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Nucleophilic Addition and Various Species Formed in the Cu(II)–NCO$^-$–3(5)-Methylpyrazole System

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Abstract

From the Cu(II)–NCO$^-$–3(5)-methylpyrazole (mpz) system two compounds $Cu(NCO)_2(mpz)_2$ and four compounds $Cu(mpz{\cdot}NCO)_2$ were isolated. The latter compounds contain carbamoylmethylpyrazolate anions as chelate ligands and are coligand isomers of the cyanate compounds. According to the results of indirect structural methods, the $Cu(NCO)_2(mpz)_2$ complexes have pseudooctahedral structures and differ in their polyhedron distortions. The $Cu(mpz{\cdot}NCO)_2$ complexes show tetragonally distorted six or five coordinate structures, possibly differing also by the methyl group position on the pyrazole ring.

Introduction

In the last years nucleophilic addition between cyanate group and pyrazole or its methyl derivatives in the Cu(II), Ni(II) or Co(II) coordination sphere has been studied in detail [1]. It has been shown that for the given central atom electronic and steric properties of the pyrazole ligands, controlled by the substituents on the pyrazole ring, exert a considerable influence on the possibility and course of these reactions. Therefore it appears very interesting to investigate the Cu(II)–NCO$^-$ system with 3(5)-methylpyrazole which is expected to have its electronic and steric properties somewhere between pyrazole alone and 3,5-dimethylpyrazole already studied [1a, b] as to their nucleophilic addition behaviour.

In the present paper we report and characterize various products isolated from the system of Cu(II)–NCO$^-$–3(5)-methylpyrazole (mpz). Since these products could only be prepared as polycrystalline materials without any ability to overgrow into single crystals, we investigated them using X-ray powder diffractions and various physical techniques.

Experimental

Preparation

α-$Cu(NCO)_2(mpz)_2$

A cool solution (≈5 °C) of 10 mmol of $Cu(NO_3)_2\cdot 3H_2O$ in 15 cm^3 of water was treated with a cool solution of 23 mmol of KNCO in 20 cm^3 of water. Under stirring and cooling a solution of 25 mmol of mpz in 20 cm^3 of methanol was added. The precipitated pale blue crystalline powder was collected by suction, washed with a small amount of 1:1 methanol–water mixture and dried in a desiccator over KOH.

β-$Cu(NCO)_2(mpz)_2$

The preparation procedure was the same as for the α-isomer, only the solutions used were warm (40 °C).

α-$Cu(mpz{\cdot}NCO)_2$

A suspension of 8 mmol of freshly obtained $Cu(NCO)_2$(2,4-lutidine) [2] and of 20 mmol of mpz in 20 cm^3 of methanol was stirred for one hour at room temperature. The violet crystalline powdery precipitate was separated, washed and dried over KOH.

β-$Cu(mpz{\cdot}NCO)_2$

After separation of α-$Cu(mpz{\cdot}NCO)_2$ the filtrate was left to stand for some days in a refrigerator. A grass green crystalline powder was formed which was collected by suction, washed and dried.

γ-$Cu(mpz{\cdot}NCO)_2$

When α-$Cu(NCO)_2(mpz)_2$ is left to stand for several months it gradually changes and a gray–green powder is formed as a final product.

δ-$Cu(mpz{\cdot}NCO)_2$

By recrystallization of α-$Cu(NCO)_2(mpz)_2$ from hot methanol solution a dark green microcrystalline precipitate was obtained.

Analysis

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

Physical Measurements

Infrared [1d], far-infrared [3], solid state electronic [4] and ESR spectra [5], as well as X-ray

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TABLE I. Analytical Data and Room Temperature Magnetic Moments

Complex	Colour	Found (%)				μ_{eff} (BM)^b
		C	H	N	Cu	
		38.52^a	3.88^a	26.96^a	20.38^a	
α-Cu(NCO)$_2$(mpz)$_2$	pale blue	38.31	3.82	26.61	20.15	1.84
β-Cu(NCO)$_2$(mpz)$_2$	turquoise blue	38.26	3.88	26.90	20.25	1.78
α-Cu(mpz·NCO)$_2$	violet	37.96	3.83	26.67	20.41	1.87
β-Cu(mpz·NCO)$_2$	grass green	39.21	4.11	26.95	20.20	1.93
γ-Cu(mpz·NCO)$_2$	grey–green	38.67	3.92	26.78	20.18	1.85
δ-Cu(mpz·NCO)$_2$	dark green	38.30	3.87	26.35	20.52	1.93

^{a}Calculated for $C_{10}H_{12}N_6O_2Cu$. ^{b}Calculated by the relation $\mu_{eff} = 2.83[(\chi_M^{corr} - N_A\alpha)T]^{1/2}$, where $N_A\alpha = 60 \times 10^{-6}$ cgsu mol^{-1} is the temperature independent paramagnetism.

powder diffraction patterns [6] and room temperature magnetic susceptibilities [7] were obtained as described in the cited papers.

Results and Discussion

X-ray Diffractions

The X-ray powder diffraction patterns of all compounds under investigation are shown in Fig. 1. In the diagrams of α- and β-Cu(NCO)$_2$(mpz)$_2$ significant differences only appear in the intensities of the diffraction lines. The diffractions of α- and γ-Cu(mpz·NCO)$_2$ show some similar features. On the other hand, the diffractions of β- and δ-Cu(mpz·NCO)$_2$ show that their crystal structures are considerably different, apparently in connection with structure differences between the relevant species present.

Infrared Spectra

The infrared spectra of the compounds under study were checked by comparison with the spectra of free [8, 9] as well as of coordinated mpz [9]; the frequencies of typical vibrations are listed in Table II.

Both isomers of Cu(NCO)$_2$(mpz)$_2$ exhibit cyanate vibrations revealing terminal nitrogen bonded NCO groups, with the possibility to form additional weak bonding using their oxygens [10]. The positions of the ν(NH) vibration prove hydrogen bonding [9] (with NCO groups of other complex units). The mpz vibrations of these compounds are substantially consistent with those reported for complexed mpz by Reedijk [9]. The differences between the α- and β-form in all ligand vibrations, if any, are quite unimportant.

All compounds Cu(mpz·NCO)$_2$ instead of the cyanate bands have new bands well known to be diagnostic of the carbamoyl group as a part of the anionic chelate ligand [1] (see Fig. 3b below). This new ligand is formed by nucleophilic addition between the cyanate carbon and the pyrazole imine nitrogen with a simultaneous transfer of the imine hydrogen, probably to the carbamoyl nitrogen [1b].

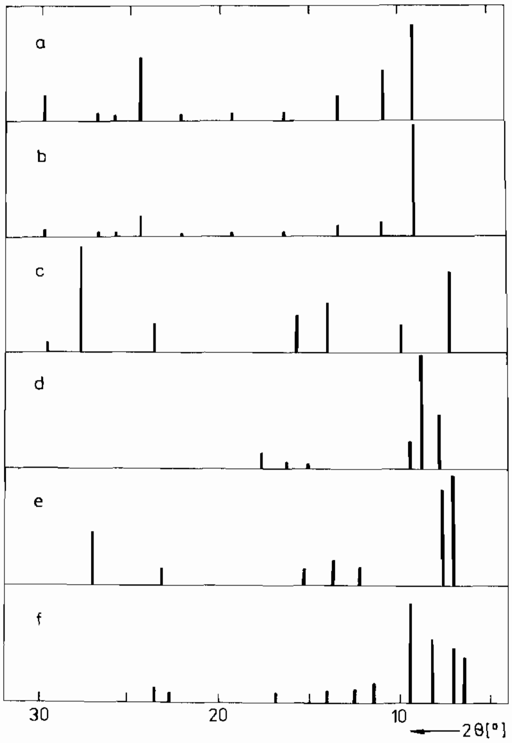


Fig. 1. X-ray diffraction patterns of (a) α-Cu(NCO)$_2$(mpz)$_2$, (b) β-Cu(NCO)$_2$(mpz)$_2$, (c) α-Cu(mpz·NCO)$_2$, (d) β-Cu(mpz·NCO)$_2$, (e) γ-Cu(mpz·NCO)$_2$, (f) δ-Cu(mpz·NCO)$_2$.

In the carbamoylmethylpyrazolate compounds, many vibrations of the methylpyrazole constituent are significantly changed with respect to the Cu(NCO)$_2$(mpz)$_2$ compounds. This applies above all to the C–H and ring stretches which are mostly shifted to lower frequencies, and to the C–H deformations (in plane and out of plane) as well as to the ring bendings, usually shifted in the opposite direction. There are certain differences between α- and γ-Cu(mpz·NCO)$_2$ in the intensities and splittings of

TABLE II. Important Vibrational Frequencies (4000–400 cm^{-1})

Complex	ν(NH)	ν_{as}(NCO)	ν(CO)	ν_s(NCO)	ν(CN)	ν(CN$_{ring}$)	δ(NCO)	γ(NCO)
α-Cu(NCO)$_2$(mpz)$_2$	3299vs	2238vs		1350m[a]			615mw[a]	
		2196vs		1342sh[a]			601mw[a]	
β-Cu(NCO)$_2$(mpz)$_2$	3298vs	2238vs		1348m[a]			615m[a]	
		2190vs		1340sh[a]			601m[a]	
α-Cu(mpz·NCO)$_2$	3263ms 3241ms		1704vs		1363vs	1195m	[b]	503m
	3219sh				1353vs			
β-Cu(mpz·NCO)$_2$	3254mw 3218mw		1703vs		1364vs	1199m	[b]	506m
γ-Cu(mpz·NCO)$_2$	3263ms 3240ms		1704vs		1365vs	1198ms	[b]	500w
	3217ms				1349vs			
δ-Cu(mpz·NCO)$_2$	3347ms 3263m		1700sh		1367sh	1207ms[a]	[b]	508w
	3175m		1676vs(?)			1189m[a]		

[a] One of both bands may belong to mpz. [b] Not determined because of the proximity of mpz bands.

several mpz bands, very likely due to crystal effects.

On the other hand, considerable differences between α, β- and δ-Cu(mpz·NCO)$_2$ were found for many mpz vibrations. First of all there are differences in frequencies or/and splittings of the ring stretches (especially R_1, R_2, R_3) and deformations (R_7, R_8, R_9), further in the number of the C–CH$_3$ stretches, CH$_3$ and C–H deformations and also in frequencies of some of these vibrations, as well as still other smaller distinctions. The shifts in the mpz frequencies could be provoked by changes in the mpz system electron distribution which may be induced by various Cu–N(ring) bond strengths, as well as by the presence of the methyl group either in the 5- or in the 3-position. The latter effect would even cause distinctions in frequency splittings owing to a different symmetry in each case. Further, various crystal symmetry effects, issuing from the respective factor-groups [11], potentially also contribute to distinctions in splittings.

For the N–H stretching vibrations there is again a close resemblance in the case of the α- and γ-isomer and dissimilarities of these two isomers compared with the β- and δ-isomer, as well as of the latter two forms between each other. This has apparently to do with the Cu–NH bond strength and especially with the adaptation of the –NH···O=hydrogen bonding [9].

To obtain further structural informations, the far-infrared spectra up to 50 cm^{-1} were measured for α-Cu(NCO)$_2$(mpz)$_2$, as well as for α- and γ-Cu(mpz·NCO)$_2$. The assignment of the Cu–N stretching vibrations causes some difficulties, because at not largely different frequencies the C–CH$_3$ deformation bands also occur [9]. However, with respect to the intensities of the bands present for α-Cu(NCO)$_2$(mpz)$_2$, the 386 cm^{-1} band can be tentatively assigned to the Cu–NCO stretch [10] and the 282 cm^{-1} band to the Cu–N(mpz) stretch [9]. A broad, finely splitted band at *ca.* 120 cm^{-1} apparently involves the Cu–OCN stretch [3, 12] which, being rather high, indicates a relatively strong axial interaction (*cf.* 'Ligand Field Spectra').

In the spectrum of α-Cu(mpz·NCO)$_2$, again based on the relative band intensities, the bands at 372 and 260 cm^{-1} are ascribable to the Cu–N(chain) and Cu–N(ring) stretches, respectively [1a–c]. The ≈120 cm^{-1} region is blank but at 90 cm^{-1} a band appears which almost surely belongs to the Cu–O stretch. Thus, axial interaction in this complex is much weaker than in its cyanate isomer, in accordance with the already made ascertainment [13]. The far-infrared spectrum of γ-Cu(mpz·NCO)$_2$ is almost identical with that of the α-isomer.

ESR Spectra

The ESR spectral parameters of the compounds studied are presented in Table III. Both Cu(NCO)$_2$(mpz)$_2$ complexes exhibit ESR spectra of an axial type with very similar $g_\parallel$ values, slightly below 2.25. Nevertheless, the $g_\perp$ value of the β-isomer is by ≈0.025 lower than in the case of the α-form, which is reflected in the considerably higher value of the *G* parameter [14]. Furthermore, the spectrum is in this case visibly flattened and the $g_\parallel$ value is badly resolved (Fig. 2). These distinctions may be connected mainly with a stronger exchange interaction [14], as well as with a greater distortion of the ligand arrangement, especially in the equatorial plane [15]. Anyway, the ESR features reveal for both isomers the $d_{x^2-y^2}$ Cu(II) atom ground state.

From the group of carbamoylmethylpyrazolate compounds, β-Cu(mpz·NCO)$_2$ displays an orthorhombic ESR spectrum. The *G* parameter value shows that the *g* values are somewhat affected by exchange coupling, however, the lowest *g* factor, g_1, is still consistent with the $d_{x^2-y^2}$ ground state [14].

The ESR spectra of other forms of Cu(mpz·NCO)$_2$ consist of single lines, with the peak-to-peak

TABLE III. ESR and Electronic Spectral Data

Complex	g_1 or $g_\perp$	g_2	g_3 or $g_\parallel$	G^a	$\tilde{\nu}_{max}$ (μm^{-1})
α-$Cu(NCO)_2(mpz)_2$	2.070		2.246	3.51	≈0.70 – ≈1.05sh 1.55 ≈2.35sh,br
β-$Cu(NCO)_2(mpz)_2$	2.046		2.248	5.39	1.50 ≈2.36sh,br
α-$Cu(mpz{\cdot}NCO)_2$		2.076^b			1.74 ≈1.91sh ≈2.4 – ≈2.6sh
β-$Cu(mpz{\cdot}NCO)_2$	2.035	2.106	2.221	3.14^c	≈1.24 1.46 ≈2.4 – ≈2.8
γ-$Cu(mpz{\cdot}NCO)_2$	2.023^d		2.139^d		1.73br ≈2.2 – ≈2.6sh
δ-$Cu(mpz{\cdot}NCO)_2$	2.034^d		2.154^d		1.65 2.69br

[a] Calculated by the relation $G = (g_\parallel - 2)/(g_\perp - 2)$. [b] The value at the inflection point of the pseudoisotropic line. [c] For the calculation the $g_\perp$ value was equalled to $1/2(g_1 + g_2)$. [d] The value at the extreme of the derivative curve.

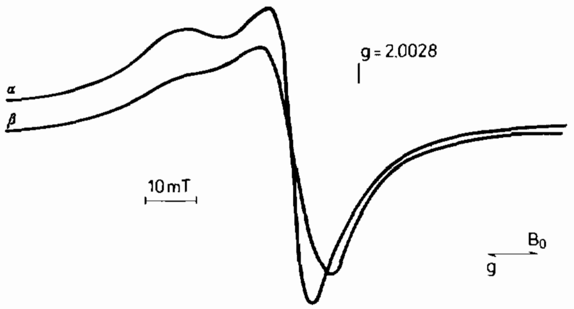
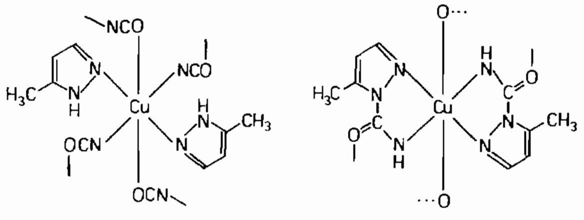


Fig. 2. ESR spectra of α- and β-$Cu(NCO)_2(mpz)_2$.



(a) (b)

Fig. 3. Principles of structure building for complexes (a) $Cu(NCO)_2(mpz)_2$ and (b) $Cu(mpz{\cdot}NCO)_2$ (the methyl group can occupy also the 3-position; see text).

line width between 14.5 and 18.0 mT, mostly having shoulders in the region of *ca.* 325–330 mT. Exchange coupling between structurally unequivalent Cu(II) atoms is the most important factor responsible for such ESR behaviour [14], suggesting only some bonding interaction between the basic structure units. Similar behaviour was ascertained for two isomers of $Cu(pz{\cdot}NCO)_2$ (pz = pyrazole) [1a].

Magnetic Moments and Ligand Field Spectra

The room temperature magnetic moments (Table I) of all compounds are above the 'spin-only' value for Cu(II), but the range of their values is relatively great and can be mainly conditioned by difference in the mean ligand field strength and by exchange coupling present.

The ligand field spectral data are listed with the UV absorptions in Table III. The ligand field spectrum of α-$Cu(NCO)_2(mpz)_2$ is indicative of a pseudooctahedral, not a very distorted coordination of the Cu(II) atom [10, 14a, 16], similar to the case of α-$Cu(NCO)_2(pz)_2$ [1a]. The d ← d spectrum of the β-form has, compared with the previous case, its maximum shifted by 0.05 μm^{-1} towards lower energies; the near IR shoulder is disappearing. We suppose both compounds to be built by *trans*-planar structure units which are completed to elongated octahedra by end-to-end asymmetrically bridging NCO groups [17] (Fig. 3a). As has been proved by Reedijk [18], mpz in the coordinated state has the methyl group always in the sterically favourable 5-position.

The β-isomer is probably more distorted, either in the equatorial plane (*cf.* ESR spectrum), or asymmetrically in the axial direction approaching the 4 + 1 + 1 coordination [14a, 19], or both. In consequence of these distortions the mean ligand field affecting the Cu(II) atom can be weakened, thus causing the red shift of the d ← d band maximum as observed. The relatively greater stability of the β-isomer agrees with its less symmetrical configuration.

The α- and γ-isomers of $Cu(mpz{\cdot}NCO)_2$ being powder crystallographically related, have also very closely localized their broad ligand field bands tailing into the IR region. The main difference is that the band of the γ-form has only a very flat saddle at about 1.92 μm^{-1} due to the high wavenumber absorption beginning already in this region. Regardless of these particularities, both compounds most likely exhibit axially strongly distorted structures [14a, 19] which are formed by the equatorially coordinated carbamoylmethylpyrazolate anions and have the carbamoyl oxygens of the adjacent moieties in axial positions (Fig. 3b). The fact, that certain axial interaction actually takes place, is corroborated by the far IR and ESR spectral data (see before).

For β-$Cu(mpz{\cdot}NCO)_2$ the position of the d ← d band shouldered on the low wavenumber side is well consistent with a five coordinate, approximately square pyramidal stereochemistry around Cu(II)

[14a, b, 19, 20]. The principle of the structure building is apparently very similar as for the α- and γ-isomers but only one copper(II) axial position is occupied by the carbamoyl oxygen. Nevertheless, with respect to the infrared finding, it is possible that the methyl group is in the 3-position on the pyrazole ring and on account of its steric influence, the five coordination is then stabilized. The ligand field band of δ-Cu(mpz$\cdot$NCO)$_2$ is, in comparison with the previous one, shifted by *ca.* 0.2 μm^{-1} to higher wavenumbers and has no observable shoulder. A pronounced tetragonal, five or six coordinate configuration is probable for this isomer which might be somehow an intermediate between those of the α- or γ- and β-form.

Conclusions

In the Cu(II)–NCO$^-$–mpz system a nucleophilic addition between mpz and NCO in the Cu(II) coordination sphere runs and besides cyanato complexes, carbamoylmethylpyrazolato compounds as their coligand isomers [1c, 13] are formed. This shows that mpz behaves in this reaction similarly to pyrazole [1a] and rather differently from 3,5-dimethylpyrazole [1b]. Both compounds Cu(NCO)$_2$(mpz)$_2$ are typical distortion isomers [21], the formation of which is connected with the plasticity of the Cu(II) coordination sphere [22]. The structure differences between α- and γ-Cu(mpz$\cdot$NCO)$_2$ also indicate a distortion isomerism, even though the crystallographic dissimilarity is greater. On the other hand, β- and δ-Cu(mpz$\cdot$NCO)$_2$ having entirely different crystal structures exhibit coordination polyhedra distinct from each other, and also from those of the foregoing isomers. It should be noted that this alteration is conditioned by various positions of the methyl group on the pyrazole ring of the chelate ligand.

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