

## A NEW MODIFICATION OF POLYMERIC 1:2 COMPLEX OF COPPER(II) AZIDE WITH PYRIDINE CONTAINING SIMULTANEOUS $\mu(1,1)$ AND $\mu(1,3)$ BRIDGING AZIDO LIGANDS BETWEEN COPPER(II) CENTRES

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**Abstract**—A new modification of the polymeric  $[\text{Cu}(\text{pyridine})_2(\text{N}_3)_2]_n$  complex has been synthesized and characterized by spectroscopic and X-ray crystallographic methods. The structure of the monoclinic crystals contains two copper(II) centres occupying special positions. Cu(1) and also N(1), C(3) of pyridine molecule 1, and N(2), C(6) of pyridine molecule 2 are located on a two-fold rotation axis at  $[1/2, y, 1/4]$ . Cu(2) is located at the inversion centre  $[3/4, 3/4, 1/2]$ . Both copper(II) centres are six-coordinated and the coordination polyhedra are distorted tetragonal bipyramids. Both copper(II) atoms are simultaneously bridged by  $\mu(1,1)$  and  $\mu(1,3)$  azido ligands [Cu—N from 2.001(5) to 2.660(4) Å]. The  $\mu(1,3)$  bridging azido ligand is symmetrical whereas the  $\mu(1,1)$  group is asymmetric but both are almost linear  $[178.5(5)$  and  $176.4(5)^\circ$ , respectively]. The IR spectrum reveals two different azido ligands and the electronic spectrum is presented and discussed.

The compound  $\text{Cu}(\text{pyridine})_2(\text{N}_3)_2$  was first prepared by Dennis and Isham,<sup>1</sup> and other methods of preparation have since been published.<sup>2,3</sup> The products obtained have been described as brown, brownish-green or green. According to Cirulis and Straumanis,<sup>3</sup> there are two modifications of  $\text{Cu}(\text{pyridine})_2(\text{N}_3)_2$ , the green and the brown, both, however are reported to give the same powder photographs. An X-ray structure determination of the green modification was determined by Agrell<sup>4</sup> in 1969, but nothing has been mentioned about the other modification.

During the course of our investigation of metal azide complexes containing various substituted

pyridine ligands<sup>5-11</sup> we have frequently observed some differences in the IR and electronic spectra of such copper(II) azide pyridine modifications. Consequently we have undertaken a thorough investigation of these modifications and have now succeeded in preparing crystals of the brownish-green modification which are suitable for X-ray crystallography. In the present paper we report the synthesis and characterization of this modification as elucidated by spectroscopic and X-ray crystallographic methods.

### EXPERIMENTAL

*Preparation of the brownish-green  $[\text{Cu}(\text{pyridine})_2(\text{N}_3)_2]_n$  complex*

Copper(II) nitrate trihydrate (0.735 g, 3 mmol) in 2 cm<sup>3</sup> water was mixed together with pyridine

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(0.630 g, 8 mmol) in 40 cm<sup>3</sup> acetone. NaN<sub>3</sub> (0.275 g, 5 mmol) in 10 cm<sup>3</sup> water was added dropwise to the above mixture which was then filtered. The filtrate was allowed to stand in an open conical flask in normal atmosphere for several weeks until almost dry, and then brownish-green crystals separated. Found: C, 39.0; H, 3.4; N, 36.4; Cu, 20.9. Calc.: C, 39.3; H, 3.3; N, 36.6; Cu, 20.8%.

Procedures and instruments used for other measurements are as described previously.<sup>12,13</sup>

### 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 32 reflections in the 2 $\theta$  range 15–25°. Data were collected at 297(1) K using graphite crystal-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å) and the  $\omega$ -scan technique. The intensities were corrected for Lorentz and polarization effects in the usual way, absorption<sup>14</sup> and also intensity decay corrections were included in the data reduction procedure (intensities of standard reflections dropped to 46% during X-ray exposure). Crystallographic data are given in Table 1.

The structure was solved by Patterson superposition methods and subsequent Fourier analyses.

Table 1. Crystallographic data and processing parameters

Molecular formula	C <sub>10</sub> H <sub>10</sub> N <sub>8</sub> Cu
Molecular weight	305.79
Crystal system	Monoclinic
<i>a</i> (Å)	12.710(4)
<i>b</i> (Å)	14.147(5)
<i>c</i> (Å)	14.089(6)
$\beta$ (°)	100.99(3)
<i>V</i> (Å <sup>3</sup> )	2487(2)
Space group	C2/c (No. 15)
<i>Z</i>	8
<i>F</i> (000)	1240
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	1.76
<i>D</i> <sub>calc</sub> / <i>D</i> <sub>obs</sub> (mg m <sup>-3</sup> )	1.633/1.62(2)
Approx. crystal size (mm)	0.65 × 0.15 × 0.12
Data collection limits	± <i>h</i> , <i>k</i> , <i>l</i> ; 2 $\theta$ < 49°
Scan mode	$\omega$ -scan, $\Delta\omega = 1.80^\circ$
<i>F</i> <sub>0</sub> > 3 $\sigma$ ( <i>F</i> <sub>0</sub> )	1081
Least squares parameters	181
<i>R</i>	0.032
<i>R</i> <sub>w</sub>	0.032
Weighting scheme	1.337 $\sigma^{-2}$ ( <i>F</i> <sub>0</sub> )
Residual extrema in final difference map (e Å <sup>-3</sup> )	+0.27 ~ -0.23

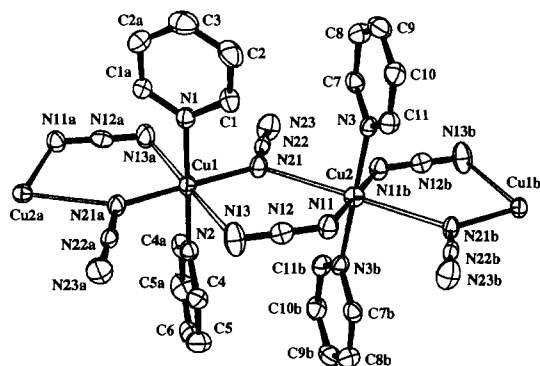


Fig. 1. Brownish-green modification of Cu(pyridine)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub> (1): the sequence of  $\mu(1,1)$ - and  $\mu(1,3)$ -azide bridges within a chain of polyhedra. Symmetry code according to Table 2. Cu—N distances > 2.50 Å are indicated by open stick bonds.

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,<sup>14</sup> SHELX-76,<sup>15</sup> SHELXS-86,<sup>16</sup> PLATON<sup>17</sup> and THE XRAY SYSTEM<sup>18</sup> were used for computations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.<sup>19</sup> 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.

## DISCUSSION

In accordance with previous studies<sup>1–3</sup> we isolated the brownish-green 1:2 complex of copper(II) azide with pyridine from acetone-aqueous medium. We obtained different X-ray powder data for this brownish-green compound (1) when compared with the published X-ray powder data of the green compound (2).<sup>4</sup>

The principal structural features of the present complex are given in Fig. 1. The structure of the brownish-green crystals (1) contains two copper(II) centres occupying special positions. Cu(1) and also N(1), C(3) of pyridine molecule 1, and N(2), C(6) of pyridine molecule 2 are located on a two-fold rotation axis at [1/2, *y*, 1/4]. Cu(2) is located at the inversion centre [3/4, 3/4, 1/2]. Both copper(II) are six-coordinated and the coordination polyhedra are distorted tetragonal bipyramids. Each pair of copper(II) centres are simultaneously bridged by two

Table 2. Selected bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

Cu(1)—N(1)	2.061(5)	Cu(1)—N(2)	2.034(5)
Cu(1)—N(13)	2.627(5)	Cu(1)—N(21)	1.998(4)
Cu(2)—N(11)	2.001(5)	Cu(2)—N(21)	2.660(4)
Cu(2)—N(3)	2.003(4)	N(11)—N(12)	1.175(7)
N(12)—N(13)	1.166(7)	N(21)—N(22)	1.205(6)
N(22)—N(23)	1.149(7)	Cu(1) $\cdots$ Cu(2)	4.280(2)
N(1)—Cu(1)—N(13)	89.8(1)	N(1)—Cu(1)—N(21)	90.2(1)
N(13)—Cu(1)—N(21)	87.2(2)	N(11)—Cu(2)—N(21)	88.6(2)
N(11)—Cu(2)—N(3)	89.6(2)	N(21)—Cu(2)—N(3)	90.1(1)
N(12)—N(11)—Cu(2)	119.4(4)	N(13)—N(12)—N(11)	178.5(5)
Cu(1)—N(13)—N(12)	108.4(4)	Cu(1)—N(21)—Cu(2)	133.0(2)
Cu(1)—N(21)—N(22)	119.7(4)	Cu(2)—N(21)—N(22)	105.8(3)
N(21)—N(22)—N(23)	176.4(6)		

Symmetry code: (a)  $1-x, y, 1/2-z$ ; (b)  $3/2-x, 3/2-y, 1-z$ .

different  $\mu(1,1)$  and  $\mu(1,3)$  azides giving rise to one-dimensional chains of copper(II) polyhedra with common corners. These chains of polyhedra are arranged in layers parallel to the  $ac$  plane of the unit cell (Fig. 2). In the chains of polyhedra the  $\mu(1,1)$  and the  $\mu(1,3)$  azide ligands are *trans* to each other. The two other sites of the distorted tetragonal bipyramids are occupied by two pyridine molecules at Cu—N distances from 2.003(4) to 2.061(5)  $\text{\AA}$ . The azide group N(11)—N(12)—N(13), which acts in the  $\mu(1,3)$  fashion, is symmetrical whereas N(21)—N(22)—N(23), behaving as a  $\mu(1,1)$  bridging azide, is asymmetric with  $\Delta d = 0.056 \text{ \AA}$  ( $\Delta d$  is the difference between two N—N distances in an azide group). Both azides, however, are almost linear [ $\angle \text{N—N—N} = 178.5(5)$  and  $176.4(6)^\circ$ , respectively].

As compared with the green  $[\text{Cu}(\text{pyridine})_2(\text{N}_3)_2]_n$  complex (2),<sup>4</sup> crystals of the present brownish complex (1) are monoclinic, space group  $C2/c$  whereas crystals of complex 2 are orthorhombic, space group  $Cmc2$ . The volume of the unit cell of complex 1 is almost exactly twice the cell volume ( $1213.1 \text{ \AA}^3$ ) of the green modification (2), which is consistent

with 8 formula units in 1 and 4 formula units in 2. Although both complexes 1 and 2 are similar they differ in some subtle aspects. Complex 2 contains only one type of distorted octahedral copper(II) centre and the two crystallographically different azides are terminal and  $\mu(1,1,3)$  bridging azides, which is different from 1 as mentioned above. The Cu—N(py) distances [2.041(12)  $\text{\AA}$ ] and two Cu—N(N<sub>3</sub>) [1.971(26) and 2.010(20)  $\text{\AA}$ ] in complex 2 are similar to, whereas the other two Cu—N(N<sub>3</sub>) [2.496(21) and 2.761(25)  $\text{\AA}$ ] are different to the corresponding values in complex 1. In contrast to complex 1 both azido groups in 2 are asymmetric with  $\Delta d = 0.06$  and  $0.04 \text{ \AA}$  for the terminal and  $\mu(1,1,3)$  azides, respectively.

The structure of the title complex differs from those of the other structurally characterized 1:2 copper(II) azide complexes of pyridine derivative ligands, 4-methylpyridine (3),<sup>20</sup> 3-methylpyridine (4)<sup>21</sup> and 2-benzoylpyridine (5)<sup>22</sup> although all of them contain six-coordinated copper(II) centres. The chelating bidentate nature of 2-benzoylpyridine forces the two azide groups to be terminally coordinated giving rise to a monomeric

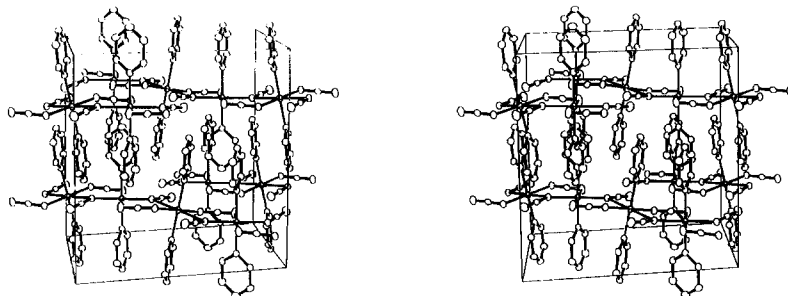


Fig. 2. Unit cell plot of  $\text{Cu}(\text{pyridine})_2(\text{N}_3)_2$  (1), viewed along the  $c$ -axis of the unit cell.

structure of the  $[\text{Cu}(\text{2-benzoylpyridine})_2(\text{N}_3)_2]$  complex (5).<sup>22</sup> The 4-methylpyridine complex features oligomeric edge-sharing chains of polyhedra in which all azido groups, except one terminal group, act as  $\mu(1,1)$  bridging ligands.<sup>20</sup> In the structure of complex 4 the position of the methyl group does not permit such successive  $\mu(1,1)$  azido ligands but allows only the sequence  $\mu(1,1)$ ,  $\mu(1,3)$ ,  $\mu(1,3)$  followed by  $\mu(1,1)$ , and so on. The influence of the methyl group on the relative orientation of the 3-methylpyridine molecules in the polymer is noticeable from Fig. 1 in ref. 21. The structure of the present complex is novel in that two copper(II) centres are simultaneously bridged by  $\mu(1,1)$  and  $\mu(1,3)$  azido ligands.

Structures with a cyclic  $\text{Cu}_2\text{N}_2$  ring are common in the literature of  $\text{CuL}(\text{N}_3)_2$  and  $\text{CuL}_2(\text{N}_3)_2$  [ $\text{L}$  = nitrogen donor ligands and the two azides are  $\mu(1,1)$  bridges] with  $\text{Cu}\cdots\text{Cu}$  separation ranging from 3.08 Å in  $[\text{Cu}(\text{N}_3)_2]_n$ <sup>23</sup> which has infinite chains of planar  $\text{Cu}(\text{N}_3)_2$  units to 3.78 Å in  $\text{CuL}'(\text{N}_3)_2$  [ $\text{L}'$  = (2-aminoethyl)pyridine].<sup>24</sup> Di- $\mu$ -1,3 azido bridges forming an eight-membered  $\text{Cu}(\text{N}_3)_2$  ring may easily force separation of the copper atoms to  $> 5$  Å as found in  $[\text{Cu}(\text{tmen})(\text{N}_3)_2]_2$  (tmen = tetramethylethylenediamine) [ $\text{Cu}\cdots\text{Cu} = 5.004(2)$  Å]<sup>25</sup> and  $[\text{Cu}_2(\text{Me}_6\text{dien})_2(\text{N}_3)_2](\text{BPh}_4)_2$  [ $\text{Cu}\cdots\text{Cu} = 5.227(7)$  Å].<sup>26</sup> The  $\text{Cu}\cdots\text{Cu}$  distance of 4.280(2) Å found in the present complex is longer than the corresponding values in the former complexes but much shorter than those in the latter eight-membered ring complexes. This  $\text{Cu}\cdots\text{Cu}$  separation may be compared with dimeric copper(II) complexes containing  $\mu(1,3)$  and  $\mu(0)$  ligands where the bridging oxygen atom belongs to an alkoxide group,  $[\text{Cu}_2(\text{L-Et})(\text{N}_3)](\text{BF}_4)_2$  [ $\text{Cu}\cdots\text{Cu} = 3.615(3)$  Å].<sup>27</sup>

Although the green  $[\text{Cu}(\text{pyridine})_2(\text{N}_3)_2]_n$  modification contains terminal and  $\mu(1,1,3)$  bridging azides, its IR absorption spectrum has been found to exhibit only a single band at  $2030\text{ cm}^{-1}$  associated with the  $\nu_{\text{as}}\text{N}_3$  mode.<sup>4</sup> The position of this band is not consistent with the  $\nu_{\text{as}}\text{N}_3$  vs  $\Delta d$  relationship reported by Agrell,<sup>28</sup> which predicts two bands around  $2065$  and  $2050\text{ cm}^{-1}$  according to  $\Delta d$  values. The IR spectrum of this brownish complex (1) shows two bands at  $2101\text{ cm}^{-1}$  (m) and  $2030\text{ cm}^{-1}$  (vs). The lower frequency band may be assigned to the  $\nu_{\text{as}}\text{N}_3$  mode of the  $\mu(1,3)$  symmetric azido group,<sup>29,30</sup> whereas the  $2101\text{ cm}^{-1}$  is due to the  $\mu(1,1)$  asymmetric azide, although the position of the latter is not consistent with Agrell's relationship.<sup>28</sup> As found for the green complex (2), we could not locate any absorption band due to  $\nu_s\text{N}_3$  in the region  $1350$ – $1250\text{ cm}^{-1}$  owing to the absorption of the pyridine moiety. In the far IR spectrum we

tentatively assigned to the metal-ligand vibrations the following frequencies<sup>31</sup> ( $\text{cm}^{-1}$ );  $365\text{ m}$ ,  $340\text{ w}$  to  $\nu\text{Cu}-\text{N}(\text{N}_3)$  and the band at  $265\text{ m}$  to  $\nu\text{Cu}-\text{N}(\text{py})$ . Corresponding bands for the green complex (2) have been reported at  $372\text{ m}$  and  $270\text{ vs}$ .<sup>11</sup>

Figure 3 shows the electronic spectrum of the solid complex (1). For comparison we also included the spectrum of the green modification (2). The spectrum of complex 2 shows the  $d-d$  transition band at  $ca\ 15,151\text{ cm}^{-1}$ , whereas that of complex 1 exhibits the corresponding band at  $ca\ 14,610\text{ cm}^{-1}$ , suggesting a strong tetragonal distortion<sup>32,33</sup> in complex 1. While complex 2 shows a pronounced shoulder on the high frequency side of the main  $d-d$  band at  $ca\ 17,543\text{ cm}^{-1}$ , the spectrum of 1 shows a pronounced shoulder on the low frequency side of the charge transfer band at  $ca\ 18,182\text{ cm}^{-1}$ . Copper(II) azido complexes of pyridine derivatives possessing cyclic  $\text{Cu}_2\text{N}_2$  units usually show a distinct absorption band in the range  $17,000$ – $20,000\text{ cm}^{-1}$  due to  $\mu(1,1)\text{N}_3 \rightarrow \text{Cu}$  CT transition.<sup>11,34</sup> In fact, neither complex 1 nor complex 2 possess the cyclic  $\text{Cu}_2\text{N}_2$  units or di- $\mu(1,1)$  azido ligands. Complex 1 possesses mono- $\mu(1,1)$  in addition to the  $\mu(1,3)$  azido ligand between each pair of copper(II) atoms, whereas complex 2 has one azido ligand which functions as  $\mu(1,3)$  between two copper(II) atoms and as  $\mu(1,1)$  between one of the copper(II) atoms and a third copper(II) centre. Thus, in effect both complexes contain a mono- $\mu(1,1)$  bridging azido ligand, and the shoulders in both cases may be taken as evidence for a mono- $\mu(1,1)$  bridging azide in copper(II) azido complexes.

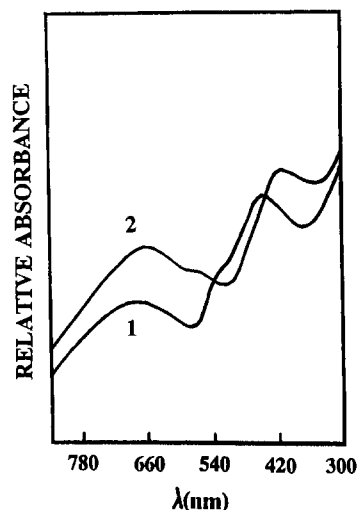


Fig. 3. Reflectance spectra of solid  $\text{Cu}(\text{pyridine})_2(\text{N}_3)_2$  complexes: (1) brownish-green modification; (2) green modification.

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