Formation of a New Ligand by Addition of 3,5-Dimethylpyrazole to the Cyanate Group in a Copper(II) Complex: Crystal and Molecular Structure of α-Bis(1-carbamoyl-3,5-dimethylpyrazolato)copper(II) and the Physical Properties of Two Isomeric Forms†

By **Fedor Valach,* Jiří Kohout, Michal Dunaj-Jurčo, Mária Hvastijová,** and **Ján Gažo,** Department of Inorganic Chemistry, Slovak Technical University, 880 37 Bratislava, Czechoslovakia

Two forms (α and β) of the compound [Cu(dmpz.NCO)$_2$] (dmpz = 3,5-dimethylpyrazole) have been prepared and the structure of the α form established by single-crystal *X*-ray analysis. The crystals are monoclinic, space group $P2_1/c$, with a = 13.697(7), b = 14.759(7), c = 7.463(7) Å, β = 114.01(3)°, and Z = 8. The structure has been solved by the heavy-atom method and refined by full-matrix least squares to R = 0.052 for 1 760 independent reflections. The compound consists of nearly planar molecules, in which two 1-carbamoyl-3,5-dimethylpyrazolate anions are co-ordinated to the Cu^{II} atom, the Cu–N distances being 1.926(8), 1.908(1), 1.985(8), and 1.990(8) Å. This new ligand originates from a nucleophilic addition of the dmpz molecule to the NCO group in the Cu^{II} co-ordination sphere. Both forms have been studied by i.r., solid-state electronic and e.s.r. spectroscopy, and by variable-temperature magnetic susceptibility measurements. The results obtained show that substantially the same molecules are present in the β as in the α form, but an appreciable out-of-plane interaction of the Cu^{II} atoms with potential donor atoms of other molecules takes place.

IN the course of a systematic study [1] of cyanatocopper(II) complexes with organic nitrogen ligands a compound of the stoicheiometric composition [Cu(dmpz·NCO)$_2$] (dmpz = 3,5-dimethylpyrazole) was prepared in two (α and β) isomeric forms. The i.r. spectra of both forms in the solid state and in dimethylformamide solution indicated [2] that in these compounds a new bonding mode of the NCO group was apparently present. The compound α-[Cu(dmpz·NCO)$_2$] was therefore subject to single-crystal *X*-ray analysis, the results of which are presented in this paper; a preliminary report has been published.[2] Both isomers were also investigated by several physical methods in order to obtain information on the nature of the structural differences.

EXPERIMENTAL

Preparations.—α-[Cu(dmpz·NCO)$_2$]. A suspension of freshly obtained [3] [Cu(NCO)$_2$(2,4Me$_2$-py)] (2,4Me$_2$-py = 2,4-dimethylpyridine) (30 mmol) and of 3,5-dimethylpyrazole (76 mmol) in methanol (60 cm^3) was stirred for 1 h at 5 °C. The cold suspension was quickly sucked off and left to stand in a refrigerator. After 20 h violet *needles* were collected by suction, washed with pure methanol, and dried in a desiccator over K[OH] (Found: C, 42.1; H, 4.75; Cu, 18.6; N, 24.75. $C_{12}H_{16}CuN_6O_2$ requires C, 42.4; H, 4.75; Cu, 18.7; N, 24.75%).

β-[Cu(dmpz·NCO)$_2$]. A suspension of [Cu(NCO)$_2$(2,4Me$_2$-py)] (15 mmol) and of 3,5-dimethylpyrazole (62.4 mmol) in methanol (70 cm^3) was stirred for 1 h at 50 °C, while maintaining the initial volume with methanol. The crude pale blue solid was sucked off and the filtrate was left to stand in a refrigerator. After 3 d the deep blue *flakes* which had separated were collected by suction, washed with methanol, and dried in a desiccator over K[OH] (Found: C, 42.3; H, 4.65; Cu, 18.6; N, 24.7%).

Both isomers are sparingly soluble in common organic solvents, except dimethylformamide. Their *X*-ray powder diffraction patterns are quite different.

Crystal Data.—α-$C_{12}H_{16}CuN_6O_2$, M = 339.84, Monoclinic, a = 13.697(7), b = 14.759(7), c = 7.463(7) Å, β = 114.01(3)°, U = 1 508.7 Å^3, D_m = 1.440 g cm^{-3} (by flotation), Z = 8, D_c = 1.63 g cm^{-3}, $F(000)$ = 700, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 16.6 cm^{-1}, space group $P2_1/c$ (C_{2h}^5, no. 14) from systematic absences on Weissenberg films.

Unit-cell dimensions and reflection intensities were measured on a Syntex four-circle $P2_1$ computer-controlled diffractometer equipped with a graphite monochromator. Least-squares refinement of four position angles for 15 reflections gave an orientation matrix for further intensity measurements. The intensities were measured in the range $0 < 2\theta \leqslant 55°$ using a θ—2θ scan technique with a variable scan rate from 4.88 to 29.3° min^{-1}. The scan range of each reflection was from 2θ(Mo-$K_{\alpha1}$) − 1° to 2θ(Mo-$K_{\alpha2}$) + 1°. The background was measured on both sides of this interval for a time equal to half that required to record the intensity. The intensity I is given as [total scan count − (sum of background counts)/background-to-scan ratio] × scan rate. A standard deviation σ(I) was determined as [total scan count + (sum of background counts)/(background-to-scan ratio)^2]$^{\frac{1}{2}}$ × scan rate. The intensities of two selected reflections were measured as standards after every 98 diffractions. 3 453 Measured reflections including systematic absences were reduced to 1 760 independent reflections for which $I > 1.96\sigma(I)$. The intensities were corrected for Lorenz-polarization, but not for absorption (μR = 0.14).

Solution and Refinement of the Structure.—The structure was solved by the heavy-atom method and refined by full-matrix least squares with an anisotropic approximation for non-hydrogen atoms until values of R = 0.071 and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ = 0.095 were obtained, where $w = [\sigma^2(F_o) + (0.035\,F_o)^2]^{-1}$, with a limitation of (sin θ)/λ ⩽ 0.5. Positional parameters for the hydrogen atoms were obtained by difference-Fourier synthesis and the positions of two hydrogen atoms for each methyl group were calculated. Hydrogen-atom parameters were refined together with the parameters of the other atoms. This refinement gave R = 0.052 and R' = 0.069. The highest maximum in the difference maps was 0.58 e Å^{-3}. The atomic scattering factors of Cromer and Waber [4] were used. All calculations were performed using XTL programs.[5]

Structure factors, thermal parameters, and the deviations

---

† No reprints available.

of the atoms from the least-squares planes are summarized in Supplementary Publication No. SUP 22621 (37 pp.).*

Physical Measurements.—Infrared spectra of solid samples were recorded on a Perkin-Elmer 225 spectrophotometer, using Nujol mulls between KBr windows (400—4 000 cm^{-1}) and polyethylene sheets (200—450 cm^{-1}). The NCO bands were checked by comparison with spectra reported[6] for pure 3,5-dimethylpyrazole. Solid-state electronic spectra were recorded as diffuse reflectance on a Cary 14 spectrophotometer with $Mg[CO_3]$ as reference. Magnetic susceptibilities were determined by the Gouy method on an apparatus equipped with a Cahn RM-2 electrobalance. The powder samples were measured at about 15 temperatures from that of liquid nitrogen to room temperature, at a field strength of 9.9 kOe.† The effective magnetic moments, $\mu_{eff.}$, were calculated from the corrected molar susceptibilities, χ_M', by subtracting the temperature-independent paramagnetism, $N_A\alpha = 4N_A\mu_B^2/\Delta$, where Δ is the energy of the *d–d* band maximum. E.s.r. spectra were obtained as described previously.[7]

RESULTS AND DISCUSSION

Description of the Structure of α-[Cu(dmpz·NCO)$_2$].—The crystal structure consists of discrete, nearly planar molecules with the geometry shown in Figure 1. The molecules are held together in the crystal by van der Waals forces. Figure 2 shows the arrangement of the molecules in the unit cell. Positional parameters of the symmetrically independent atoms are listed in Table 1.

TABLE 1

Positional parameters with standard deviations in parentheses

Atom	x/a	y/b	z/c
Cu	0.780 3(1)	0.306 7(1)	0.348 0(2)
N(1)	0.882 9(5)	0.398 2(5)	0.359 3(10)
C(1)	0.979 1(8)	0.373 3(6)	0.380 7(11)
O(1)	0.061 1(5)	0.416 0(4)	0.414 7(9)
N(2)	0.689 2(6)	0.219 4(5)	0.390 4(11)
C(2)	0.593 2(9)	0.242 7(6)	0.369 5(13)
O(2)	0.519 7(6)	0.198 6(5)	0.376 7(10)
N(3)	0.896 5(6)	0.225 9(5)	0.349 7(10)
N(4)	0.656 9(5)	0.386 6(5)	0.313 3(10)
N(5)	0.982 8(6)	0.274 9(5)	0.358 8(9)
N(6)	0.577 9(6)	0.338 2(5)	0.336 3(10)
C(3)	0.061 3(7)	0.222 1(7)	0.352 4(12)
C(4)	0.021 4(8)	0.134 7(6)	0.337 0(13)
C(5)	0.921 2(8)	0.138 3(6)	0.335 9(12)
C(6)	0.164 9(8)	0.255 6(7)	0.357 8(12)
C(7)	0.846 1(8)	0.065 2(6)	0.319 4(14)
C(8)	0.520 5(7)	0.476 5(6)	0.268 6(14)
C(9)	0.492 6(7)	0.393 1(7)	0.309 0(12)
C(10)	0.379 7(7)	0.030 2(6)	0.230 3(12)
C(11)	0.394 0(8)	0.362 1(8)	0.326 4(16)
C(12)	0.316 2(7)	0.043 0(6)	0.270 7(15)
H(1)	0.843(8)	0.053(7)	0.429(15)
H(2)	0.876(7)	0.003(7)	0.313(13)
H(3)	0.770(6)	0.095(5)	0.218(11)
H(4)	0.149(6)	0.296(4)	0.259(10)
H(5)	0.194(8)	0.203(7)	0.336(13)
H(6)	0.210(9)	0.273(7)	0.483(17)
H(7)	0.362(5)	0.313(4)	0.245(90)
H(8)	0.339(8)	0.417(7)	0.300(14)
H(9)	0.409(7)	0.348(6)	0.452(14)
H(10)	0.358(6)	0.097(6)	0.330(11)
H(11)	0.288(7)	0.014(7)	0.355(12)
H(12)	0.272(6)	0.067(5)	0.158(10)
H(13)	0.521(3)	0.012(3)	0.263(6)
H(14)	0.058(5)	0.100(5)	0.341(10)
H(15)	0.881(8)	0.452(7)	0.368(15)
H(16)	0.693(10)	0.153(8)	0.381(17)

The carbon atom of each NCO group is bonded to one nitrogen atom of the pyrazole ring to give a new anionic ligand. This ligand is chelated to copper(II) through the nitrogen atoms of the NCO group and of the ring. Bond lengths and angles are given in Tables 2 and 3.

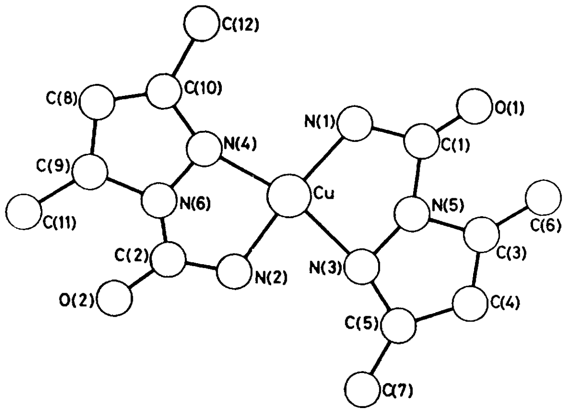

FIGURE 1 Molecular geometry of α-[Cu(dmpz·NCO)$_2$]

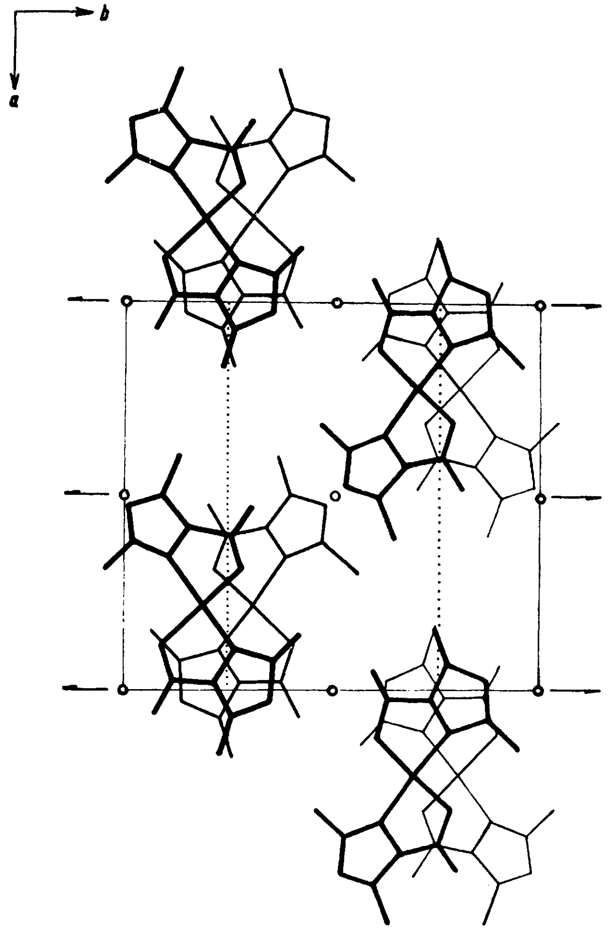

FIGURE 2 Packing diagram for α-[Cu(dmpz·NCO)$_2$]

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

† Throughout this paper: 1 Oe = 1 $cm^{-\frac{1}{2}}$ $g^{\frac{1}{2}}$ s^{-1}; 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

TABLE 2

Interatomic distances (Å)

(*i*) CuN_4 polyhedron			
Cu–N(1)	1.926(8)	Cu–N(3)	1.985(8)
Cu–N(2)	1.908(1)	Cu–N(4)	1.990(8)
(*ii*) Pyrazolate ligand (1)			
N(1)–C(1)	1.313(14)	C(3)–C(6)	1.487(15)
N(1)–H(15)	0.792(7)	C(3)–C(4)	1.388(14)
C(1)–O(1)	1.220(13)	C(4)–C(5)	1.370(16)
C(1)–N(5)	1.465(11)	C(5)–C(7)	1.461(14)
N(5)–N(3)	1.363(11)	C(5)–N(3)	1.352(11)
N(5)–C(3)	1.345(13)	Mean C–H	0.92 ± 0.21 *
(*iii*) Pyrazolate ligand (2)			
N(2)–C(2)	1.306(16)	C(9)–C(11)	1.481(16)
N(2)–H(16)	0.987(7)	C(9)–C(8)	1.358(13)
C(2)–O(2)	1.218(14)	C(8)–C(10)	1.367(15)
C(2)–N(6)	1.432(12)	C(10)–C(12)	1.493(14)
N(6)–C(9)	1.368(13)	C(10)–N(4)	1.316(12)
N(6)–N(4)	1.363(11)	Mean C–H	0.92 ± 0.18 *

* Maximum deviation from the mean.

TABLE 3

Bond angles (°)

(*i*) CuN_4 polyhedron			
N(1)–Cu–N(4)	99.0(3)	N(3)–Cu–N(2)	99.8(3)
N(1)–Cu–N(3)	81.5(3)	N(2)–Cu–N(4)	81.0(3)
(*ii*) Pyrazolate ligand (1)			
Cu–N(1)–C(1)	119.2(6)	C(1)–N(5)–C(3)	130.0(8)
N(1)–C(1)–O(1)	132.4(9)	N(3)–N(5)–C(3)	112.4(7)
N(1)–C(1)–N(5)	110.0(8)	Cu–N(3)–N(5)	111.0(5)
N(5)–C(1)–O(1)	117.6(8)	Cu–N(3)–C(5)	143.1(6)
N(5)–C(3)–C(6)	125.1(8)	N(5)–N(3)–C(5)	105.8(7)
N(5)–C(3)–C(4)	104.3(8)	N(3)–C(5)–C(7)	121.6(8)
C(6)–C(3)–C(4)	130.6(9)	C(4)–C(5)–C(7)	129.9(9)
C(3)–C(4)–C(5)	108.9(9)	C(4)–C(5)–N(3)	108.6(8)
C(1)–N(5)–N(3)	117.6(7)		
(*iii*) Pyrazolate ligand (2)			
Cu–N(2)–C(2)	119.8(7)	C(11)–C(9)–C(8)	130.4(9)
N(2)–C(2)–O(2)	131.6(10)	C(8)–C(10)–C(12)	127.7(9)
N(2)–C(2)–N(6)	110.5(9)	C(8)–C(10)–N(4)	110.3(8)
N(6)–C(2)–O(2)	117.9(9)	C(12)–C(10)–N(4)	122.0(8)
C(2)–N(6)–C(9)	131.6(8)	C(10)–N(4)–Cu	143.4(7)
C(2)–N(6)–N(4)	118.0(7)	C(10)–N(4)–N(6)	106.2(7)
C(9)–N(6)–N(4)	110.2(7)	N(6)–N(4)–Cu	110.4(5)
N(6)–C(9)–C(11)	124.0(9)	C(9)–C(8)–C(10)	107.7(9)
N(6)–C(9)–C(8)	105.6(8)		

The oxygen atoms O(1) and O(2) of the NCO groups are not involved in bonding interactions with other Cu^{II} atoms, because the Cu–O distances for the adjacent molecules are greater than 3.3 Å.[8] The distances (4.09 Å) between the adjacent Cu^{II} do not indicate any metal–metal interaction. Four nitrogen atoms from the two anionic ligands form a distorted square-planar co-ordination around the Cu^{II} atom. The Cu–N bond lengths are consistent with those in planar complexes comprising a CuN_4 chromophore.[9] The NCO groups are bent and each atom is in a non-equivalent sp^2 hybridisation state. The N(1)–C(1), C(1)–O(1), N(2)–C(2), and C(2)–O(2) bond lengths are somewhat greater than the corresponding lengths in cyanate compounds of known crystal structure [10-13] and suggest double-bond character. On the other hand, the C(1)–N(5) and C(2)–N(6) lengths indicate essentially single bonds.

Reaction between dmpz and $[NCO]^-$ *in the Copper*(II) *Co-ordination Sphere.*—During the formation of $[Cu(dmpz{\cdot}NCO)_2]$ a nucleophilic addition of the dmpz molecule to the NCO group apparently takes place. It may be supposed that bonding of both dmpz and $[NCO]^-$ to Cu^{II} provides favourable conditions for such a reaction that does not occur in the absence of such bonding. A large difference in the Cu–N(dmpz) and Cu–N(NCO) bond strengths is to be expected, owing to steric hindrance of the dmpz ligand and the plasticity of the copper(II) co-ordination sphere.[8] Thus, the abundance of electron density in the dmpz ring caused by the two electron-releasing methyl groups may provoke attack on the cyanate carbon by the nucleophilic ring nitrogen (with intramolecular transfer of its hydrogen, *cf.* Table 2).

The compound 1-carbamoyl-3,5-dimethylpyrazole can be released from a suspension of the chelate complex in water by the action of H_2S. In dimethylformamide solution the C(chain)–N(ring) bond is broken and a cyanate compound is formed.[2]

Physical Results.—*Infrared spectra.* In the i.r. spectra (>400 cm^{-1}) of the compounds under investigation several bands belonging to the dmpz part of the chelate ligand are considerably changed compared with the relevant bands of pure 3,5-dimethylpyrazole.[6] Furthermore, clear-cut distinctions between many bands may be seen in the spectra of the α and β forms. The most striking feature is the appearance of very strong bands at *ca.* 1 690 cm^{-1}, associated with the asymmetric stretch of the bent NCO chain of the ligand. The strong bands at *ca.* 1 355 cm^{-1} are then attributable to the symmetric stretch of the same chain. Tentative assignments of other NCO group bands can be made as follows: *ca.* 755 cm^{-1}, deformation; *ca.* 510 cm^{-1}, in-plane rocking NCO vibration. The strong bands at *ca.* 1 215 cm^{-1} are thought to be due to the C(chain)–N(ring) stretching vibration. The medium sharp band appearing in the spectrum of the α form at 3 326 cm^{-1} may be assigned to the ν(NH) vibration. The corresponding band of the β form undergoes a large shift to lower frequencies, occurring at 3 298 cm^{-1}.

The far-i.r. spectral data with tentative assignments of the Cu–N stretching bands, based on results of Reedijk *et al.* [14] and our work,[15] are listed in Table 4.

Solid-state electronic spectra. In the ligand-field region [Figure 3(*a*)] both forms exhibit a single band with a broad low-wavenumber shoulder, which is better resolved for the α form. The effectively square-planar co-ordination without any out-of-plane interaction, as determined for the α form, must cause a strong splitting of the *d*-orbital set and thus explains the high energy of the *d–d* band. The form and width of the shoulder between *ca.* 1.45 and *ca.* 1.70 μm^{-1} appear to indicate two

TABLE 4

Far-i.r. spectra (200—400 cm^{-1}) for α- and β-$[Cu(dmpz{\cdot}NCO)_2]$ [a]

Specification	ν(Cu–N)	Other bands
α	363s,[b] 316vs [c]	282m, 220s
β	365s,[b] 360s,[b] 311s [c]	276m, 216s

[a] s = Strong, m = medium, v = very. [b] Mainly the Cu–N(chain) stretch. [c] Mainly the Cu–N(ring) stretch.

d–d transitions, these being most likely[9,16] the $d_{x^2-y^2}\leftarrow d_{xy}$ and $d_{x^2-y^2}\leftarrow d_{z^2}$ transitions; the energy of the latter is directly dependent[17-19] on the tetragonal distortion. The band maximum would then involve the $d_{x^2-y^2}\leftarrow d_{xz}$ and $d_{x^2-y^2}\leftarrow d_{yz}$ transitions, of similar energy.

The d–d band shoulder of the β form, between *ca.* 1.35 and *ca.* 1.55 μm^{-1}, is shifted by *ca.* 0.13 μm^{-1} to lower wavenumbers compared with the α form. The band maximum for the β form is also shifted to lower wavenumbers by 0.08 μm^{-1}. These changes suggest an appreciable reduction of the tetragonal distortion for the β when compared with the α form. Because of this,[16,18,19] the $d_{x^2-y^2}\leftarrow d_{z^2}$ transition energy decreases and the same is true to a lesser degree for the $d_{x^2-y^2}\leftarrow d_{xz}$, d_{yz} transition energies; the $d_{x^2-y^2}\leftarrow d_{xy}$ transition energy changes only slightly. The reduced tetragonal distortion in the β form might be caused by some out-of-plane interaction of the Cu^{II} atom with potential donor atoms of other [Cu(dmpz·NCO)$_2$] molecules, *e.g.* with the carbamoyl oxygens. Interaction of this kind can be achieved by suitable molecular stacking in the crystal structure. Thus it may be concluded that α- and β-[Cu(dmpz·NCO)$_2$] represent further examples of distortion isomerism.[8,20]

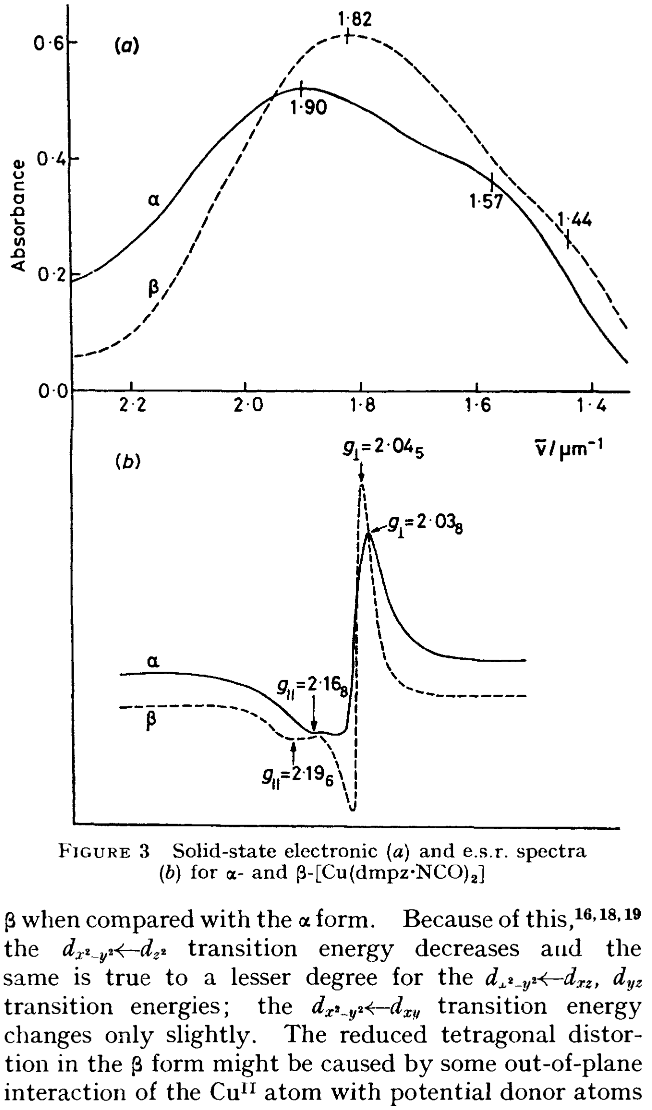

FIGURE 3 Solid-state electronic (*a*) and e.s.r. spectra (*b*) for α- and β-[Cu(dmpz·NCO)$_2$]

In the charge-transfer region of the spectra weak bands occur with maxima at 2.91 and 2.89 μm^{-1} for the α and β forms, respectively.

E.s.r. spectra. The X-band e.s.r. spectra of both forms of [Cu(dmpz·NCO)$_2$] in the polycrystalline state [Figure 3(*b*)] are of the axial type, and the g values were determined by the method of Kneubühl.[21]

The spectra of the two forms differ considerably in line shape. That of α-[Cu(dmpz·NCO)$_2$] is perceptibly broadened and the $g_{\parallel}$ band is rather poorly resolved. From the crystal structure it is evident that a significant exchange coupling between the Cu^{II} atoms cannot occur. Therefore, dipolar coupling and an unresolved copper hyperfine interaction are probably the main factors[22] causing the observed line broadening. Nevertheless, the g values obtained represent the correct molecular g factors (approximated because of the powder technique). From the low symmetry of the Cu^{II} atom environment a $g_{\perp}$ anisotropy is to be expected,[23] but under the given conditions this should not be resolved. The g values are rather low[9,24] even for a planar CuN_4 system with a comparatively strong covalency, including π bonding. A possible reason for the reduction of $g_{\perp}$ would be some orbital hybridisation in the ground-state wavefunction,[23] which occurs in low-symmetry copper(II) complexes, and giving a g_x value nearer to 2. The reason for the low $g_{\parallel}$ value is, however, not obvious. Only by assuming that the $d_{x^2-y^2}\leftarrow d_{xy}$ transition has the maximum d–d band energy and that the orbital-reduction factor $k_{\parallel}$ falls to *ca.* 0.7, according to the approximate D_{4h} symmetry expression,[9,18] can we obtain a value of *ca.* 2.17 for $g_{\parallel}$, close to that found. Single-crystal spectral and e.s.r. measurements would allow a better insight into the electronic properties of this compound.

Although the crystal structure of β-[Cu(dmpz·NCO)$_2$] is unknown, its polycrystalline g values are probably meaningful since the value of the G parameter [$= (g_{\parallel} - 2)/(g_{\perp} - 2)$] (refs. 9 and 18) is 4.36, *i.e.* >4. This compound exhibits a slightly higher $g_{\perp}$ value and a remarkably higher $g_{\parallel}$ value than the α form. This might be expected[24] if an appreciable out-of-plane interaction exists in the β form. It is noteworthy that very similar differences were ascertained[25] between the g values of the two isomers of [Cu(NCO)$_2$(2,4Me$_2$-py)$_2$], one of which according to other results has a strongly tetragonal and the other a pseudo-octahedral configuration.

Magnetic susceptibilities. The corrected molar susceptibilities were fitted to the Curie–Weiss law, $\chi_M' - N_A\alpha = C(T + \theta)^{-1}$, using the standard linear least-squares method. The Curie and Weiss constants obtained are listed in Table 5, together with the room-temperature values of χ_M' and $\mu_{eff.}$. The magnetic properties of both forms of [Cu(dmpz·NCO)$_2$] are very similar. The temperature-independent $\mu_{eff.}$ values cal-

TABLE 5

Magnetic data for α- and β-[Cu(dmpz·NCO)$_2$]

Specification	$10^6\chi_M'$/cm^3 mol^{-1}	$\mu_{eff.}$/B.M.	C/cm^3 K mol^{-1}	θ/K
α	1 402 [a]	1.78 [a]	0.386 0	−11.5
β	1 409 [b]	1.78 [b]	0.385 7	−8.1

[a] At 294 K. [b] At 292 K.

culated as 2.83 $C^{\frac{1}{2}}$ are both equal to 1.76 B.M., so that they are at the lower limit of the $\mu_{eff.}$ values for copper(II) systems with an orbitally non-degenerate ground state.[26]

We thank Dr. K. Bukietyńska from the Institute of Chemistry, University of Wrocław, for the measurements of the solid-state electronic spectra, Dr. J. Mroziński from the same Institute for the susceptibility measurements, and Dr. L. Omelka from the Department of Physical Chemistry, Slovak Technical University, Bratislava, for recording the e.s.r. spectra.

[8/2060 *Received, 28th November,* 1978]

REFERENCES

[1] J. Kohout, M. Hvastijová, and J. Gažo, *Co-ordination Chem. Rev.*, 1978, **27**, 141.

[2] J. Kohout, F. Valach, M. Hvastijová, M. Dunaj-Jurčo, and J. Gažo, *J.C.S. Chem. Comm.*, 1976, 903.

[3] J. Kohout, M. Quastlerová-Hvastijová, M. Kohútová, and J. Gažo, *Monatsh.*, 1971, **102**, 350.

[4] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] F. Ahmed, M. Pippy, W. Busing, H. Levy, D. Cromer, J. Waber, H. Hope, B. Klewe, A. C. Larson, K. Trueblood, P. Gantzel, R. A. Sparks, M. Woolfson, P. Main, G. Germain, A. Zalkin, and U. C. Berkeley, XTL System of Computer Programs.

[6] A. Zecchina, L. Cerutti, S. Coluccia, and E. Borello, *J. Chem. Soc.* (*B*), 1967, 1363.

[7] J. Kohout, M. Quastlerová-Hvastijová, and J. Gažo, *Inorg. Chim. Acta*, 1974, **8**, 241.

[8] J. Gažo, I. B. Bersuker, J. Garaj, M. Kabešová, J. Kohout, H. Langfelderová, M. Melník, M. Serátor, and F. Valach, *Co-ordination Chem. Rev.*, 1976, **19**, 253.

[9] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[10] W. C. Dohlen and G. B. Carpenter, *Acta Cryst.*, 1955, **8**, 646.

[11] D. Britton and J. D. Dunitz, *Acta Cryst.*, 1965, **18**, 426.

[12] F. Valach, M. Dunaj-Jurčo, J. Garaj, and M. Hvastijová, *Coll. Czech. Chem. Comm.*, 1974, **39**, 380.

[13] F. Valach, M. Dunaj-Jurčo, J. Garaj, and P. Nemčok, *Proc. 4th Conf. Co-ordination Chem.*, *Smolenice-Bratislava, ČSSR,* 1973, p. 114; F. Valach, M. Handlovič, and M. Dunaj-Jurčo, unpublished work.

[14] J. Reedijk, J. C. A. Windhorst, N. H. M. van Ham, and W. L. Groeneveld, *Rec. Trav. chim.*, 1971, **111**, 234.

[15] M. Hvastijová, J. Kohout, and J. Gažo, unpublished work.

[16] R. J. Fereday, *J. Chem. Soc.* (*A*), 1971, 3035.

[17] A. A. G. Tomlinson, B. J. Hathaway, D. E. Billing, and P. Nicholls, *J. Chem. Soc.* (*A*), 1969, 65.

[18] I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc.* (*A*), 1968, 1678.

[19] B. J. Hathaway, D. E. Billing, P. Nicholls, and I. M. Procter, *J. Chem. Soc.* (*A*), 1969, 319.

[20] J. Gažo, *Pure Appl. Chem.*, 1974, **38**, 279.

[21] F. K. Kneubühl, *J. Chem. Phys.*, 1960, **31**, 1074.

[22] K. E. Hyde, P. L. Bocko, M. Lynch, R. Adams, and G. Kokoszka, *Inorg. Chim. Acta*, 1976, **19**, 51.

[23] M. A. Hitchman, *J. Chem. Soc.* (*A*), 1970, 4.

[24] D. W. Smith, *J. Chem. Soc.* (*A*), 1970, 3108.

[25] M. Quastlerová-Hvastijová, J. Kohout, J. Gažo, and F. Valach, *J. Inorg. Nuclear Chem.*, 1976, **38**, 705.

[26] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.