

Crystal structure and magnetic properties of bis(2,2'-bipyridine) azido copper(II) perchlorate

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The title compound has been synthesized and its crystal structure has been solved at room temperature. It crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 7.853(1) \text{ \AA}$, $b = 10.177(1) \text{ \AA}$, $c = 13.651(4) \text{ \AA}$, $\alpha = 74.57(1)^\circ$, $\beta = 88.49(1)^\circ$, $\gamma = 80.675(4)^\circ$, and $Z = 2$. The structure consists of isolated $[\text{Cu}(\text{bipy})_2\text{N}_3]^+$ cations (bipy = 2,2'-bipyridine) and perchlorate anions. The metallic cation environment has a distorted trigonal-bipyramidal geometry. The EPR spectrum is rhombic, which indicates that the distortion with respect to the perfect trigonal bipyramid is sufficiently pronounced to mix z^2 - and x^2-y^2 -type orbitals in the ground state. The temperature dependence of the molar magnetic susceptibility has been investigated in the 300–2.2 K temperature range.

Introduction

Azido copper(II) complexes have been investigated extensively in the last few years (Kahn and Boillot, 1985). Azido has been used to mimic the peroxo ion in copper(II)-containing oxygen carriers like hemocyanine (McKee *et al.*, 1981) and may be present in met-hemocyanine and met-tyrosinase (Solomon, 1981). It also exhibits quite exceptional structural and magnetic properties when bridging two copper(II) ions. Indeed, it has been shown experimentally and rationalized theoretically that when azido bridges in an end-to-end fashion, it favors a strong antiferromagnetic interaction, and when it bridges in an end-on fashion, it favors a ferromagnetic interaction (Charlot *et al.*, 1986; Comarmond *et al.*, 1982).

In the course of our synthetical work on azido copper(II) compounds, we have isolated well shaped crystals of the title compound. This paper reports on the crystal structure and the magnetic properties of this compound.

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Experimental

Synthesis

2×10^{-3} Mol of bipy = 2,2'-bipyridine and 10^{-3} mol of copper(II) perchlorate were dissolved in 20 ml of a 50/50 mixture acetonitrile-methanol. Then, 10^{-3} mol of sodium azide was added. The solution turned immediately from blue to green. It was filtered. Well-shaped single crystals of $[\text{Cu}(\text{bipy})_2(\text{N}_3)](\text{ClO}_4)$ were obtained by slow evaporation. Anal. calcd for $\text{C}_{20}\text{H}_{16}\text{N}_7\text{O}_4\text{ClCu}$: C, 46.4; H, 3.1; N, 18.9; O, 12.4, Cl, 6.8; Cu, 12.3. Found: C, 46.3; H, 3.1; N, 18.9; O, 12.1; Cl, 6.8; Cu, 12.2.

Crystallographic data collection and refinement of the structure

The X-ray structure determination was carried out at room temperature, on a crystal sealed in a Lindeman glass capillary. Diffraction data were collected on an Enraf-Nonius CAD-4F diffractometer, with the $w/2\theta$ scan technique. Information concerning the crystallographic data collection is given in Table 1. Lattice parameters were refined with 25 reflections in the range $40^\circ \leq \theta \leq 45^\circ$. The compound is very sensitive to exposure of X-rays; from the three crystals used for data

Table 1. Experimental and refinement conditions

Formula	[Cu(NC ₅ H ₄ —H ₄ C ₅ N) ₂ N ₃]ClO ₄
Space group	$P\bar{1}$
Unit cell parameters	$a = 7.853(1) \text{ \AA}$ $b = 10.177(1) \text{ \AA}$ $c = 13.651(4) \text{ \AA}$ $\alpha = 74.57(1)^\circ$ $\beta = 88.49(1)^\circ$ $\gamma = 80.675(4)^\circ$ $V = 1037.60 \text{ \AA}^3$
Number formula unit/cell	$Z = 2$
Mol. wt.	517.388
D_m	$1.64(4) \text{ g cm}^{-3}$
D_x	1.66 g cm^{-3}
Cryst. shape	prismatic
Cryst. size	0.40, 0.25, 0.15 mm
Radiation : Cu $K\alpha$	1.5418 \AA
Monochromator	graphite
Abs. coeff. μ	30.76 cm^{-1}
$(\sin \theta/\lambda)_{\max}$	0.637 \AA^{-1}
Reference reflections	$18\bar{1}, 11\bar{4}, 538$
Number of reflections measured	5260
Number of unique reflections	4060
Number of reflections in refinement (m)	$3199 > 2\sigma(F)$
Number of variable parameters (n)	346
Agreement factors:	
$R(F) = \Sigma F_o - F_c / \Sigma F_o $	4.71 %
$R_w(F) = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$	6.40 %
$S = [\Sigma w(F_o - F_c)^2 / m - n]^{1/2}$	1.21

collection, only one retained enough stability to afford 5260 reflections before a decay of about 30% of the intensity occurred, as revealed by three standards measured every hundred reflections. To get more accuracy, the data were collected partly from the second hemisphere of reflection, the second set being measured after the first one. Decay was then corrected for by scaling. The averaged intensities led to $R_{\text{int}} = 3.7\%$. This low value strongly suggests that the decay correction was reasonable. The data were then corrected for Lorentz-polarization effects, but the rather low absorption coefficient, the quasi isotropic crystal shape, and the impossibility to use the crystal after data collection made this correction unavailing. The structure was solved by direct methods using the program MULTAN (Germain *et al.*, 1971). All nonhydrogen atoms were located after a Fourier synthesis. The structure was refined by the full-matrix least-squares method. The weighting scheme used was: $w^{-1}(F_o) = \sigma^2 \text{count}(F_o) + (0.025F_o)^2$. Scattering factors including real anomalous dispersion correction for Cu and Cl were taken from the *International*

Tables of Crystallography. The nonhydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were determined from a Fourier-difference synthesis, and introduced in refinement with isotropic thermal factors, set equal to 1.5 those of the bound carbon atoms, and were not allowed to vary. The last difference-Fourier synthesis did not show any significant feature. Final agreement factors are given in Table 1.

EPR and magnetic data

The X-band powder EPR spectra were recorded with a ER 200D Bruker spectrometer equipped with a helium continuous-flow cryostat, a hall probe and a frequency meter. The magnetic measurements were carried out with a Faraday-type magnetometer equipped with a helium continuous-flow cryostat. HgCo(NCS)₄ was used as a susceptibility standard. Diamagnetic correction was estimated as $-250 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

Description of the structure

The atomic positions and thermal parameters are given in Tables 2 and 3. Figure 1 shows the coordination around the copper atom.

The unit cell contains two formula units. The structure consists of $[Cu(bipy)_2N_3]^+$ discrete monomeric cationic units and ClO_4^- anions. Each copper(II) ion (see Table 4) is bound to five nitrogen atoms: N(1) of the azido group, N(11) and N(12), and N(21) and N(22), respectively, of the two bipy ligands. The bond lengths and angles around each copper(II) ion show that the resulting coordination geometry is best described as a distorted trigonal bipyramid. The atoms N(1), N(11), N(21) are in the basal trigonal plane with the copper atom deviating by 0.035 Å from it, while N(12) and N(22) occupy the axial positions. The trigonal axis N(12)—Cu—N(22) does not show too much deviation from linearity, and the nitrogen atoms are nearly equidistant from the basal plane. The angles in the trigonal plane depart by a maximum of 15° from the theoretical 120° value. The Cu—N(1) bond length, shorter than the two other Cu—N bonds of the basal plane, involves the azido group. The angles between the Cu—N axial directions with the Cu—N basal plane directions depart by a maximum of 10° from the theoretical 90° value. The mean least-squares planes of the two bipy ligands make an angle of 76°. The angles between these planes and the basal plane are equal to 80° and 90°, respectively.

The values of the angles and distances in N_3^- (Table 5) are consistent with the values in other compounds containing terminal azido groups (Agnus *et al.*, 1979; Agrell, 1966, 1969; Bkouche-Waksman *et al.*, 1983; Bushnell and Khan, 1974). The N_3^- ion is essentially linear, with the Cu—N(1)—N(2) angle comparable to those found in references above; the longer N—N bond length involves the nitrogen atom linked to the copper atom.

The bond lengths within the bipyridine ligand (Table 5) are in agreement with the reported values for the complex $Cu(N_3)_2(bipy)$ (Bushnell and Khan, 1974). The angles of the six membered rings deviate of less than 3° from 120°; the other angles are less regular as expected, and all are comparable with reported values.

The least squares planes show that individually each aromatic ring is planar but the angle between the two rings of the same bipy is equal to 5.6° in both ligands. This departure from planarity, related to rotation about the C—C bond between the six membered rings to

Table 2. Fractional atomic coordinates : For nonhydrogen atoms ($\times 10^4$) and for hydrogen atoms ($\times 10^2$), and equivalent thermal parameters (\AA^2) with esd's in parentheses

	x	y	z	B_{eq}^*
Cu	4356.6	1225.4(4)	2379.5(3)	3.06(1)
Cl	8444(12)	6498.1(8)	2919.8(6)	3.93(2)
O(1)	428(6)	5694(4)	3885(2)	6.9(1)
O(2)	603(6)	7917(3)	2917(4)	7.8(1)
O(3)	2625(5)	6074(4)	2726(3)	7.0(14)
O(4)	-226(5)	6298(4)	2160(3)	6.6(1)
N(1)	1927(4)	1065(4)	2815(3)	4.4(1)
N(2)	721(4)	1480(3)	2249(2)	3.7(1)
N(3)	-469(5)	1880(4)	1712(3)	5.5(1)
N(11)	5934(3)	669(3)	1238(2)	3.0(1)
N(12)	3693(4)	2876(3)	1225(2)	3.0(1)
N(21)	5944(4)	2023(3)	3221(2)	3.0(1)
N(22)	5252(4)	-464(3)	3453(2)	3.2(1)
C(11)	5695(4)	1626(3)	331(2)	2.8(1)
C(12)	6637(5)	2465(4)	-511(3)	3.6(1)
C(13)	7834(5)	278(4)	-435(3)	4.1(1)
C(14)	8069(5)	-702(4)	495(3)	4.2(1)
C(15)	7117(5)	-469(3)	1312(3)	3.6(1)
C(16)	4370(4)	2836(3)	322(2)	2.9(1)
C(17)	3838(5)	3871(4)	-550(3)	3.9(1)
C(18)	2613(5)	4988(4)	-487(3)	4.2(1)
C(19)	1985(5)	5058(3)	448(3)	3.8(1)
C(110)	2505(5)	3976(3)	1286(3)	3.5(1)
C(21)	6831(4)	1049(3)	3897(2)	3.1(1)
C(22)	7973(5)	1364(5)	4608(3)	4.3(1)
C(23)	8280(6)	2720(5)	4412(4)	4.9(1)
C(24)	7403(5)	3712(4)	3603(3)	4.4(1)
C(25)	6237(5)	3326(4)	3044(3)	3.8(1)
C(26)	6427(5)	-363(3)	4110(2)	3.1(1)
C(27)	7188(5)	-1517(4)	4856(3)	4.2(1)
C(28)	6745(6)	-2795(4)	4887(3)	4.7(1)
C(29)	5535(6)	-2881(4)	4208(3)	4.5(1)
C(210)	4775(5)	-1700(4)	3504(3)	4.0(1)
H(12)	63	21(1)	-11(1)	5.4
H(13)	84.1	2(1)	-10(1)	6.1
H(14)	90.1	-16(1)	6(1)	6.2
H(15)	73(1)	-10(1)	20(1)	5.4
H(17)	43(1)	39(1)	-12(1)	5.9
H(18)	23(1)	56(1)	-10(1)	6.3
H(19)	11(1)	57(1)	5.1	5.7
H(110)	21(1)	40(1)	20(1)	5.3
H(22)	85(1)	6(1)	52(1)	6.5
H(23)	91(1)	29(1)	48(1)	7.4
H(24)	76(1)	46(1)	34(1)	6.6
H(25)	56(1)	40(1)	25(1)	5.7
H(27)	79(1)	-13(1)	54(1)	6.3
H(28)	72(1)	-35(1)	53(1)	7.0
H(29)	52(1)	-38(1)	42(1)	6.8
H(210)	39(1)	-17(1)	30(1)	5.9

$$B_{eq}^* = (4/3) \sum_i \sum_j \beta_{ij} a_i^* a_j^*$$

Table 3. Anisotropic thermal parameters ($\times 10^4$)^a

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	149.0(9)	68.9(5)	38.0(3)	-14.7(5)	-8.8(4)	-2(3)
Cl	2202(2)	858(8)	452(5)	-301(9)	-70(7)	-77(5)
O(1)	393(10)	172(5)	58(2)	-72(6)	10(4)	5(3)
O(2)	400(10)	83(3)	153(4)	-24(5)	-67(5)	-29(3)
O(3)	225(7)	217(6)	118(3)	-30(5)	8(4)	-66(4)
O(4)	322(9)	195(6)	73(2)	-37(6)	-457(34)	-42(3)
N(1)	165(6)	130(4)	52(2)	-23(4)	3(3)	6(2)
N(2)	152(5)	88(3)	60(2)	-13(3)	7(3)	-20(2)
N(3)	174(7)	141(5)	101(3)	6(1)	-33(4)	-35(3)
N(11)	123(4)	78(3)	43(2)	-11(3)	-7(2)	-9(2)
N(12)	145(5)	68(3)	38(2)	-13(3)	-7(2)	-6(2)
N(21)	150(5)	76(3)	37(2)	-28(3)	0(2)	-9(2)
N(22)	163(5)	70(3)	41(2)	-18(3)	-5(2)	-2(2)
C(11)	124(5)	73(3)	39(2)	-21(3)	-7(2)	-10(2)
C(12)	166(6)	101(4)	46(2)	-26(4)	4(3)	-21(2)
C(13)	160(6)	125(4)	61(2)	-25(4)	14(3)	-44(3)
C(14)	132(6)	101(4)	82.3(3)	-8.4	0(3)	-35(3)
C(15)	149(6)	78(3)	59(2)	-7(3)	-5(3)	-12(2)
C(16)	134(5)	73(3)	39(2)	-17(3)	-6(2)	-8(3)
C(17)	213(7)	90(4)	40(2)	-11(4)	-8(3)	0(2)
C(18)	191(7)	85(4)	57(2)	-5(4)	-16(3)	9(2)
C(19)	170(6)	74(3)	60(2)	-6(4)	-10(3)	-6(2)
C(110)	167(6)	81(3)	46(2)	-2(4)	0(3)	-11(2)
C(21)	126(5)	102(4)	35(2)	-9(3)	2(2)	-19(2)
C(22)	145(6)	151(5)	57(2)	5(4)	-15(3)	-37(3)
C(23)	173(7)	167(6)	79(3)	-44(5)	9(4)	-60(4)
C(24)	185(7)	124(5)	72(3)	-60(5)	20(4)	-41(3)
C(25)	201(7)	91(4)	50(2)	-54(4)	12(3)	-16(2)
C(26)	136(5)	84(3)	34(2)	9(3)	2(2)	-7(2)
C(27)	177(7)	110(4)	46(2)	29(4)	-5(3)	2(2)
C28	227(9)	85(4)	59(3)	26(4)	15(4)	10(2)
C(29)	229(8)	70(3)	68(3)	-9(4)	26(4)	-3(2)
C(210)	210(7)	75(3)	54(2)	-30(4)	6(3)	-6(2)

^aThe form of the anisotropic thermal parameter is $\exp - [(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2) + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

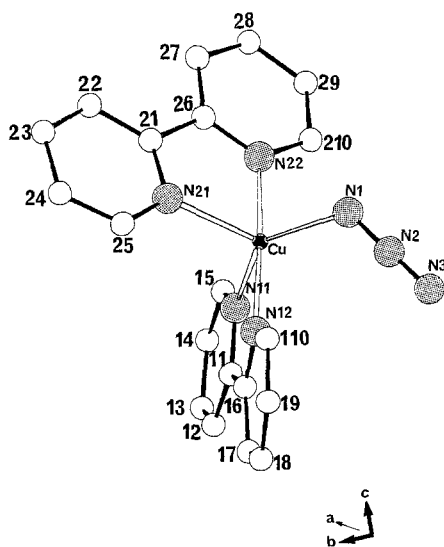


Fig. 1. ORTEP view of the $[\text{Cu}(\text{bipy})_2\text{N}_3]^+$ cation. The white circles labeled only by numbers stand for carbon atoms; the dotted circles stand for nitrogen atoms.

respect the coordination to copper was already observed (Bushnell and Khan, 1974).

The angles and distances in the perchlorate ion (Table 6) are consistent with the values found in the

Table 4. Distances (\AA) and angles ($^\circ$) with esd's in parentheses around the copper atom

Cu—N(1)	2.002(2)	Cu—N(21)	2.105(2)
Cu—N(11)	2.104(2)	Cu—N(22)	1.980(2)
Cu—N(12)	1.982(2)		
N(1)—Cu—N(11)	135.0(1)	N(11)—Cu—N(21)	105.5(1)
N(1)—Cu—N(12)	94.6(1)	N(11)—Cu—N(22)	94.6(1)
N(1)—Cu—N(21)	119.4(1)	N(12)—Cu—N(21)	99.9(1)
N(1)—Cu—N(22)	91.1(1)	N(12)—Cu—N(22)	173.8(1)
N(11)—Cu—N(12)	79.6(1)	N(21)—Cu—N(22)	79.4(1)
Cu—N(1)—N(2)	123.1(3)	Cu—N(21)—C(21)	113.5(2)
Cu—N(11)—C(11)	112.9(2)	Cu—N(21)—C(25)	128.0(2)
Cu—N(11)—C(15)	128.5(2)	Cu—N(22)—C(26)	117.5(2)
Cu—N(12)—C(16)	117.1(2)	Cu—N(22)—C(210)	122.2(2)
Cu—N(12)—C(110)	123.8(2)		

Table 5. Selected bond distances (Å) and angles (°) with esd's in parentheses in the ligands

N(1)–N(2)	1.187(5)	N(1)–N(2)–N(3)	178.9(4)
N(2)–N(3)	1.154(5)		
<i>bipyridine 1</i>			
cycle 1.1	N(11)–C(11)	1.352(4)	cycle 2.1
	C(11)–C(12)	1.383(5)	
	C(12)–C(13)	1.387(5)	
	C(13)–C(14)	1.385(6)	
	C(14)–C(15)	1.378(6)	
C(15)–N(11)	1.344(4)	C(25)–N(21)	1.341(4)
cycle 1.2	N(12)–C(16)	1.337(4)	cycle 2.2
	C(16)–C(17)	1.385(5)	
	C(17)–C(18)	1.385(5)	
	C(18)–C(19)	1.372(5)	
	C(19)–C(110)	1.377(5)	
	C(110)–N(12)	1.356(4)	
C(11)–C(16)	1.476(4)	N(22)–C(26)	1.338(4)
N(11)–C(11)–C(12)	121.8(3)	C(21)–C(21)–C(22)	122.1(3)
C(11)–C(12)–C(13)	119.4(3)	C(21)–C(22)–C(23)	119.0(4)
C(12)–C(13)–C(14)	118.6(4)	C(22)–C(23)–C(24)	118.6(4)
C(13)–C(14)–C(15)	119.2(3)	C(23)–C(24)–C(25)	118.9(4)
C(14)–C(15)–N(11)	122.4(3)	C(24)–C(25)–N(21)	123.0(3)
C(15)–N(11)–C(11)	118.5(3)	C(25)–N(21)–C(21)	118.4(3)
N(11)–C(11)–C(16)	114.7(3)	N(21)–C(21)–C(26)	114.1(3)
N(12)–C(16)–C(17)	121.3(3)	N(22)–C(26)–C(27)	121.2(3)
C(16)–C(17)–C(18)	119.6(3)	C(26)–C(27)–C(28)	118.4(3)
C(17)–C(18)–C(19)	118.9(3)	C(27)–C(28)–C(29)	119.7(4)
C(18)–C(19)–C(110)	119.1(3)	C(28)–C(29)–C(210)	119.7(3)
C(19)–C(110)–N(12)	122.0(3)	C(29)–C(210)–N(22)	120.7(4)
C(110)–N(12)–C(16)	118.9(3)	C(210)–N(22)–C(26)	120.3(3)
N(12)–C(16)–C(11)	115.4(3)	N(22)–C(26)–C(21)	115.4(3)

Table 6. Bond distances (Å) and angles (°) in the perchlorate anion and smallest contact distances with esd's in parentheses

perchlorate anion			
Cl–O(1)	1.415(4)	Cl–O(3)	1.434(4)
Cl–O(2)	1.424(3)	Cl–O(4)	1.427(4)
O(1)–Cl–O(2)	109.6(3)	O(2)–Cl–O(3)	108.5(3)
O(1)–Cl–O(3)	108.9(3)	O(2)–Cl–O(4)	110.6(4)
O(1)–Cl–O(4)	109.3(2)	O(3)–Cl–O(4)	110.0(2)
Smallest contact distances between perchlorate anion and the ligands of the complex cation, and between ligands.			
O(1)–C(23) ^{ia}	3.419(6)	N(22)–C(15) ^{ic}	3.235(5)
O(2)–C(15) ^{ib}	3.455(6)	N(1)–N(22)	2.842(4)
O(2)–N(1) ^{ic}	3.493(5)	N(1)–N(12)	2.928(4)
O(3)–C(110)	3.277(5)	N(1)–C(110)	3.231(5)
O(4)–C(19) ^{id}	3.274(5)	N(1)–C(210)	3.235(5)
N(11)–N(22)	3.003(4)	N(2)–N(12)	3.044(5)
N(21)–N(12)	3.130(4)	N(2)–C(110)	3.069(5)

^(ia) $1 - x, 1 - y, 1 - z$ ^(ib) $-1 + x, 1 + y, z$ ^(ic) $x, -1 + y, z$ ^(id) $1 + x, y, z$

literature. The smallest contact distances between perchlorate anion and ligands of the complex cation, and between ligands are given in Table 6. The interesting structural feature is that the shortest Cu \cdots Cu($1 - x, -y, 1 - z$) distance, equal to 6.964(2) Å, is associated with the stacking of two centrosymmetrically related pyridine 2 planes at 3.38 Å from each other, with a noticeable overlapping as illustrated in Fig. 2. The intermolecular distances C22 \cdots C210, C26 \cdots C26 and C28 \cdots N21 involving atoms belonging to bipy groups are rather short, namely 3.37, 3.41, and 3.47 Å, respectively, which reveals some π - π interaction between aromatic rings.

Discussion

Five coordinate copper(II) complexes of the type [Cu(bipy)₂X]Y where X is a monodentate ligand and Y a counteranion are now well documented, in particular thanks to the work carried out by Hathaway (Foley *et*

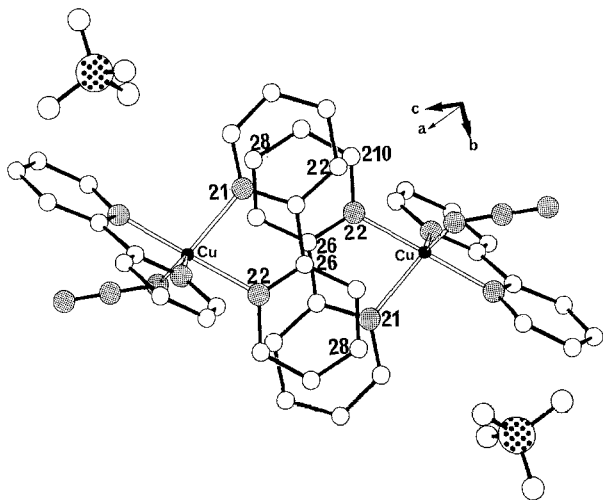


Fig. 2. ORTEP view in the plane of bipyridine 2 showing the stacking of two centrosymmetrically related planes. Small and large dotted circles stand for nitrogen and chlorine atoms, respectively. White circles stand for carbon or oxygen atoms, indifferently.

al., 1984; Hathaway and Billing, 1970; Tyagi and Hathaway, 1981, 1983; Tyagi *et al.*, 1984). According to the nature of X, Y, and of eventual noncoordinated solvent molecules, the geometry is that of a more or less distorted trigonal bipyramid. In the present case, the situation is very close to that encountered, for instance, with $[\text{Cu}(\text{bipy})_2(\text{NH}_3)](\text{BF}_4)$ (Dudley *et al.*, 1974), $[\text{Cu}(\text{bipy})_2(\text{CN})(\text{NO}_3) \cdot 2\text{H}_2\text{O}]$ (Tyagi and Hathaway, 1983) and $[\text{Cu}(\text{bipy})_2(\text{NCS})(\text{BF}_4)]$ (Tyagi and Hathaway, 1981). The X-band powder EPR spectrum was recorded at several temperatures in the range 300–4.2 K. At room temperature, the spectrum is rhombic with $g_1 = 2.02$, $g_2 = 2.14$, and $g_3 = 2.23$, as shown in Fig. 3. It does not vary significantly upon cooling down. From the EPR data, it appears that the ground state of the $[\text{Cu}(\text{bipy})_2(\text{N}_3)]^+$ cation is not purely of the z^2 -type, z being the axis of the trigonal bipyramid. The distortion with respect to the perfect D_{3h} geometry is too pronounced, which couples the z^2 - and x^2-y^2 -type states. It is worth noting that an almost pure z^2 -type state has been reported for $[\text{Cu}(\text{bipy})_2\text{Cl}](\text{PF}_6) \cdot \text{H}_2\text{O}$ (Tyagi and Hathaway, 1984). In this compound, the bond angles in the equatorial plane range from 116° to 124° instead of 105° to 135° in $[\text{Cu}(\text{bipy})_2(\text{N}_3)](\text{ClO}_4)$.

The molar magnetic susceptibility of $[\text{Cu}(\text{bipy})_2(\text{N}_3)](\text{ClO}_4)$ has also been measured in the 300–2.2 K temperature range. Down to ca. 10 K, the product $\chi_M T$ of the molar magnetic susceptibility by the temperature is constant and equal to $0.420(5) \text{ cm}^3 \text{ K mol}^{-1}$, which closely follows what is expected for isolated copper(II) ions, i.e., $\chi_M T = N\beta^2 g^2 / 4K$, the symbols having their usual meaning. The average value of

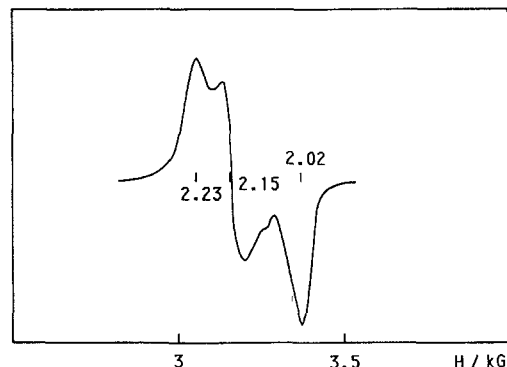


Fig. 3. X-band powder EPR spectrum for $[\text{Cu}(\text{bipy})_2\text{N}_3](\text{ClO}_4)$.

the g -factor deduced from the magnetic data is $g = 2.12$, in agreement with the EPR data. Indeed, $(g_1^2 + g_2^2 + g_3^2)/3$ is equal to 2.13. Upon cooling down further below 10 K, $\chi_M T$ smoothly decreases to reach $0.380(10) \text{ cm}^3 \text{ K mol}^{-1}$ at 2.2 K. This low temperature behavior is due to very weak intermolecular interactions within the crystal lattice.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60746 (28 pages).