X-Ray and Infrared Evidence of New Ligand Formation by Addition of 3,5-Dimethylpyrazole to the Cynate Group in a Copper(II) Complex

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Summary Two forms of the compound [Cu(NCO)$_2$ (dmpz)$_2$] have been prepared (dmpz = 3,5-dimethylpyrazole); in the nearly planar molecules of the α-form the uncoordinated dmpz nitrogen atom is linked to the carbon atom of the NCO group, thus forming a new chelating ligand with a bent NCO skeleton.

WE have prepared two forms (α and β) of the compound [Cu(NCO)$_2$(dmpz)$_2$] (dmpz = 3,5-dimethylpyrazole), obtained by treating a suspension of Cu(NCO)$_2$(2,4-lutidine) in methanol[1] with 3,5-dimethylpyrazole at 5 and 50°C, respectively, followed by crystallization of the filtrates in a refrigerator. The α-form, violet needles, shows λ_{max} (diffuse reflectance, MgCO$_3$) 344, 526, and 642sh nm, 10^6 χ_M

(294 K) 1402 c.g.s.u. and the β-form, deep-blue flakes, λ_{max} (as before) 345, 550, and 703sh nm, $10^6 \chi_M$ (292 K) 1409 c.g.s.u. Both are sparingly soluble in organic solvents except dimethylformamide (DMF). Their *X*-ray powder patterns are quite different.

TABLE. I.r. frequencies (in cm^{-1}) and assignments for the NCO system in α- and β-forms of [Cu(NCO)$_2$ (dmpz)$_2$].[a]

	ν_{as}	ν_s[b]	δ[b]	ρ
α	1694vs, br[c] 2221s, br[d]	1357s	756sh, 752s	512sh, 507m
β	1689vs, br[c] 2224vs, br[d]	1354s	758s	508s

[a] s = strong, m = medium, w = weak, br = broad, v = very, sh = shoulder. [b] The proximity of 3,5-dimethylpyrazole bands renders this assignment less certain. [c] Unresolved splitting appears and the average frequency is given. [d] Measured for a saturated DMF solution.

In the i.r. spectra of both forms (Table) the ν_{as} (NCO) frequency occurs at *ca.* 1690 cm^{-1}, but it attains its usual value[2] (*ca.* 2200 cm^{-1}) after both compounds have been dissolved in DMF. In order to elucidate the reasons for these remarkable changes, we have carried out a single-crystal analysis of α-[Cu(NCO)$_2$ (dmpz)$_2$].

The experimental data were obtained on a Syntex four-circle P2$_1$ computer-controlled diffractometer using Cu-K_α radiation. Crystals of α-Cu(C$_6$H$_8$N$_3$O)$_2$ are monoclinic, space group $P2_1/c$, with a = 13·697(7), b = 14·759(7), c = 7·463(3) Å, β = 114·01(3)°, D_m = 1·62 g cm^{-3} (by flotation), Z = 8, D_c = 1·63 g cm^{-3}. The structure was solved by the heavy-atom technique and was refined by a full-matrix least-squares procedure to R 0·121 for 1760 independent non-zero observed reflections.

The structure consists of discrete Cu(dmpz.NCO)$_2$ units (Figure), which are held together by van der Waals interactions and hydrogen bonds. The whole Cu(dmpz.NCO)$_2$ unit is nearly planar and the ligands are formed by bonding contact between one nitrogen atom of the dmpz molecule and a carbon atom of the NCO group. The ligands are bis-*trans*-co-ordinated to the copper(II) through the 'cyanate' and 'pyridine' nitrogen atoms. The Cu–N(NCO) and Cu–N(dmpz) bond lengths (Figure) are similar to the Cu–N bond lengths in other planar Cu^{II} complexes.[3] The NCO skeleta are bent, with their oxygen atoms out of the Cu^{II} co-ordination sphere.

During formation of the complex nucleophilic addition of the dmpz molecule to the NCO group apparently takes place, with transfer of the imino-hydrogen to this group. Each atom of the NCO entity is approximately sp^2-hybridised and the bond distances suggest largely double bond character. For this reason the hydrogen is probably transferred to the nitrogen rather then to the oxygen of the NCO group; it seems, however, to be involved in the N · · · O hydrogen bonds between adjacent Cu(dmpz.NCO)$_2$ molecules.

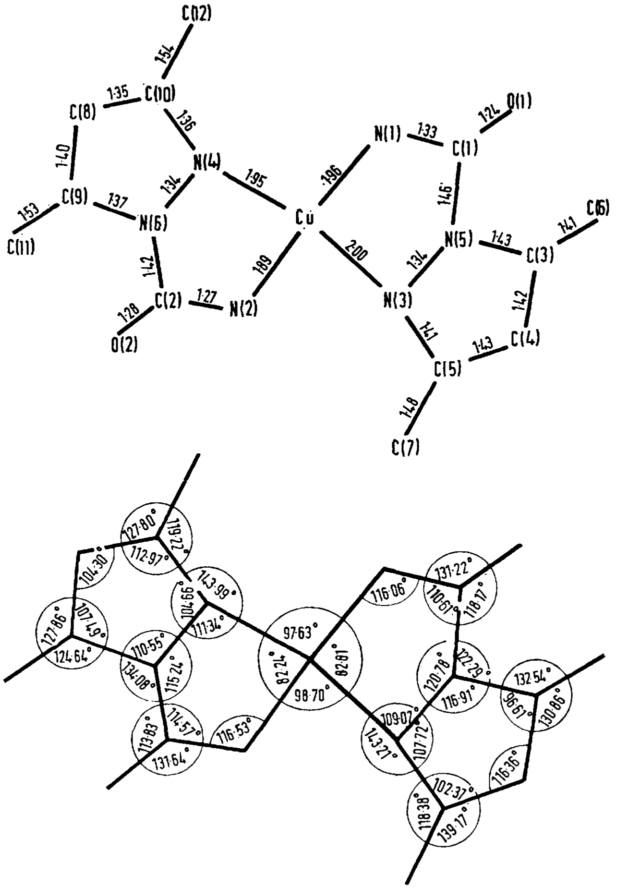

FIGURE. Bond lengths (Å) and angles in the structural unit of α-[Cu(NCO)$_2$(dmpz)$_2$].

These structural features of the NCO system explain the positions of the ν_{as} (NCO) and other NCO vibrations (Table). Strong bands at *ca.* 1215 cm^{-1} would correspond to the stretching vibration of the (NCO)C–N(dmpz) linkage, which essentially a single bond in character. This bond is broken upon dissolution in DMF, giving normal linear NCO groups.

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