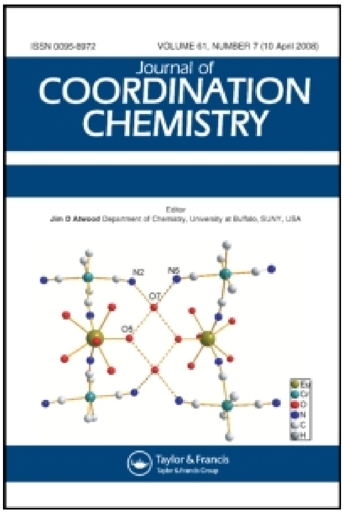

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CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF A POLYMERIC (μ-1,3-AZIDO) COPPER(II) COMPOUND, *catena*-[Cu(BIPYRIMIDINE)(μ-1,3-N_3)(N_3)]$_n$

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The X-ray structure of the title compound has been determined together with spectroscopical measurements. The structure forms an infinite alternating one-dimensional polymeric structure *via* the μ-1,3-bridging azido anion and chelating bipym ligands.

Keywords: Bridging-azido; polymer; copper(II); bipyrimidine; X-ray structure

INTRODUCTION

2,2′-Bipyrimidine (hereafter abbreviated as bipym) is a very useful tool in synthesizing dinuclear copper(II) complexes and can act both as a didentate chelating or as a bridging bis-didentate ligand.[1] On the other hand the azide group is a very versatile anion which can coordinate to copper(II) either in a monodentate or bridging fashion to yield mono- or polynuclear species. Two bridging modes of N_3^- are known, end-to-end (μ-1,3) and end-on (μ-1,1), of which the latter is the more common.[2,10]

Until now only two copper(II) crystal structures are known containing both bipyrimidine ligand and the azido anion, *i.e.*, [Cu_2(bipym)(N_3)$_4$] which

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contains[2] bridging bipym ligands, monodentate azide anions and end-to-end azide bonding, and $[Cu_2(bipym)_3(N_3)_2(CH_3OH)_2](CF_3SO_3)_2(CH_3OH)_2$ which contains[3] bis-didentate and didentate bipym ligands and monodentate coordinating azido anions.

In this paper we describe the first polynuclear compound, $[Cu(bipym)(\mu\text{-}1,3\text{-}N_3)(N_3)]_n$, in which bipym acts as a didentate ligand and the azide anions as monodentates and bridging in an end-to-end (μ-1,3) fashion.

EXPERIMENTAL

Preparation

The title compound was prepared according to the following procedure. Some 1.2 mmol of Cu(II) triflate and 1.2 mmol of bipym were each dissolved in 10 cm^3 of methanol and carefully mixed together. Then, a solution of 1.2 mmol sodium azide dissolved in *ca* 0.5 cm^3 of water was added slowly to the copper(II) bipym solution in such a way that no precipitate formed. If a little precipate tended to form the addition was stopped. The solution was filtered and left to stand for some days. Then it was filtered again and after some weeks green crystals separated, and which were isolated by filtration and dried in air.

Anal. Calcd. for $CuC_8H_6N_{10}$(%): C, 31.43; H, 1.98; N, 45.81; Cu, 20.78. Found: C, 31.60; H, 1.98; N, 46.35; Cu, 19.84.

Physical and Analytical Measurements

C, H, N and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland. Electronic spectra were obtained on a Perkin-Elmer 330 spectrophotometer using the diffuse reflectance technique, with MgO as reference. X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as standard. FTIR spectra were obtained on a Bruker 113v infrared spectrophotometer for KBr disks (4000–400 cm^{-1}, mirror velocity 0.166 cm/s, resolution 2 cm^{-1}).

Crystal Structure Determination

X-ray diffraction data were collected on a Enraf-Nonius CAD4T diffractometer at 150 K [rotating anode, 60 kV, 50 mA, graphite-monochromated MoKα radiation, ω-scan mode, $\theta_{max} = 27.5°$]. Unit-cell parameters were checked for the presence of higher lattice symmetry.[4] A total of 2844 reflections were scanned. The structure was solved by direct methods (SHELXS86).[5] Neutral atom scattering factors and anomalous dispersion factors[6] were used. Calculations were performed with programs SHELXL93[7] and PLATON[8] on a DEC-5000 cluster. The structure refined on F^2 to $R_1 = 0.043$ for 1948 reflections with $F_o > 4\sigma(F_o)$ ($wR_2 = 0.100$ for 2491 unique reflections, $\Delta\rho < 0.76\,\text{e/Å}^3$).

RESULTS AND DISCUSSION

Crystal Structure

Crystal data: [($C_8H_6N_{10}Cu$): $FW = 305.75$, green, crystal size: $0.05 \times 0.08 \times 0.63$ mm, triclinic, space group P-1, $a = 5.0128(7)$, $b = 10.190(2)$, $c = 11.578(3)$ Å, $\alpha = 68.329(14)°$, $\beta = 84.065(14)°$, $\gamma = 87.645(11)°$, $V = 546.7(2)$ Å^3, $Z = 2$, *dens.* (*calc*) $= 1.857\,\text{g cm}^{-1}$, $F(000) = 306$, $\mu(\text{MoK}\alpha) = 20.0\,\text{cm}^{-1}$.

Figure 1 shows the structure with the atom labelling scheme; relevant bond distances and bond angles are given in Table I. Atomic positions are listed in Table II. The title compound consists of a copper ion with square pyramidal geometry; the square plane is formed by two nitrogen atoms of a bipym ligand (Cu1–N11 2.010(3), Cu1–N21 2.027(3) Å), a nitrogen atom of a monodentate azide anion (Cu1–N4 1.945(3) Å) and a nitrogen atom of the end-to-end bridging azide anion (Cu1–N3a 1.963(3) Å). The fifth

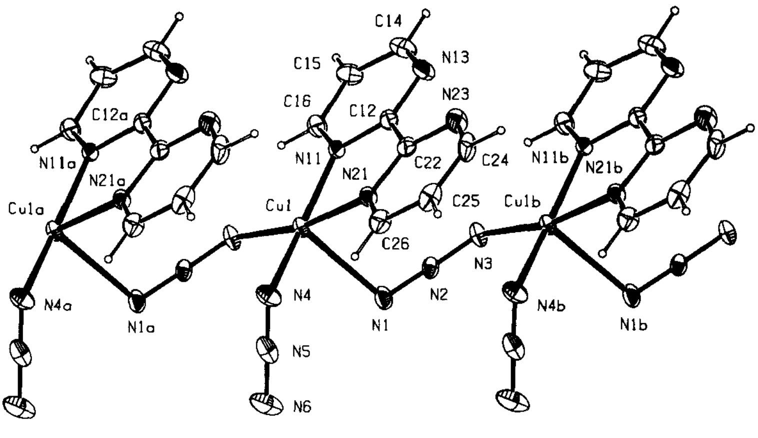

FIGURE 1 ORTEP 30% probability plot of $[\text{Cu(bipym)}(\mu\text{-}1,3\text{-}N_3)(N_3)]_n$ with the atom labelling scheme. Atoms marked with "a" and "b" are generated by translation symmetry.

TABLE I Selected bond distances and angles

Bond distances (Å)			
Cu(1)–N(1)	2.437(3)	N(1)–N(2)	1.155(4)
Cu(1)–N(4)	1.945(3)	N(2)–N(3)	1.200(4)
Cu(1)–N(11)	2.010(3)	N(4)–N(5)	1.196(5)
Cu(1)–N(21)	2.027(3)	N(5)–N(6)	1.155(5)
Cu(1)–N(3)a	1.963(3)		
Bond angles (deg)			
N(1)–Cu(1)–N(4)	93.99(13)	N(3)a–Cu(1)–N(21)	167.91(14)
N(1)–Cu(1)–N(11)	90.92(12)	Cu(1)–N(1)–N(2)	107.5(3)
N(1)–Cu(1)–N(21)	90.47(12)	N(1)–N(2)–N(3)	177.8(4)
N(1)–Cu(1)–N(3)a	97.57(12)	Cu(1)b–N(3)–N(2)	122.9(3)
N(4)–Cu(1)–N(11)	171.61(14)	Cu(1)–N(4)–N(5)	117.0(3)
N(4)–Cu(1)–N(21)	92.99(14)	N(4)–N(5)–N(6)	177.0(4)
N(3)a–Cu(1)–N(4)	95.42(14)	Cu(1)–N(11)–C(12)	115.2(3)
N(11)–Cu(1)–N(21)	80.16(13)	Cu(1)–N(11)–C(16)	126.8(3)
N(3)a–Cu(1)–N(11)	90.66(13)		

TABLE II Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $[Cu(bipym)(\mu\text{-}1,3\text{-}N_3)(N_3)]_n$

Atom	*x/a*	*y/b*	*z/c*	*U*(eq) (Å^2)
Cu(1)	0.55133(9)	0.17203(5)	0.23784(4)	0.0144(1)
N(1)	0.8444(6)	0.2368(3)	0.3634(3)	0.0200(11)
N(2)	1.0432(6)	0.1754(3)	0.3630(3)	0.0153(10)
N(3)	1.2453(6)	0.1075(3)	0.3650(3)	0.0190(11)
N(4)	0.4168(7)	0.3632(3)	0.1599(3)	0.0209(12)
N(5)	0.3869(6)	0.4336(3)	0.2232(3)	0.0216(12)
N(6)	0.3591(8)	0.5068(4)	0.2796(4)	0.0341(12)
N(11)	0.7044(6)	−0.0246(3)	0.2928(3)	0.0147(10)
N(13)	1.0813(6)	−0.1571(3)	0.2537(3)	0.0221(12)
N(21)	0.8564(6)	0.1997(3)	0.1018(3)	0.0161(10)
N(23)	1.2429(6)	0.0832(4)	0.0460(3)	0.0229(12)
C(12)	0.9357(7)	−0.0398(4)	0.2275(3)	0.0168(12)
C(14)	0.9858(8)	−0.2678(4)	0.3529(4)	0.0252(12)
C(15)	0.7501(8)	−0.2625(4)	0.4236(4)	0.0229(12)
C(16)	0.6123(7)	−0.1364(4)	0.3909(3)	0.0186(12)
C(22)	1.0198(7)	0.0878(4)	0.1184(3)	0.0173(12)
C(24)	1.2962(7)	0.2026(5)	−0.0535(4)	0.0259(14)
C(25)	1.1391(8)	0.3216(4)	−0.0795(3)	0.0235(12)
C(26)	0.9172(8)	0.3166(4)	0.0029(3)	0.0213(12)

U(eq)* = 1/3 of the trace of the orthogonalized *U* tensor.

position is also occupied by a nitrogen of the end-to-end bridging azide anion (Cu1–N1 2.437(3) Å).

The angles of the square plane are 171.61(14)° (N4–Cu1–N11) and 167.91(14)° (N3a–Cu1–N21), in which the Cu atom lies only 0.117(1) Å above the plane towards N1, with an angle N1–Cu1–N11 of 90.92(12)°. The Cu atoms are at a long distance of 5.0128(7) Å from each other, while

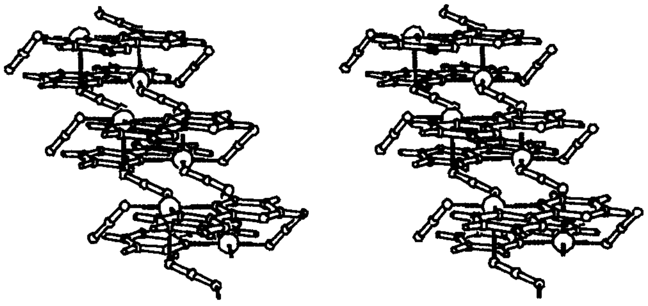

FIGURE 2 Stereo drawing of the structure along the *z* axis showing the alternating chain.

each azido anion is almost linear (N1–N2–N3 177.8(4)°, N4–N5–N6 177.0(4)°). All other bipym and azido distances and angles are consistent with those reported in the literature.[2,3,9,11]

The structure forms an alternating one-dimensional polymeric structure *via* the μ-1,3-bridging azido anion (see stereo drawing, Figure 2) in which the N6 atom of the monodentate azido anion forms weak hydrogen bonding contacts with neighbouring C atoms of the bipyrimidine rings (C14–H14···N6a 3.202(6), C25–H25···N6b 3.304(6) Å). This packing is uncommon as in most structures with the same chromophore (CuN_4N_{azide}) and square pyrimidal geometry the azide anion tends to form a μ-1,1-bridge to produce a sheet-like polymeric structure.[12,13]

Infrared Spectroscopy

Characteristic asymmetric N_3 stretching vibrations are found at 2062 and 2031 cm^{-1}; the higher frequency can be assigned to bridging N_3 and the lower frequency to the terminal N_3 anion.[12,14,15] The symmetric N_3 stretching vibration is found at 1344 cm^{-1} as a split band of medium intensity. Characteristic vibrations of the bipym ligand are found as a *quasi*-symmetric doublet at 1594–1557 cm^{-1}, which is diagnostic for the didentate coordinated bipym ligand.[11]

Electronic Spectroscopy

Ligand field spectra shows a broad band centred at $15.9 \times 10^3\,cm^{-1}$, typical for Cu(II) with square-pyrimidal geometry.[16,17] The EPR signal shows an uneventful spectrum for a $d_{x^2-y^2}$ ground state[19] with an unresolved $g_{\parallel}$ (measured as a solid at RT of $g_{\perp}$ 2.06 and $g_{\parallel}$ of 2.21), indicative of exchange narrowing.

This structure almost matches the dinuclear copper compound $[Cu_2(L^1)_2(N_3)_3]Cl \cdot 2H_2O$ (in which $L^1 = \{$1-(imidazol-4-yl)-2-[(2-pyridylmethylene)amino]ethane$\}$).[18,19] The latter has the same basic chromophore, the same square pyrimidal geometry in which the apical nitrogen atom from the bridging μ-1,1-azido anion has a distance of 2.465(6) Å, the same EPR spectrum and a d–d transition at $14.7 \times 10^3\,cm^{-1}$. However, it is a dinuclear compound (with a Cu–Cu distance of 6.785(6) Å) probably forced by the tridentate ligand (whereas bipyrimidine is a didentate ligand).

Supplementary Material

Tables of atomic coordinates, bond lengths and angles for all atoms, thermal parameters and tables of calculated and observed structure factors are available as supplementary material and may be obtained from one of the authors (A.L.S.).

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