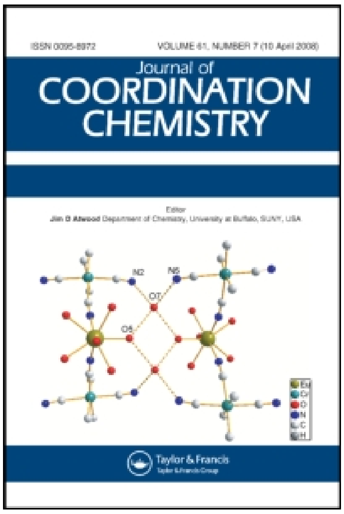

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Syntheses and Crystal Structures of Two One-Dimensional Chain Copper Benzoylacetone Complexes Bridged Through Azobispyridine Ligands

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SYNTHESES AND CRYSTAL STRUCTURES OF TWO ONE-DIMENSIONAL CHAIN COPPER BENZOYLACETONE COMPLEXES BRIDGED THROUGH AZOBISPYRIDINE LIGANDS

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Two copper complexes [Cu(bzac)$_2$(4,4′-azpy)]·H_2O (**1**) and [Cu(bzac)$_2$(3,3′-azpy)] (**2**) (bzac = benzoylacetone, 4,4′-azpy = 4,4′-azobispyridine, 3,3′-azpy = 3,3′-azobispyridine) have been synthesized and characterized. The crystal structures were determined by X-ray diffraction analysis. In crystals of Complexes **1** and **2**, the copper atoms have distorted octahedral symmetry. The two compounds possess very similar one-dimensional linear chains linked through the rod-like 4,4′-azpy or 3,3′-azpy ligands.

Keywords: Crystal structure; One-dimensional chain; Copper complexes; Azobispyridine; Benzoylacetone

INTRODUCTION

Self-assembly of coordination polymers from basic building blocks is of considerable interest because of their intriguing diverse architectures and potential applications in catalysis and advanced materials such as magnetic, optic and electronic materials [1–4]. The reaction of a metal complex with two vacant or substitutable coordination sites with a bridging ligand is the most common and effective synthetic method to obtain one-dimensional chain compounds. Bridging ligands such as 4,4′-azobispyridine and 3,3′-azobispyridine link metal ions to form infinite configurations [5–7].

Many β-diketonates such as acetylacetone, 1,1,1-trifluoro-3-(2-thenyl)acetone and hexafluoroacetylacetone complexes have been reported [8–15]. In the present work, by using a mixed ligand system containing a β-diketonate ligand benzoylacetone (bzac) and 4,4′-azobispyridine (4,4′-azpy) or 3,3′-azobispyridine (3,3′-azpy) as a

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bridging ligand, two one-dimensional chain copper complexes [Cu(bzac)$_2$(4,4′-azpy)] · H_2O (**1**) and [Cu(bzac)$_2$(3,3′-azpy)] (**2**) have been synthesized and characterized.

EXPERIMENTAL

Physical Measurements

Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyser. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 400–4000 cm^{-1} region. Electronic spectra were recorded in DMF solution on a Shimadzu 3100 spectrophotometer.

Materials and Reagents

All reagents were of AR grade and used without further purification. 4,4′-Azobispyridine (4,4′-azpy) and 3,3′-azobispyridine (3,3′-azpy) were prepared following the literature method [16]. Cu(bzac)$_2$ was prepared by the literature method [17].

Synthesis of [Cu(bzac)$_2$(4,4′-azpy)] · H_2O (1)

[Cu(bzac)$_2$(4,4′-azpy)] · H_2O was prepared from Cu(bzac)$_2$ and 4,4′-azpy. A 95% ethanol solution (20 mL) of 4,4′-azpy (0.184 g, 1 mmol) and DMF solution (10 mL) of [Cu(bzac)$_2$] (0.386 g, 1 mmol) were mixed and stirred for 10 min, and the resulting solution was allowed to stand at room temperature. After two weeks, green prismatic crystals of [Cu(bzac)$_2$(4,4′-azpy)] · H_2O (**1**) suitable for X-ray diffraction were obtained. Yield 86%. Elemental analysis confirmed the organic content (Found: C, 61.02; H, 4.71; N, 9.46%. Calcd. for $C_{30}H_{28}CuN_4O_5$: C, 61.27; H, 4.80; N, 9.53%).

Synthesis of [Cu(bzac)$_2$(3,3′-azpy)] (2)

The compound was prepared following the same procedure as for **1**, except that 4,4′-azpy was replaced by 3,3′-azpy. Yield 81%. Elemental analysis confirmed the organic content (Found: C, 63.14; H, 4.51; N, 9.68%. Calcd. for $C_{30}H_{26}CuN_4O_4$: C, 63.21; H, 4.60; N, 9.83%).

Crystal Structure Determination

Single crystals with dimensions 0.23 × 0.21 × 0.20 mm for Complex **1** and 0.21 × 0.20 × 0.17 mm for Complex **2** were selected for data collection at 193(2) K, using a Rigaku CrystalClear with graphite monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Data were collected by the ω-scan technique. The structures were solved by direct methods and refined using a full-matrix least-squares method (SHELX-97) [18]. The positions of all remaining non-hydrogen atoms were obtained from successive Fourier syntheses. The positions of hydrogen atoms were calculated using idealized geometry. No attempt was made to locate the hydrogen atoms of water. The parameters of the crystal, data collection and refinement are given in Table I. Atomic coordinates of non-hydrogen atoms of Complexes **1** and **2** are given

TABLE I Crystal data and structure refinement for Compounds **1** and **2**

Compound	[Cu(bzac)$_2$(4,4′-azpy)] · H_2O (**1**)	[Cu(bzac)$_2$(3,3′-azpy)] (**2**)
Empirical formula	$C_{30}H_{28}CuN_4O_5$	$C_{30}H_{26}CuN_4O_4$
Temperature (K)	193	193
Formula weight (g mol^{-1})	588.10	570.09
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	C222$_1$	P1
a (Å)	18.745(4)	7.0930(14)
b (Å)	19.817(4)	8.6620(17)
c (Å)	15.015(3)	11.335(2)
α (°)	90.00	75.96(3)
β (°)	90.00	76.40(3)
γ (°)	90.00	89.52(3)
Volume (Å^3)	5577.6(19)	655.8(2)
Z	8	1
D (mg/cm^3)	1.401	1.444
Absorption coefficient (mm^{-1})	0.830	0.877
F(000)	2440	295
Crystal size (mm^3)	0.23 × 0.21 × 0.20	0.21 × 0.20 × 0.17
θ range for data collection	3.10–27.48°	3.11–27.48°
Index ranges	$-23 \le h \le 24$, $-25 \le k \le 25$, $-19 \le l \le 19$	$-8 \le h \le 9$, $-11 \le k \le 10$, $-14 \le l \le 14$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Independent reflections	6398	4365
Goodness-of-fit on F^2	1.133	1.037
Final R_1 and wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0585$, $wR_2 = 0.1102$	$R_1 = 0.0689$, $wR_2 = 0.1861$
R_1 and wR_2 indices (all data)	$R_1 = 0.0705$, $wR_2 = 0.1144$	$R_1 = 0.0709$, $wR_2 = 0.1876$
Largest diff. peak and hole	0.348 and –0.328 e/Å^3	2.653 and –0.496 e/Å^3

1: $W = 1/[\sigma^2(Fo^2) + (0.0531P)^2 + 2.6356P]$, $P = [Fo^2 + 2Fc^2]/3$, **2**: $W = 1/[\sigma^2(Fo^2) + (0.0940P)^2 + 3.4085P]$, $P = [Fo^2 + 2Fc^2]/3$.

in Tables II and III, respectively. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC numbers for **1** and **2** are 190123 and 190124, respectively.

RESULTS AND DISCUSSION

Crystal Structure

The two compounds have similar linear chain structures, which are formed by bridging 4,4′-azpy or 3,3′-azpy ligands connecting the Cu(bzac)$_2$ units.

The selected bond lengths and angles of Complexes **1** and **2** are listed in Table IV. Part of the structure of Complex **1** is shown in Fig. 1. The Cu atom is in a greatly distorted octahedral environment with four shorter and two longer bonds. The four shorter bonds [Cu(1)–O(1) 1.944(2) Å, Cu(1)–O(2) 2.017(3) Å, Cu(1)–O(3) 1.947(2) Å and Cu(1)–O(4) 2.006(3) Å] are formed by four oxygen atoms of two bzac ligands. These bonds form a square-planar arrangement. The bond angles O(1)–Cu(1)–O(2), O(1)–Cu(1)–O(4), O(2)–Cu(1)–O(3) and O(3)–Cu(1)–O(4) are 91.72(10)°, 87.59(11)°, 88.19(10)° and 92.46(10)°, respectively. O_4 planes are co-planar with mean deviation from plane of 0.0397 Å and the Cu(II) atom is displaced slightly above the plane by 0.0461 Å. Some coordination bond distances found in relevant Cu(II) complexes

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **1**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Cu(1)	3332(1)	1495(1)	1273(1)	22(1)
O(1)	2726(1)	825(1)	1840(2)	25(1)
O(2)	3656(1)	1855(1)	2462(2)	29(1)
O(3)	3935(1)	2170(1)	706(2)	26(1)
O(4)	2935(1)	1186(1)	101(2)	32(1)
O(5)	5000	2714(2)	2500	45(1)
O(6)	1963(2)	0	0	40(1)
N(1)	4232(2)	717(2)	1223(3)	34(1)
N(2)	5870(2)	−714(2)	1302(3)	49(1)
N(3)	5698(2)	−1313(2)	1336(3)	41(1)
N(4)	7380(2)	−2718(2)	1345(2)	34(1)
C(1)	3522(2)	2186(2)	3961(3)	42(1)
C(2)	3304(2)	1762(2)	3178(2)	24(1)
C(3)	2762(2)	1285(2)	3298(2)	27(1)
C(4)	2524(2)	829(2)	2650(2)	21(1)
C(5)	1980(2)	303(2)	2885(2)	24(1)
C(6)	1901(2)	48(2)	3747(3)	31(1)
C(7)	1402(2)	−453(2)	3916(3)	37(1)
C(8)	978(2)	−702(2)	3240(3)	37(1)
C(9)	1050(2)	−446(2)	2392(3)	35(1)
C(10)	1549(2)	50(2)	2214(2)	28(1)
C(11)	2596(3)	1253(2)	−1406(3)	50(1)
C(12)	3014(2)	1509(2)	−622(2)	30(1)
C(13)	3454(2)	2078(2)	−742(3)	34(1)
C(14)	3887(2)	2371(2)	−95(2)	25(1)
C(15)	4344(2)	2967(2)	−327(2)	25(1)
C(16)	4238(2)	3353(2)	−1091(3)	33(1)
C(17)	4664(2)	3909(2)	−1259(4)	42(1)
C(18)	5212(2)	4079(2)	−685(3)	42(1)
C(19)	5322(2)	3692(2)	66(3)	34(1)
C(20)	4891(2)	3145(2)	250(2)	30(1)
C(21)	4915(2)	882(2)	1331(4)	45(1)
C(22)	5455(2)	415(2)	1366(4)	53(1)
C(23)	5288(2)	−256(2)	1271(4)	42(1)
C(24)	4587(2)	−442(2)	1158(4)	46(1)
C(25)	4080(2)	60(2)	1134(3)	44(1)
C(26)	6692(2)	−2900(2)	1386(3)	39(1)
C(27)	6133(2)	−2446(2)	1402(3)	39(1)
C(28)	6291(2)	−1770(2)	1352(3)	34(1)
C(29)	7002(2)	−1570(2)	1305(3)	35(1)
C(30)	7514(2)	−2062(2)	1302(3)	36(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

are summarized in Table V for comparison. The Cu–O bond lengths are consistent with those in Cu(bzac)$_2$ [17], Cu(acac)$_2$(4,4′-bipy) [8], Cu(TTA)$_2$(4,4′-bipy) [9], Cu(TTA)$_2$(pyz) [10], [Cu(TTA)$_2$](btrz) [11] and Cu(hfac)$_2$(pyz) [12], but shorter than the Cu–O distances in some hfac complexes [Cu(hfac)$_2$(mpydz)$_2$] [13], [Cu(hfac)$_2$(pyz)$_2$] [14], [Cu(hfac)$_2$(cnpy)] [14], [Cu(hfac)$_2$(bpea)] [14], [Cu(hfac)$_2$(bpt)] [14]. The two longer bonds are for Cu to nitrogen atoms of bridging 4,4′-azpy, Cu(1)–N(1) is 2.286(3) Å and Cu(1)–N(4)A is 2.373(3) Å. Those values are consistent with the Cu–N distances in Cu(TTA)$_2$(4,4′-bipy) [9], Cu(TTA)$_2$(pyz) [10] and [Cu(TTA)$_2$](btrz) [11], while shorter than the Cu–N distances in Cu(acac)$_2$(4,4′-bipy) [8] and Cu(hfac)$_2$(pyz) [12] and longer than those in some hfac copper complexes [13,14].

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) for **2**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Cu(1)	7553(2)	7340(2)	3002(2)	21(1)
O(1)	5917(12)	5618(11)	2871(8)	30(2)
O(2)	9640(12)	7031(9)	1670(8)	27(2)
O(3)	9223(11)	9074(9)	3096(7)	23(2)
O(4)	5433(10)	7640(10)	4406(8)	25(2)
N(1)	6108(15)	9274(12)	1547(8)	26(2)
N(2)	8982(15)	15322(13)	−5522(10)	30(2)
N(3)	7904(16)	11992(13)	−1489(9)	30(2)
N(4)	7208(12)	12594(10)	−2406(8)	20(2)
C(1)	4221(15)	9437(12)	1672(10)	21(2)
C(2)	3304(17)	10351(15)	856(11)	37(3)
C(3)	4483(13)	11326(12)	−295(10)	18(2)
C(4)	6545(15)	11119(12)	−424(11)	24(2)
C(5)	7229(16)	10196(14)	477(12)	31(3)
C(6)	10940(20)	15297(17)	−5724(11)	35(3)
C(7)	11735(14)	14342(14)	−4761(10)	32(3)
C(8)	10590(20)	13526(16)	−3700(11)	39(3)
C(9)	8650(17)	13458(13)	−3503(8)	25(2)
C(10)	7867(15)	14487(13)	−4462(9)	23(2)
C(11)	4963(19)	3250(15)	2323(11)	34(3)
C(12)	6418(17)	4593(14)	2251(10)	24(2)
C(13)	8236(15)	4580(14)	1431(12)	27(2)
C(14)	9700(15)	5887(12)	1118(10)	21(2)
C(15)	11563(15)	5825(11)	152(9)	20(2)
C(16)	11546(18)	5287(16)	−939(11)	32(3)
C(17)	13302(19)	5219(15)	−1752(12)	31(3)
C(18)	15009(19)	5888(16)	−1652(12)	32(3)
C(19)	15105(18)	6370(17)	−580(15)	46(4)
C(20)	13258(18)	6406(15)	247(11)	29(3)
C(21)	10049(17)	11410(16)	3544(13)	35(3)
C(22)	8623(17)	10044(13)	3796(11)	24(2)
C(23)	6847(17)	9879(13)	4668(9)	21(2)
C(24)	5376(16)	8805(14)	4898(10)	24(2)
C(25)	3542(16)	8880(14)	5834(11)	28(3)
C(26)	3454(17)	9464(13)	6869(11)	25(2)
C(27)	1700(20)	9354(19)	7808(12)	42(3)
C(28)	−3(18)	8911(17)	7546(14)	39(3)
C(29)	170(15)	8216(14)	6560(10)	29(2)
C(30)	1780(15)	8318(14)	5621(11)	26(2)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

O(1), O(2), C(2), C(3) and C(4) are co-planar with a mean deviation from plane of 0.0230 Å. The dihedral angle between this plane and the phenyl ring plane is 27.1°. O(3), O(4), C(12), C(13) and C(14) are also co-planar with a mean deviation from plane of 0.0035 Å. The dihedral angle between this plane and the phenyl ring plane is 16.1°.

4,4′-Azpy ligands are trans in Complex **1**. The dihedral angle between the two pyridyl groups of the 4,4′-azpy ligand is 11.0°. The Cu atoms are bridged by 4,4′-azpy ligands with the nearest Cu···Cu separation being 13.639 Å within the chain (Fig. 2). The separations of metal ions between the two neighboring chains are 7.050 and 7.258 Å, respectively.

Part of the structure of Complex **2** is shown in Fig. 3. Cu has an elongated octahedral geometry. The equatorial plane is defined by four O atoms from two chelated bzac ligands with a mean deviation from plane of 0.0151 Å and the Cu(II) atom is above

TABLE IV Selected bond lengths (Å) and angles (°) for the Complexes **1** and **2**

Complex **1**	
Cu(1)–O(1)	1.944(2)
Cu(1)–O(3)	1.947(2)
Cu(1)–N(1)	2.286(3)
Cu(1)–O(2)	2.017(2)
Cu(1)–O(4)	2.006(3)
Cu(1)–N(4)A	2.373(3)
O(1)–Cu(1)–O(2)	91.72(10)
O(1)–Cu(1)–O(4)	87.59(11)
O(2)–Cu(1)–O(4)	175.06(12)
O(1)–Cu(1)–N(1)	89.14(11)
O(3)–Cu(1)–N(1)	91.24(11)
O(1)–Cu(1)–N(4)A	89.35(11)
O(3)–Cu(1)–N(4)A	90.27(11)
N(1)–Cu(1)–N(4)A	178.48(13)
O(1)–Cu(1)–O(3)	179.62(12)
O(2)–Cu(1)–O(3)	88.19(1)
O(3)–Cu(1)–O(4)	92.46(10)
O(2)–Cu(1)–N(1)	92.58(12)
O(4)–Cu(1)–N(1)	92.30(12)
O(2)–Cu(1)–N(4)A	87.32(12)
O(4)–Cu(1)–N(4)A	87.78(12)
Complex **2**	
Cu(1)–O(2)	1.919(8)
Cu(1)–O(4)	1.983(8)
Cu(1)–N(2)A	2.496(10)
Cu(1)–O(1)	1.952(10)
Cu(1)–O(3)	1.959(8)
Cu(1)–N(1)	2.450(8)
O(1)–Cu(1)–O(2)	93.0(4)
O(1)–Cu(1)–O(4)	87.5(4)
O(2)–Cu(1)–O(4)	178.7(4)
O(1)–Cu(1)–N(1)	90.5(4)
O(3)–Cu(1)–N(1)	89.0(4)
O(1)–Cu(1)–N(2)A	88.2(3)
O(3)–Cu(1)–N(2)A	92.3(3)
N(1)–Cu(1)–N(2)A	178.7(5)
O(1)–Cu(1)–O(3)	178.8(5)
O(2)–Cu(1)–O(3)	85.9(4)
O(3)–Cu(1)–O(4)	93.6(3)
O(2)–Cu(1)–N(1)	92.0(3)
O(4)–Cu(1)–N(1)	89.2(3)
O(2)–Cu(1)–N(2)A	88.0(3)
O(4)–Cu(1)–N(2)A	90.8(4)

Symmetry code: A $x-1/2$, $y+1/2$, z for **1**. A x, $y-1$, $z+1$ for **2**.

the plane by 0.0061 Å, while the axial positions are occupied by two N atoms from two different 3,3′-azpy ligands arranged trans. The Cu–O bond lengths are similar to the distances found in **1**, while the Cu–N bond lengths are longer than those in **1** and correspond to the Cu–N distances in Cu(acac)$_2$(4,4′-bipy) [8] and Cu(hfac)$_2$(pyz) [12]. The dihedral angle between the two pyridyl groups of the 3,3′-azpy ligand is 3.0°. The Cu atoms are bridged by the 3,3′-azpy ligands with the closest Cu $\cdots$ Cu intra-chain

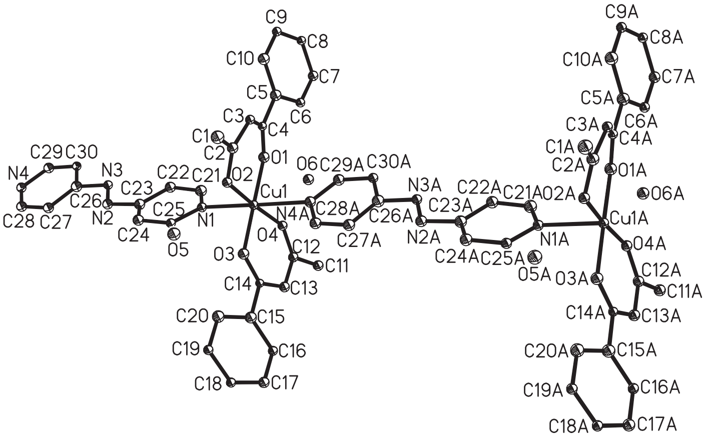

FIGURE 1 Local coordination of Cu in Complex **1** with 30% thermal ellipsoids.

TABLE V Comparison of coordination bond distances

Complex	*Cu–O in equatorial plane* (Å)	*Cu–N in axial direction* (Å)	*References*
$Cu(bzac)_2$	1.914(5)–1.931(5)		[17]
$Cu(acac)_2(4,4'\text{-bipy})$	1.948(3)–1.965(3)	2.449(3)–2.452(3)	[8]
$Cu(TTA)_2(4,4'\text{-bipy})$	1.983(4)–2.096(5)	2.201(8)	[9]
$Cu(TTA)_2(pyz)$	1.945(3)–1.970(3)	2.34(1)	[10]
$[Cu(TTA)_2](btrz)$	1.936(2)–1.950(2)	2.290(3)	[11]
$Cu(hfac)_2(pyz)$	1.924(7)–2.004(7)	2.529(9)	[12]
$[Cu(hfac)_2(mpydz)_2]$	2.009(3)–2.228(4)	2.043(4)	[13]
$[Cu(hfac)_2(pyz)_2]$	1.995(4)–2.225(4)	2.097(4)	[14]
$[Cu(hfac)_2(cnpy)]$	1.991(4)–2.184(4)	2.097(4)	[14]
$[Cu(hfac)_2(bpea)]$	2.114(7)–2.129(8)	2.014(7)	[14]
$[Cu(hfac)_2(bpt)]$	2.038(6)–2.203(7)	1.992(6)	[14]
$[Cu(bzac)_2(4,4'\text{-azpy})]\cdot H_2O$	1.944(2)–2.017(2)	2.286(3)–2.373(3)	This work
$[Cu(bzac)_2(3,3'\text{-azpy})]$	1.919(8)–1.983(8)	2.450(8)–2.496(10)	This work

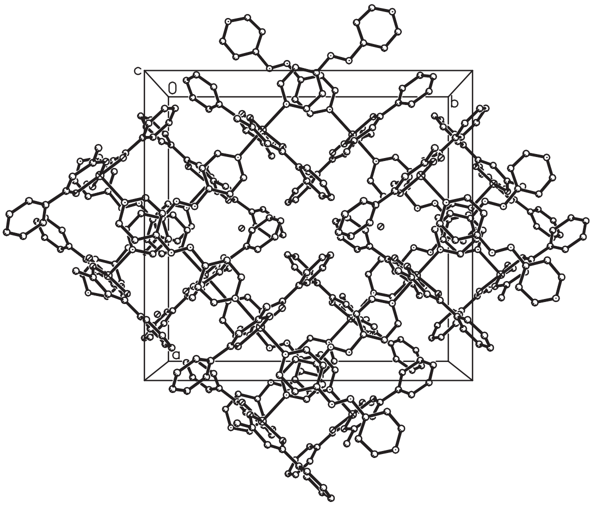

FIGURE 2 View of the one-dimensional chain in Complex **1**.

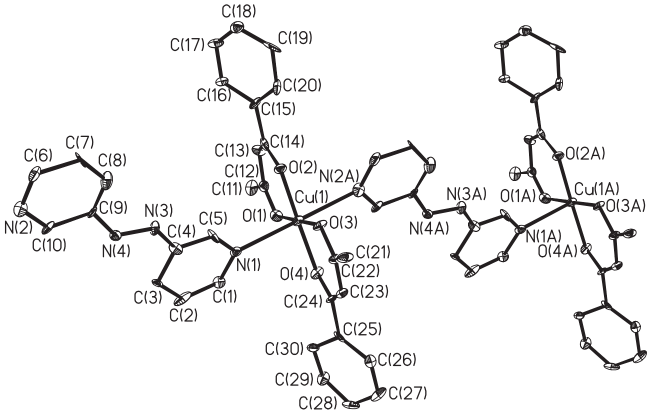

FIGURE 3 Local coordination of Cu in Complex **2** with 30% thermal ellipsoids.

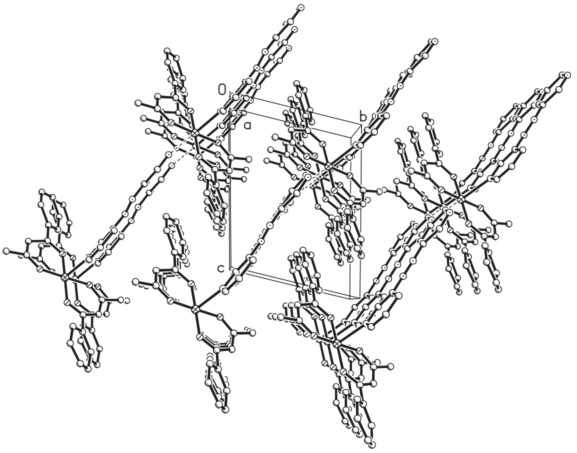

FIGURE 4 View of the one-dimensional chain in Complex **2**.

separation being 12.485 Å (Fig. 4). The neighboring inter-chain Cu···Cu distances are 7.093 and 8.662 Å.

The two compounds possess very similar one-dimensional linear chains linked through the rod-like 4,4′-azpy or 3,3′-azpy ligands. Solvent water molecules are disordered with two positions occupied 0.50 and 0.50 in **1**. Hydrogen bonding interactions are observed between solvent water and the O atom of bzac ligands (O(5)···O(2) 3.040 Å, O(6)···O(4) 2.976 Å) in **1**. One unexpected feature is that no solvent or guest molecules are included in the void between chains and no hydrogen bonding interactions are observed in **2**.

Infrared and Electronic Spectra

The IR spectrum of Complex **1** shows bands at: 3530 (s), 3479 (m), 3083 (m), 3163 (s), 2967 (w), 1590 (s), 1559 (s), 1514 (s), 1485 (s), 1454 (s), 1416 (s), 1285 (s), 1219 (s), 1111 (m), 1073 (m), 1026 (w), 999 (s), 957 (m), 845 (vs), 760 (vs), 718 (vs), 691 (m), 617 (w), 567 (m), 540 (m) and 459 (m) cm^{-1}. The IR spectrum of Complex **2** shows bands: 3063 (w), 1590 (s), 1563(s), 1508 (s), 1485 (s), 1454 (s), 1408 (s), 1300 (w), 1208 (w), 1177 (m), 1111 (w), 1019 (m), 957 (m), 853 (w), 822 (m), 772 (m), 706 (s), 610 (w), 544 (m) and 459 (m) cm^{-1}. A strong peak at 3530 cm^{-1} for **1** belongs to the water. The strong peaks at 1416 cm^{-1} for **1** and 1408 cm^{-1} for **2** belong to the $\mathrm{N}=\mathrm{N}$ stretch vibration of azo group [5–7, 16]. The strong peak at 1590 cm^{-1} for **1** and **2** is attributed to coordinated bzac liagands.

The DMF solution electronic spectra show two broad peaks at 287 and 468 nmr for **1** and 309 and 443 nmr for **2**. The low-energy peak is assigned as a d–d transition of copper(II) and the high-energy absorption is assigned to ligand-to-copper(II) charge transfer.

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