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PREPARATION, SPECTRAL AND CRYSTAL STRUCTURE STUDY OF POLYMERIC 1:1 AND DIMERIC 1:2 COMPLEXES OF COPPER(II) AZIDE WITH PYRIDINE-*N*-OXIDE AND 3-ACETYLPYRIDINE, [Cu(PYRIDINE-*N*-OXIDE)$(N_3)_2]_n$ AND [Cu(3-ACETYLPYRIDINE)$_2(N_3)_2]_2$

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Abstract—The synthesis and characterization of two new complexes of copper(II) azide, 1 : 1 with pyridine-*N*-oxide (**1**) and 1 : 2 with 3-acetylpyridine (**2**) are described. The structure of complex **1** features five-coordinated copper in a distorted tetragonal pyramidal environment with N(11), N(11a), N(21) and N(21b) of the two $\mu(1,1)$ bridging azido ligands in basal sites [Cu—N from 2.003(3) to 2.026(3) Å] and O(1) of the pyridine-*N*-oxide molecule occupying the apical position [Cu—O = 2.185(3) Å]. The chains of polyhedra are directed along the *a* axis of the unit cell. The dimeric molecule of **2**, which possesses a crystallographic inversion centre, contains both terminal and $\mu(1,1)$ bridging azido groups. Each copper(II) atom is further coordinated by two nitrogen atoms from 3-acetylpyridine molecules to give a distorted square pyramid. The IR and electronic spectra of the solid complexes are given and discussed.

The interaction between copper(II) azide and pyridine has been reported to produce different modifications of a *polymeric* 1:2 complex and the products described as brown, brownish-green or green.[1-3] Additionally, a brown 1 : 1 complex has been reported.[4] X-ray structure determinations, however, have shown that while the green and brownish-green modifications contain distorted octahedral copper(II) atoms, the two azide groups are crystallographically distinct with different structural environments. In the green form of the $Cu(py)_2(N_3)_2$ complex, one azide ligand is monodentate whereas the other coordinates asymmetrically to three different metal centres.[5] In the structure of the brownish-green form, each pair of copper atoms are simultaneously bridged by $\mu(1,1)$ and $\mu(1,3)$ azido ligands.[6] In fact these different modifications of the 1 : 2 copper(II) azide complex of pyridine reflect the versatile nature of the N_3^- ion as a ligand which can bind metal atoms in different coordination modes as has been described elsewhere.[7] Such versatility manifests itself in the substantial array of copper(II) azide complexes of monosubstituted pyridine ligands that have been prepared, structurally characterized and shown to have a wide variety of stoichiometries, solid state stereochemistries and varying degrees of oligomerization.[8,9] Although copper(II) azide complexes of disubstituted and other pyridine

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derivatives have been reported, to our knowledge the literature contains no example of copper(II) azide complexes of the corresponding *N*-oxide derivatives. In this paper we report the synthesis and characterization of the first example of such complexes, the 1 : 1 copper(II) azide of pyridine-*N*-oxide along with the corresponding 1 : 2 complex of 3-acetylpyridine as elucidated by X-ray crystallographic and spectroscopic methods.

EXPERIMENTAL

Preparation of polymeric [Cu(*pyridine*-N-*oxide*)$(N_3)_2]_n$ *complex* (**1**)

Copper(II) nitrate trihydrate (0.48 g, 2 mmol) dissolved in ethanol (*ca* 30 cm^3) and pyridine-*N*-oxide (0.30 g, 3.5 mmol) were mixed together followed by addition of an aqueous solution of NaN_3 (0.32 g, *ca* 5 mmol, in 5 cm^3) with continuous stirring. The brown solution mixture was concentrated and the filtrate allowed to stand over several weeks to yield crystals of the complex. Crystals suitable for X-ray measurements were prepared by mixing the components in the above molar ratio in acetone (40 cm^3) and the final green mixture allowed to stand for 2–3 days to produce the complex. Found: C, 24.3; H, 2.4; N, 40.0; Cu, 26.7. Calc.: C, 24.7; H, 2.1; N, 40.4; Cu, 26.2%.

Preparation of [Cu(3-*acetylpyridine*)$_2(N_3)_2]_2$ *complex* (**2**)

To a mixture of copper(II) nitrate trihydrate (0.96 g, 4 mmol) and 3-acetylpyridine (1.21 g, 10 mmol) in ethanol (40 cm^3), an aqueous solution (10 cm^3) of NaN_3 (0.45 g, 7 mmol) was dropwise added. The green mixture was boiled for several minutes and allowed to stand for *ca* 3 weeks until black crystals separated. Found: C, 42.8; H, 3.5; N, 28.9; Cu, 16.7. Calc.: C, 43.1; H, 3.6; N, 28.7; Cu, 16.3%.

The experimental procedures and instruments used for various measurements are as described previously.[10]

X-ray crystallography

Lattice parameters of both compounds have been determined by least-squares refinement of X-ray powder patterns at 298(1)K [Philips APD 1700 powder diffractometer, Cu-$K\alpha$ radiation (λ = 1.54178 Å)] with silicon (NIST 640b) as an internal standard. Single crystal intensity data were collected with a modified STOE four-circle diffractometer using graphite crystal-monochromatized Mo-$K\alpha$ radiation (λ = 0.71069 Å) and the ω-scan technique. The intensities were corrected for Lorentz and polarization effects, and for absorption.[11] 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. The hydrogen atoms were included in the final refinement cycles on calculated positions. The programs DIFABS,[11] SHELX-76,[12] SHELXS-86,[13] PLATON[14] and THE XRAY SYSTEM[15] were used for computations. Analytical expressions of netural-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] Selected bond distances and bond angles are given in Table 2. Positional parameters, anisotropic displacement parameters, hydrogen atom coordinates, a full list of bond lengths and angles and observed and calculated structure factors have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

The principal structural features of polymeric [Cu(pyridine-*N*-oxide)$(N_3)_2]_n$ (**1**) are illustrated in Figs 1 and 2. The structure features five-coordinate copper(II). Each copper atom is coordinated by four nitrogen atoms, N(11), N(11a), N(21) and N(21b) of the two μ(1, 1) bridging azido groups in the basal sites [Cu—N from 2.003(3) to 2.026(3) Å] and O(1) of pyridine-*N*-oxide molecule occupying the apical position [Cu—O(1) = 2.185(3) Å]. The stereochemistry about each copper atom is best described as a distorted tetragonal pyramid. The chains of polyhedra are directed along the *a* axis of the unit cell. Both azido ligands are linear and asymmetric (Table 2).

The structure of complex **1** differs from corresponding $CuL(N_3)_2$ complexes with L = 3-picoline (3-pic),[17] 2-picoline[18] and diethylnicotinamide (DENA).[19] The stereochemistry about each copper atom in the 3-pic complex is a distorted trigonal bipyramid and the asymmetric unit contains three distinct μ(1, 1) bridging azido ligands: two azides lying on the same crystallographic diad bridge a pair of copper atoms whereas a third azide group asymmetrically links alternate copper atoms to yield an infinite zigzag chain.[17] Although the 1 : 1 complex of 2-pic possesses a distorted square pyramidal geometry around each copper atom, one of the azide groups function in the μ(1, 1) mode giving rise to a cyclic Cu_2N_2 system whereas the other bridges metal atoms of neighbouring Cu_2N_2 units in

Table 1. Crystallographic data and processing parameters

Compound	1	2
Molecular formula	$C_5H_5N_7OCu$	$C_{14}H_{14}N_8O_2Cu$
Molecular weight	242.69	389.86
Crystal system	Triclinic	Monoclinic
a (Å)	6.112(3)	7.950(3)
b (Å)	7.309(4)	13.145(7)
c (Å)	10.162(5)	15.650(7)
α (°)	87.66(3)	
β (°)	78.07(3)	81.74(3)
γ (°)	78.56(2)	
V (Å^3)	435.4(4)	1619(1)
Space group	P-1 (No. 2)	$P2_1/c$ (No. 14)
Z	2	4
F(000)	242	796
μ(Mo-$K\alpha$) (mm^{-1})	2.49	1.38
D_{calc}/D_{obs} (Mg m^{-3})	1.851/1.86(2)	1.600/1.60(2)
Approx. crystal size (mm)	0.65 × 0.12 × 0.16	0.45 × 0.45 × 0.20
Data collection limits	$\pm h, \pm k, l$; $2\theta < 55°$	$\pm h, k, l$; $2\theta < 60°$;
Scan mode	ω-scan, $\Delta\omega = 1.50°$	ω-scan, $\Delta\omega = 1.5°$
$F_o > 3\sigma(F_o)$	1421	2403
Least squares parameters	132	258
R	0.036	0.041
R_w	0.037	0.038
Weighting scheme	$1.206\sigma^{-2}$ (F_o)	$1.831\sigma^{-2}(F_o)$
Residual extrema in final difference map (e Å^{-3})	+0.74/−0.81	+0.42/−0.62

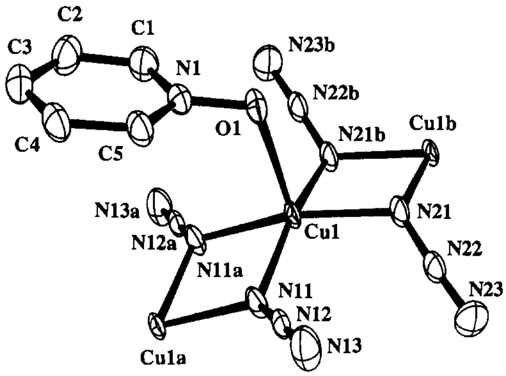

Fig. 1. Tetragonal pyramidal environment of the copper(II) centre and the atom numbering scheme of $[Cu(C_5H_5NO)(N_3)_2]_n$ (1) (symmetry code according to Table 2).

an asymmetric $\mu(1,3)$ fashion resulting in polymeric chains.[18] In the DENA complex the coordination about each copper atom is an elongated octahedron. One of the two crystallographically independent azide groups acts in the $\mu(1, 1)$ mode forming a planar four-membered Cu_2N_2 ring and the other functioning as a $\mu(1, 1, 3)$ bridging ligand interlinks the Cu_2N_2 units into a corrugated chain. The backbone of the chains is built up of Cu_2N_2 rings and virtually planar eight-membered $Cu(N_3)_2$ rings.[19]

Dimeric molecules of 2 contain both terminal and $\mu(1, 1)$ bridging azido ligands (Figs 3 and 4). Each copper atom is further coordinated by two 3-acetylpyridine molecules *via* their N(1) and N(2) atoms. The stereochemistry about each Cu atom is best described as a distorted square pyramid, with the N(11) of the bridging azide at its apex at a Cu—N bond length of 2.391(3) Å. Both azido groups are linear within experimental error. In conformity to the general trend of coordinated azides,[20] the $\mu(1,1)$ azido group is asymmetric [N(11)—N(12) = 1.201(4) and N(12)—N(13) = 1.156(4) Å]. The terminal azide ligand, however, is symmetrical (Table 2). Terminal symmetric azides are known in other azido complexes, e.g. $[Fe(N_3)_5]^{2-}$.[21] The 3-acetyl groups are slightly bent out of the pyridine planes [torsion angles: C(3)—C(2)—C(6)—C(7) = 8.2(5)°, C(1)—C(2)—C(6)—O(1) = 8.9(5)°, C(10)—C(9)—C(13)—C(14) = −15.4(5)°, C(8)—C(9)—C(13)—O(2) = −15.2(5)°].

In most aspects complex 2 is structurally similar to the di-$\mu(1, 1)$ azido-bis[azido(2-aminopyridine)aqua]dicopper(II), 3, of $P-1$ molecular symmetry, which also features distorted square

Table 2. Selected bond distances (Å) and bond angles (deg)

[Cu(pyridine-*N*-oxide)$(N_3)_2]_n$ (**1**)			
Cu(1)···Cu(1a)	3.120(2)	Cu(1)···Cu(1b)	3.071(2)
Cu(1)—O(1)	2.185(3)	Cu(1)—N(11)	2.005(3)
Cu(1)—N(21)	2.003(3)	Cu(1)—N(11a)	2.026(3)
Cu(1)—N(21b)	2.012(3)	O(1)—N(1)	1.333(4)
N(11)—N(12)	1.193(5)	N(12)—N(13)	1.137(5)
N(21)—N(22)	1.209(5)	N(22)—N(23)	1.143(5)
N(11)—Cu(1)—N(21b)	165.3(1)	N(21)—Cu(1)—N(11a)	166.4(1)
O(1)—Cu(1)—N(11)	98.3(1)	O(1)—Cu(1)—N(21)	98.7(1)
O(1)—Cu(1)—N(11a)	94.9(1)	O(1)—Cu(1)—N(21b)	96.3(1)
N(11)—Cu(1)—N(21)	99.7(1)	N(11)—Cu(1)—N(11a)	78.6(1)
N(21)—Cu(1)—N(21b)	80.2(1)	Cu(1)—O(1)—N(1)	115.1(2)
O(1)—N(1)—C(1)	119.4(3)	O(1)—N(1)—C(5)	119.7(3)
Cu(1)—N(11)—N(12)	128.7(3)	Cu(1)—N(11)—Cu(1a)	101.4(2)
N(12)—N(11)—Cu(1a)	127.9(3)	N(11)—N(12)—N(13)	179.2(4)
Cu(1)—N(21)—N(22)	125.3(3)	Cu(1)—N(21)—Cu(1b)	99.8(2)
N(22)—N(21)—Cu(1b)	121.3(3)	N(21)—N(22)—N(23)	177.6(4)
[Cu(3-acetylpyridine)$_2(N_3)_2]_2$ (**2**)			
Cu···Cu′	3.336(2)	Cu—N(11′)	2.002(3)
Cu—N(1)	2.003(3)	Cu—N(2)	2.020(3)
Cu—N(11)	2.391(3)	Cu—N(21)	1.978(4)
O(1)—C(6)	1.211(4)	O(2)—C(13)	1.222(5)
N(11)—N(12)	1.201(4)	N(12)—N(13)	1.156(4)
N(21)—N(22)	1.175(5)	N(22)—N(23)	1.170(6)
N(1)—Cu—N(2)	170.1(1)	N(1)—Cu—N(11)	94.4(1)
N(1)—Cu—N(21)	90.4(1)	N(2)—Cu—N(21)	88.1(1)
N(1)—Cu—N(11′)	91.3(1)	N(2)—Cu—N(11)	95.5(1)
N(2)—Cu—N(11′)	90.4(1)	N(11)—Cu—N(21)	96.9(1)
N(11)—Cu—N(11′)	81.6(1)	N(21)—Cu—N(11′)	177.8(2)
Cu—N(11)—N(12)	127.8(2)	Cu—N(11)—Cu′	98.4(1)
N(12)—N(11)—Cu′	129.8(2)	N(11)—N(12)—N(13)	177.5(4)
Cu—N(21)—N(22)	122.5(3)	N(21)—N(22)—N(23)	176.9(5)
C(2)—C(6)—O(1)	119.9(3)	0(1)—C(6)—C(7)	122.2(3)
C(9)—C(13)—O(2)	119.2(3)	O(2)—C(13)—C(14)	122.3(4)

Symmetry code of compound **1**: (a) $-x, -y, 1-z$; (b) $1-x, -y, 1-z$; compound **2**: (′) $1-x, 1-y, 1-z$.

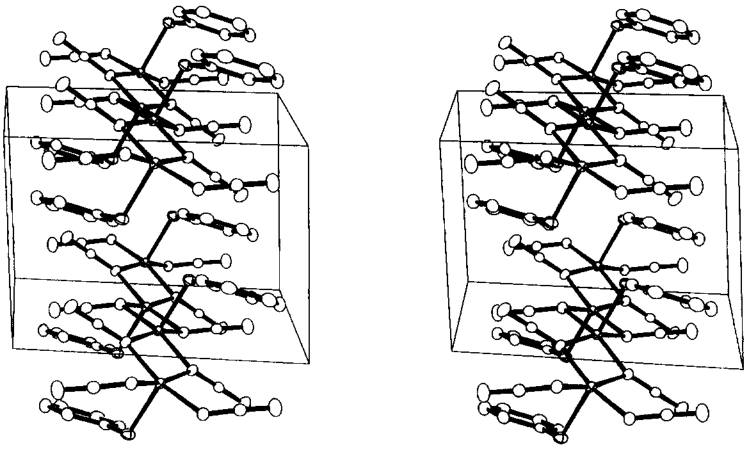

Fig. 2. Packing plot of $[Cu(C_5H_5NO)(N_3)_2]_n$ (**1**) viewed along the *a* axis of the unit cell.

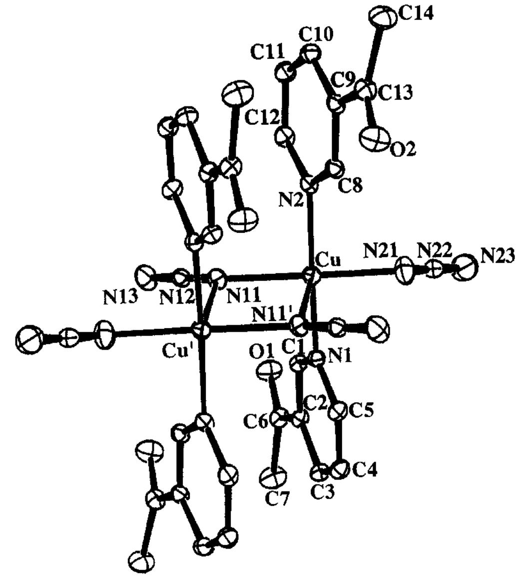

Fig. 3. Coordination figure and atom numbering scheme of $[Cu(3\text{-acetylpyridine})_2(N_3)_2]_2$ (**2**). Unlabelled atoms are related by a centre of inversion.

pyramidal copper(II).[22] Despite the difference in the apical ligated atom in these two dimeric copper(II) complexes, there is remarkably good agreement between corresponding bond distances within the coordination polyhedron about each copper. The relevant dimensions reported for **3**: Cu—N(L) = 2.001(2) Å, Cu—N(bridging azide) = 2.018(2) Å, Cu—N(terminal azide) = 1.962(3) and 2.003(3) Å, and Cu—$O(H_2O)$ = 2.371(2) Å may be compared with those of **2** listed in Table 2. Both complexes, however, differ in that the terminal as well as bridging azido ligands are asymmetric [N—N = 1.201(3) and 1.137(3) Å for bridging azide and N—N = 1.180(4) and 1.143(5) Å for terminal azide] and the Cu—N—Cu' in the cyclic Cu_2N_2 ring is greater in complex **3** [103.1(1)°] than Cu—N(11)—Cu' in **2** [98.4(1) Å].

The present complex **2** differs from 1:2 copper(II) azide complexes of other pyridine ligands, e.g. $Cu(py)_2(N_3)_2$ (two forms),[5,6] $Cu(3\text{-pic})_2(N_3)_2$,[23] and $Cu(4\text{-pic})_2(N_3)_2$.[24] All of these complexes possess distorted octahedral copper atoms and the py and 3-pic complexes are polymeric whereas the 4-pic complex features oligomeric edge-sharing chain of polyhedra.

The Cu···Cu distance of 3.336(2) Å with the cyclic Cu_2N_2 units in structure **2** is much longer than corresponding values [3.120(2) and 3.071(2) Å] found in complex **1**. These values are shorter than that reported for $Cu(3\text{-pic})_2(N_3)_2$[23] [3.546(2) Å]. In fact the Cu···Cu separations in copper(II) azide complexes fall in the range from 3.78 Å in $CuL'(N_3)_2$ (L' = (2-aminoethyl)pyridine)[25] to 3.08 Å in $[Cu(N_3)_2]_\infty$ which has infinite chains of planar $Cu(N_3)_2$ units.[9] One of the two Cu···Cu distances in the pyridine-*N*-oxide complex is shorter than that of the latter $[Cu(N_3)_2]_\infty$, thus this is the shortest Cu—Cu distance known in structurally characterized $CuL(N_3)_2$ or $CuL_2(N_3)_2$ complexes.

Pertinent IR spectral bands are given in Table 3. The IR absorption spectrum of **1** exhibits two strong bands at 2094 and 2039 cm^{-1}, associated with the $\nu_{as}N_3$ mode. The positions of these bands are not consistent with the $\nu_{as}N_3$ *vs* Δd (Δd is the difference between two N—N distances in an azide group) relationship reported previously.[26] In contrast to this result, the position of the two $\nu_{as}N_3$ frequencies in the spectrum of complex **2** are consistent with such a relationship. The higher frequency band is due to the $\mu(1, 1)$ azido group with $\Delta d = 0.045$ Å, whereas the 2020 cm^{-1} band is related to the symmetrical terminal azido ligand. Both complexes, however, exhibit a medium to strong band in the region 1350–1270 cm^{-1} associated with ν_sN_3, which is an indication of the asym-

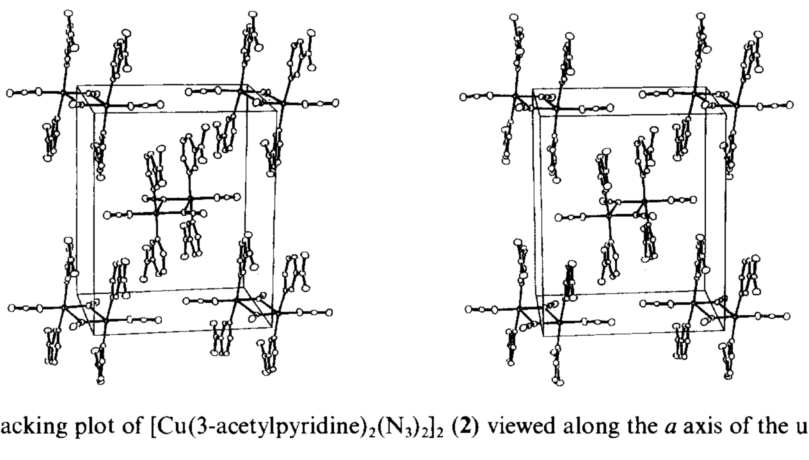

Fig. 4. Packing plot of $[Cu(3\text{-acetylpyridine})_2(N_3)_2]_2$ (**2**) viewed along the *a* axis of the unit cell.

Table 3. Infrared spectral data

Frequency (cm^{-1})		Assignments
1	**2**	
2094 vs	2050 vs	$\nu_{as}(N_3)$
2039 vs	2020 vs	
1286 s	1335 m	$\nu_s(N_3)$
578 m		$\delta(N_3)$
368 ms	365 m	$\nu(Cu—N_3)$
342 ms	345 ms	
320 s		$\nu(Cu—O)$
	260 s	$\nu(Cu—N(L))$
	235 s	

s, strong; m, medium, v, very.

metric nature of the azido ligands. In the far IR region, we tentatively assigned the bands in the ranges 370–340 cm^{-1} and 270–230 cm^{-1} to νCu—N(N_3) and νCu—N(L) modes, respectively, with the band at 320 cm^{-1} in complex **1** as due to νCu—O(L).[27,28]

The electronic spectra of solid complexes **1** and **2** are given in Fig. 5. The spectrum of complex **1** shows a strong absorption band at 26,315 cm^{-1}, a pronounced shoulder at *ca* 22,471 cm^{-1} and a distinct absorption band of moderate intensity at 18,018 cm^{-1}. Complex **2** exhibits a strong band at 25,000 cm^{-1} and a moderate intensity band at 18,690 cm^{-1}. These absorption bands are due to LMCT transitions from N_3^- to copper(II). Copper(II) azido complexes of pyridine derivative ligands usually exhibit a distinct absorption band of moderate intensity in the range 17,000–20,000 cm^{-1}, the appearance of which has been taken as a strong evidence of the existence of binuclear cyclic Cu_2N_2 units.[23,29] Bate *et al.*[30] on the basis of the transition dipole vector coupling model have predicted two and four azide-to-copper(II) charge transfer transitions for terminal and μ(1, 1) or μ(1, 3) bridging copper(II) azide complexes, respectively. In metal azide hemocyanin, assuming a bridging μ(1, 3) structure, three azide-to-copper(II) charge transfer transitions are observed, which are similar to those given here for the pyridine-*N*-oxide complex. Both complexes however, exhibit an asymmetric *d-d* absorption band at 13,157 cm^{-1} and 14,285 cm^{-1} for complexes **1** and **2**, respectively. These spectra are consistent with five-coordinate copper(II) environments.[31,32]

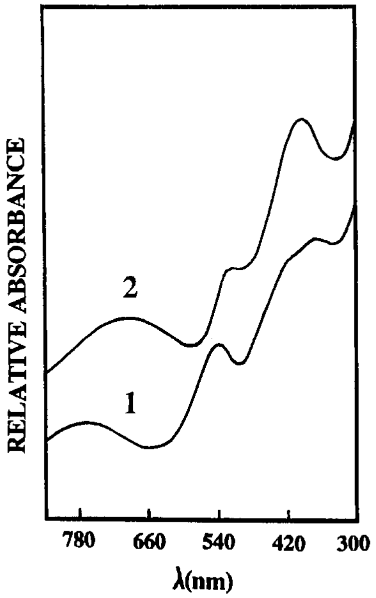

Fig. 5. Reflectance spectra of solid complexes: (1) $[Cu(C_5H_5NO)(N_3)_2]_n$; (2) $[Cu(3\text{-acetylpyridine})_2(N_3)_2]_2$.

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REFERENCES

1. L. M. Dennis and H. J. Isham, *J. Am. Chem. Soc.* 1907, **29**, 19.
2. W. Strecker and E. Schwinn, *J. Prakt. Chem.* 1939, **152**, 207.
3. A. Cirulis and M. Straumanis, *Z. Anorg. Allg. Chem.* 1943, **251**, 349.
4. M. A. S. Goher, *Acta Chim. Hung.* 1988, **125**, 877.
5. I. Agrell, *Acta Chem. Scand.* 1969, **23**, 1667.
6. F. A. Mautner and M. A. S. Goher, *Polyhedron* 1995, in press.
7. M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta* 1985, **99**, 223.
8. F. A. Mautner and M. A. S. Goher, *Polyhedron* 1994, **13**, 2141.
9. N. A. Bailey, D. E. Fenton and C. H. McLean, *Inorg. Chim. Acta* 1991, **179**, 1.
10. M. A. S. Goher, F. A. Mautner and A. Popitsch, *Polyhedron* 1993, **12**, 2557.
11. N. Walker and D. Stuart, *Acta Cryst.* 1983, **A39**, 158.
12. G. M. Sheldrick, SHELX-76. *A Program for Crystal Structure Determination.* University Chemical Laboratory, Cambridge (1976).
13. G. M. Sheldrick, SHELXS-86. Universität Göttingen, F.R.G. (1986).
14. A. L. Spek, in *Computational Crystallography* (Edited by D. Sayre), p. 528. Clarendon Press, Oxford (1982).
15. J. M. Stuart, The X-RAY SYSTEM, version of 1976, Technical Report TR-466. University of Maryland, College Park (1976).
16. *International Tables for X-ray Crystallography*, Vol.

IV, pp. 99 and 149. Kynoch Press, Birmingham (1974).

17. M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta* 1984, **89**, 119.
18. M. A. S. Goher and F. A. Mautner, *Z. Naturforsch.* 1991, **46b**, 687.
19. M. A. S. Goher, R.-J. Wang and T. C. W. Mak, *J. Mol. Struct.* 1991, **243**, 179.
20. Z. Dori and R. F. Ziolo, *Chem. Rev.* 1973, **73**, 247.
21. J. Drummond and J. S. Wood, *J. Chem. Soc., Chem. Commun.* 1969, 1373.
22. M. A. S. Goher and T. C. W. Mak, *Inorg. Chim. Acta* 1984, **85**, 117.
23. F. A. Mautner and M. A. S. Goher, *Polyhedron* 1992, **11**, 2537.
24. M. A. S. Goher and F. A. Mautner, *Cryst. Res. Technol.* 1992, **27**, 817.
25. R. Söderquist, *Acta Cryst.* 1968, **B24**, 450.
26. I. Agrell, *Acta Chem. Scand.* 1971, **25**, 2965.
27. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds.* John Wiley, New York (1978).
28. L. S. Gelfand, L. Pytlewski, A. N. Speca, C. M. Mikulski and N. M. Karayannis, *J. Inorg. Nucl. Chem.* 1980, **42**, 209.
29. F. A. Mautner, M. A. S. Goher and A. E. Abdou, *Polyhedron* 1993, **12**, 2815.
30. J. E. Bate, P. K. Ross, T. J. Thamann, C. A. Reed, K. D. Karlin, T. N. Sorell and E. I. Solomon, *J. Am. Chem. Soc.* 1989, **111**, 5198.
31. L. Sacconi and L. Bertini, *Inorg. Chem.* 1966, **5**, 1520.
32. A. Mangia, M. Nardilli, C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.* 1972, 2483.