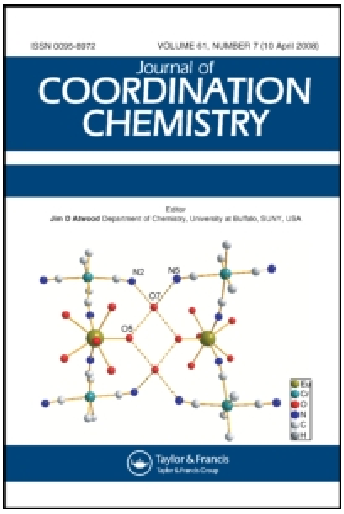

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Synthesis, Characterization and Crystal Structure of a One-Dimensional Chain Copper Bipyridine Complex Bridged Through an Azobispyridine Ligand

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A ONE-DIMENSIONAL CHAIN COPPER BIPYRIDINE COMPLEX BRIDGED THROUGH AN AZOBISPYRIDINE LIGAND

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The copper complex $\{[Cu(2,2'\text{-bpy})(azpy)(H_2O)(ClO_4)\}_n$ **1** (2,2′-bpy=2,2′bipyridine, azpy=4,4′-azopyridine), has been synthesized and characterized. X-ray analysis reveals that copper is coordinated by two N atoms of 2,2′-bpy, two N atoms from two bridging azpy ligands, one O atom of coordinated water and O atom from ClO_4^- and has a distorted octahedral coordination environment in complex **1**. Copper ions are linked to each other through bridging azpy ligands to form a one-dimensional chain. Stacking the one-dimensional chains results in the formation of rhombic channels with *ca.* 6 Å × 6 Å. Variable-temperature magnetic susceptibility studies show that there is a weak antiferromagnetic interaction between the copper ions.

Keywords: Crystal structure; Copper complex; Azobispyridine; Bipyridine

INTRODUCTION

Crystal engineering of supramolecular architectures sustained by coordination covalent bonds or hydrogen bonds represents a rapidly expanding field that offers potential for development of new classes of functional solids [1,2]. It is now established that the architectures of coordination polymers can be reliably predicted, since previously known metal coordination environments are propagated into one-, two-, and three-dimensional motifs with rigid multitopic organic "spacer" ligands. The formation of an open framework structure based on coordination chemistry with zeolite-like molecular-sized channels, cavities and pores is of current interest [3–5]. A convenient path to

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obtain polymeric structures is to use a bifunctional ligand, such as pyrazine, 4,4′-bipyridine and 4,4′-azobispyridine, to link metal ions to form an infinite configuration [6–20]. In the present work, we report the crystal structure of a one-dimensional chain copper complex, $\{[Cu(2,2'\text{-bpy})(azpy)(H_2O)(ClO_4)](ClO_4)\}_n$ **1**.

EXPERIMENTAL

Physical Measurements

Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region. ESR spectra were recorded on a Er2000-SRC instrument. Magnetic susceptibilities were measured in the solid state using a CAHN-2000 Faraday balance with $[Ni(en)_2]S_2O_3$ as a standard at 6000 G magnetic field.

Preparation

A solution of 2,2′-bpy (0.156 g, 1.0 mmol) in 20 mL H_2O/EtOH (1 : 1, v/v) was added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1.0 mmol) in 10 mL H_2O, then a solution of 4,4′-azobispyridine (azpy) [21] (0.184 g, 1.0 mmol) in 20 mL H_2O/EtOH (1 : 1, v/v) was added to the above solution with stirring. After about two weeks, the product $\{[Cu(2,2'\text{-bpy})(azpy)(H_2O)(ClO_4)](ClO_4)\}_\infty$ was obtained in 85% yield. The deep-green crystals suitable for x-ray diffraction analysis were isolated by slow evaporation of the solution at room temperature. *Anal.* calcd. for $C_{20}H_{18}Cl_2CuN_6O_9$ (%): C, 38.69; H, 2.90; N, 13.54. Found: C, 38.43; H, 2.62; N, 13.25.

Crystal Structure Determination

A deep-green single crystal of $\{[Cu(2,2'\text{-bpy})(azpy)(H_2O)(ClO_4)](ClO_4)\}_\infty$ with approximate dimensions $0.75 \times 0.35 \times 0.075$ mm was mounted on a glass fibre and used for data collection. Cell constants for data collection were obtained by least-squares refinement of diffraction data from 25 reflections in the range $12.99° < \theta < 14.94°$ using an Enraf-Nonius CAD4 four-circle diffractometer. Data were collected at 293(2) K using with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) and ω-2θ scan mode, and were corrected for Lorentz and polarization effects. A semi-empirical absorption correction (Psi scan) was made. The structure was solved by direct methods (SHELX-86 [22]) and refined with full-matrix least-squares technique (SHELX-93 [23]). The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated using idealized geometry. A summary of the crystal data, experimental details and refinement result are listed in Table I. Atomic coordinates of non-hydrogen atoms are given in Table II. Complete tables of atomic coordinates and thermal parameters, excluding structure factors, are available from the authors upon request.

TABLE I Crystal data and structure refinement for complex **1**

Empirical formula	$C_{20}H_{18}Cl_2CuN_6O_9$
Temperature	293(2) K
Formula weight	620.84
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.071(2)
b (Å)	9.114(2)
c (Å)	17.051(3)
α (°)	87.75(3)
β (°)	83.63(3)
γ (°)	75.91(3)
Volume (Å^3)	1208.9(4)
Z	2
D_{calc} (g/cm^3)	1.706
Absorption coefficient	1.189 mm^{-1}
F(000)	630
Crystal size	0.75 × 0.35 × 0.075 mm
θ range for data collection	1.20°–25.97°
Index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $0 \le l \le 20$
Refinement method	Full-matrix least-sqaures on F^2
Data/restraints/parameters	4721/0/343
Goodness-of-fit on F^2	1.052
Final $R1$ and wR^2 [$I > 2\sigma(I)$]	0.0633, 0.1673
$R1$ and $wR2$ indices (all data)	0.0840, 0.1794
Largest diff. Peak and hole	0.881 and −0.806 eÅ^{-3}

$W = 1/[\sigma^2(Fo^2) + (0.1058P)^2 + 1.0420P]$, $P = [Fo^2 + 2Fc^2]/3$.

RESULTS AND DISCUSSION

Crystal Structure

The selected bond lengths and angles are listed in Table III. The X-ray analysis reveals that the copper ion has a distorted octahedral coordination environment in complex **1** (Fig. 1). Copper is coordinated by two N atoms (N1 and N2) of 2,2′-bpy and two N atoms (N3 and N5) from two bridging ligand azpy [Cu(1)–N(1),1.990(4) Å; Cu(1)–N(2), 2.021(4) Å; Cu(1)–N(3), 2.004(4) Å; Cu(1)–N(5), 2.026(4) Å] at equatorial positions and one O(1) atom of water and one O(13) atom from ClO_4^-[Cu(1)–O(1), 2.414(4) Å; Cu(1)–O(13), 2.817(9) Å] at the apical positions. The coordination mode of the octahedron is similar to [Cu(2,2′-bpy)(4,4′-bpy)$(ClO_4)_2$] [24], but with the difference of two oxygen atoms at apical positions from H_2O and ClO_4^- in title complex, and from two ClO_4^- in the latter.

Azpy exhibits a *trans*-form. The coordination plane defined by Cu(1), N(1), N(2), N(3) and N(5) is poorly coplanar and the mean derivation from the least squares plane is 0.2731 Å. Cu(1), N(1), N(2), N(3) and N(5) deviate from the mean plane −0.1126, −0.3076, −0.3621, −0.2625 and −0.3205 Å, respectively. Cu(1), N(1) and N(3) are below the mean plane while N(2) and N(5) are above the mean plane. The angles N(1)–Cu(1)–N(3) and N(2)–Cu(1)–N(5) are 167.8(2)° and 153.2(2)°, respectively, which are 12° and 27° deviation from 180.0°, respectively. The angles N(1)–Cu(1)–N(2), N(3)–Cu(1)–N(2), N(1)–Cu(1)–N(5) and N(3)–Cu(1)–N(5) are 80.8(2)°, 94.6(2)° and 93.9(2)°, respectively. The angle O(1)–Cu(1)–O(13A) is 163.8(2)°. The dihedral angle

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement ($\text{Å} \times 10^3$) for compound **1**; U(eq) is defined as one third of trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cu(1)	19555(1)	5304(1)	7363(1)	33(1)
Cl(1)	23098(2)	5935(2)	8700(1)	61(1)
Cl(2)	15989(2)	1593(2)	6441(1)	61(1)
O(1)	16826(5)	5472(4)	6868(2)	52(1)
O(11)	24272(9)	6245(10)	8115(6)	159(4)
O(12)	24113(13)	5289(13)	9263(6)	189(4)
O(13)	22170(10)	5124(8)	8353(7)	176(4)
O(14)	21960(9)	7364(8)	8917(4)	127(3)
O(21)	16352(16)	619(9)	5818(5)	202(6)
O(22)	15925(7)	3077(5)	6125(3)	81(1)
O(23)	14429(8)	1475(9)	6834(4)	123(2)
O(24)	17258(9)	1231(10)	6955(6)	169(4)
N(1)	20628(5)	4150(4)	6394(2)	34(1)
N(2)	20805(5)	6804(4)	6830(2)	38(1)
N(3)	18174(5)	6760(4)	8178(2)	36(1)
N(4)	14940(7)	10177(6)	9675(3)	62(1)
N(5)	19421(5)	3454(4)	8043(2)	32(1)
N(6)	19319(5)	220(4)	9844(2)	39(1)
C(1)	20327(7)	2838(5)	6184(3)	43(1)
C(2)	20986(8)	2205(6)	5464(3)	53(1)
C(3)	21994(8)	2882(7)	4944(3)	55(1)
C(4)	22280(7)	4237(6)	5153(3)	47(1)
C(5)	21596(6)	4837(5)	5888(3)	36(1)
C(6)	21803(6)	6290(5)	6167(3)	35(1)
C(7)	22932(7)	7074(6)	5788(3)	53(1)
C(8)	23073(8)	8401(7)	6109(4)	58(2)
C(9)	22085(8)	8912(6)	6784(4)	58(2)
C(10)	20964(7)	8093(6)	7138(3)	51(1)
C(11)	17128(6)	8037(5)	7921(3)	46(1)
C(12)	16116(7)	9111(6)	8415(4)	55(1)
C(13)	16121(7)	8884(6)	9206(4)	54(2)
C(14)	17160(7)	7576(7)	9493(3)	56(2)
C(15)	18184(6)	6551(6)	8952(3)	43(1)
C(16)	17960(6)	3336(5)	8461(3)	37(1)
C(17)	17905(6)	2269(5)	9050(3)	40(1)
C(18)	19422(6)	1276(5)	9214(3)	33(1)
C(19)	20924(6)	1344(5)	8758(3)	39(1)
C(20)	20884(6)	2444(5)	8183(3)	37(1)

TABLE III Selected bond lengths (Å) and angles (°) for complex **1**

Cu(1)–N(1)	1.990(4)	Cu(1)–N(2)	2.021(4)
Cu(1)–N(3)	2.004(4)	Cu(1)–N(5)	2.026(4)
Cu(1)–O(1)	2.414(4)	Cu(1)–O(13)	2.817(9)
N(1)–Cu(1)–N(3)	167.8(2)	N(1)–Cu(1)–N(2)	80.8(2)
N(3)–Cu(1)–N(2)	94.6(2)	N(1)–Cu(1)–N(5)	95.3(2)
N(3)–Cu(1)–N(5)	93.9(2)	N(2)–Cu(1)–N(5)	153.2(2)
N(1)–Cu(1)–O(1)	86.8(2)	N(3)–Cu(1)–O(1)	84.5(2)
N(2)–Cu(1)–O(1)	112.5(2)	N(5)–Cu(1)–O(1)	93.6(2)
N(1)–Cu(1)–O(13)	107.1(2)	N(3)–Cu(1)–O(13)	82.9(2)
N(2)–Cu(1)–O(13)	78.8(2)	N(5)–Cu(1)–O(13)	77.1(2)
O(1)–Cu(1)–O(13)	163.8(2)		

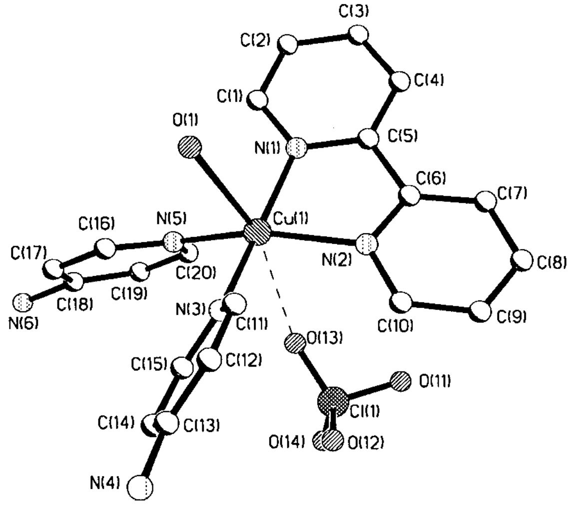

FIGURE 1 The local coordination of copper in complex **1** with 30% thermal ellipsoids.

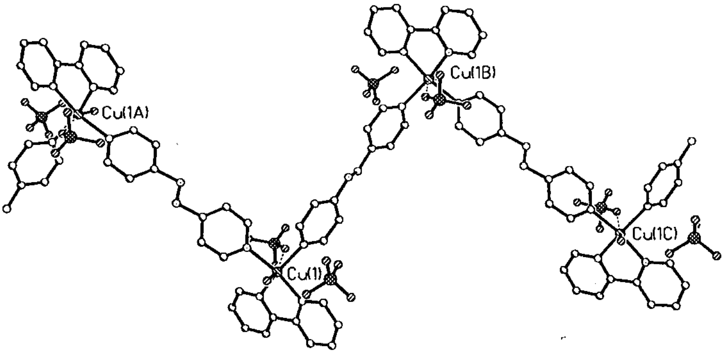

FIGURE 2 Viewing of the one-dimensional chain structure in complex **1**.

between the O(1), Cu(1) and O(13) plane and equatorial coordination plane is 96.1°. From the bond lengths and angles, we can see that copper has a distorted octahedral geometry. Two pyridyl rings of 2,2′-bpy are not coplanar with a dihedral angle 9.5°. N(1) and N(2) pyridyl rings are not coplanar with the Cu(1) coordination plane. The two pyridyl rings of azpy are coplanar but not coplanar with Cu(1) coordination plane.

Each copper ion is coordinated by two azpy ligands and each azpy links two copper ions, which result in the formation of a one-dimensional zigzag chain (Fig. 2). The distance between two adjacent Cu(II) atoms linked by azpy is 12.997 Å for Cu(1) and Cu(1A) and 12.887 Å for Cu(1) and Cu(1B). The distance of two alternative copper ions in the same chain (for example, between Cu(1) and Cu(1C)) is 18.049 Å. The angle Cu(1A)–Cu(1)–Cu(1B) is 88.4°C. The copper is coordinated by O(1) atom of water molecule and O(13) atom of perchlorate at the apical positions. Each coordinated water molecule forms two hydrogen bonds with O(11) and O(22) of perchlorate [O(1)–O(11), 2.773 Å; O(1)–O(22), 2.844(6) Å]. the zigzag chains are linked *via* perchlorate through hydrogen bonding [O(1)–O(11)] and coordination bonding [O(13)–Cu] to form a rhombus channel *ca.* 6 Å × 6 Å (Fig. 3). Although there is overlap between the 2,2′-bpy molecules and between azpy molecules, the pyridyl rings of the 2,2′-bpy molecules and of the azpy molecules are not involved in π–π interactions due to the long distances. This structure is different from the similar one-dimensional chain complexes [20,27]. $\{[Fe(azpy)(NCS)_2(MeOH)_2]\cdot azpy\}_n$ is a one-dimensional chain structure and forms a two-dimensional structure *via* hydrogen bonding and π–π interactions [20]. $[Cu(dmp)(4,4'\text{-}bpy)]BF_4\cdot MeCN$ and $[Cu(dmp)(bpe)]BF_4$ (dmp=2,9-dimethyl-1,10-phenanthroline, bpe=trans-1,2-bis(pyridin-4-yl)ethene) are one-dimensional zig-zag chain structures and π–π stacking interactions occur in these two complexes [27].

Infrared Spectra, ESR and Magnetic Measurements

IR spectra of **1** show bands as follows: 3458 m, 3114 m, 3088 m, 1657 w, 1611 v, 1570 s, 1539 w, 1498 m, 1476 s, 1444 v, 1423 v, 1318 s, 1248 w, 1235 w, 1224 w, 1172 m, 1099 v, 1062 v, 1030 s, 930 m, 852 m, 817 m, 770 m, 731 m, 662 w, 643 m, 622 v, 580 m, 553 w, 530 w and 472 w cm^{-1}. The N=N stretch vibration of the azo [21,25] group appears

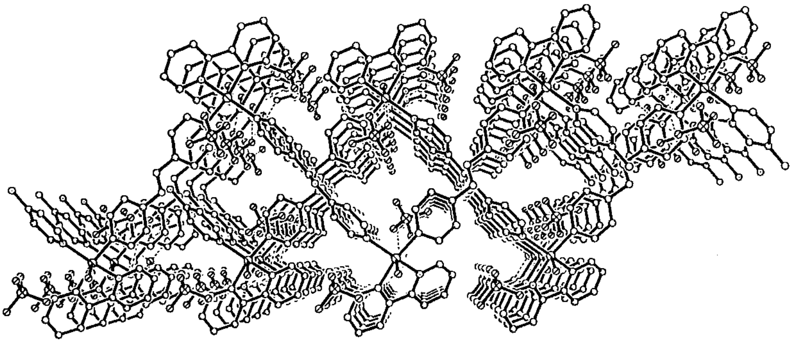

FIGURE 3 The structure of stacking of one-dimensional chain of complex **1**.

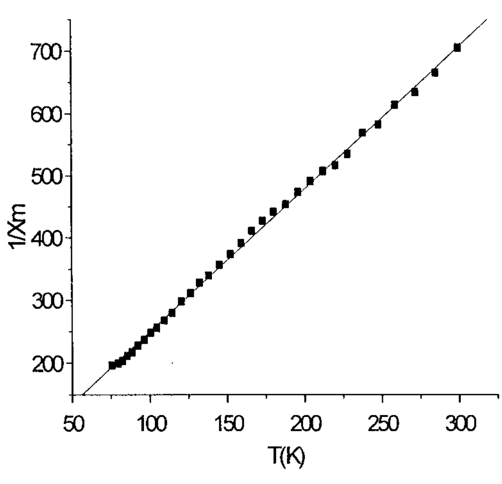

FIGURE 4 Plot of $1/\chi_m$ *vs.* T for the compound **1**.

as a strong peak at 1423 cm^{-1}. The strong absorption band in 1099, 1062 and 1030 cm^{-1} for perchlorates, suggests that there are two kinds of perchlorates: free and unidentate [26]. The ESR spectrum shows a typical axically symmetric signal with $g_{\|} = 2.311$ and $g_{\perp} = 2.053$.

Variable-temperature magnetic susceptibility studies in the temperature range 75–300 K showed that complex **1** obeys the Curie–Weiss law (Fig. 4), $x_m = C/(T - \theta)$, with values of $\theta = -10.99\,\mathrm{K}$, $\mathrm{C} = 0.448\,\mathrm{emu\,K\,mol^{-1}}$. This indicates that there is a weak antiferromagnetic interaction between the copper ions through the azpy bridging in complex **1**.

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