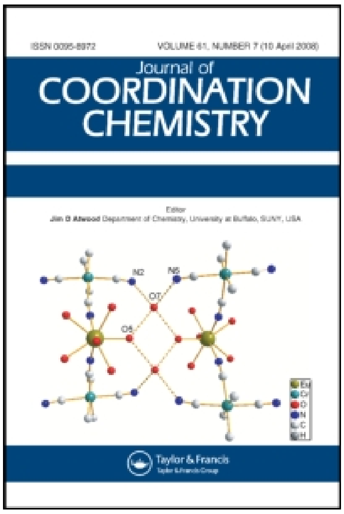

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Copper(II) azide complexes with mono-anionic tridentate Schiff-base ligands: monomer *versus* dimer

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Three new copper(II) complexes $[CuL^1N_3]_2$ (**1**), $[CuL^2N_3]$ (**2**) and $[CuL^3N_3]$ (**3**) with three very similar tridentate Schiff base ligands [$HL^1 =$ 6-diethylamino-3-methyl-1-phenyl-4-azahex-3-en-1-one, $HL^2 =$ 6-amino-3-methyl-1-phenyl-4-azahex-3-en-1-one and $HL^3 =$ 6-amino-3-methyl-1-phenyl-4-azasept-3-en-1-one] have been synthesized and structurally characterized by X-ray crystallography. In complex **1** half of the molecules are basal-apical, end-on azido bridged dimers and the remaining half are square-planar monomers whereas all the molecules in complexes **2** and **3** are monomers with square-planar geometry around Cu(II). A competition between the coordinate bond and H-bond seems to be responsible for the difference in structure of the complexes.

Keywords: Copper(II); Schiff base; Azide; Crystal structure; H-bonding

1. Introduction

The rational design and synthesis of polynuclear coordination complexes are of continuing interest for developing new functional molecular-based materials [1]. For this purpose azide-bridged complexes received considerable attention because azide can bridge the metal centers in a variety of ways to yield di-nuclear, tetra-nuclear, 1-D, 2-D and 3-D compounds [2–10] and a small change in the co-ligands can lead to astonishing variation in the structure of the resulting complexes [11]. The end-on, azido bridged basal-apical copper(II) complexes deserve special mention as their magneto structural correlation is still not clear and thus the synthesis and magnetic study of such

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complexes are a subject of recent interest [12]. A group of mono-negative N_2O donor tridentate Schiff-base blocking ligands, the mono-condensation product of acetylacetone or salicylaldehyde and diamines usually yield double EO azido-bridged, basal-apical dimers in all cases [12d, e]. In those complexes the H-bonding between the amine hydrogen and the azide or phenolic (enolic) oxygen plays a very important role on packing of the molecules and also on their magnetic properties. Recently, we found that replacement of acetylacetone by 1-benzoylacetone in this type of ligand has a very significant effect on the structure of the tri-nuclear copper(II) complexes [13a]. The increased nonbonding interactions due to the presence of a phenyl ring instead of methyl group seems to be responsible for such changes.

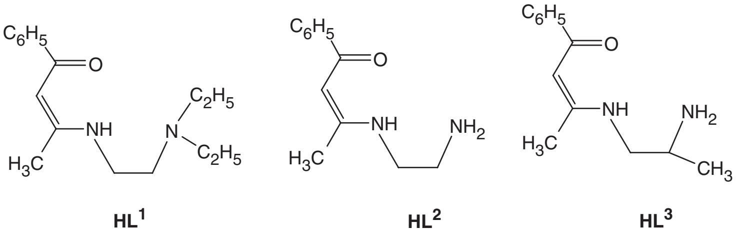
The results have inspired us to investigate if this increased steric effect can bring about change in the structure of azido bridged Cu(II) complexes. As H-bonding is also very important in these type of compounds, we designed the ligand in such a way that one (HL^1) is not capable of formation of H-bond while the other two (HL^2 and HL^3) have free amine hydrogen to from H-bonds (scheme 1). Here, we report the synthesis, spectral study and crystal structure of three copper(II) azide compounds with these three ligands. The results reveal a very intriguing competition between the coordination bond and H-bonding, the two most important forces on which the supramolecular chemistry as a whole and the self-assembly of the molecules in particular are based.

2. Experimental

Three mono-condensed ligands HL^1, HL^2 and HL^3 have been synthesized in our laboratory by the methods described below. All chemicals were of reagent grade and used without further purification.
Caution! Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

2.1. *Synthesis of ligands*

Preparation of HL^1 [6-diethylamino-3-methyl-1-phenyl-4-azahex-3-en-1-one], HL^2 [6-amino-3-methyl-1-phenyl-4-azahex-3-en-1-one] and HL^3 [6-amino-3-methyl-1-phenyl-4-azasept-3-en-1-one]. HL^1 was prepared by condensation of the NH_2 group of



Scheme 1. Structure of the ligands.

N,*N*-diethyl-1,2-ethanediamine (0.96 mL, 10 mmol) with 1-benzoylacetone (1.62 g, 10 mmol), in methanol (30 mL) under reflux for 3 h. The ligand was not isolated; the yellow colored methanol solution was used directly for complex formation. Ligands HL^2 and HL^3 were prepared by the single condensation of the NH_2 group of 1,2-ethanediamine (0.67 mL, 10 mmol) and 1,2-propanediamine (0.85 mL, 10 mmol), respectively with 1-benzoylacetone (1.62 g, 10 mmol) under the condition of high dilution in chloroform [13]. After reaction, the chloroform was evaporated under reduced pressure to yield semi-solid HL^2 and solid HL^3. Methanol solutions of these ligands were used for complex formation.

2.2. *Synthesis of complexes [CuL^{1}N$_3$] (1), [CuL^{2}N$_3$] (2) and [CuL^{3}N$_3$] (3)*

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (3.7 g, 10 mmol) in methanol (20 mL) was added to a stirred solution of each of the ligands, HL^1, HL^2 and HL^3 (10 mmol) in methanol (10 mL). Triethylamine (1.7 mL, 10 mmol) was then added, dropwise, to this solution with constant stirring. The resulting solution was filtered to remove a small amount of colloidal precipitate that was formed immediately after addition of triethylamine, and sodium azide (0.78 g 12 mmol), dissolved in water-methanol mixture (5 mL, 1 : 4, v/v) was added to the filtrate and stirred. Separation of desired products as greenish solid took place for all three compounds in an hour. They were filtered and recrystallized from dry methanol. Single crystals of the compounds were obtained by slow evaporation of the methanol solution in a refrigerator. Single crystals of **1** are cubic whereas **2** and **3** are hexagonal.

Complex 1. Yield: 2.3 g (60%). Anal. Calcd for $C_{16}H_{23}CuN_5O$: C, 52.66; H, 6.35; N, 19.19; Cu, 17.41. Found: C, 52.94; H, 6.22; N, 19.51; Cu, 17.26%. λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 654 (348); IR: ν(C=N), 1592 cm^{-1}, ν(N–N), 2043 cm^{-1}.

Complex 2. Yield: 2.5 g (80%). Anal. Calcd for $C_{12}H_{15}CuN_5O$: C, 46.67; H, 4.90; N, 22.68; Cu, 20.58. Found: C, 46.96; H, 4.76; N, 22.53; Cu, 20.04%. λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 601 (105); IR: ν(N–H), 3132, 3208 and 3298 cm^{-1}, ν(C=N), 1597 cm^{-1}, ν(N–N), 2060 cm^{-1}.

Complex 3. Yield: 2.6 g (80%). Anal. Calcd for $C_{13}H_{17}CuN_5O$: C, 48.32; H, 5.27; N, 21.68; Cu, 19.67. Found: C, 48.92; H, 4.96; N, 21.57; Cu, 19.13%. λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 596(108); IR: ν(N–H), 3131, 3200 and 3261 cm^{-1}, ν(C=N), 1595 cm^{-1}, ν(N–N), 2062 cm^{-1}.

2.3. *Physical measurements*

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer and the copper contents in all the complexes were estimated spectrophotometrically. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1200–350 nm) were recorded in a Hitachi U-3501 spectrophotometer.

2.4. *Crystallographic studies*

Independent reflections for the complexes were measured with Mo-Kα radiation using a Siemens SMART CCD diffractometer for **1** and a MAR research Image Plate System for **2** and **3**. Data analysis for **1** was carried with the SHELXTL program [14] and the structure was solved by direct methods with SHELXTL. Absorption corrections were carried out using SADABS [15] and the structure was then refined to convergence on F^2 using SHELXTL. The non-hydrogen atoms were refined with anisotropic thermal parameters.

Suitable single crystals of complexes **2** and **3** were positioned at 70 mm from the Image Plate. A total of 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [16]. The structures were solved using direct methods with the SHELX86 program [17]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the DIFABS program [18]. The structures were refined on F^2 using SHELXL [19]. The crystal structure illustrations were generated using the ORTEP-3 program [20]. All crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *IR and electronic spectra*

The coordination mode of azide to transition metal is usually detected by the intense I.R. band due to $\nu_{as}(N_3)$ which occurs above 2000 cm^{-1}. In general, it appears above

Table 1. Crystal data and structure refinement of **1**–**3**.

	1	**2**	**3**
Formula	$C_{16}H_{23}CuN_5O$	$C_{12}H_{15}CuN_5O$	$C_{13}H_{17}CuN_5O$
M	364.93	308.84	322.86
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2/n$	$Pccn$
a (Å)	9.80(1)	17.43(2)	21.32(2)
b (Å)	12.73(1)	7.48(1)	17.59(2)
c (Å)	15.06(1)	20.45(2)	7.64(1)
α (°)	87.39(1)	90	90
β (°)	76.35(1)	95.63(1)	90
γ (°)	77.55(1)	90	90
V/(Å^3)	1783.2(1)	2653(5)	2864.5(6)
Z	4	8	8
D_c (g cm^{-3})	1.359	1. 547	1.497
μ (mm^{-1})	1.2 [Mo-Kα]	1.529 [Mo-Kα]	1.5 [Mo-Kα]
R(int)	0.025	0.051	0.097
No. of unique data	6094	4559	2610
No. of data with $I > 2\sigma(I)$	4731	3459	2008
R_1, wR_2	0.0850, 0.2278	0.0999, 0.1805	0.0819, 0.1433
Goodness-of-fit on F^2	1.055	1.217	1.201

2055 cm^{-1} for the μ_2-1,1-azide bridge and below 2055 cm^{-1} for the terminal ion [12a, d]. However complex **1** shows a strong absorption band at 2043 cm^{-1}, although it contains two types of azide ion. The position of the ν_{as} depends upon the difference between the two N–N distances ($\Delta d'$) of the azide group. In the present complex the $\Delta d'$ (0.021 and 0.026 Å for dimeric unit, A and monomeric unit, B respectively) is expectedly lower than that of symmetric μ_2-1,1-azide bridged complexes and hence the ν_{as} band appears at lower wave number. Complexes **2** and **3** also show a single absorption band at 2060 and 2062 cm^{-1}, respectively, consistent with the presence of only one type of azide i.e. terminal azide ion in the structures (vide structure description).

The bands corresponding to azomethine (C=N) are distinct in all the three complexes and occur at 1592, 1597 and 1595 cm^{-1} for **1**, **2** and **3**, respectively. Complexes **2** and **3** show three sharp bands at 3132, 3208, 3298 cm^{-1} and 3131, 3200, 3261 cm^{-1}, respectively, characteristic of NH_2.

The reflectance electronic spectra of all three complexes display a single absorption band at 654, 601 and 596 nm in methanol, respectively. The positions of these bands are consistent with their structures [21].

3.2. *Description of structures of complexes 1, 2 and 3*

3.2.1. Complex 1.

The structure determination reveals that **1** consists of one independent centrosymmetric dimer (A) and a monomer (B) in the asymmetric unit. A view of the dimeric unit is given in figure 1. Selected bond lengths and angles for **1** are summarized in table 2. In the dimer of **1** two distorted square-pyramidal copper(II) centers are bridged by two centrosymmetrically related azides in asymmetric, basal-apical, end-on fashion leading to relatively small Cu $\cdots$ Cu distances (3.566 Å). Within the dimeric unit each of the two trigonally-distorted, square-pyramidal copper(II) centers is coordinated equatorially by three ligating atoms N(4), N(5) and O(1), of the tridentate Schiff-base ligand and a nitrogen atom, N(1), of one of the bridging azide. A second nitrogen, N(1)′, from the centrosymmetrically related bridging azide coordinates axially at a rather long distance furnishing elongated square pyramidal (4 + 1) geometry. In the monomeric unit of the asymmetric part (B), the metal atom is in a square planar four-coordinate environment being bonded to three atoms of the tridentate ligand O(2), N(9) and N(10) and a terminal azide anion N(6). The axial Cu(II)-nitrogen (of centrosymmetrically related azide) distance is 3.126 Å, which is too long to be considered as a bond. The four basal bond distances of the asymmetric unit A are slightly greater than those of B (table 2). The axial coordination of azide in A seems to cause this difference.

The four basal donor atoms [O(1), N(1), N(4) and N(5)] in the dimeric unit deviate from the mean coordination plane through them by 0.353(5), −0.077(6), −0.119(6) and 0.415(5) Å, respectively. The copper(II) ion is displaced 0.014(1) Å from the plane towards the apical atom N1′. The distortions of the coordination polyhedron from the square pyramid to the trigonal bipyramid have been calculated by the Addison parameter (τ) [22] as an index of the degree of trigonality. The τ value for the unit A is 0.30. The monomer (B) is approximately planar with the atoms in the CuN3O equatorial planes. The four coordinating atoms N(2), N(6), N(9) and N(10) deviate form the coordination plane through them by 0.287(5), −0.303(10), −0.117(6) and 0.409(6) Å, respectively. The copper(II) is displaced 0.016(1) Å from

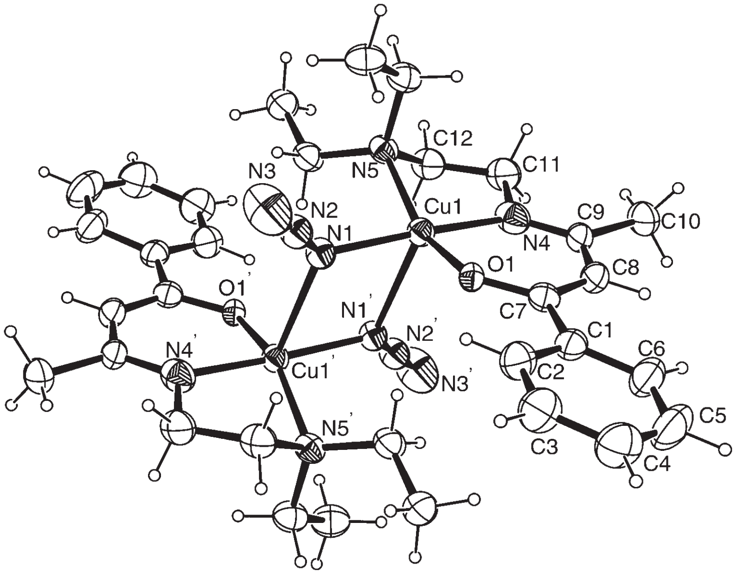


Figure 1. ORTEP-3 view of the dimer A of **1** with ellipsoids at 20% probability.

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

1(A)		**1**(B)	
Cu1–O1	1.940(5)	Cu2–O2	1.914(5)
Cu1–N1	2.005(6)	Cu2–N10	2.096(6)
Cu1–N4	1.967(6)	Cu2–N9	1.940(6)
Cu1–N5	2.102(6)	Cu2–N6	1.970(9)
Cu1–N1′	2.508(6)		
O1–Cu1–N4	92.7(2)	O2–Cu2–N10	159.2(2)
O1–Cu1–N5	156.8(2)	O2–Cu2–N6	91.7(3)
O1–Cu1–N1′	105.3(2)	O2–Cu2–N9	94.1(2)
O1–Cu1–N1	89.7(2)	N9–Cu2–N10	85.5(2)
N1–Cu1–N5	95.5(2)	N9–Cu2–N6	167.9(3)
N1–Cu1–N1′	76.2(2)	N6–Cu2–N10	92.8(3)
N1–Cu1–N4	174.9(2)		
N4–Cu1–N5	83.9(2)		
N4–Cu1–N1′	98.9(2)		
N1′–Cu1–N5	97.8(2)		
Cu1–N1–Cu1′	103.8(3)		

Designates the symmetry related atom at $-x$, $1-y$, $1-z$ for complex **1**.

the plane.The five-membered chelate ring incorporating the dimethylene fragment from the starting diamine assumes envelope conformation on N(5) within the dimer with puckering parameters [23] $q = 0.455(7)$ Å and $\phi = 315.6(9)^\circ$ in complex **1** and in the monomeric part the same ring is twisted on C(31)$\cdots$C(32) with puckering parameters $q = 0.451(9)$ Å and $\phi = 95.6(7)^\circ$.

The bridging Cu_2N_2 network in the dimer of **1** is exactly planar as dictated by symmetry. Due to formation of basal-apical μ_2-1,1-N_3 bridging, the bridging Cu–N bond length is significantly different ($\triangle d = 0.503$). The bridging N_3^- anions are quasi-linear; the N–N–N angles are 177.5(5)° for dimer and 176.4(6)° in the monomer.

3.2.2. *Complexes* **2** *and* **3**

There are two monomers (C) and (D) in the asymmetric unit in **2** but they have similar geometries and one molecule (C) is shown in figure 2. The structure of **3** has only one monomer in the asymmetric unit which is shown in figure S1 (supporting information). The metal atom in both complexes is in a square planar four-coordinate environment being bonded to three atoms of the tridentate ligand N(11), N(14) and O(18) and a terminal azide anion N(400). Molecular dimensions for both structures are given in table 3 and are very similar. The molecules are approximately planar with the atoms in the CuN_3O equatorial planes being planar to within 0.03 Å. Despite the planar structures and therefore the lack of steric repulsions, there are no close axial contacts to the metal atoms less than 3.1 Å (axial metal-nitrogen (azide) distances are 3.463, 3.500 and 3.599 Å in (C) and (D) of **2** and **3**, respectively).

The five-membered chelate ring incorporating the dimethylene fragment from the starting diamine assumes envelope conformation on C(12) with puckering parameters [23] $q = 0.424(10)$ and 0.358(6) Å and $\phi = 252.9(10)$ and 249.0(8)° in (C) of **2** and in **3** respectively. In unit (D) of **2**, the same ring assumes envelope conformation on C(32) with puckering parameters $q = 0.408(10)$ and $\phi = 67.9(11)$.

The bond distances and angles between the copper atom and the donor sites of the tridentate ligand and azide are within the range of values normally found for such systems [12]. However, there are two significant differences, first the bond length between amine nitrogen and Cu(II) of **1** (both in the asymmetric units A and B) is greater than that of other complexes. The presence of two bulky ethyl groups on amine nitrogen seems to be responsible for this difference. Second, the bridging Cu–N–Cu angles (103.8) in the asymmetric unit A of **1** is significantly greater compared to the range (86–94) found previously [12]. It seems likely that the presence of the phenyl ring in the carbonyl fragment of the Schiff-base ligand of **1** compared to methyl groups in the previous compounds as well as the presence of two ethyl group in the diamine part of L^1 have increased the non-bonded interactions and led to this significant change.

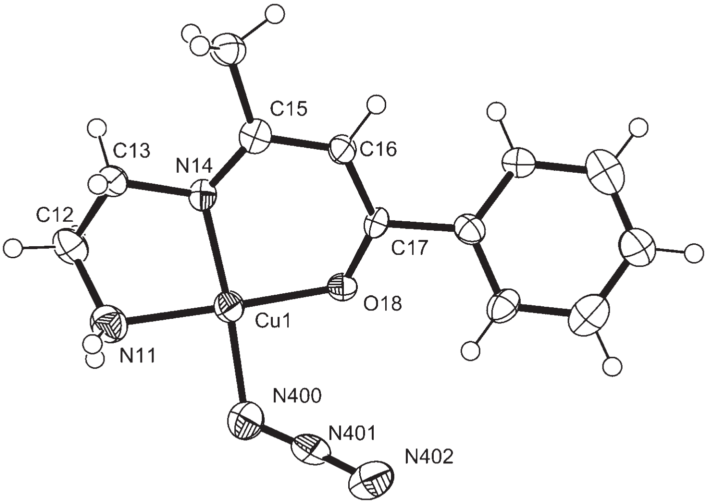


Figure 2. ORTEP-3 view of the asymmetric unit C of **2** with ellipsoids at 30% probability.

Table 3. Selected bond lengths (Å) and angles (°) for **2** and **3**.

	2(C)	**2**(D)	**3**
Cu1–O18	1.937(7)	–	1.914(5)
Cu1–N11	2.012(9)	–	2.014(6)
Cu1–N14	1.933(7)	–	1.951(5)
Cu1–N400	1.979(9)	–	1.995(7)
Cu2–N34	–	1.964(7)	–
Cu2–O38	–	1.941(7)	–
Cu2–N31	–	2.005(9)	–
Cu2–N300	–	2.004(10)	–
O18–Cu1–N11	177.0(3)	–	178.2(2)
O18–Cu1–N14	94.7(3)	–	93.8(2)
O18–Cu1–N400	90.3(3)	–	90.7(2)
N11–Cu1–N14	84.2(3)	–	84.8(2)
N11–Cu1–N400	90.9(4)	–	90.6(2)
N14–Cu1–N400	175.0(3)	–	175.4(2)
N400–N401–N402	176.9(10)	–	177.4(7)
N34–Cu2–N300	–	175.4(3)	–
N31–Cu2–N300	–	91.5(4)	–
O38–Cu2–N34	–	94.5(3)	–
O38–Cu2–N300	–	89.6(3)	–
O38–Cu2–N31	–	177.7(3)	–
N31–Cu2–N34	–	84.3(3)	–
N300–N301–N302	–	176.7(11)	–

Two different monomers in the asymmetric unit of **2** are linked by strong hydrogen bonds using four available hydrogen atoms [H(11a), H(11b), H(31a) and H(31b)] of two asymmetric units resulting in a one-dimensional network (figure 3, table 4). H(11a) and H(31b) of the nitrogen N(11) and N(31) that are coordinated to Cu(1) and Cu(2), respectively, are involved in strong N–H$\cdots$N hydrogen bond formation with the coordinated azide nitrogen atoms N(400′) and N(300′) from centrosymmetrically related ($3/2-x$, y, $3/2-z$) asymmetric units. H(11b) of the nitrogen N(11) is involved in bifurcated N–H$\cdots$N hydrogen bond formation with the nitrogen atoms N(300) and N(301) of same azide. H(31a) of the nitrogen N(31) is also involved in bifurcation forming strong N–H$\cdots$N hydrogen bonds with nitrogen N(400) and N(401) of the same azide of centrosymmetrically related asymmetric unit ($x, 1+y, -z$).

In **3**, two centrosymmetrically ($1/2-x$, $1/2-y$, z) related monomeric units are linked via a strong N11–H11a$\cdots$N400′ hydrogen bond resulting in a dimeric entity having long Cu$\cdots$Cu distance, 5.606 Å. The other H-atom on N11 (H11b) is involved in a weaker H-bond ($1/2-x$, y, $-1/2+z$) with the coordinated N of the azide ion (N400″) of the neighboring dinuclear entity to result in a similar H-bonding network as in **2** (figure 4, table 4). The H-bonding patterns of **2** and **3** show an interesting difference from those of similar Schiff base complexes of Cu(II) containing acetylacetone or salicyladehyde [12d, e]. In those dimers, one of the H-atoms in the amine nitrogen is invariably involved in an intra-dimer N–H$\cdots$O hydrogen bond with the ligating oxygen of the corresponding tridentate Schiff-base ligand that acts as an additional bridge to bind the two monomeric units in the azide-bridged dinuclear entities. In contrast, although there are two H-atoms in the amine nitrogen of **2** and **3**, none is involved in H-bonding with the oxygen atom of the corresponding tridentate ligand.

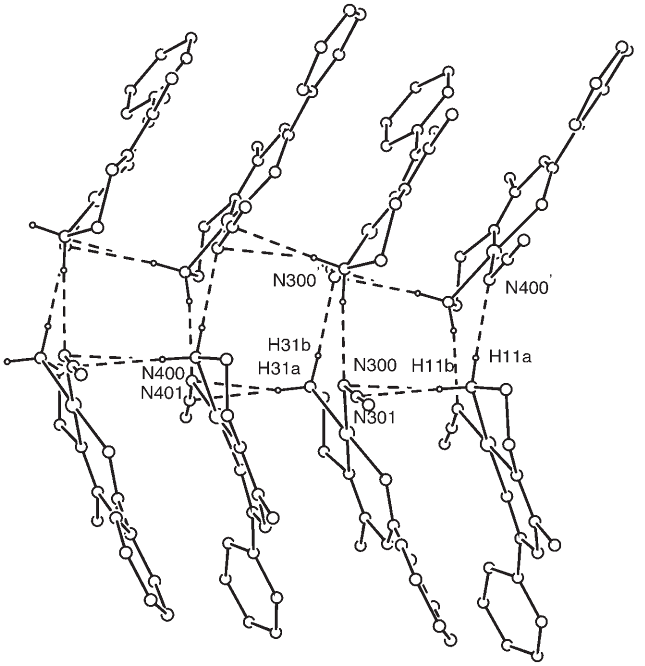


Figure 3. Extended hydrogen-bonding network of **2**. Symmetry transformations: $' = 3/2 - x,\ y,\ 3/2 - z$; $'' = x,\ 1 + y,\ z$.

Table 4. Hydrogen bonding distances (Å) and angles (°) for **2** and **3**.

Compound	D–H···A	D–H	D···A	A···H	∠D–H···A
2	N11–H11b···N300	0.899	3.423(16)	2.545	166
	N11–H11b···N301	0.899	3.397(14)	2.515	167
	N11–H11a···N400^{j}	0.899	3.068(13)	2.198	163
	N31–H31b···N300^{j}	0.900	3.096(13)	2.224	163
	N31–H31a···N400^{k}	0.899	3.414(15)	2.559	159
	N31–H31a···N401^{k}	0.899	3.341(13)	2.447	172
3	N11–H11a···N400^{m}	0.899	3.179(9)	2.311	162
	N11–H11b···N400^{n}	0.900	3.451(10)	2.565	168

Symmetry elements: (j) $3/2 - x,\ y,\ 3/2 - z$; (k) $x,\ 1 + y,\ z$; (m) $1/2 - x,\ 1/2 - y,\ z$; (n) $1/2 - x,\ y,\ -1/2 + z$.

3.3. *Discussion*

Crystal structures of the three compounds clearly show that in **1** half of the molecules are dimers and the remaining half are monomers whereas in **2** and **3** no dimeric molecule is formed. On the other hand, when acetylacetone was used instead of 1-benzoylacetone, invariably basal-apical, dinuclear μ_2-1,1-N_3 copper(II) complexes resulted [12(d, e)]. Therefore, to a first approximation one may consider that the nonbonding interactions of the phenyl ring prevent the monomeric units forming dimers in these complexes. However, the steric factor alone cannot explain the dimer formation only in **1** but not in **2** or **3**. In fact, HL^1 is the bulkiest among the three ligands as it contains two ethyl groups on nitrogen and therefore **1** should have the least possibility to dimerize. As a result, other factors such as H-bonding interaction and

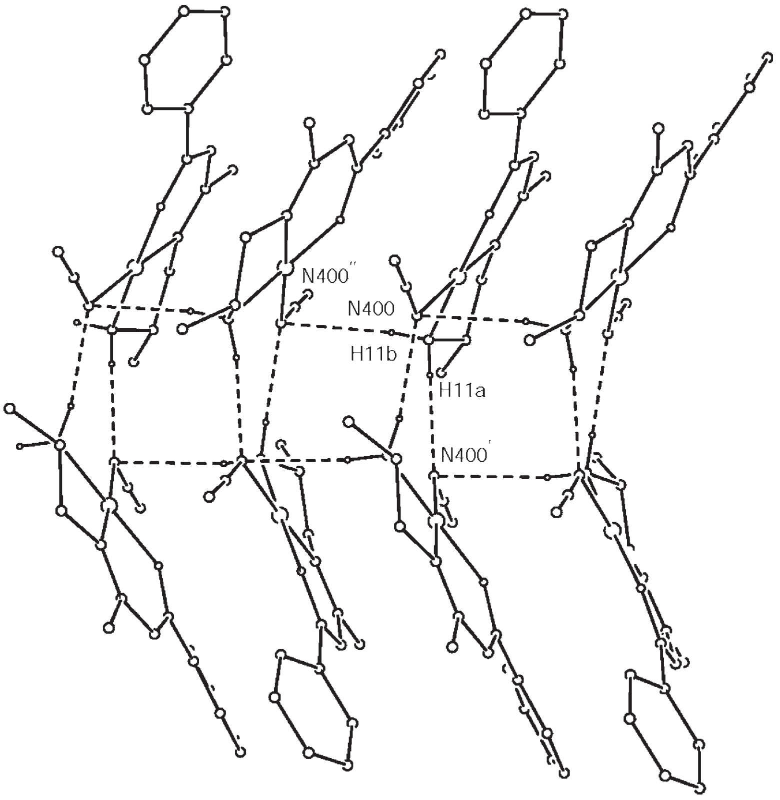


Figure 4. Extended hydrogen-bonded network of **3**. Symmetry transformations: $' = 1/2 - x,\ 1/2 - y,\ z$; $'' = 1/2 - x,\ y,\ -1/2 + z$.

strength of the coordinate bond are also needed for formation of dimer. The dimeric entity is formed as the coordinated basal azide of a monomer bridges another monomeric unit in axial position and vice versa [12d, e]. Cu(II) being a d^9 system with an active Jahn–Teller effect can have a very long axial bond but as the bond gets longer, it becomes weaker and its dissociation can take place easily to facilitate other weak interactions. Complexes **2** and **3** can form H-bonds as there are hydrogen atoms on the amine nitrogen. However, the strength of H-bond depends upon the relative orientation and bulkiness of the molecule and on the nature of the acceptor atoms. As the molecule gets bulkier, the increased nonbonding interactions make the axial bond longer in the dimer and also constrain the intermolecular H-bond formation. The mononeric units, however, can orient themselves relatively easily to facilitate stronger H-bond formation. Therefore, monomers are the preferred structures when loss in energy due to dissociation of a long and weak axial bond is offset by the gain in H-bond strength (as in complexes **2** and **3**), i.e. a stronger H- bond is formed, at the expense of the coordination bond, a rare phenomenon in coordination chemistry. Complex **1** cannot form an H-bond and therefore the weakly associated dimeric structure of half of the molecules is preferred. Replacement of the ethyl groups of L^1 by methyl, reduces the steric demand of the ligand and expectedly all the molecules of the resulting compound are dimeric [24].

4. Conclusion

The crystal structure determination of the three compounds reveals that the group of mononegeative, N_2O donor tridentate Schiff-base ligands can produce mononuclear complxes on reaction with Cu(II) azide although most of the compounds reported previously with this type of ligand are end-on azido bridged dimers. The steric demand and the H-bonding ability of the ligands seem to be the determining factors for monomeric versus dimeric structural preferences.

Supplementary data

Crystallographic data (excluding structure factors) for complexes, **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 610128 (Complex **1**), 610129 (Complex **2**) and 610130 (Complex **3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/deposit; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033.

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