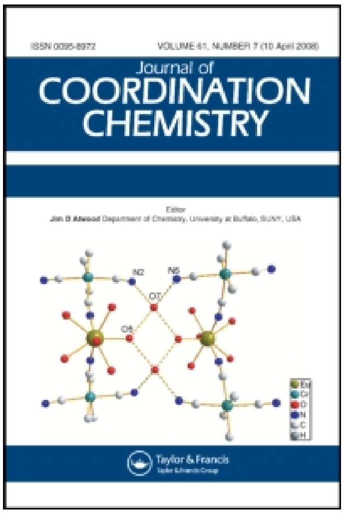

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Solvent-controlled synthesis and crystal structures of a pair of azido-bridged copper(II) complexes constructed from 1-[(3-dimethylaminopropylimino)methyl]naphthalen-2-ol

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A pair of azido-bridged copper(II) complexes, $[Cu_2L_2(\mu_{1,1}\text{-}N_3)_2]$ (**1**) and $[Cu_2L_2(\mu_{1,3}\text{-}N_3)_2] \cdot H_2O$ (**2**) (HL = 1-[(3-dimethylaminopropylimino)methyl]naphthalen-2-ol), have been obtained from an identical synthetic procedure and starting materials with solvents as the only independent variable. Complex **1** was synthesized and crystallized using the anhydrous methanol, while **2** was synthesized and crystallized using 95% ethanol. Both complexes show interesting self-assembled structures in their crystals as elucidated by X-ray analysis. The end-on azido-bridged dinuclear **1** crystallizes in the $P\bar{1}$ space group. The end-to-end azido–bridged polymeric **2** crystallizes in the $P2_1/c$ space group.

Keywords: Synthesis, Schiff base; Copper(II) complex; Crystal structure; Azide

1. Introduction

Polynuclear complexes containing bridging ligands are of interest because of their interesting molecular topologies and may be designed with specific functionalities [1–3]. Versatile coordination modes of the ambidentate azide, an extensively studied building block in the multi-dimensional complexes, can bridge two or more metal ions in the $\mu_{1,1}$ (end-on, EO), $\mu_{1,3}$ (end-to-end, EE), $\mu_{1,1,3}$, and many other modes, resulting in polynuclear complexes [4, 5]. The versatile features of azide bridges may lead to topologies which are difficult to obtain with bridging ligands such as thiocyanate or cyanide. A major obstacle to more comprehensive study of such azido-based polymeric coordination complexes is the lack of rational synthetic procedures; with the present state of knowledge it is not possible to determine which coordination mode will be adopted by the azide and whether the sought-after alternating structure will be formed [6–8]. The design and synthesis of novel coordination architectures controlled by varying the reaction conditions (including temperature [9–11], metal/ligand ratio [12], pH values [13], solvents [14], and counter anions [15, 16]) are of great interest in coordination chemistry. Appropriate control of the reaction conditions makes it possible to construct new materials with useful properties. In this article, we report the

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synthesis of a pair of azido-bridged copper(II) complexes, $[Cu_2L_2(\mu_{1,1}\text{-}N_3)_2]$ (**1**) and $[Cu_2L_2(\mu_{1,3}\text{-}N_3)_2] \cdot H_2O$ (**2**), from an identical synthetic procedure and starting materials but with different solvents.

2. Experimental

2.1. *Materials and methods*

All chemicals (reagent grade) were commercially available and used without further purification. The Schiff-base ligand HL was synthesized according to the literature [5]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region.

2.2. *Preparation of 1*

To an anhydrous methanol solution (5 cm^3) of $Cu(CH_3COO)_2 \cdot H_2O$ (20.0 mg, 0.1 mmol) was added a methanol solution (10 cm^3) of HL (25.6 mg, 0.1 mmol) and a methanol solution (5 cm^3) of NaN_3 (6.5 mg, 0.1 mmol), with stirring. The mixture was stirred for 10 min at room temperature and filtered. Upon keeping the filtrate in air for 3 days, blue block-shaped crystals of **1**, suitable for X-ray crystal determination, formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield: 32%. Anal. Calcd for $C_{32}H_{38}Cu_2N_{10}O_2$ (%): C, 53.2; H, 5.3; N, 19.4. Found: C, 52.9; H, 5.5; N, 19.7.

2.3. *Preparation of 2*

Complex **2** was prepared by similar procedure as described for **1**, only with the solvent methanol replaced by 95% ethanol, resulting in block-shaped crystals of **2**. Yield: 22%. Anal. Calcd for $C_{32}H_{40}Cu_2N_{10}O_3$ (%): C, 52.0; H, 5.4; N, 18.9. Found: C, 52.4; H, 5.6; N, 18.8. The final product yields were calculated according to the amount of HL used.

2.4. *X-ray crystallography*

X-ray intensities of **1** and **2** were collected using a Bruker Smart CCD area detector equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. Empirical absorption corrections were applied using the SADABS program [17]. Both structures were solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL [18]. All non-hydrogen atoms were refined anisotropically. Atoms H3A, H3B, H3C and H3D in **2** were located in a difference Fourier map and refined isotropically, with O–H distances restrained to 0.84(1) Å and $H \cdots H$ distances restrained to 1.37(2) Å. All other H atoms were placed in geometrically ideal positions and constrained to ride on their parent atoms. The lattice water molecule in **2** is disordered over two distinct sites with occupancies of 0.600(2) and 0.400(2). The crystallographic data for the two complexes are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystallographic and experimental data for **1** and **2**.

Complex	**1**	**2**
Chemical formula	$C_{32}H_{38}Cu_2N_{10}O_2$	$C_{32}H_{40}Cu_2N_{10}O_3$
Formula weight	721.80	739.82
Crystal shape/color	Block/blue	Block/blue
Crystal size (mm^3)	0.35 × 0.28 × 0.20	0.28 × 0.26 × 0.16
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	8.502(2)	10.716(1)
b	9.890(2)	12.931(2)
c	10.307(2)	25.034(2)
α	106.412(2)	90.00
β	93.248(2)	99.343(2)
γ	105.414(2)	90.00
V (Å^3)	793.3(3)	3422.9(7)
Z	1	4
λ(Mo-Kα) (Å)	0.71073	0.71073
T (K)	298(2)	298(2)
μ(Mo-Kα) (mm^{-1})	1.388	1.291
T(min)	0.6422	0.7138
T(max)	0.7687	0.8201
Reflections/parameters	3516/210	7665/450
Goodness of fit on F^2	1.087	1.020
R_1, wR_2 [$I \geq 2\sigma(I)$][a]	0.0309, 0.0800	0.0683, 0.1584
R_1, wR_2 (all data)[a]	0.0348, 0.0822	0.1146, 0.1827

[a] $R_1 = \sum|F_o| - |F_c|/\sum|F_o|$, $wR_2[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Compound **1**			
Cu1–O1	1.919(2)	Cu1–N1	1.957(2)
Cu1–N2	2.114(2)	Cu1–N3	2.348(2)
Cu1–N3^i	2.007(2)		
O1–Cu1–N1	90.2(1)	O1–Cu1–N3^i	86.0(1)
N1–Cu1–N3^i	175.7(1)	O1–Cu1–N2	155.0(1)
N1–Cu1–N2	90.9(1)	N3^i–Cu1–N2	93.4(1)
O1–Cu1–N3	103.2(1)	N1–Cu1–N3	99.4(1)
N3–Cu1–N3^i	79.6(1)	N2–Cu1–N3	101.2(1)
Compound **2**			
Cu1–O1	1.912(4)	Cu1–N1	1.981(4)
Cu1–N2	2.072(4)	Cu1–N3	2.004(5)
Cu1–N10	2.355(5)	Cu2–O2	1.921(4)
Cu2–N6	1.982(4)	Cu2–N7	2.081(4)
Cu2–N8	2.011(4)	Cu2–N5^{ii}	2.385(5)
O1–Cu1–N1	88.5(2)	O1–Cu1–N3	88.9(2)
N1–Cu1–N3	155.3(2)	O1–Cu1–N2	176.3(2)
N1–Cu1–N2	92.9(2)	N3–Cu1–N2	88.3(2)
O1–Cu1–N10	91.5(2)	N1–Cu1–N10	97.3(2)
N3–Cu1–N10	107.3(2)	N2–Cu1–N10	91.7(2)
O2–Cu2–N6	88.9(2)	O2–Cu2–N8	88.3(2)
N6–Cu2–N8	154.3(2)	O2–Cu2–N7	175.6(2)
N6–Cu2–N7	95.1(2)	N8–Cu2–N7	87.3(2)
O2–Cu2–N5^{ii}	91.9(2)	N6–Cu2–N5^{ii}	94.3(2)
N8–Cu2–N5^{ii}	111.4(2)	N7–Cu2–N5^{ii}	89.5(2)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-1+x, y, z$.

3. Results and discussion

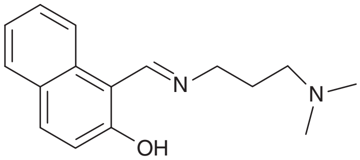
To design structures of transition metal complexes, the ligands and the solvents used in the synthesis are important [19]. In this article, we used the tridentate Schiff-base ligand HL (as shown in scheme (I)), a NNO donor. Recently, we reported a dinuclear copper(II) complex derived from HL with thiocyanate anions [20]. The azide ligand is a well-known bridging group, readily bridging different metal ions through the terminal donor atoms, forming polynuclear complexes. The two complexes reported in this article, together with the thiocyanato-bridged dinuclear copper(II) complex we reported previously, indicate that the azide is a better bridging ligand than thiocyanate.

Complexes **1** and **2** were synthesized under the same synthetic procedures, demonstrating that the same reactants can be used to obtain different structures by varying only the solvent used in synthesis and crystallization. The coordination numbers of each copper(II) in the two complexes are the same, but the bridging modes of the azide groups are different.

3.1. *Structures of 1 and 2*

The single-crystal X-ray structural analysis shows that both complexes are azido-bridged copper(II) compounds. The asymmetric unit of the end-on, azido-bridged dinuclear **1** consists of one half of the molecule with the other half generated by the inversion symmetry (figure 1). The asymmetric unit of the end-to-end azido-bridged polymeric **2** consists of two [CuL($\mu_{1,3}$-N$_3$)] moieties and one disordered lattice water (figure 2). Each Cu is in a square-pyramidal coordination, with the NNO donor set of the Schiff-base ligand and the terminal N atom [for **1**: N3^{i}, symmetry code: (i) $1-x$, $-y$, $-z$; for **2**: N3 for Cu1 and N8 for Cu2] of a bridging azide ligand defining the basal plane, and one terminal N atom [for **1**: N3; for **2**: N10 for Cu1 and N5^{ii} for Cu2, symmetry code: (ii) $-1+x$, y, z] of another bridging azide ligand occupying the apical position. The Schiff bases in both **1** and **2** are tridentate *via* the phenolate O, imine N and amine N. In **1**, the bridging azide anions are monodentate ligating two different but symmetry-related Cu atoms through end-on coordination, while in **2**, the bridging azide anions are bidentate ligating two adjacent Cu atoms through end-to-end coordination.

Significant distortion of each square pyramid is revealed by bond lengths and angles between the apical and basal donor atoms (table 2). The apical Cu–N bond lengths are much longer than usual; the other bond lengths are within normal ranges and comparable to the corresponding values observed in other Schiff-base copper(II)



Scheme 1. Ligand HL.

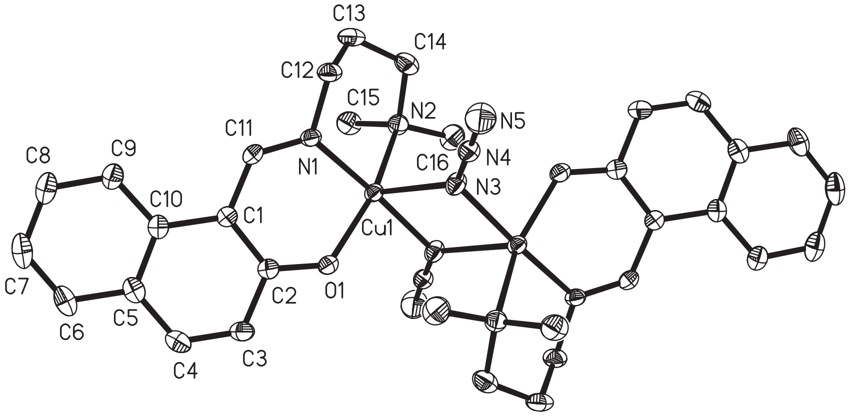


Figure 1. Molecular structure of **1**. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. Unlabelled atoms are at the symmetry-related positions $1-x$, $-y$, $-z$.

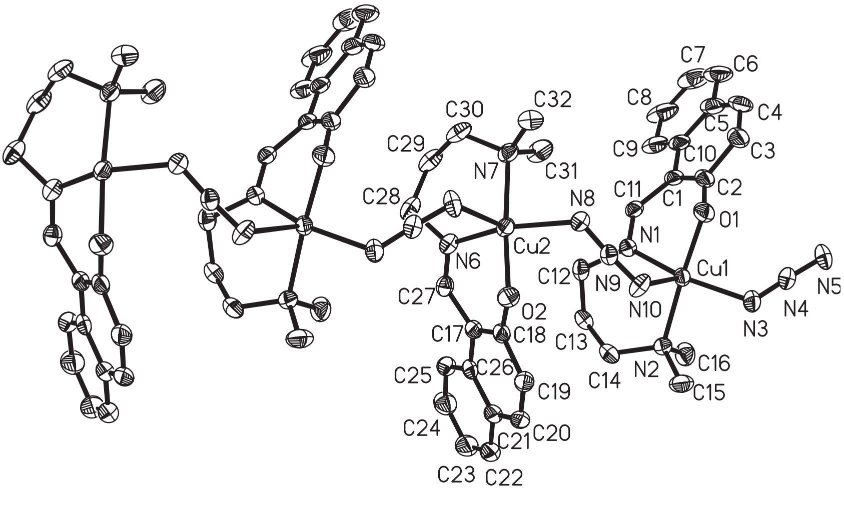


Figure 2. Complex **2** with displacement ellipsoids drawn at the 30% probability level and H atoms omitted for clarity. Unlabelled atoms are at the symmetry-related positions $-1+x$, y, z.

complexes [4, 5, 19, 21, 22]. For **1**, the deviation of Cu1 from the least-squares plane defined by the basal donor atoms is 0.208(2) Å. For **2**, the deviation of Cu1 from the least-squares plane defined by the basal donor atoms is 0.239(2) Å, and that for Cu2 is 0.228(2) Å. The distance for $\mathrm{Cu1}\cdots\mathrm{Cu1}^{\mathrm{i}}$ is 3.352(2) Å in **1**, and 5.335(2) Å for $\mathrm{Cu1}\cdots\mathrm{Cu2}$ and 5.466(2) Å for $\mathrm{Cu1}^{\mathrm{ii}}\cdots\mathrm{Cu2}$ in **2**. The bridging azide groups are nearly linear and show bent coordination with copper(II) [in **1**, N3–N4–N5 = 178.2(2)°, Cu1–N3–N4 = 137.1(2)°, $\mathrm{Cu1}^{\mathrm{i}}$–N3–N4 = 122.4(2)°; and in **2**, N3–N4–N5 = 177.3(6)°, N8–N9–N10 = 176.0(5)°, Cu1–N3–N4 = 124.5(4)°, Cu1–N10–N9 = 115.2(4)°, Cu2–N8–N9 = 123.4(4)°, Cu2–$\mathrm{N5}^{\mathrm{ii}}$–$\mathrm{N4}^{\mathrm{ii}}$ = 117.2(4)°]. The chelate rings formed by Cu1, N1, C12–C14, and N2 in **1** and in **2**, and by Cu2, N6, C28–C30, and N7 have chair conformations. In **1**, the diagonally positioned atoms, Cu1 and C13, are shifted from the least-squares plane defined by N1, N2, C12, and C14 by −0.960(2) and 0.662(6) Å, respectively. In **2**, the distances of the two diagonally positioned atoms, Cu1 and C13, from the least-squares plane defined by N1, N2, C12, and C14 are 0.758(2) and −0.690(6) Å, respectively; the distances of the two diagonally positioned atoms, Cu2 and C29, from the least-squares plane defined by N6, N7, C28, and C30 are 0.680(2) and −0.703(6) Å, respectively.

In the crystal structure of **1**, the molecules are stacked along the *c* axis with no short contacts (figure 3). In the crystal structure of **2**, the molecules are linked through bridging azide groups, forming polymeric chains running along the *a* axis (figure 4).

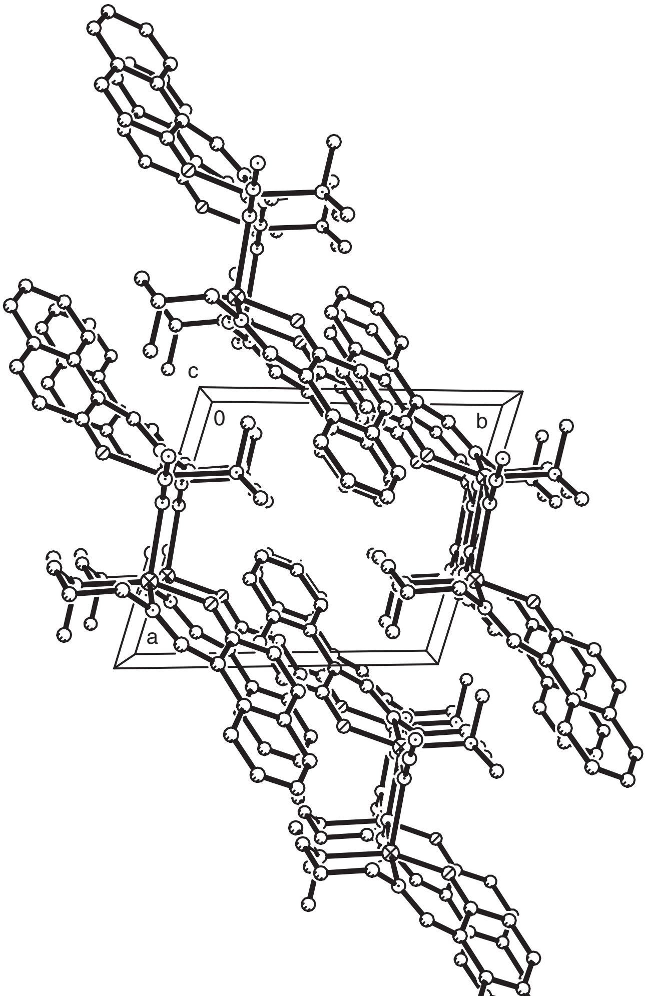


Figure 3. The molecular packing of **1**, viewed along the *c* axis.

3.2. *IR spectra of 1 and 2*

The IR spectra of the Schiff-base ligand and the two complexes provide information about the metal–ligand bonding. The assignments are based on typical group frequencies. The weak absorption at 3372 cm^{-1} for HL is assigned to ν(O–H). The strong absorption band at 1627 cm^{-1} in the spectrum of HL is assigned to the azomethine group, ν(C=N) [23]. This band shifts to lower wavenumbers in the complexes, 1612 cm^{-1} for **1** and 1617 cm^{-1} for **2**, attributed to coordination of the nitrogen of azomethine to the metal. The phenolic ν(C–O) strong band at 1200 cm^{-1} in the free ligand [24] appears at 1172 and 1181 cm^{-1} in the complexes. These bands

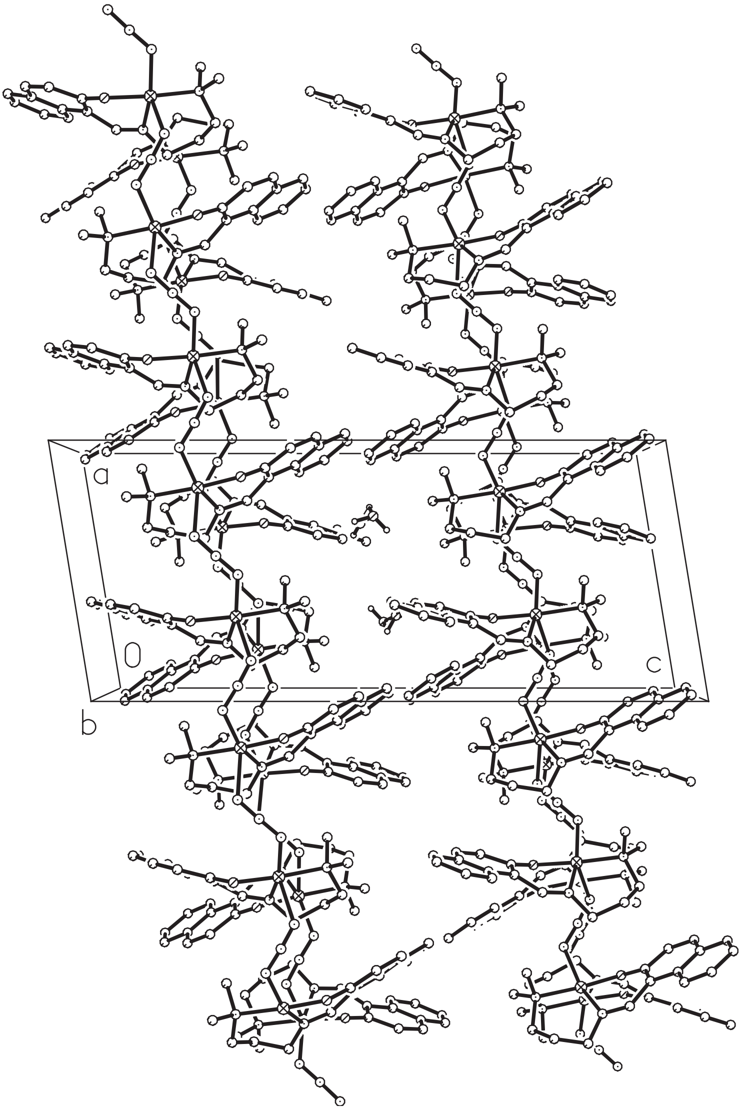


Figure 4. The molecular packing of **2**, viewed along the *b* axis.

assigned to the skeletal vibrations related to the phenolic oxygen of the Schiff bases are known to shift to lower frequency when the phenolic oxygen coordinates to metal ions. Other weak bands in the region 470–475 cm^{-1} for both complexes can be assigned to ν(Cu–O) [25] and provide further evidence for coordination through the deprotonated phenolic oxygens. The strong absorption indicative of the end-on azide groups in **1** is at 2097 cm^{-1}, and that indicative of end-to-end azide groups in **2** is at 2072 cm^{-1}.

Supplementary material

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 638101 and 638102. Copies of these data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033).

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