

Cyanato copper(II) complexes with pyridine: synthesis and characterization of two isomeric forms

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Abstract

A new solid isomeric form (α) of $\text{Cu}(\text{NCO})_2\text{py}_2$ was obtained as a first reaction product of copper nitrate, potassium cyanate and pyridine. This form can be transformed into the already known β form by recrystallization. Comparison of the spectroscopic and spectromagnetic properties of the two isomers suggests the absence of significant intermolecular interactions in the α form, the β one being characterized by a pseudo-bridging position of the NCO groups. The difference in the relative orientation of the tetragonal axes of the copper centers is responsible for different exchange coupling effects between the metal ions.

Introduction

Exchange interaction effects, frequently observed in copper(II) complexes, were found to depend on the mutual orientation of the molecules in the crystal structure. They are sometimes so peculiar as to be a tool for differentiating the isomeric forms of a given compound [1].

We recently found that the exchange interaction variations of Cu(II) centers, included in phosphate glasses, give rise to significant variations of their electrical properties. Different conduction models can, therefore, be associated with the predominance of either one or the other orientation of the Cu(II) centers [2]. Such relationships among copper centers are most probably also implied in the superconducting properties of the appropriate materials [3].

For these reasons it seems important to report any current investigation into detecting interaction effects between Cu(II) centers and in relating those effects to the symmetry of copper sites.

A different exchange coupling between copper atoms can be assigned to different isomeric forms of a given copper complex; cyanato copper(II) complexes with nitrogen organic ligands are one of the largest classes of molecules characterized by this type of isomerism [4]. However the bis pyridine derivative $\text{Cu}(\text{NCO})_2(\text{py})_2$ was reported as a single

crystalline form [4]. We report the synthesis procedure of a new isomeric form, $\alpha\text{-Cu}(\text{NCO})_2(\text{py})_2$, its spectroscopic and spectromagnetic properties being used for comparison with the already described isomer, conveniently called the β form [4].

Experimental

$\alpha\text{-Cu}(\text{NCO})_2(\text{py})_2$

A solution of 2.42 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 25 ml H_2O was mixed with a solution of 1.62 g KNCO in 25 ml H_2O ; then 1.6 ml pyridine were added under stirring and the precipitate was allowed to stand. The pale violet micaceous product was separated by filtering, then washed with H_2O (30 ml), $\text{C}_2\text{H}_5\text{OH}$ (10 ml) and diethylether (20 ml). Finally it was dried under vacuum for 2 h. *Anal.* Calc.: C, 47.14; H, 3.27; N, 18.33. Found: C, 46.76; H, 3.18; N, 18.38%. Pyridine was lost at 180 °C, in a 1:2 Cu:py molar ratio.

$\beta\text{-Cu}(\text{NCO})_2(\text{py})_2$

The α form was dissolved in an excess of pyridine. On dilution with water, navy blue crystalline needles precipitated; these showed a composition identical to the α form. Single crystal X-ray diffraction data

are consistent with those reported in the literature [4]. The α form converts to the powder of β , if allowed to stand in moist conditions.

Physicochemical characterization

The X-ray diffraction patterns were taken with a powder diffractograph using Cu $K\alpha$ radiation. Thermogravimetric analyses were performed with a DuPont 951 thermal analyzer. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer, using sintered KBr-product disks. Diffuse reflectance spectra were recorded on a Beckman DK-2A spectrophotometer. The magnetic susceptibility measurements were performed by a Faraday-Cahn system equipped with an automatic temperature control system. The ESR spectra were recorded on a Varian E-109 spectrometer equipped with an Oxford automatic temperature control system; the g values were standardized by DPPH.

Results and discussion

The X-ray diffraction patterns of the two isomeric forms of $\text{Cu}(\text{NCO})_2(\text{py})_2$ are shown in Fig. 1. The differences in the diffraction pattern of the violet α isomer with respect to the β one mainly occur in the region between the 8° and 11° diffraction angles, where very strong peaks are detectable; for the β compound the region containing strong diffraction intensities is around 15° .

In the electronic spectra of both isomers (Fig. 2), a broad band is present in the region between 800 and 600 nm, the asymmetrical shape being indicative

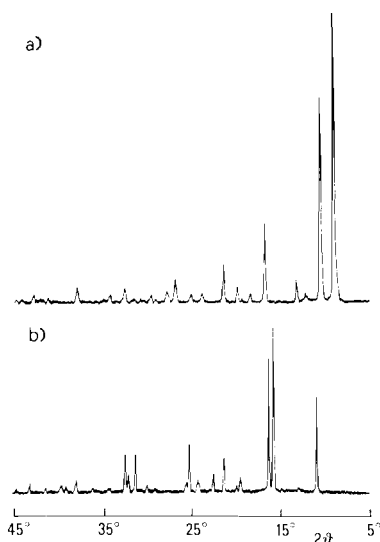


Fig. 1. X-ray diffraction patterns of $\text{Cu}(\text{NCO})_2(\text{py})_2$: (a) α form, (b) β form.

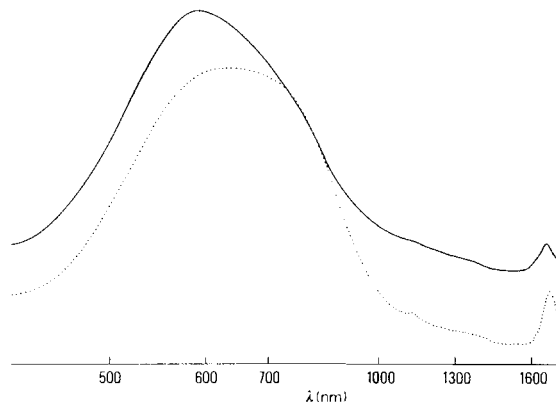


Fig. 2. Electronic spectra of $\text{Cu}(\text{NCO})_2(\text{py})_2$: —, α form; ..., β form.

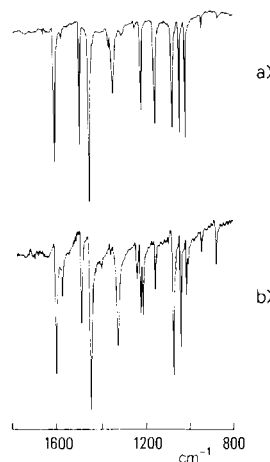


Fig. 3. IR spectra of $\text{Cu}(\text{NCO})_2(\text{py})_2$: (a) α form, (b) β form.

of a distorted cubic symmetry around the bivalent copper. Two transitions are distinguishable though a third one is expected owing to the presumed tetragonal symmetry of the copper complexes (${}^2B_{1g} \rightarrow {}^2E_g$, ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$).

A difference of 40 nm in λ_{max} was found in the two isomers ($\lambda_{\text{max}}(\alpha) < \lambda_{\text{max}}(\beta)$).

Significant differences are also present in the IR region of the pyridine out-of-plane bending vibrations (Fig. 3). The spectrum of the violet product is quite similar to that of pure pyridine, while for the blue one the band at 1200 cm^{-1} is clearly split into two components.

The α form is also different from the β one in its electron spin resonance behaviour (Fig. 4): in fact it shows a normal axial spectrum ($g_{\parallel} = 2.22$, $g_{\perp} = 2.05$), while a reversed near isotropic spectrum ($g = 2.16$) is observed for the β isomer.

The magnetic susceptibility measurements, performed in the temperature range 298–70 K, show that both compounds follow the Curie–Weiss law.

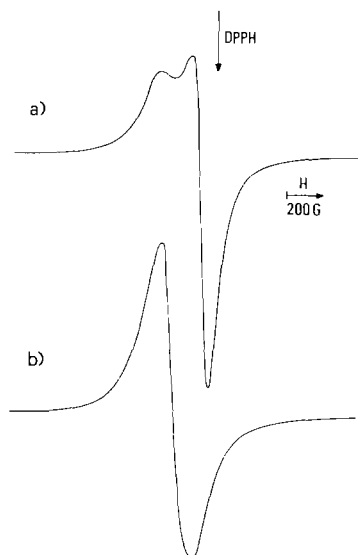


Fig. 4. ESR spectra of $\text{Cu}(\text{NCO})_2\text{py}_2$: (a) α form, (b) β form.

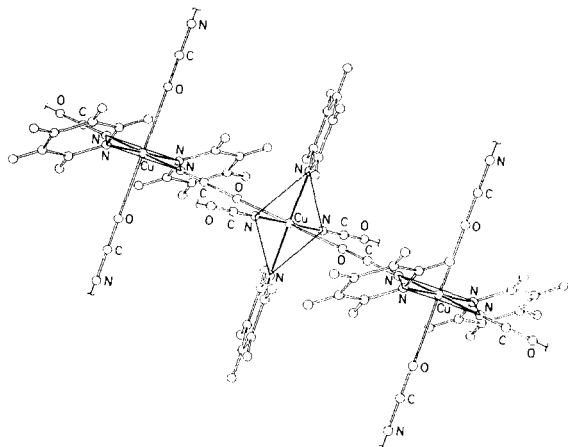


Fig. 5. Molecular scheme of $\beta\text{-Cu}(\text{NCO})_2\text{py}_2$.

Differences among the isomers are not significant and it seems impossible to differentiate one product from the other one on the basis of these data (Table 1).

A comparative examination of the results obtained from the physicochemical analyses suggests that, though the ground state is the same for both isomers, $(xz)^2(yz)^2(xy)^2(z^2)^2(x^2-y^2)$, they have a different electronic structure. For the β compound the spectro-

magnetic characterization is consistent with the crystal structure of $\text{Cu}(\text{NCO})_2(\text{py})_2$ reported in the literature [4]; in fact the reversed ESR spectrum indicates that an exchange interaction effect is active between molecules occupying non-equivalent positions in the unit cell and having their tetragonal axes inclined one to the other (Fig. 5).

The pseudo-bridging position of the NCO groups, whose N and O atoms interact with different copper centers, is responsible for the coupling exchange. The splitting of the pyridine ligand vibrations observed in the IR spectrum agrees with the non-equivalent position of these ligands in the unit cell.

For the α form, in the absence of suitable crystals, the spectromagnetic behaviour is indicative of a parallel orientation of the tetragonal axes. This is consistent both for magnetically isolated square planar unities and for polymeric chains connected through N atoms bridging two copper centers, the structure proposed for the γ form of $\text{Cu}(\text{NCO})_2(2,4\text{-lutidine})_2$ [5]. However the tetragonal distortion, as derived from the absorption frequencies of the electronic spectra, is higher for $\alpha\text{-Cu}(\text{NCO})_2(\text{py})_2$ than for the β form; this excludes the hypothesis that hexacoordinated Cu(II) centers expected in polymeric chains are present in the α form.

The results found for the $\text{Cu}(\text{NCO})_2(\text{py})_2$ isomers allow some comments on the structures proposed for the three isomers of $\text{Cu}(\text{NCO})_2(2,4\text{-lutidine})_2$ [5]. The pseudo-bridging interaction, though limited, suggested for the α and β forms of the lutidine derivative, similar to that reported in Fig. 5 for ($\beta\text{-Cu}(\text{NCO})_2(\text{py})_2$), is ruled out by the absence of a reverse ESR spectrum in these lutidine compounds. In fact the α and β form of the lutidine derivative show a normal trend of resonances, with $g_{\parallel} > g_{\perp} > 2$, while the suggested bridge position of NCO through N and O atoms should produce misalignment of the tetragonal axes and either inversion or isotropy in the spectra resonance lines. More consistent with the ESR spectrum and the exchange interaction effects observed by the magnetic susceptibility measurements is the structure containing nitrogen-bridging ligands proposed for $\gamma\text{-Cu}(\text{NCO})_2(2,4\text{-lutidine})_2$.

In conclusion our results show that small differences in the synthesis procedures, e.g. conventional crystallization techniques, may induce significant modifications in the coordination sphere of Cu(II) derivatives, comparable to the change of a ligand. A knowledge of these peculiarities allows a better un-

TABLE 1. Magnetic properties of the isomers of $\text{Cu}(\text{NCO})_2\text{py}_2$

Isomer	C (cgsK/mol)	ϑ (K)	$\chi_M(\text{corr}) \times 10^6$ (298 K)	μ_{eff} (BM)
α	0.4675	-1.2	1575	1.949
β	0.4748	-1	1599	1.929

derstanding of the electronic behaviour of copper(II) ions in solid materials.

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