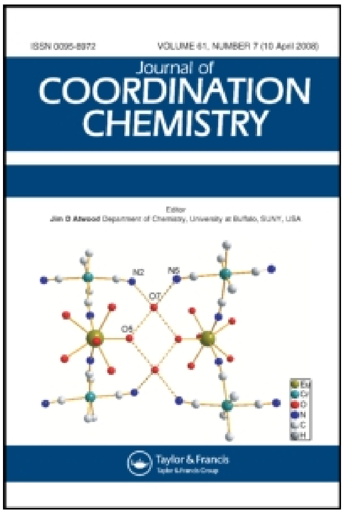

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Copper(II) complexes with singly condensed tridentate Schiff-base ligands incorporating 1-benzoylacetone

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Copper(II) complexes with singly condensed tridentate Schiff-base ligands incorporating 1-benzoylacetone

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Two copper(II) complexes $[CuL^1Cl]_n$ (**1**) and $[CuL^2Cl]$ (**2**) with singly condensed tridentate Schiff-base ligands [HL^1 = 6-amino-3-methyl-1-phenyl-4-azahex-3-en-1-one and HL^2 = 6-diethylamino-3-methyl-1-phenyl-4-azahex-3-en-1-one] have been synthesized and structurally characterized by X-ray crystallography. Complex **1** is a single-chloro-bridged one-dimensional polymer, whereas **2** is a monomeric square-planar complex. The H-bonding interactions of the amine hydrogen and the non-bonding interactions of phenyl groups in the Schiff base play important roles for the structural variations.

Keywords: Copper(II); Schiff base; 1-Benzoylacetone; Crystal structure; Electrochemical behavior

1. Introduction

Since the first reports on the synthesis of 7-amino-4-methyl-5-azahept-3-en-2-one (AMAH) [1, 2] and 8-amino-4-methyl-5-azaoct-3-en-2-one (AMAO) [3], monocondensation products of 2,4-pentanedione with 1,2-ethanediamine and or 1,3-propanediamine, respectively, these ‘half units’ have been used extensively to synthesize mono-, di- or trinuclear transition metal complexes and also as precursors for preparation of unsymmetrical quadridentate Schiff-base ligands [4–10]. Recently, we synthesized the analogous tridentate Schiff bases by monocondensation of 1-benzoylacetone with 1,2-diaminoethane or 1,2-diaminopropane under similar conditions and used those ligands to synthesize copper(II) complexes [11–13]. In those studies we observed that the structure and properties of the resulting complexes may be very different from their acetoacetyl analogues. For example, the acetylacetone-derived tridentate Schiff bases, on reaction with copper(II) azide, invariably yielded double

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end-on azido bridged basal-apical dimers [14], whereas their benzoylacetone analogues produced monomeric compounds [12]. The benzoylacetone-derived Schiff bases are more susceptible to hydrolysis during complex formation and can result in ternary compounds containing the hydrolyzed products e.g. diamine and benzoylacetone [11]. In the hydroxo-bridged trinuclear copper(II) complexes of such ligands, replacement of acetylacetone-derived Schiff base by their benzoylacetone analogue gives remarkable changes in their magnetic properties (antiferromagnetic to ferromagnetic) [13].

There are only two chloro-bridged copper(II) complexes containing acetylacetone-derived N_2O donor Schiff base ligands reported in the literature [15, 16]. In both cases, the chloride ion bridges the copper centers in basal-apical manner resulting in centrosymmetric dimeric species. In this paper, we report synthesis, crystal structure, spectral properties and electrochemical behavior of two new copper(II) chloride complexes with benzoylacetone-derived Schiff bases, HL^1 (6-amino-3-methyl-1-phenyl-4-azahex-3-en-1-one) and HL^2 (6-diethylamino-3-methyl-1-phenyl-4-azahex-3-en-1-one). The structures of the complexes are very different from the reported acetylacetone-derived complexes [15, 16].

2. Experimental

Two mono-condensed ligands, HL^1 and HL^2, have been synthesized in our laboratory by the methods described below. The diamines and 1-benzoylacetone were purchased from Lancaster Chemical Co. The chemicals were of reagent grade and used without further purification.

2.1. *Preparation of HL^1 [6-amino-3-methyl-1-phenyl-4-azahex-3-en-1-one] and HL^2 [6-diethylamino-3-methyl-1-phenyl-4-azahex-3-en-1-one]*

HL^1 was prepared by condensation of one of the NH_2 groups of 1,2-ethanediamine with 1-benzoylacetone in chloroform by high-dilution technique [11, 13]. A solution of 1-benzoylacetone (1.62 g, 10 mmol) in chloroform (50 mL) was added dropwise to a solution of 1,2-ethanediamine (0.67 mL, 10 mmol) in chloroform (50 mL) at room temperature. After addition, the solution was stirred for an additional 3 h and chloroform was evaporated under reduced pressure. The resultant semi-solid product was collected as the ligand and dissolved in methanol (30 mL) for synthesis of the complex.

HL^2 was prepared by condensation of the NH_2 group of *N*,*N*-diethyl-1,2-ethanediamine (0.96 mL, 10 mmol) with 1-benzoylacetone (1.62 g, 10 mmol) in methanol (30 mL) [12] under reflux for 2 h. The ligand was not isolated and the methanolic solution was used directly for formation of the complex.

2.2. *Synthesis of complexes $[CuL^1Cl]_n$ (1) and $[CuL^2Cl]$ (2)*

A solution of $CuCl_2 \cdot 2H_2O$ (1.705 g, 10 mmol) was added to a stirred solution of each of the ligands, HL^1 and HL^2 (10 mmol) in methanol (10 mL). The resulting solutions were filtered to remove the small amount of colloidal precipitates that formed immediately. The bluish-green crystalline solid products for both compounds separated on keeping the filtrate at room temperature for several days. The precipitated complexes were collected by filtration and recrystallized from methanol. X-ray quality single crystals of **1** were obtained as bluish-green prisms by slow diffusion of diethylether into an acetonitrile solution of the complex, whereas those of **2** were obtained as greenish-black prisms by slow diffusion of n-hexane into a dichloromethane solution of **2**.

Complex 1: Yield: 1.9 g (56%). Anal. Calcd for $C_{12}H_{15}ClCuN_2O$: C, 47.68; H, 5.00; N, 9.27; Cu, 21.02. Found: C, 47.94; H, 5.12; N, 9.11; Cu, 21.26%. λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 602(117); IR: ν(C=N), 1510 cm^{-1}, ν(N–H), 3179 and 3293 cm^{-1}. Magnetic moment (at 25°C), $\mu_{eff} = 1.74$ BM.

Complex 2: Yield: 1.7 g (47%). Anal. Calcd for $C_{16}H_{23}ClCuN_2O$: C, 53.62; H, 6.47; N, 7.82; Cu, 17.73. Found: C, 53.71; H, 6.53; N, 7.61; Cu, 17.83%. λ_{max}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) (methanol), 579 (137); IR: ν(C=N), 1503 cm^{-1}. Magnetic moment (at 25°C), $\mu_{eff} = 1.78$ BM.

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. Cyclic voltammetry was carried out using Sycopel model AEW2 1820F/S instrument. The measurements were performed at 300 K in acetonitrile solutions containing 0.2 M TEAP and 10^{-3} M Cu(II) complex deoxygenated by bubbling with nitrogen. The working, counter, and reference electrodes used were a platinum wire, a platinum coil, and an SCE. The magnetic susceptibility measurements were done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants.

2.4. *Crystallographic studies*

Data were collected at room temperature on a Bruker AXS Smart single crystal diffractometer with CCD (area detector) using Cu-Kα radiation. The absorption correction was performed with the method inserted in SHELXTL-NT V5.1 [17]. The structure was solved by direct methods with the software SHELXTL-NT V5.1 inserted in the Bruker AXS software [17]. The nonhydrogen atoms were refined anisotropically while the hydrogen atoms, either located from difference electron density maps or placed geometrically, were refined with isotropic thermal parameters. Neutral atom scattering factors were taken from Cromer and Weber [18] and anomalous dispersion effects were included in Fcalc [19]. The crystallographic illustrations were prepared using ORTEP-3 [20]. Significant crystallographic data are summarized in table 1 and selected bond distances and angles in table 2.

Table 1. Crystal data and structure refinement of **1** and **2**.

	1	**2**
Formula	$C_{12}H_{15}ClCuN_2O$	$C_{16}H_{23}ClCuN_2O$
M	302.26	358.36
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pna21*
Unit cell dimensions (Å, °)		
a	25.713(3)	11.588(3)
b	7.158(3)	13.335(3)
c	13.446(3)	10.754(3)
α	90	90
β	90	90
γ	90	90
V(Å^{-3})	2474.8(1)	1661.8(7)
Z	8	4
D_{Calcd} g^{-1} cm^{-3}	1.622	1.432
μ (mm^{-1})	4.347 [Cu-Kα]	3.325 [Cu-Kα]
No. of unique data	2311	2361
No. of data with $I > 2\sigma(I)$	1191	2313
$R1$, $wR2$	0.0468, 0.1189	0.0418, 0.1166
Goodness of fit on F^2	0.811	1.131

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

	1	**2**
Cu(1)–Cl	2.299(2)	2.239(1)
Cu(1)–O(1)	1.907(4)	1.906(4)
Cu(1)–N(3)	1.992(6)	2.066(4)
Cu(1)–N(6)	1.956(4)	1.937(3)
Cu(1)–Cl^b	3.124(2)	
Cl–Cu(1)–O(1)	90.94(13)	89.72(12)
Cl–Cu(1)–N(3)	91.60(16)	94.67(10)
Cl–Cu(1)–N(6)	164.83(13)	166.66(10)
Cl–Cu(1)–Cl^b	109.70(5)	
O(1)–Cu(1)–N(3)	174.8(2)	168.45(15)
O(1)–Cu(1)–N(6)	93.83(17)	92.43(15)
O(1)–Cu(1)–Cl^b	93.50(13)	
N(3)–Cu(1)–N(6)	84.9(2)	85.76(14)
N(3)–Cu(1)–Cl^b	81.34(16)	
N(6)–Cu(1)–Cl^b	84.40(13)	

Symmetry element; $^b = 1 - x, 1/2 + y, 1/2 - z$.

3. Results and discussion

3.1. *IR and electronic spectra*

The bands corresponding to azomethine (C=N) are distinct in both complexes at 1510 and 1503 cm^{-1} for **1** and **2**, respectively. Complex **1** shows sharp bands at 3197 and 3293 cm^{-1}, characteristic of NH_2. Complex **2** contains no significant peaks in the region 3100 to 3300 cm^{-1} as there is no free –NH_2 group. The electronic spectra of the two complexes display a single absorption at 602 and 579 nm, respectively, in methanol. The positions of these bands are consistent with their structures [21, 22]. The appearance of similar d-d transition in **1** and **2** indicates that semi-coordinated

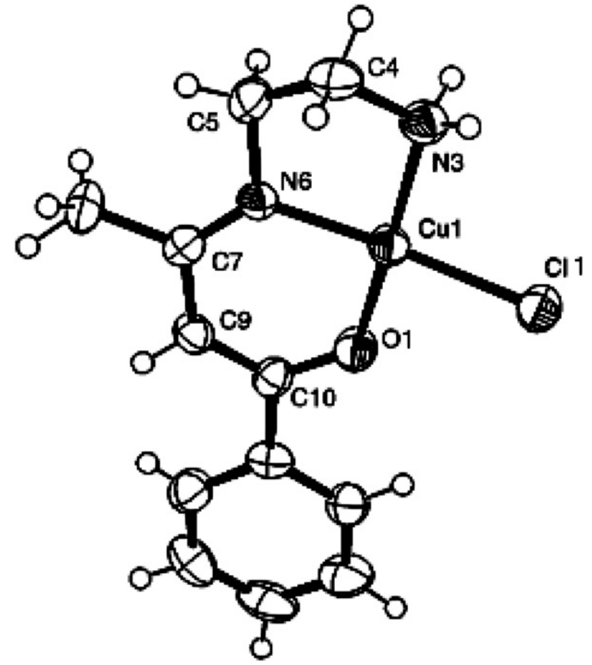


Figure 1. The structure of **1** with ellipsoids at 50% probability.

character of the chloride to the axial position of copper does not significantly affect the coordination geometry around the Cu(II) in **1**.

3.2. *Structure description*

The structures of **1** and **2** are shown in figures 1 and 2, respectively, with common atom numbering scheme. For both compounds, the structures consist of a [CuLCl] asymmetrical unit. The basic coordination environment of the complexes is square planar, with the deprotonated tridentate Schiff base occupying three coordination sites and the fourth coordination site by chloride. In **1**, this apical chloride coordinates very weakly to the axial position of the copper of another unit ($1-x$, $1/2+y$, $1/2-z$) at a distance of 3.124(2) Å, resulting in a singly chloro-bridged polymeric chain (figure 3). Although the distance is very long, because it is less than the sum of the van der Waals radii for copper(II) and chlorine (3.25 Å), a weak bond is considered to be formed [23]. In this complex, the four basal donor atoms [O(1), N(3), N(6) and Cl] deviate from the mean coordination plane by 0.171(4), 0.178(5), −0.192(4) and −0.157(1) Å, respectively. The copper(II) is displaced 0.0924(7) Å from the plane towards the apical chloride as usual for square pyramidal geometry. The Addison parameter ($\tau = 0.17$) of the complex shows that there are slight distortions of the coordination polyhedron from the square pyramid to trigonal bipyramidal geometry [24].

In **2**, the four donors [O(1), N(3), N(6) and Cl] deviate from the mean coordination plane by −0.222(3), −0.208(4), 0.237(3) and 0.193(1) Å, respectively. The copper(II) ion is displaced by 0.0195(6) Å from the same plane. In this complex, the tetrahedral

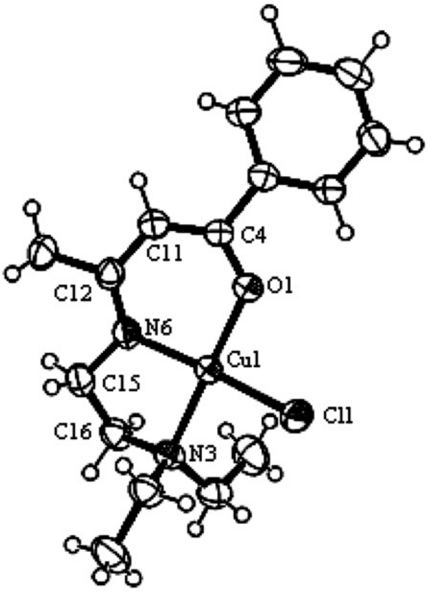
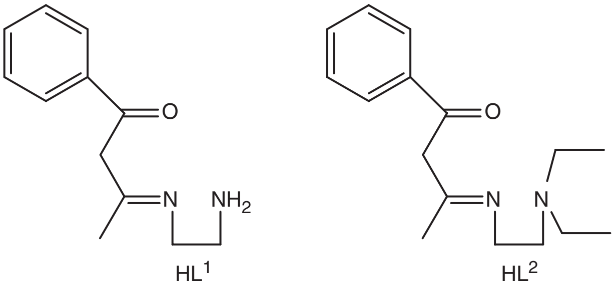


Figure 2. The structure of **2** with ellipsoids at 50% probability.



Scheme 1. The ligands.

distortion is apparent since one pair of diagonal donors clearly lies below the plane while the other pair is above the plane with the metal ion in the mean plane. The dihedral angles between the two planes [N(6)–Cu–O(1) and N(3)–Cu–Cl] is 16.87° compared with 0° for a perfectly square-planar arrangement and 90° for a perfect tetrahedral arrangement.

The six-membered benzoylacetone rings around the copper are essentially planar with no atoms deviating from the least square plane by 0.017 Å and 0.011 Å for complexes **1** and **2**. The mean plane of this ring is not coplanar with the benzene plane; the angle between the two planes is 8.61° and 5.66° for **1** and **2**, respectively. The five-membered rings incorporating the ethylene fragment from the starting diamine are not planar, but twisted on C(4) and C(5) for **1** and assumes an envelope conformation on C(16) for **2**. The puckering parameters [25, 26] are $q = 0.364(7)$ and 0.413(4) Å and $\phi = 262.0(7)$ and 250.1(5)° for **1** and **2**, respectively.

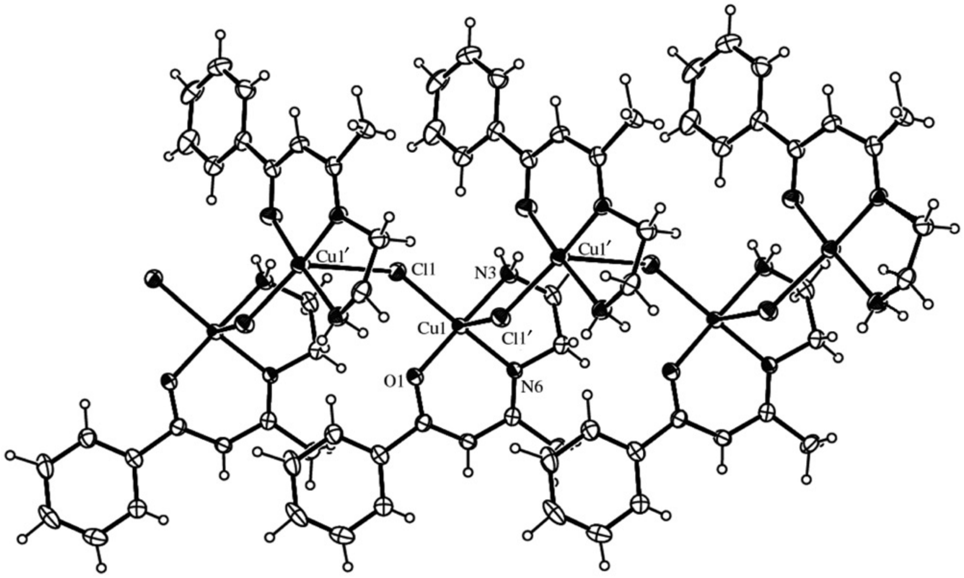


Figure 3. The structure showing one-dimensional single chloride bridges in **1** with ellipsoids at 30% probability. Symmetry element: $' = 1 - x,\ 1/2 + y,\ 1/2 - z$.

The structure of these two complexes can be compared with those of the acetylacetone-derived Schiff base complexes of copper(II). Two such complexes are reported with 8-amino-5-aza-4-methyl-3-octene-2-one [15] and 7-amino-4-methyl-5-azahept-3-en-2-one [16]. In both cases, the compounds are double basal-apical chloro-bridged dimers. As described above, the structure of the present complexes are different: **1** is a single chloro-bridged one-dimensional chain, whereas **2** is a monomer. In **1**, the bridging Cu–Cl(apical) distance is rather large (3.124 Å) compared to 2.782 and 2.837 Å in the two reported dichloro-bridged complexes [15, 16]. Thus, the effect of non-bonding interactions of the phenyl group on the variation of the molecular structure is obvious. The single chloro-bridged Cu(II) complex with tridentate ligand is rare. We found only one such complex, $[Cu(pamh)Cl]_n$, where Hpamh is the hydrazone of 2-pyridine-carboxaldehyde and aroylhydrazine [27]. The bridging Cu–Cl distance (2.782 Å) in this complex is appreciably shorter and the Cu–Cl–Cu bridge angle (117.60°) is smaller (123.55°) than that in **1**.

Both the hydrogen atoms (H3a and H3b) on N3 of **1** are involved in hydrogen bonding interactions (figure 4, table 3). H3a is involved in a hydrogen bond with O(1)′ ($1 - x,\ 1/2 + y,\ 1/2 - $z) of a neighboring unit in the same chain. Thus, two units in the one-dimensional chain are linked both by H-bond and chloride bridge. H3b is engaged in hydrogen bonding with the chloride of symmetry related unit ($x,\ 1/2 - y,\ 1/2 + z$) in a neighboring chain to result in a two-dimensional hydrogen-bonded polymeric structure.

Neither complex shows significant π-stacking interaction between the aromatic rings, though molecules of **1** are assembled via $C_{sp}^2 - H\cdots\pi$ binding contacts to generate a two-dimensional network. Each molecule of **1** interacts with symmetry related ($x,\ 1/2 - y,\ -1/2 + z$) neighboring molecules by weak $C_{sp}^2 - H\cdots\pi$ (phenyl)

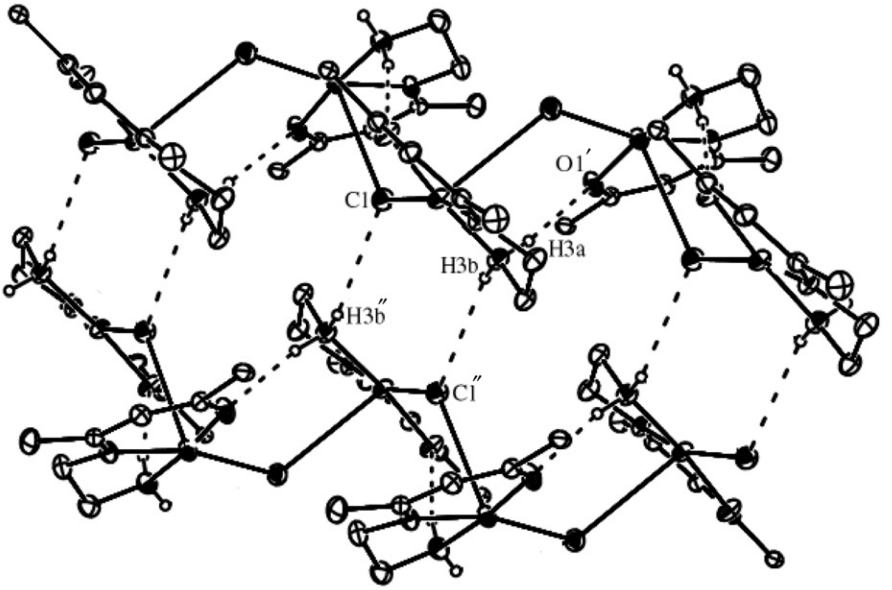


Figure 4. Extended hydrogen-bonded network of **1** (with ellipsoids at 45% probability). Symmetry elements: $' = 1 - x,\ 1/2 + y,\ 1/2 - z$ and $'' = x,\ 1/2 - y,\ 1/2 + z$.

Table 3. Hydrogen bonding distances (Å) and angles (°) for 1.

D–H···A	D–H	D···A	A···H	∠D–H···A
N3–H3a···O11′	0.92(8)	3.32(1)	2.42(7)	170(6)
N3–H3a···Cl″	0.77(3)	3.61(7)	2.93(1)	149.2(2)

Symmetry elements: $' = 1 - x,\ 1/2 + y,\ 1/2 - z$; $'' = x,\ 1/2 - y,\ 1/2 + z$.

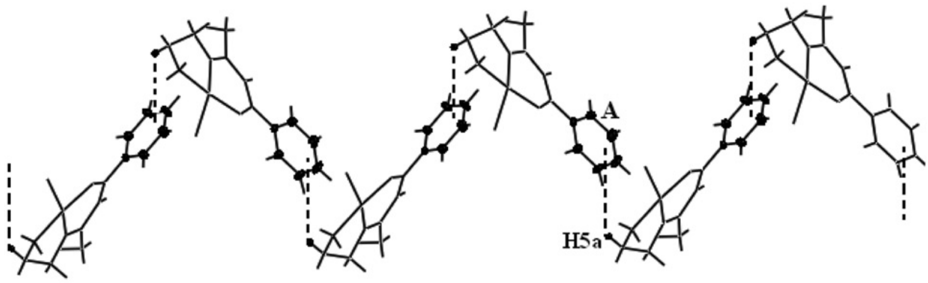


Figure 5. Crystal packing of **1** showing the supramolecular one-dimensional chain generated from C–H/π interaction.

supramolecular bonds (the distance H5a···centroid A is 2.94(5) Å, angle between C5–H5a···C_g (ring A) is 142(4)° and the distance C5···C_g (ring A) is 3.73(1) Å; figure 5). The $C^2_{sp} - H \cdots \pi$ contact distance is typical for this type of interaction [28, 29].

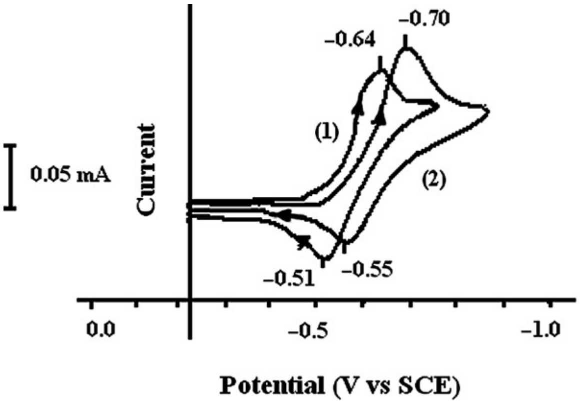


Figure 6. The cyclic voltammogram of **1** and **2** in acetonitrile (scan rate $100\,\mathrm{mV\,s^{-1}}$).

3.3. *Electrochemical study*

The cyclic voltammograms of the complexes are recorded in acetonitrile (figure 6). The two complexes show quasi-reversible Cu(II)/Cu(I) reductive responses. The reduction potential for **1** is −0.64 V (E_{pc}); the corresponding E_{pa} value was observed at −0.51 V. The $E_{1/2}$ value of **1** is −0.575 V (*versus* SCE). Under identical experimental conditions the potential values for **2** are −0.70 V (E_{pc}), −0.55 V (E_{pa}) and −0.625 V ($E_{1/2}$) (*versus* SCE). The electrochemical properties of copper(II) complexes have been studied extensively [27, 30, 31]. In four-coordinate systems, Cu(II) and Cu(I) have very distinct preference for square and tetrahedral geometry, respectively [31]. This preference is well reflected in the redox behavior of these systems. The more distortion in the coordination geometry towards tetrahedral, the higher is the anodic shift of the Cu(II)/Cu(I) redox potentials [31]. The observed $E_{1/2}$ values for the present complexes are within the range of similar complexes. However, the axial bond of the bridging chloride in **1** is very weak and may undergo bond cleavage in solution during the electrochemical study to form four-coordinate species like **2**. It is difficult to correlate the observed $E_{1/2}$ values for the complexes with their solid-state structural parameters.

4. Conclusion

Differences in the structures of **1** and **2** from their acetylacetone analogues suggest that the nonbonding interactions of the phenyl ring prevent formation of dimeric units. In **1**, the chloride coordinates very weakly to the axial position of copper(II) to form a polymeric chain compound. The H-bond between H3a and O(1) also provides additional stability to the chain structure. The Schiff-base ligand of **2** is even more sterically demanding as two additional ethyl groups are present on the amine nitrogen. As a consequence, the complex exists as a monomer. This study, thus, clearly shows that the steric requirement of ligands can alter the bridging of linking atoms and must be considered in designing polynuclear metal complexes.

Supporting information

Significant crystallographic data are summarized in table 1. CCDC Nos 661576 (complex **1**) and 661577 (complex **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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