of the hydrogen originally bonded on the imine nitrogen.

In the far-i.r. region of both Cu(tmpz.NCO)$_2$ and Cu(NCO)$_2$(pz)$_2$ some bands may be tentatively assigned, as is given in Table II. In the spectra of α- and β-Cu(tmpz.NCO)$_2$ the bands are found at 315 and 304 cm^{-1}, and 336, 318 and 303 cm^{-1}, respectively, which cannot be definitely assigned, as free tmpz absorbs at 338 cm^{-1}. However, very probably at least some of these bands, together with the bands at $\approx$350 cm^{-1}, belong to the skeletal Cu—N vibration with main contribution of the Cu—N(chain) stretch. The Cu—N(ring) stretch contributes then prevailingly to the Cu—N vibration bands at $\approx$225 cm^{-1}. It is interesting to note, that this stretching frequency compared with the analogous frequency for Cu-(dmpz.NCO)$_2$[2] is lower by ca. 90 cm^{-1}. This is apparently caused not only by increase of the ligand mass owing to a further methyl group, but also by some decrease of the Cu—N(ring) bond strength. In the case of Cu(NCO)$_2$(tmpz)$_2$ the assignment is more straightforward: the band at 374 cm^{-1} is prevailingly due to the Cu—NCO stretch[7,12] and the band at 244 cm^{-1} to the Cu—N(tmpz) stretch. Because of a number of bands present, the far-i.r. region of Cu(NCO)$_2$(tmpz) appears to be rather confused; a strong band at 380 cm^{-1} is assignable to the Cu—NCO stretch.

Electronic and ESR Spectra

The wavenumbers of the band maxima in the solid state electronic spectra together with the g-values from the ESR spectra are listed in Table III.

The ligand field band of α-Cu(tmpz.NCO)$_2$ is by its shape and position very similar to that of α-Cu(dmpz.NCO)$_2$, whose structure was solved[1,2] by X-ray methods. Therefore, the structure of α-Cu(tmpz.NCO)$_2$ is apparently closely related, *i.e.* formed by *trans*-square-planar molecules, in which two 3,4,5-trimethyl-1-carbamoylpyrazolate anions are bonded to the Cu(II) atom by their chain and ring nitrogens. Between these molecules no distinct axial interaction takes place in the crystal structure.

The electronic spectrum of β-Cu(tmpz.NCO)$_2$ is quite different from the foregoing one. On the descending branch from the u.v. region two broad expressive absorptions appear at *ca.* 22600 and 16400 cm^{-1}; a third, unresolved one is perceptible at 13100 cm^{-1}. Since the planar CuN$_4$-systems have their d $\leftarrow$ d-band maxima at the highest energies,[13] considering the d $\leftarrow$ d-spectrum of the α-form it seems reasonable to suppose the $\approx$22600 cm^{-1} band to be some low energy CT-transition. In this case the d $\leftarrow$ d-transitions of

TABLE III
Electronic and ESR spectral data for the solid complexes

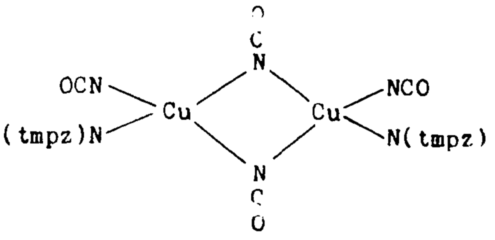
Compound	$10^{-3}\,\tilde{\nu}_{max}$(cm^{-1})[a]	$g_\parallel$	$g_\perp$
α-Cu(tmpz.NCO)$_2$	$\approx$16.0sh, 18.8, $\approx$28.1sh	2.189	2.048
β-Cu(tmpz.NCO)$_2$	$\approx$13.1sh, $\approx$16.4sh, $\approx$22.6sh, $\approx$27.7sh	2.196	2.047
Cu(NCO)$_2$(tmpz)$_2$	$\approx$10.4sh, 13.0, $\approx$23.1sh, 28.4	2.306	2.058
Cu(NCO)$_2$(tmpz)	$\approx$11.1sh, 12.9, $\approx$22.8sh	—	—

[a] sh = shoulder.

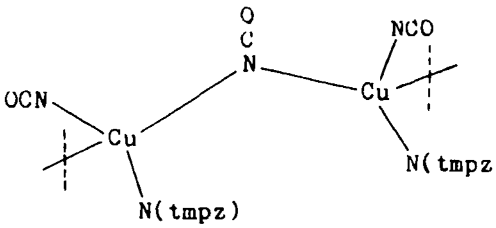
β-Cu(tmpz.NCO)$_2$ appear shifted by $\approx$2500 cm^{-1} to lower energies with respect to the α-form.

These shifts might be connected either with a fall of the ligand field strength affecting the Cu(II) atom, or with the presence of some effective axial interaction between the structure units. However, taking into account the d $\leftarrow$ d-transition energy observed, we are inclined to assume that the planar Cu(tmpz.NCO)$_2$ species go in axial interactions, most likely *via* the carbamoyl oxygens. These interactions, accepted also for β-Cu(dmpz.NCO)$_2$,[2] strongly reduce the axial distortion, and the low-energy jump of the d $\leftarrow$ d-spectrum is thus easy to understand. On the other hand, in the far-i.r. spectrum no band can be unequivocally assigned to the Cu—O(chain) stretch. Nevertheless, this can be accidentally degenerate with some other vibration in this region.

The compound Cu(NCO)$_2$(tmpz)$_2$ and Cu(NCO)$_2$(tmpz) exhibit rather similar electronic spectra. Their d $\leftarrow$ d - band positioned in the near. -i.r. region indicates[14] a distorted tetrahedral N$_4$ environment of the central Cu(II) atom. While Cu(NCO)$_2$(tmpz)$_2$ obviously consists of mononuclear molecules, Cu(NCO)$_2$(tmpz)$_2$ must be in some way polymeric. Thus, it can contain binuclear species (I), similar to *e.g.* [Cu$_2$(NCO)$_6$]$^{2-}$,[8] or polynuclear chains (II), both with bridging and terminal NCO groups.



(I)



(II)

The ESR spectra of α- and β-Cu(tmpz.NCO)$_2$ are of normal axial type. The values of the G parameter $[= (g_\parallel - 2)/(g_\perp - 2)]$[13,15] are 3.94 and 4.17, respectively. Thus, the g values indicate a $d_{x^2-y^2}$ ground state of the central Cu(II) atom. The g values of the α-form are relatively low, though not insomuch as for α-Cu(dmpz.NCO)$_2$.[2] The β-form shows very similar g values as β-Cu(dmpz.NCO)$_2$.[2] A significantly higher $g_\parallel$ value than that of the α-form is almost certainly a consequence of axial bondings in this compound.[2,16]

Cu(NCO)$_2$(tmpz)$_2$ also exhibits a normal axial ESR spectrum, but its g values (especially $g_\parallel$) are considerably high. This fact, however, agrees fairly well with the postulated pseudotetrahedral stereochemistry.[17]

DISCUSSION

The Cu(II)-NCO$^-$-tmpz system allows the isolation of two isomers of Cu(tmpz.NCO)$_2$ with 3,4,5-trimethyl-1-carbamoylpyrazolate ligands, further, of the compound Cu(NCO)$_2$(tmpz)$_2$ with cyanate and 3,4,5-trimethylpyrazole ligands and also of the compound Cu(NCO)$_2$-(tmpz).

The compounds $Cu(tmpz.NCO)_2$ and $Cu(NCO)_2(tmpz)_2$ show an isomeric pair of the same kind as of $Cu(pz.NCO)_2$ and $Cu(NCO)_2(pz)_2$,[3] which were classified as ligand isomers (in a broader sense). Occurrence of such isomers is connected with the existence of tmpz or pz and NCO as independent ligands as well as with the bond formation between them in the coordination sphere. more adequately isomers of such type might be designated as *coligand* isomers.

The isomeric pair of α- and β-$Cu(tmpz.NCO)_2$ is stereochemically closely related to α- and β-$Cu(dmpz.NCO)_2$[2] and can be considered for an extreme case of distortion isomerism due to the plasticity of the Cu(II) atom coordination sphere[18] (one isomeric form is planar and the other – pseudooctahedral). It may be expected, that the electronic properties of dmpz.NCO and tmpz.NCO ligands are commensurate to one another and the additional 4-methyl group shows rather crystallostructural than stereochemical influence.

The formation of the stable $Cu(NCO)_2(tmpz)_2$ species with pseudotetrahedral geometry is probably a consequence of the considerable basicity of the tmpz ligand[19] and its steric hindrance. The basicity forces this ligand to form a tight bond with the Cu(II) atom but the steric hindrance acts against them. Thus, a compromise between the steric factor and the ligand field stabilization results in the tetrahedral distortion of the planar ligand arrangement. From this point of view also the existence of the 1 : 1 cyanato compound can be rationalized.

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