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Polymeric complexes of copper(II) azide and 2,5-dimethylpyridine without and with solvent molecules. Synthesis, spectral and structural characterization of [Cu(2,5-dimethylpyridine)$(N_3)_2]_n$ and [Cu(2,5-dimethylpyridine)$(N_3)_2(H_2N\text{-}CHO)]_2$

Mohamed A. S. Goher,[a]* Franz A. Mautner[b] and Najeeb A. Al-Salem[a]

[a]Department of Chemistry, Faculty of Science, Kuwait University, P.O. Box 5969 Safat, 13060 Kuwait

[b]Institut fur Physikalische und Theoretische Chemie, Technische Universitat, Graz, A-8010 Graz, Austria

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Abstract—Catina di-μ(1,1)-azido[di-μ(1,1)-azidobis(2,5-dimethylpyridine)dicopper(II)] (**1**) and di-μ(1,1)-azidobis[azido(2,5-dimethylpyridine)(formamide)]dicopper(II) (**2**) were synthesized and characterized by spectroscopic and crystallographic methods. In the triclinic complex **1** the copper(II) centres are penta-coordinated by four nitrogen atoms from the azido ligands [Cu—N distances = 1.980(3)–2.249(4) Å] and a fifth nitrogen from the organic molecule at a Cu—N bond length of 2.038(4) Å. Both azido ligands function as μ(1,1) bridges to form chains of polyhedra along the crystallographic *a* axis. The dimeric molecule **2**, which possesses a crystallographic inversion centre, contains both terminal and μ(1,1) bridging azido ligands. Each copper(II) atom is further coordinated by a 2,5-dimethylpyridine molecule [Cu—N = 1.998(4) Å] and a formamide molecule *via* its carbonyl oxygen atom [Cu—O = 2.356(4) Å] to give a distorted square pyramid. The IR absorption spectra reveal asymmetric azido ligands in both complexes, O-bonded formamide and hydrogen bonds as well, in **2**. The solid and solution electronic spectra of both complexes exhibit more than one strong $N_3^- \rightarrow Cu^{II}$ charge-transfer transition band. The room-temperature EPR spectra of powdered samples and DMF solutions were recorded and discussed. © 1997 Elsevier Science Ltd

Keywords: copper(II) azide; 2,5-dimethylpyridine; complexes; spectra; crystal structure.

2-Picoline, otherwise known as 2-methylpyridine, forms only a polymeric 1 : 1 copper(II) azide complex [1], whereas 3- and 4-picolines form polymeric 1 : 2 in addition to the 1 : 1 complexes with copper(II) azide [2–5]. This difference was reported as due to the steric hindrance of the methyl group in position 2 in the pyridine ring. On the other hand, the reactions between copper(II) azide and disubstituted pyridine ligands have been reported to yield different types of copper(II) azido complexes. For example, while the reaction of copper(II) nitrate with 3,4-dimethylpyridine in the presence of sodium azide afforded a 1 : 1 complex [6], a similar reaction with 3,5-dimethylpyridine afforded a dimeric 1 : 2 complex; $[Cu(NO_3)\,(N_3)L_2]_2$ containing simultaneous bridging azido and nitrato ligands [7]. 2,6-Dimethylpyridine, which possesses a steric hindrance much greater than 2-methylpyridine, however, yielded a polymeric 2 : 3 complex with copper(II) azide [6], whereas 2,4,6-trimethylpyridine, also known as *s*-collidine, with steric hindrance similar to that of the former ligand, produced a monomeric 1 : 2 copper(II) azide complex [8]. Steric hindrance is, therefore, not the only factor that plays an important role in the synthesis of such copper azide complexes. As a consequence, we investigated the complex formation between copper(II) azide and 2,5-dimethylpyridine, otherwise known as 2,5-lutidine (hereafter abbreviated as 2,5-DMPy). During the preparative work, we isolated a 1 : 1 complex whose

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*Author to whom correspondence should be addressed.

elemental analysis and IR spectrum suggest that it crystallizes with an additional formamide molecule. In the present paper we describe these two new 1 : 1 copper(II) azide complexes of 2,5-DMPy without and with solvent molecules, as elucidated by spectroscopic and crystallographic methods.

EXPERIMENTAL

2,5-DMPy was purchased from Aldrich and other chemicals were of analytical grade quality.

Preparation of polymeric $[Cu(2,5\text{-}DMPy)(N_3)_2]_n$ complex (**1**)

Copper(II) perchlorate hexahydrate (0.78 g, 3 mmol) dissolved in ethanol (*ca* 30 cm^3) and 2,5-DMPy (1.07 g, 1 mmol) were mixed together, followed by addition of an aqueous solution of NaN_3 (0.48 g, 7.5 mmol, in 5 cm^3) with continuous stirring. The brown solution was filtered and the filtrate allowed to stand in a refrigerator until black needle-like crystals of the complex separated. Yield 45%. Found: C, 35.9; H, 4.2; N, 36.8; Cu, 23.2. Calc.: C, 35.8; H, 4.1; N, 36.5; Cu, 23.6 %.

Preparation of $[Cu(2,5\text{-}DMPy)(N_3)_2(OCH\text{-}NH_2)]_2$ complex (**2**)

To a mixture of copper(II) perchlorate hexahydrate (1.05 g, 4 mmol) and 2,5-DMPy (1.07 g, 10 mmol) in acetone (30 cm^3), an aqueous solution of NaN_3 (0.65 g, 10 mmol, in 5 cm^3) was added dropwise. This mixture was filtered and the brown precipitate was dissolved in formamide and allowed to stand in a refrigerator until black crystals of the complex obtained. Addition of *ca* 5 cm^3 formamide to the filtrate and standing in a refrigerator produced similar crystals. Found: C, 32.4; H, 4.0; N, 37.0; Cu, 21.5. Calc.: C, 32.0; H, 4.0; N, 37.4; Cu, 21.2%.

Procedures and instruments used for other physical measurements are as described previously [9].

X-ray crystallography

A modified STOE four-circle diffractometer was used for single crystal X-ray measurements. Orientation matrix and Lattice parameters were obtained by least-squares refinement of the diffraction data from 35 reflections in the 2θ range 10–27°. Data were collected at 293(2) K using graphite crystal-monochromatized Mo-K_α radiation ($\lambda = 0.71069$ Å) and the ω-scan technique. The intensities were corrected for Lorentz and polarization effects in the usual way. Crystallographic data are given in Table 1.

The structures were solved by Patterson superposition methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to the non-hydrogen atoms in full-matrix least-squares refinements. Hydrogen-atom positions were obtained from *F* maps and included in the final refinement cycles by use of geometrical constraints. The programs SHEXLTL [10] and PLATON [11] were used for computations. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated [12]. Selected bond distances and bond angles are given in Tables 2 and 3. Positional parameters, anisotropic displacement parameters, hydrogen-atom coordinates, a full list of bond lengths and angles have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

The reaction of copper(II) azide with 2,5-DMPy in ethanol or acetone afforded a 1 : 1 complex regardless of the molar ratio of the components used. Crystallization of the complex from, or addition of formamide to the solution which contains the complex, leads to the formation of a new 1 : 1 complex with one formamide molecule. Both complexes are black and very similar and could not be distinguished from one another, even under a microscope. These complexes are insoluble in many polar and non-polar solvents indicating their polymeric nature. They are, however, freely soluble in DMSO and DMF and partially soluble in acetone giving rise to non-conducting solutions.

Structure

A plot and atom numbering scheme of $[Cu(2,5\text{-}DMPy)(N_3)_2]_n$ **1** are given in Fig. 1. The coordination of the copper(II) atom by 2,5-DMPy and azido ligands may be described as distorted square pyramid with N(11) atom at its apex. In the asymmetric unit, $\mu(1,1)$ azido groups [N(21)—N(22)—N(23) and N(21a)—N(22a)—N(23a)] lying on the same crystallographic diad bridge a pair of copper atoms [Cu(1) and Cu(1b)] related by an inversion centre forming a planar Cu_2N_2 ring, whereas $\mu(1,1)$ azido ligands [N(11)—N(12)—N(13) and N(11b)—N(12b)—N(13b)] link Cu(I) and Cu(1b) atoms forming another Cu_2N_2 ring, giving rise to chains of copper polyhedra along the *a* axis of the unit cell. The shortest and longest metal–ligand bonds are Cu—N(11) = 1.980(3) and Cu—N(11a) = 2.249(4) Å, respectively, while the other three are virtually equal at 1.985(4)–2.050(4) Å (Table 2) and compare well with corresponding distances in other copper(II) azido complexes of pyridine derivative ligands [1–9]. Both $\mu(1,1)$ azido ligands are asymmetric [N(11)—N(12) =

Table 1. Crystallographic data and processing parameters

Compound	1	2
Molecular formula	$C_7H_9CuN_7$	$C_{16}H_{24}Cu_2N_{16}O_2$
Molecular weight	254.75	599.60
Colour and habit	Black prism	Green prism
System, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	5.761(2)	7.617(3)
b (Å)	9.646(4)	7.852(4)
c (Å)	9.886(4)	12.073(4)
α (°)	83.99(3)	79.01(3)
β (°)	77.81(3)	72.17(2)
γ (°)	83.81(3)	71.06(2)
V (Å)	532.0(4)	646.8(3)
Z	2	1
μ(Mo-K_α) (mm^{-1})	2.032	1.691
Transmission factors	1.000–0.411	1.000–0.437
D_{calc}/D_{obs} (Mg m^{-3})	1.590/1.59(2)	1.539/1.54(2)
Approximate crystal size (mm)	0.60 × 0.10 × 0.10	0.25 × 0.20 × 0.12
2θ range of data collection (°)	3.63–26.50	2.76–29.98
Reflections collected	2351	1701
Independent reflections/R_{int}	2014/0.0321	1504/0.0302
Parameters	141	182
Goodness-of-fit on F_0^2	1.070	1.478
R_1/wR_2	0.0469/0.1082	0.0477/0.0970
Weighting factors:[a] a/b	0.0572/0.000	0.001/0.001
Largest peak/hole (e Å^{-3})	0.475/−0.789	0.631/−0.506

[a] $w^{-1} = [\sigma^2(F_0^2) + (aP)^2 + bP]$ and $P = (F_0^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**

Cu(1)···Cu(1a)	3.137(2)	Cu(1)···Cu(1b)	3.235(2)
Cu(1)—N(11)	1.980(3)	Cu(1)—N(21)	1.985(4)
Cu(1)—N(1)	2.038(4)	Cu(1)—N(21a)	2.050(4)
Cu(1)—N(11b)	2.249(4)	N(11)—N(12)	1.182(5)
N(11)—Cu(1b)	2.249(4)	N(12)—N(13)	1.143(6)
N(21)—N(22)	1.181(6)	N(21)—Cu(1a)	2.050(4)
N(22)—N(23)	1.125(6)	N(1)—C(5)	1.337(6)
N(1)—C(1)	1.347(6)	C(1)—C(2)	1.393(7)
C(1)—C(6)	1.493(7)	C(2)—C(3)	1.362(9)
C(3)—C(4)	1.380(9)	C(4)—C(5)	1.387(7)
C(4)—C(7)	1.516(8)		
N(11)—Cu(1)—N(21)	169.5(2)	N(11)—Cu(1)—N(1)	94.3(1)
N(21)—Cu(1)—N(1)	96.1(2)	N(11)—Cu(1)—N(21a)	94.1(2)
N(21)—Cu(1)—N(21a)	77.9(2)	N(1)—Cu(1)—N(21a)	142.9(2)
N(11)—Cu(1)—N(11b)	80.4(2)	N(21)—Cu(1)—N(11b)	96.3(2)
N(1)—Cu(1)—N(11b)	104.0(1)	N(21a)—Cu(1)—N(11b)	113.0(2)
N(12)—N(11)—Cu(1)	124.4(3)	N(12)—N(11)—Cu(1b)	131.7(3)
Cu(1)—N(11)—Cu(1b)	99.6(2)	N(13)—N(12)—N(11)	178.0(5)
N(22)—N(21)—Cu(1)	128.0(3)	N(22)—N(21)—Cu(1a)	126.8(3)
Cu(1)—N(21)—Cu(1a)	102.1(2)	N(23)—N(22)—N(21)	178.5(6)

Symmetry code: (a) $-x, -y+1, -z$; (b) $-x+1, -y+1, -z$.

1.182(5), N(12)—N(13) = 1.143(6) and N(21)—N(22) = 1.181(6), N(22)—N(23) = 1.125(6) Å] and linear within experimental error (both N—N—N angles > 178°).

The Cu—N(2,5-DMPy) distance is longer than corresponding values reported in the structure of Cu(3,4-DMPy)$(N_3)_2$ [1.980(3) Å] [6], Cu(3-picoline)$(N_3)_2$ [1.997(5) Å] [2] and $[(Cu(N_3)(NO_3)(3,5\text{-DMPy})]_2$ [Cu—N(3,5-DMPy) = 2.003(3) and 2.012(3) Å] [7], but comparable with that found in the structure of Cu(2-picoline)$(N_3)_2$ [1]. The structure of the present complex **1** differs from those of polymeric Cu(2-pico-

Table 3. Selected bond lengths (Å) and angles (°) for **2**

Cu(1)···Cu(1a)	3.124(2)	Cu(1)—N(21)	1.955(5)
Cu(1)—N(2)	1.998(4)	Cu(1)—N(11a)	2.005(5)
Cu(1)—N(11)	2.019(5)	Cu(1)—O(1)	2.356(4)
N(11)—N(12)	1.198(6)	N(11)—Cu(1a)	2.005(5)
N(12)—N(13)	1.142(6)	N(21)—N(22)	1.188(7)
N(22)—N(23)	1.138(7)	O(1)—C(1)	1.225(6)
C(1)—N(1)	1.296(8)	N(2)—C(6)	1.338(7)
N(2)—C(2)	1.339(7)	C(2)—C(3)	1.387(8)
C(2)—C(7)	1.510(8)	C(3)—C(4)	1.379(8)
C(4)—C(5)	1.367(8)	C(5)—C(6)	1.380(7)
C(5)—C(8)	1.502(8)		
N(21)—Cu(1)—N(2)	97.2(2)	N(21)—Cu(1)—N(11a)	68.8(2)
N(2)—Cu(1)—N(11a)	92.0(2)	N(21)—Cu(1)—N(11)	91.4(2)
N(2)—Cu(1)—N(11)	164.2(2)	N(11a)—Cu(1)—N(11)	78.2(2)
N(21)—Cu(1)—O(1)	94.7(2)	N(2)—Cu(1)—O(1)	99.3(2)
N(11a)—Cu(1)—O(1)	90.0(2)	N(11)—Cu(1)—O(1)	93.1(2)
N(12)—N(11)—Cu(1a)	126.7(4)	N(12)—N(11)—Cu(1)	124.9(4)
Cu(1a)—N(11)—Cu(1)	101.8(2)	N(13)—N(12)—N(11)	179.4(7)
N(22)—N(21)—Cu(1)	124.1(4)	N(23)—N(22)—N(21)	176.7(6)
C(1)—O(1)—Cu(1)	121.2(4)	O(1)—C(1)—N(1)	126.5(6)
hydrogen bonds:			
O(1)···H(2)	2.00(6)	N(1)—H(2)···O(1)	177(5)
N(21)···(3)	2.11(6)	N(1)—H(3)···N(21)	161(5)

Symmetry code: (a) $-x+2, -y, -z+2$.

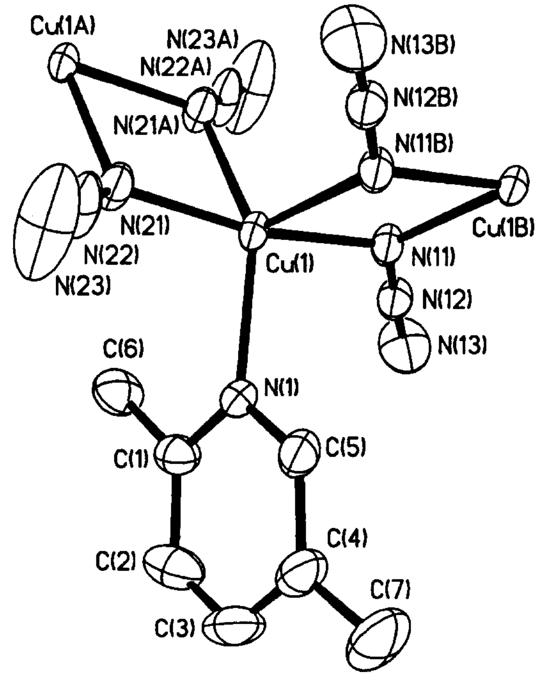

Figure 1. Molecular geometry and atom-labelling scheme of Cu(2,5-dimethylpyridine) $(N_3)_2$ (**1**).

line)$(N_3)_2$ **3** [1] and Cu(4-picoline)$(N_3)_2$ **4**, although both exhibit distorted square-pyramidal environment about each copper atom. Structure **4** contains chains of Cu_2N_2 units linked by two $\mu(1,3)$ azido groups along the short *a* axis [3], whereas the Cu_2N_2 units in structure **3** are connected *via* the $\mu(1,3)$ azides to form layers of polyhedra. The apical Cu—N distance in **1** is shorter than the corresponding distance of 2.457(3) Å in **4**, but closes that of 2.273(2) Å found in the structure of **3** [1]. The structure of **1** resembles that of catena di-$\mu(1,1)$-azido-[di-$\mu(1,1)$-azido-bis(3-picoline) dicopper(II)] [2], **5**, but also differs from it in several subtle aspects. Although complex **5** contains similar $\mu(1,1)$ azido ligands, the stereochemistry about each copper atom is distorted trigonal bipyramid and the N—N distances are close to corresponding values in **1** for one of the two azides [N—N = 1.19(2) and 1.13(3) Å] they are much longer for the other [N—N = 1.23(3) and 1.27(3) Å] with the longer N—N bond being more remote from the metal atom.

Dimeric molecules of **2** contain both terminal and $\mu(1,1)$ bridging azido ligands (Figs 3 and 4). Each five-coordinated copper atom further binds a 2,5-DMPy molecule *via* its nitrogen atom, N(2), and the carbonyl oxygen atom of a formamide molecule. The copper dimers are located at the inversion centre at the origin of the unit cell. The stereochemistry about each copper atom is best described as a distorted square pyramid, with the oxygen atom, O(1) of the formamide molecule at its apex. Both azido groups are linear within experimental error. In conformity to the general trend of coordinated azides [13–15], the $\mu(1,1)$ azido ligand is more asymmetric [N(11)—N(12) = 1.198 (6) and N(12)—N(13) = 1.142(6) Å] than the terminal azido group [N(21)—N(22) = 1.188(7) and N(22)—N(23) = 1.138(7) Å].

In most aspects complex **2** is structurally similar to

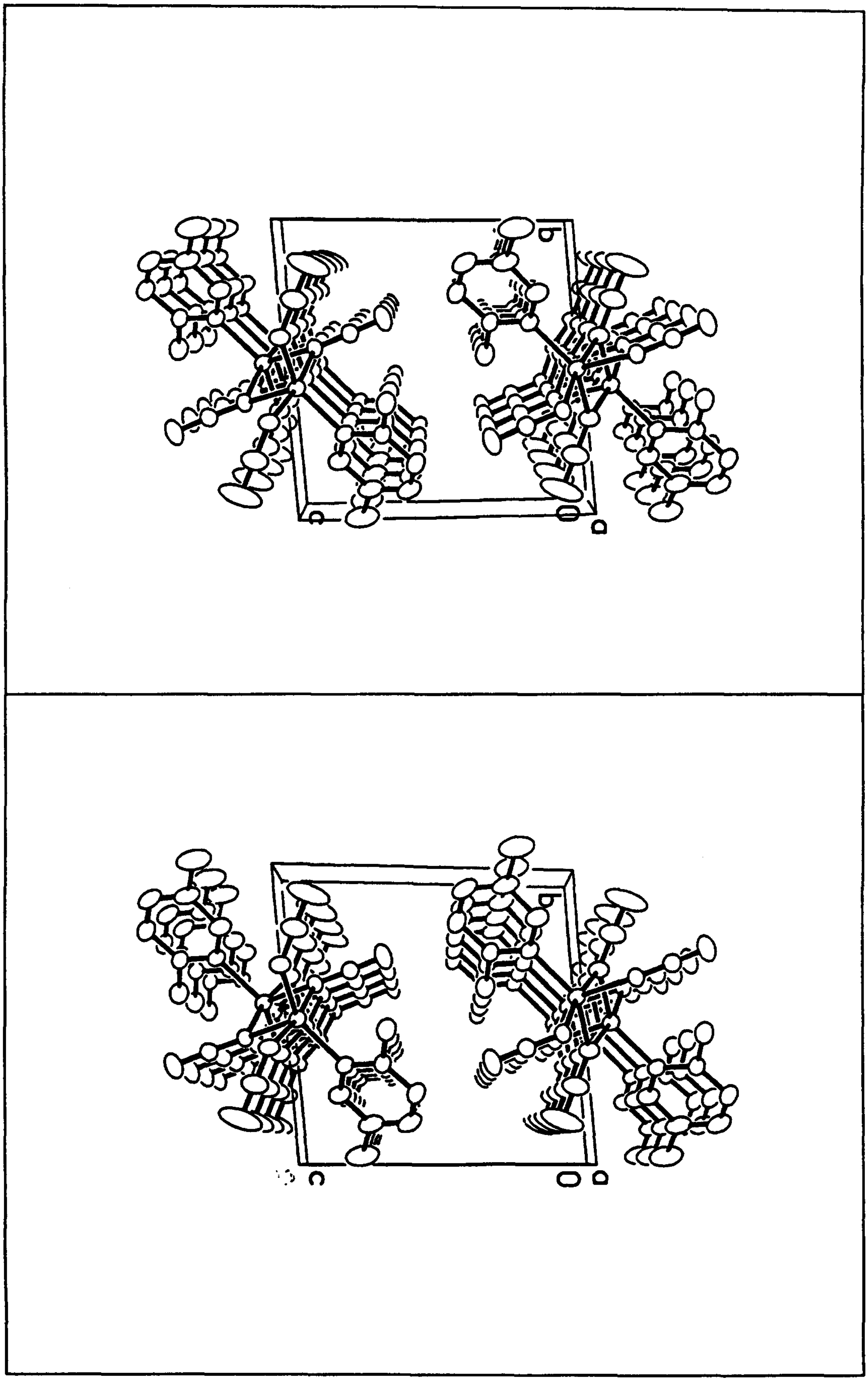

Figure 2. Packing plot of Cu(2,5-dimethylpyridine)$(N_3)_2$ (**1**), viewed along the *a* axis of the unit cell.

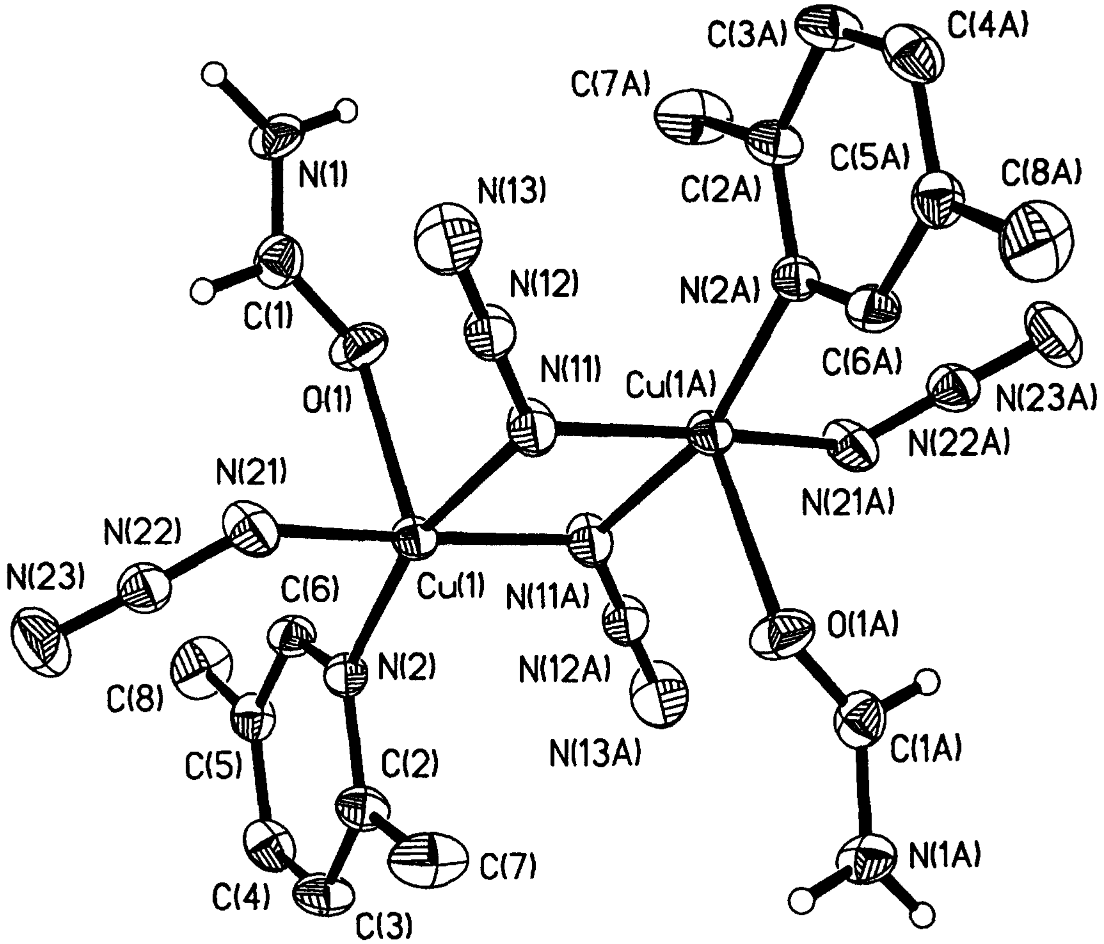

Figure 3. Molecular geometry and atom-labelling scheme of [Cu(2,5-dimethylpyridine)$(N_3)_2$(formamide)$]_2$ (**2**).

the di-μ(1,1) azido-bis [azido(2-aminopyridine)-aqua]dicopper(II) (**6**) of P −1 molecular symmetry, which also features distorted square pyramidal copper(II) [16]. There is remarkably good agreement between corresponding bond distances within the coordination polyhedron about each copper. The relevant dimensions reported for **6**: Cu—N(L) = 2.001(2), Cu—N(bridging azide) = 2.018(2), Cu—N(terminal azide) = 1.962(3) and 2.003(3), and Cu—O(H_2O) = 2.371(2) Å, may be compared with those of **2** listed in Table 3. Both complexes, however, differ in that the Cu—N—Cu angle in the cyclic Cu_2N_2 ring and Cu—N—N angles are greater in complex **6** [103.1(1) and 126.5(2), 127.2(2)°, respectively] than corresponding angles in complex **2** (Table 3).

The formamide molecule plays an important role in the structure of the present complex **2**. Besides serving as a ligand and forming a hydrogen bond of the type N—H···O between its nitrogen atom N(1) and a carbonyl oxygen atom of a neighbour dimer, it is further involved in intermolecular hydrogen bonding N(1)—H···N(21) = 3.026(8) Å with terminal azido groups of adjacent dimeric complexes. In the crystal structure (Fig. 4) the dimeric molecules are thus linked by N—H—N hydrogen bonds along the *a* axis of the unit cell. Two hydrogen bridged dimeric fomamide molecules are related by the inversion centre at [0, 1/2, 0].

Structures such as the title complexes **1** and **2** with a cyclic Cu_2N_2 ring are common in the literature of $CuL_2(N_3)_2$ and $CuL(N_3)_2$ (L = nitrogen donor ligands) with Cu···Cu separations ranging from 3.08 Å in [Cu$(N_3)_2$] [17], which has infinite chains of planar Cu$(N_3)_2$ units to 3.78 Å in CuL$(N_3)_2$ (L = (2-aminoethylpyridine) [18]. The Cu···Cu distances found in **1** and **2** are comparable to each other (Tables 2 and 3) and to those found in the structure of Cu(2-bromopyridine)$(N_3)_2$ [3.140(2) and 3.291(2) Å] [19], but shorter than that found in Cu(3-picoline)$(N_3)_2$ [3.546(2) Å] [2] and longer than 3.095(1) Å found in the structure of Cu(2-picoline)$(N_3)_2$ [1].

IR spectra

The IR spectra (Table 4) of both complexes show two absorption bands above 2000 cm^{-1} due to the

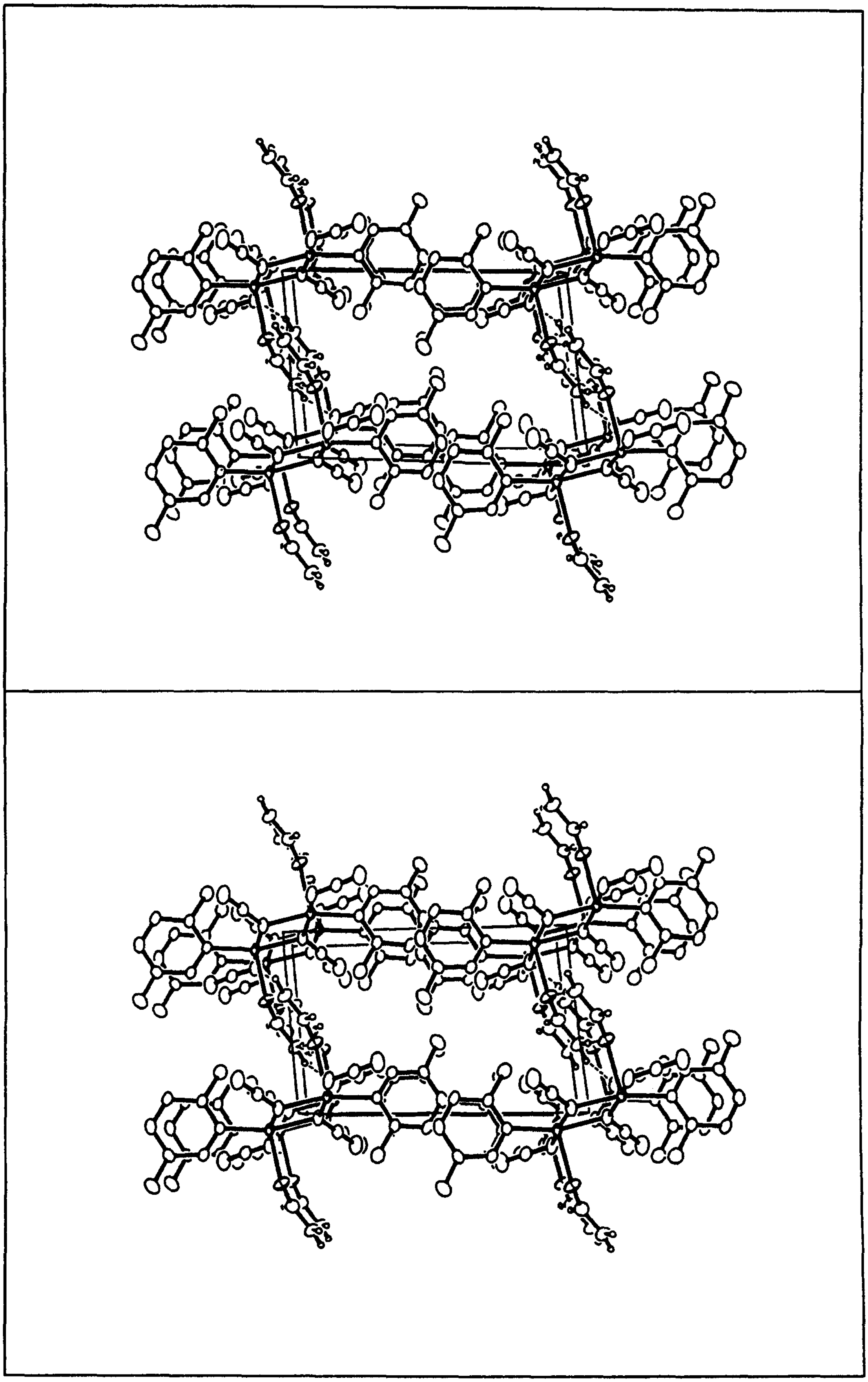

Figure 4. Packing plot of [Cu(2,5-dimethylpyridine)$(N_3)_2$(formamide)]$_2$ (**2**), viewed along the *a* axis of the unit cell.

Table 4. Azide and other vibration frequencies in complexes $[Cu(2,5\text{-}DMPy)(N_3)_2]_n$ (**1**) and $[Cu(2,5\text{-}DMPy)(N_3)_2(OHC\text{-}NH_2)]_2$ (**2**)

Frequency (cm^{-1}) 1	2	Assignments
	3320 s	$\nu NH_2 + \nu N—H\cdots O +$
	3170 s	$\nu N—H\cdots N$
	2900 m,sp	
2065vs	2075 vs	$\nu_{as}(N_3)$
2030vs	2045 vs	
	1681 vs	$\nu C{=}O$
1614 m	1611 ms	pyridine
1571 m	1575 m	pyridine
1015 s	1012 s	pyridine
1330 wm	1329 s,sp	$\nu_s(N_3)$
1281 s	1289 s,sp	
632 m	650 m	$\delta(N_3)$
585 wm	638 ms	
	601 wm	
	577 w,br	$\nu Cu—O$
390 s	380 s	ν Cu—N_3
360 ms	355 s	
235 s	245 vs	$\nu Cu—N(L)$

w = weak, m = medium, s = strong, v = very, sp = sharp, br = broad.

asymmetric azide stretching, as well as two absorption bands in the range 1350–1270 cm^{-1} associated with the $\nu_s(N_3)$ mode. The appearance of these latter bands strongly evidences the asymmetric nature of the azide ligands. Although we could not distinguish between bridging and terminal azides or between complexes **1** and **2** from these stretching vibration bands since both compounds contain $\mu(1,1)$ asymmetric azido ligands in addition to the terminal azido group in **2**, we may assign the highest $\nu_{as}(N_3)$ absorption frequencies to N(21)—N(22)—N(23) ($\Delta d = 0.056$ Å) and N(11)—N(12)—N(13) ($\Delta d = 0.056$ Å) and the other frequencies to N(11)—N(12)—N(13) ($\Delta d = 0,038$ Å) and N(21)—N(22)—N(23) ($\Delta d = 0.050$ Å) in **1** and **2**, respectively. These assignments are given on the basis of the Δd *vs* $\nu_{as}(N_3)$ relationship reported earlier [20,21]. In the far-IR region at least two medium to strong bands are observed in the range 400–330 cm^{-1} and attributed to the $\nu(Cu—N_3)$ mode. These bands are very similar to those reported for polymeric Cu(3-picoline)-$(N_3)_2$, which contains the copper atoms in a distorted trigonal bipyramidal environment [2]. The range of the $\nu(Cu—N_3)$ is very close to that found for the isoelectronic cyanato complexes of copper(II) with similar ligands [22].

In addition to the above absorption bands, the IR spectrum of complex **2** shows several absorption bands which are absent from the spectrum of complex **1**. These bands are definitely due to the formamide molecule in complex **2**. The IR spectrum of formamide shows a broad band with three peaks at 3386, 3250 and 3100 cm^{-1} in addition to a sharp band at 2880 cm^{-1}. The carbonyl stretching band appears as a broad band covers the range 1700–1660 cm^{-1}. Corresponding bands in the spectrum of complex **2** appear as sharp bands at 3320 and 3170 cm^{-1} (N—H) and 1681 cm^{-1} (C=O) suggesting coordination *via* the carbonyl oxygen.

Electronic spectra

The electronic spectra of the title complexes, **1** and **2**, measured as Nujol mulls are given in Table 5 and Fig. 5. The spectra of both complexes show a very strong absorption band around 23,000 cm^{-1} in addition to a distinct absorption band of moderate intensity around 18,900 cm^{-1}. These bands are due to $N_3^- \rightarrow Cu^{II}$ LMCT transitions. On the basis of the transition dipole vector coupling model, two and four azide-to-copper(II) charge-transfer transitions have

Table 5. Electronic spectral data[a]

Complex	Solvent	$N_3^- \rightarrow Cu^{II}$ CT (ξ)	d-d(ξ)
1	NM	22 547 vs, vbr 18 467 s,br	12,690 vbr
	DMF	26 315 (560) 24 242 (2037)	13,745 (139)
	DMSO	24 630 (1870)	13,888 (204)
2	NM	24 390 vs,vbr 19 361 s,br	14,388 vbr
	DMF	24 155 (2270)	13,698 (173)
	Acetone	24 450 (1790)	15,385 (183)
	MC	24 937 s 21 739 sh	

[a] In cm^{-1}. NM = Nujol mull. MC = methylene chloride.

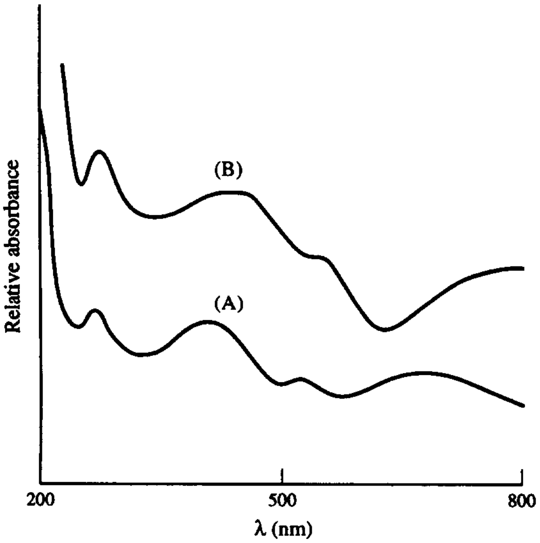

Figure 5. Electronic spectra of solid complexes: (A) Cu(2,5-dimethylpyridine)$(N_3)_2$ (**1**); (B) [Cu(2,5-dimethylpyridine)$(N_3)_2$(formamide)]$_2$ (**2**).

been predicted for terminal and μ-1,1 or μ-1,3 bridging copper(II) azide complexes [23]. Terminal copper(II) azide monomers, however, show only one feature, whereas two bands are reported for μ-1,1 and μ-1,3 dimers [23]. The present structures with di-μ(1,1) and coexistence of di-μ(1,1) and terminal azides are, therefore expected to show more than two $N_3^- \rightarrow Cu^{II}$CT bands. In fact the absorption band around 23,000 cm^{-1} is very broad and may be formed of more than one transition. Since a discrete absorption band is usually observed in the region 17,000–21,000 cm^{-1} for copper(II) complexes containing di-μ(1,1) azides [24–26], the band around 18,900 cm^{-1} in both complexes is evidently due to the μ(1,1) azide-to-copper charge transfer transitions. These spectra also exhibit *d–d* transitions as a very broad band centred around 12,690 and 13,888 cm^{-1}, for **1** and **2**, respectively, suggesting a five-coordinate copper(II) environment [27,28] for both complexes. The position of the *d–d* band in **2** is similar to that reported (see Fig. 5, ref. 29) for the polymeric 1 : 1 copper(II) azide complex of pyridine-*N*-oxide, in which copper(II) atoms have a distorted tetragonal pyramidal environment. In DMF, both complexes show a very strong band around 24,000 cm^{-1} and a shoulder around 26,315 cm^{-1} in **1** due to $N_3^- \rightarrow Cu^{II}$ CT transitions, in addition to the *d–d* absorption around 13,700 cm^{-1}. Thus in DMF, as well as in other solvents except methylene chloride (Table 5) one of the charge-transfer bands disappears (the lower frequency band), whereas the highest one is shifted to higher wave numbers in **1** or remained constant in **2**. Similar features have been observed for other copper(II) azide complexes [30].

EPR spectra

The EPR spectra of polycrystalline samples of complexes **1** and **2** have been recorded at room temperature. These spectra are of 1 g value type, with g values of 2.112 and 2.182 for **1** and **2**, respectively. A grossly misaligned set of tetragonal axes seems to be a more plausible explanation as reported for other copper(II) complexes [31]. Both complexes were dissolved in DMF and their room-temperature spectra were obtained. These spectra are very similar and that of **1** is shown in Fig. 6. It shows four hyperfine lines of uncoupled copper(II) ($I = 3$) with $A_0(Cu) = 57.2$ and 73.3 G, for **1** and **2**, respectively. There is no evidence of coupled copper(II) signals at room temperature for **1** and **2** either in the solid state or in DMF solutions. Besides DMF, we tried to use acetone, methylene chroride, methanol and DMSO as solvents. Poor resolution was observed for solvents other than DMSO and methylene chloride (for complex **2**) because of poor solubility. The DMSO and methylene chloride solutions spectra of **1** and **2** at room temperature show four EPR lines, which are similar to the DMF solution spectra.

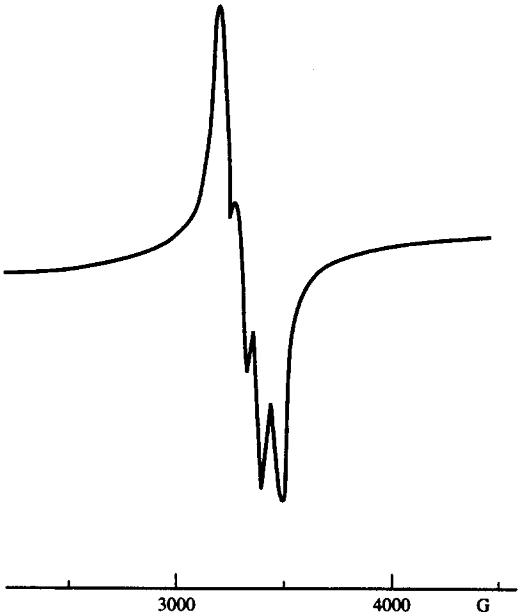

Figure 6. The DMF solution EPR spectrum of complex **1** at room temperature.

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REFERENCES

1. Goher, M. A. S. and Mautner, F. A., *Z. Naturforsch.* 1991, **46b**, 687.
2. Goher, M. A. S. and Mak, T. C. W., *Inorg. Chim. Acta*, 1984, **89**, 119.
3. Mautner, F. A. and Goher, M. A. S., *Polyhedron*, 1993, **12**, 2823.
4. Goher, M. A. S. and Mautner, F. A., *Cryst. Res. Technol.* 1992, **27**, 817.
5. Mautner, F. A. and Goher, M. A. S., *Polyhedron*, 1992, **11**, 2137.
6. Mautner, F. A. and Goher, M. A. S., *Polyhedron*, 1994, **13**, 2141.
7. Mautner, F. A. and Goher, M. A. S., *Struct. Chem.* 1994, **5**, 171.
8. Goher, M. A. S. and Mautner, F. A., *Polyhedron*, 1996, **15**, 5.
9. Goher, M. A. S., Abdou, A. E. H., Luo, B. S. and Mak, T. C. W., *J. Coord. Chem.* 1995, **36**, 71.
10. Sheldrick, G. M., SHELXTL Reference manual. Siemens Industrial Automation, Inc., U.S.A., 1994.
11. Spek, A. L., in *Computational Crystallography*, ed. D. Sayre. Clarendon Press, Oxford, 1982, p. 528.
12. *International Tables for Crystallography*, Vol. C, Tables 4.2.6.8. and 6.1.1.4. Kluwer Academic Publishers, Dordrecht, 1982.
13. Dori, Z. and Ziolo, R. F., *Chem. Rev.* 1973, **73**, 247.
14. Agrell, I., *Acta Chem. Scand.* 1969, **23**, 1667; Felt-

house, T. R. and Hendrickson, D. N., *Inorg. Chem.* 1978, **17,** 444.
15. Escuer, A., Vicente, R., El-Fallah, M. S., Solans, X. and Font-Bardia, M., *Inorg. Chem.* 1994, **33,** 1842; Escuer, A., Vicente, R., El Fallah, M. S., Solans, X. and Font-Bordia, M., *J. Chem. Soc. Dalton Trans.* 1996, 1013.
16. Goher, M. A. S. and Mak, T. C. W., *Inorg. Chim. Acta,* 1984, **85,** 117.
17. Soderquist, R., *Acta Cryst.* 1986, **B24,** 450.
18. Baily, N. A., Fenton, D. E. and McLean, C. H., *Inorg. Chim. Acta,* 1991, **197,** 1.
19. Mautner, F. A. and Goher, M. A. S., *Polyhedron,* 1992, **11,** 2537.
20. Agrell, I., *Acta Chem. Scand.* 1971, **25,** 2865.
21. Goher, M. A. S., *Acta Chim. Hung.* 1990, **127,** 213.
22. Hvastijova, M., Kohout, J., Gažo, J. and Valach, F., *J. Inorg. Nucl. Chem.* 1976, **38,** 705; Kohout, J., Kabešova, M., Hvastijova, M. and Gažo, J., *Coll. Czech. Chem. Commun.* 1978, **43,** 705.
23. Pate, J. E., Ross, P. K., Thamann, T. J., Reed, C. A., Karlin, K. D., Sorrell, T. N. and Solomon, E. J., *J. Am. Chem. Soc.* 1989, **111,** 5198.
24. Mak, T. C. W. and Goher, M. A. S., *Inorg. Chim. Acta,* 1986, **115,** 17.
25. Goher, M. A. S., *Bull. Soc. Chim. Fr.* 1987, I-49.
26. Goher, M. A. S., *Acta Chim. Hung.* 1988, **125,** 877.
27. Sacconi, L. and Bertini, L., *Inorg. Chem.* 1966, **5,** 1520.
28. Mangia, A., Nardilli, M., Pelizzi, C. and Pelizzi, G., *J. Chem. Soc., Dalton Trans.* 1972, 2483.
29. Goher, M. A. S. and Mautner, F. A., *Polyhedron,* 1995, **14,** 1751.
30. Goher, M. A. S., Al-Salem, N. A. and Mautner, F. A., *Polyhedron,* 1996, **15,** 4513.
31. Hathaway, B. J. and Billing, D. E., *Coord. Chem. Rev.* 1970, **5,** 143.