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Synthesis, characterisation and X-ray crystal structure of copper(II) complexes with unsymmetrical tetradentate Schiff base ligands: first evidence of Cu(II) catalysed rearrangement of unsymmetrical to symmetrical complex

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Abstract

The mononuclear copper(II) complexes, $[CuL^1](ClO_4)$ (**1**), and $[CuL^2](ClO_4)$ (**2**) with unsymmetrical quadridentate Schiff base ligands derived from the 1:1:1 condensation of 2,4-pentanedione, pyridine-2-carboxaldehyde and 1,2-ethanediamine (HL^1) or 1,3-propanediamine (HL^2) have been prepared and characterised. Complex **2** undergoes Cu(II)/H^+ catalysed rearrangement to $[CuL^3](ClO_4)_2$ (**3**) where L^3 is a symmetrical tetradentate Schiff base involving 1,3-propanediamine and pyridine-2-carboxaldehyde. Structures of all the three compounds have been verified by single crystal X-ray analysis. The geometry around Cu(II) is square-planar in **1** and **2** whereas that in **3** is distorted octahedral with two axially coordinated perchlorate ions.

Keywords: Asymmetrical tetradentate Schiff base; Copper(II); X-ray crystallography; Cu(II) catalysed hydrolysis

1. Introduction

Since the first reports on the synthesis of 7-amino-4-methyl-5-azahept-3-en-2-one (AMAH) [1] and 8-amino-4-methyl-5-azaoct-3-en-2-one (AMAO), [2] the monocondensation products of 2,4-pentanedione with 1,2-ethanediamine and or 1,3-propanediamine, respectively, the compounds have been used as precursors for the preparation of unsymmetrical quadridentate Schiff base ligands [3]. The monocondensation products of diamines, here after referred to as 'half-units' where one primary amine group forms an imine or enamine bond and the other is unchanged, have a potential to react with other carbonyl moieties to form unsymmetrical ligands capable of binding transition metal ions. Such singly condensed units have been prepared by several routes [1–4]. Reacting the constituents under high dilution which was employed in the present study, is a route employed earlier [1,4]. In transition-metal biosites the metal ions are often found in chemically or geometrically distinct environments. Such compounds have been suggested as useful probes for the study of low symmetry complexes related to the low symmetry sites found in metalloprotins [5]. The unsymmetrical nature of the dicopper site in hemocyanin was established [6].

In this paper we report the synthesis and characterisation of copper(II) complexes of quadridentate unsymmetrical ligands HL^1 and HL^2 derived from AMAH and AMAO by condensation of the free amine group with pyridine-2-carboxaldehyde (Scheme 1). The complex, $[CuL^2]ClO_4$, has been found to rearrange into the symmetrical complex $[CuL^3](ClO_4)_2$ (where L^3 is the

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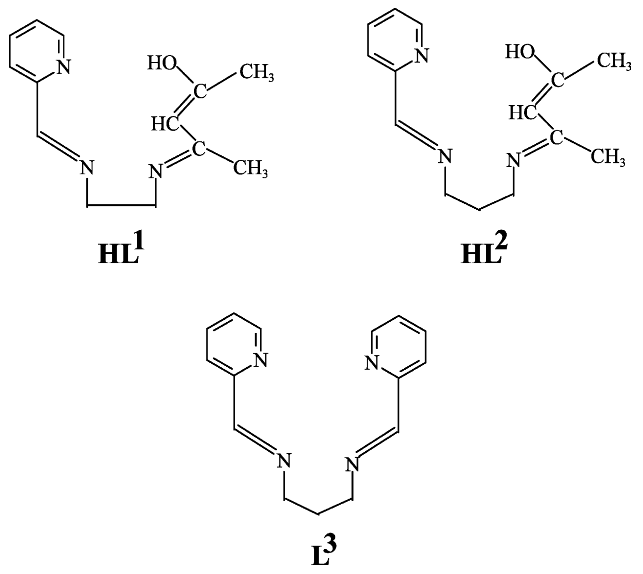


Scheme 1.

symmetrical Schiff base ligand involving 1,3-propanediamine and pyridine-2-carboxaldehyde). Unsymmetrical to symmetrical rearrangement of similar type of ligands was observed in the presence of Mn^{3+} during the synthesis of such type of complexes [7]. However, to our knowledge, till date there is no report of investigation as to whether this type of rearrangement (i) is catalysed by any other metal ion or (ii) is dependent on the ligand systems. In the present systems, we observed the first copper catalysed rearrangement, which is dependent upon the ligand systems. The structures of all the three complexes have been verified by single crystal X-ray analysis.

2. Experimental

All other chemicals were of reagent grade and used without further purification. The ‘half-units’ AMAH and AMAO were prepared as viscous oil by reported methods [1,4].

2.1. Synthesis of the complexes

2.1.1. [CuL^1]ClO$_4$ (**1**)

AMAH (10 mmol) was dissolved in methanol (50 cm^3) and pyridine-2-carboxaldehyde (1.1 g, 10 mmol) was mixed with it. The mixture was warmed at 50–60 °C for 1 h and cooled to ambient temperature. To the solution was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (3.7 g, 10 mmol) in methanol (20 cm^3) to precipitate immediately dark red solid of **1** which was recrystallised from CH_3CN–MeOH (1:1 v/v) mixture to obtain dark red single crystals suitable for X-ray diffraction. (yield: 3.146 g, 80%). Calc. for $C_{13}H_{16}CuClN_3O_5$: C, 39.69; H, 4.07; N, 10.69; Cu, 16.16. Found: C, 39.91; H, 4.17; N, 10.70; Cu 15.83%; λ_{max} (nm) (ε_{max} (dm^3 mol^{-1} cm^{-1})) (acetonitrile), 539 (255), 367 (1639); μ_{eff}, 1.73 BM.

2.1.2. [CuL^2]ClO$_4$ (**2**) and [CuL^3] (ClO$_4$)$_2$ (**3**)

Complex **2** was prepared by similar method to **1** except that AMAO was used instead of AMAH. The immediately separated product was a brown solid which was collected by filtration and was recrystallised from CH_3CN–MeOH (1:1 v/v) mixture to give dark brown single crystals of **2** suitable for X-ray diffraction (yield: 1.222 g, 30%). Calc. for $C_{14}H_{18}CuClN_3O_5$: C, 41.27; H, 4.42; N, 10.32; Cu, 15.6. Found: C, 41.43; H, 4.67; N, 10.35; Cu, 15.02%. λ_{max} (nm) (ε_{max} (dm^3 mol^{-1} cm^{-1})) (acetonitrile), 533 (130), 373 (1170); μ_{eff}, 1.77 BM.

A mixture of brown and green products started to separate out from the filtrate after approximately 20 min and only the green crystalline product after 1 h. The green product was identified as **3** and single crystals suitable for X-ray studies were obtained by diffusion of diethylether to an acetonitrile solution of the compound at room temperature (r.t.). Calc. for $C_{15}H_{16}CuCl_2N_4O_8$: C, 34.97; H, 3.11; N, 10.88; Cu, 12.34. Found: C, 35.35; H, 3.04; N, 11.12; Cu, 11.71%. The same product **3** was also obtained as a green solid by refluxing 1,3-propanediamine (0.74 g, 10 mmol) and pyridine-2-carboxaldehyde (2.2 g, 20 mmol, 1:2 molar ratio) for 2 h and then adding $Cu(ClO_4)_2 \cdot 6H_2O$ (3.7 g, 10 mmol) to the mixture. It was recrystallised from CH_3OH. (yield: 4.118 g, 80%). Calc. for $C_{15}H_{16}CuCl_2N_4O_8$: C, 34.97; H, 3.11; N, 10.88. Found: C, 35.21; H, 2.90; N, 11.02%. λ_{max} (nm) (ε_{max} (dm^3 mol^{-1} cm^{-1})) (acetonitrile), 624 (119); μ_{eff}, 1.72 BM.

2.1.3. Synthesis of **3** from **2**

2.1.3.1. Catalysed by H^+.

Two drops of 1 M perchloric acid was added to a solution of complex **2** (0.5 mmol, 0.2 g) in methanol–water (9:1 v/v) mixture (50 cm^3) and put under reflux. Within 30 min, the colour of the solution started to change into green and the green compound **3** deposited along with the brown compound **2** just above the upper meniscus of the boiling solution indicating the occurrence of the rearrangement. The solid compounds were taken back into the solution by occasional stirring. After approximately 10 h of reflux the solvent was evaporated to make the final volume approximately 2 cm^3 and cooled at r.t. when a mixture of compound **2**, **3** and $Cu(acac)_2$ were precipitated. Compound **3** was separated from the mixture by dissolving it in cold water. The residue was washed with little amount of dmf (5 cm^3) to dissolve out the unreacted **2**. The yield of compound **3** and $Cu(acac)_2$ were approximately 50 and 35%, respectively.

2.1.3.2. Catalysed by Cu^{2+}. The same experiment was performed by adding 0.005 g of $Cu(ClO_4)_2 \cdot 6H_2O$ to the solution instead of perchloric acid. Here also partial rearrangement was found to occur with approximately 30 and 20% yield of **3** and $Cu(acac)_2$, respectively.

2.1.3.3. Catalysed both by H^+ and Cu^{2+}. The experiment was again performed with the addition of both two drops of perchloric acid and 0.005 g of $Cu(ClO_4)_2 \cdot 6H_2O$. The yield of compound **3** was found to be much higher in this case (75%) along with a yield of 50% $Cu(acac)_2$.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyser and the copper contents in all the complexes were estimated spectrophtometrically [8]. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1200–350 nm) were recorded in a Hitachi U-3501spectrophotometer. Electrochemical studies were done using PAR Versastat-2. The effective magnetic moments were calculated from magnetic susceptibility measurements with an EG & G PAR vibrating sample magnetometer model 155 at r.t. and diamagnetic corrections were made using Pascal's constants.

2.3. Structure determination

The X-ray single-crystal diffraction measurements were carried out using an Enraf–Nonius CAD4 single crystal diffractometer for complex **1** and **3** and a Bruker AXS Smart single crystal diffractometer with CCD for complex **2**. The data were corrected for Lorentz, polarisation and absorption effects. The crystal structures of the three complexes were solved by direct methods using the programs SIR-97 [9] and SHELXS-97 [10] and refined by using SHELXL-97 [10]. The non-hydrogen 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 [11] and anomalous dispersion effects were included in F_{calc} [12]. The crystallographic data are summarised in Table 1. Selected bond lengths and bond angles are shown in Table 2. The crystallographic illustrations were prepared using ORTEP-3 [13].

3. Results and discussions

3.1. Infrared and electronic spectra

In the IR spectra of all the complexes no bands due to ν_{NH_2} could be observed indicating the condensation of the free amine groups. The bands corresponding to azomethine (C=N) group are distinct and occurs within 1649–1573 cm^{-1}. The lowering of the positions of the bands indicate their coordination to the metal centres. The sharp single peak at 1088 cm^{-1} for both **1** and **2** give evidence of ionic perchlorate present in both of them. The splitting of the band at 1090 cm^{-1} for **3** is indicative of coordinated perchlorate ions as substantiated in the crystal structure.

The electronic spectral data in acetonitrile solution suggest basically square planar geometry for compounds **1** and **2**. In general square-planar complexes are known to exhibit two or more band [14]. Complex **1** shows two bands at 18 553 and 27 248 cm^{-1} while the corresponding peaks for complex **2** are at 18 762 and a shoulder at 26 809 cm^{-1}. The octahedral nature of complex **3** is evident by appearance of a single broad peak at 16 026 cm^{-1} substantially lower than the two square-planar complexes [15].

3.2. Cyclic voltammetry

The cyclic voltammograms of the Cu(II) complexes show oxidation peaks at high potentials thereby suggesting stable Cu(II) complexes. The oxidation peak of complex **3** at 1.205 V is quasi reversible with the corresponding reduction peak at 1.058 V versus AgCl ($\Delta E_P = 147$ mV). No other peaks are observed on the initial anodic scan or the corresponding cathodic part. On initial cathodic scan a reduction peak at −0.17 V versus AgCl is due to Cu(II)–Cu(I) reduction with no corresponding anodic peak. The initial anodic scan of complex **1** and **2** is at 1.3 V with a corresponding cathodic peak at 1.142 V ($\Delta E_P = 158$ mV) indicative of a quasi-reversible nature. Initial cathodic scan is at −0.23 V.

3.3. Crystal structures of complexes *1, 2 and 3*

The X-ray analysis verified the structures of unsymmetrical copper(II) complexes **1** and **2** and the symmetrical complex, **3**. The ORTEP-3 views of the three complexes with atom numbering schemes are shown in Figs. 1–3. In both the complexes **1** and **2**, the deprotonated ligands L^1 and L^2 are quadridentate forming one six-membered chelate ring, and two five-membered chelate rings (6–5–5) in **1** and two adjacent six-membered chelate rings and one five-membered chelate ring (6–6–5) in **2**.

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

	[CuL^1](ClO$_4$) (**1**)	[CuL^2](ClO$_4$) (2)	[CuL^3](ClO$_4$)$_2$ (3)
Formula	$C_{13}H_{16}CuClN_3O_5$	$C_{14}H_{18}CuClN_3O_5$	$C_{15}H_{16}CuCl_2N_4O_8$
M	393.29	407.29	514.77
Crystal system	triclinic	triclinic	monoclinic
Space group	$P1$	$P1$	$C2/c$
a (Å)	10.439(3)	7.743(2)	14.037(3)
b (Å)	10.959(2)	10.767(2)	10.220(3)
c (Å)	7.674(2)	10.997(2)	15.138(4)
α (°)	92.54(3)	63.62(2)	
β (°)	91.27(2)	84.64(2)	115.15(2)
γ (°)	117.77(2)	88.66(2)	
V (Å^3)	775.1(4)	817.6(3)	1965.8(9)
Z	2	2	4
D_{calc} (g cm^{-3})	1.685	1.654	1.739
μ (mm^{-1})	3.852[Cu Kα]	1.529[Mo Kα]	4.565[Cu Kα]
Number of unique data	2940	3483	1760
Number of data with $I > 2\sigma(I)$	2478	2584	1440
R_1, wR_2	0.0539, 0.1758	0.0963, 0.2723	0.0515, 0.1684

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1**–**3**

	1	**2**	**3**
Bond lengths			
Cu–N1	2.004(3)	2.047(5)	2.026(3)
Cu–N2	1.922(5)	1.977(6)	1.982(4)
Cu–N3	1.907(3)	1.955(5)	
Cu–O	1.866(4)	1.884(5)	
Cu–O1			2.510(5)
Cl–O1	1.382(9)	1.419(7)	1.406(5)
Cl–O2	1.341(11)	1.357(12)	1.375(9)
Cl–O3	1.359(10)	1.371(14)	1.404(5)
Cl–O4	1.315(11)	1.351(9)	1.377(7)
Cl–O2A	1.322(13)		1.418(10)
Cl–O3A	1.309(11)		1.355(15)
Cl–O4A	1.369(17)		1.393(15)
Bond angles			
N1–Cu–N2	80.8(2)	79.2(2)	81.3(2)
N2–Cu–N3	85.4(2)	98.6(2)	
N3–Cu–O	97.5(2)	94.9(2)	
N1–Cu–O	96.5(1)	87.3(2)	
N1–Cu–N3	165.2(2)	174.6(2)	
N2–Cu–O	176.7(2)	166.5(2)	
N2–Cu–N2*			92.6(2)
N2*–Cu–N1*			81.3(2)
N1–Cu–N1*			104.9(2)
N1–Cu–N2*			173.1(2)

* Designates the symmetry related atom at $1-x$, y, $3/2-z$ for complex **3**.

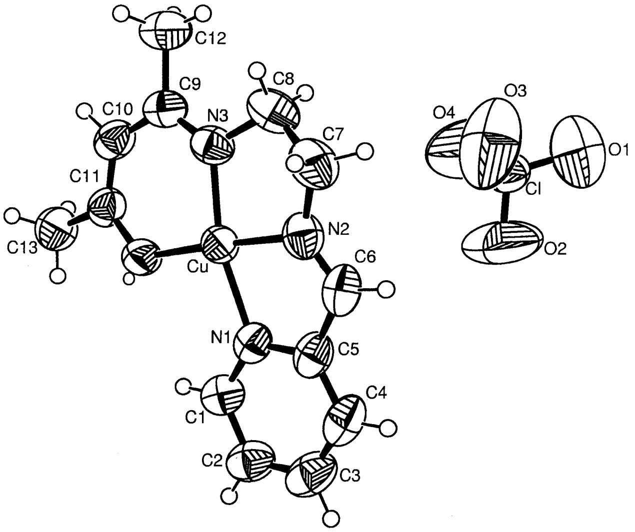


Fig. 1. ORTEP-3 view of complex **1** with the atom labelling scheme. Thermal ellipsoids are shown at 50% probability. Only the major fractions of the disordered perchlorate oxygen atoms are shown.

The copper(II) ions have square-planar co-ordination with a slight tetrahedral distortion in both the complexes **1** and **2**. The deviations of the co-ordinating atoms O, N(3), N(2), N(1) from the least-square mean plane through them are 0.042(3), −0.060(3), 0.083(4), −0.046(3) Å in complex **1** and 0.049(6), −0.040(6), 0.050(6), −0.036(5) Å in complex **2**, respectively. The deviation of copper(II) from the same plane are 0.0337(5) and 0.0463(7) Å in complex **1** and **2**, respectively.

In complex **1**, the five-membered chelate ring, Cu–N(2)–C(7)–C(8)–N(3), has a half chair conformation with the puckering parameters [16] $q_2 = 0.253(6)$ and $\phi_2 = -83.2(9)°$. In complex **2**, the carbon atom C(8) of the six-membered chelate ring, Cu–N(2)–C(7)–C(8)–C(9)–N(3), is disordered with the C(8) atom having two alternate positions, C(8) with an occupancy of 0.475(19) and C(8′) with an occupancy of 0.525(19). This causes the six-membered ring to flip between two envelope conformations [17] with $\phi = 359.0(14)°$ for Cu–N(2)–C(7)–C(8)–C(9)–N(3) and $\phi = 180.2(9)°$ for

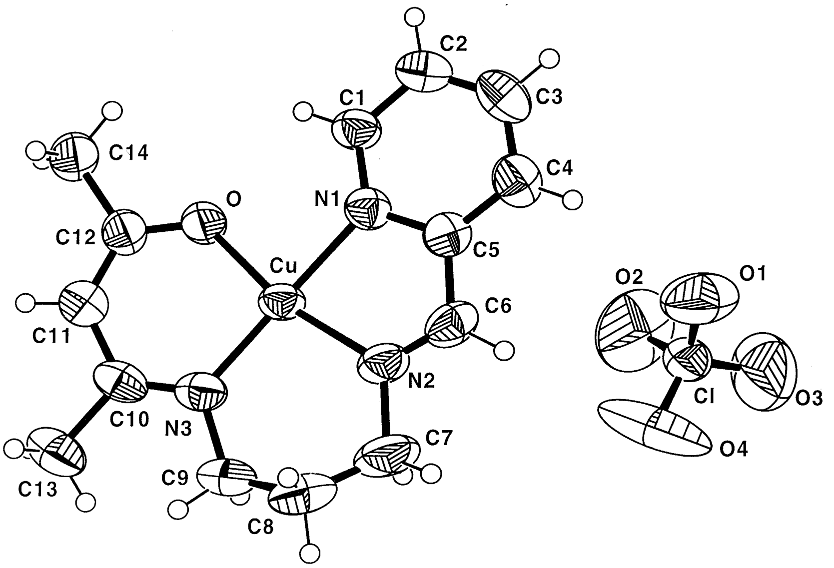


Fig. 2. ORTEP-3 view of complex **2** with the atom labelling scheme. Thermal ellipsoids are shown at 50% probability. Only the major fraction of the disordered carbon atom, C(8), of the six-membered puckered ring is shown.

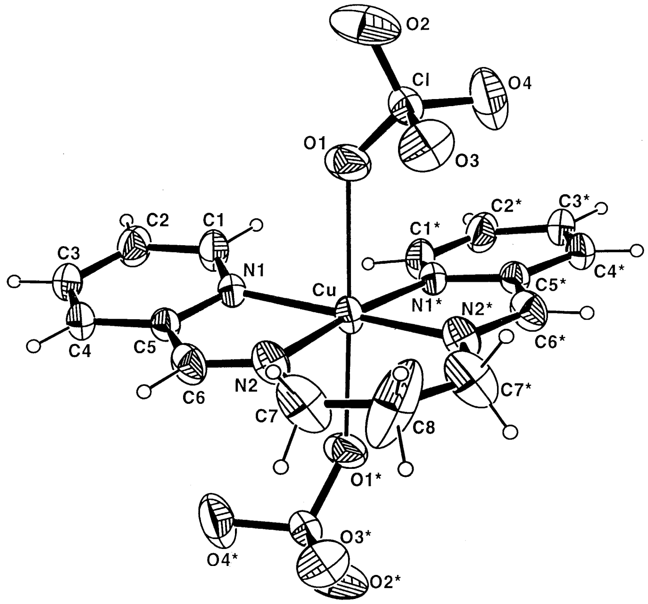


Fig. 3. ORTEP-3 view of complex **3** with the atom labelling scheme. An * denotes a symmetry related atom. For clarity, thermal ellipsoids are given at 20% probability and only the major fractions of the disordered perchlorate oxygen atoms are shown.

Cu–N(2)–C(7)–C(8′)–C(9)–N(3). The displacements of C(8) and C(8′) from the least-squares mean plane through Cu, N(2), C(7), C(9), N(3) are, respectively, $-0.534(19)$ and $+0.727(14)$ Å.

The general features of the copper co-ordination sphere are not unusual. The observed angular distortions from a regular square-planar geometry are consistent with similar distortions seen in related compounds [3,18]. For example the angles around the copper atom associated with five-membered chelate rings are invariably smaller than those associated with six-membered rings. The corresponding values observed in related structures range from 81° to 84° for five-membered rings and from 92° to 98° for six-membered rings [3,18]. The values found in the present system are within these ranges. The larger value of the N(2)–Cu–N(3) angle in complex **2** is attributed in part to the steric strain imparted to the system by the presence of the two adjacent six-memberd rings. The rather long Cu–N distances (Table 2) in complex **2** compared with those in **1** are also consistent with this.

Crystal structure of **3** reveal that the copper atom lies on a twofold axis of symmetry passing through the copper(II) and C(8). The co-ordination polyhedron around the copper atom is best described as a distorted octahedron. The four nitrogen atoms N(1), N(2) and N(2)*, N(1)* (* designates a symmetry related atom) of the quadridentate symmetrical ligand define the equatorial plane and two oxygen atoms O(1) and O(1)* of the perchlorate groups are semi-coordinated in *trans* axial position. The deviations of the component atoms N(1), N(2), N(2)*, N(1)* from the equatorial plane are $-0.048(4)$, $0.059(5)$, $-0.059(5)$, $0.048(4)$ Å, respectively, from the least-square mean plane defined by themselves. The copper atom lies in that plane. Unlike complex **2**, the saturated six-membered ring is not disordered and exhibits twist-boat with the puckering parameters [15] $q_3 = 0$, $q_2 = Q$, $\phi_2 = 90(11)^\circ$, $\theta_2 = 90(18)^\circ$. The N(2)–Cu–N(2)* angle is 92.6(17)° and is typical of six-membered chelate [3,18]. However, in comparison to the complex **2**, the angle is smaller and that is expected as its adjacent chelate rings are five-membered, causing less steric strain. It is to be mentioned here that the geometry of the complexes with other symmetrical tetradentate Schiff base ligands are different from the present one e.g. ligand involving 1,2-ethanediamine and 2,4-pentanedione shows a square-planar metal environment [19] whereas that derived from 1,2-ethanediamine and 2-pyrollecarboxaldehyde gives a binuclear copper(II) complex in which both ends of the Schiff base act as bis(bidentate) ligands [20].

For complexes **1** and **2** the molecules are packed in pairs; one on top of the other giving rise to infinite stacks along *c* and *a* directions, respectively (Figs. 4 and 5). The two molecules in each pair are centrosymmetrically related and exhibit significantly short Cu–Cu distances, 3.335(1) and 3.491(1) Å for **1** and **2**, respectively. The comparatively large distance in **2** is probably due to the presence of disorder in the saturated six-membered chelate ring preventing the molecules to be closer.

3.4. Cu(II) catalysed rearrangement of the unsymmetrical ligand, HL^2

The rearrangement was first noticed during the preparation of the complex. Addition of HL^2 to the methanolic solution of $Cu(ClO_4)_2 \cdot 6H_2O$ results immediately in the formation of the brown unsymmetrical complex **2**. When the resulting mixture was put under reflux for approximately 2 h all the brown compounds disappear and on cooling crystalline symmetrical complex **3** was isolated as sole product. It was filtered and the mother liquor was concentrated to about one-eighth of the original volume and left overnight at r.t. The crystalline product which was separated from this solution was found to be a mixture of **3** and bis(acetylacetonato)Cu(II) but no compound of the Schiff base of symmetrical combination of pent-2,4-dione with the diamine could be isolated. Such rearrangement was reported earlier by Bermijo et al. [7] for Mn(III) complexes during their synthesis which took a long period of time. However, during the synthesis all the constituents i.e. the metal ion, the ligand, the complex and most importantly the H^+ which is released during the complex formation are present in the solution. Therefore, it is very difficult to conclude whether the rearrangement took place with free ligand, the ligand bound to the metal ion and if it was catalysed by the free metal ion or by H^+. To verify the role of H^+ and Cu^{2+} ion in the hydrolysis scheme, complex **2** (0.5 mmol; 0.2 g) was dissolved in methanol–water (9:1 v/v) mixture (50 cm^3) and put under reflux for several hours but no rearrangement or colour change of the solution was observed. However, the same reaction by addition of two drops of 1 M perchloric acid or of 0.005 g of $Cu(ClO_4)_2 \cdot 6H_2O$ showed the rearranged products within 1 h as described in the Section 2.1. Thus we can infer that the presence of either free H^+ or Cu^{2+} is necessary for the rearrangement of **2** i.e. both of them can catalyse the hydrolysis of compound **2**.

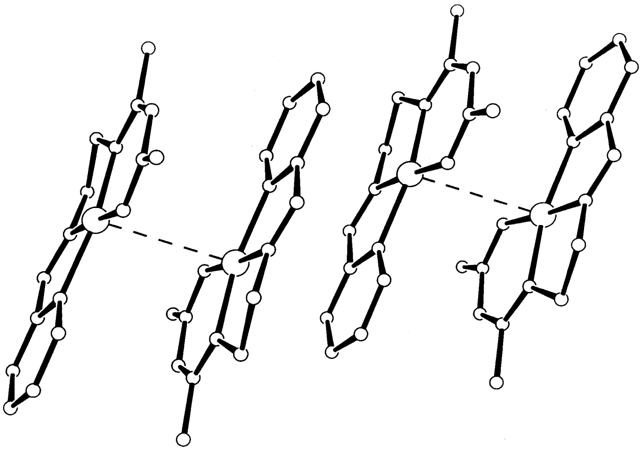


Fig. 4. Stacking of the molecules of complex **1** along the *c*-axis.

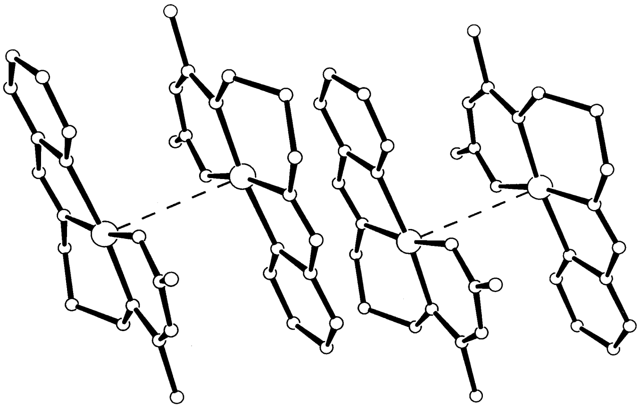
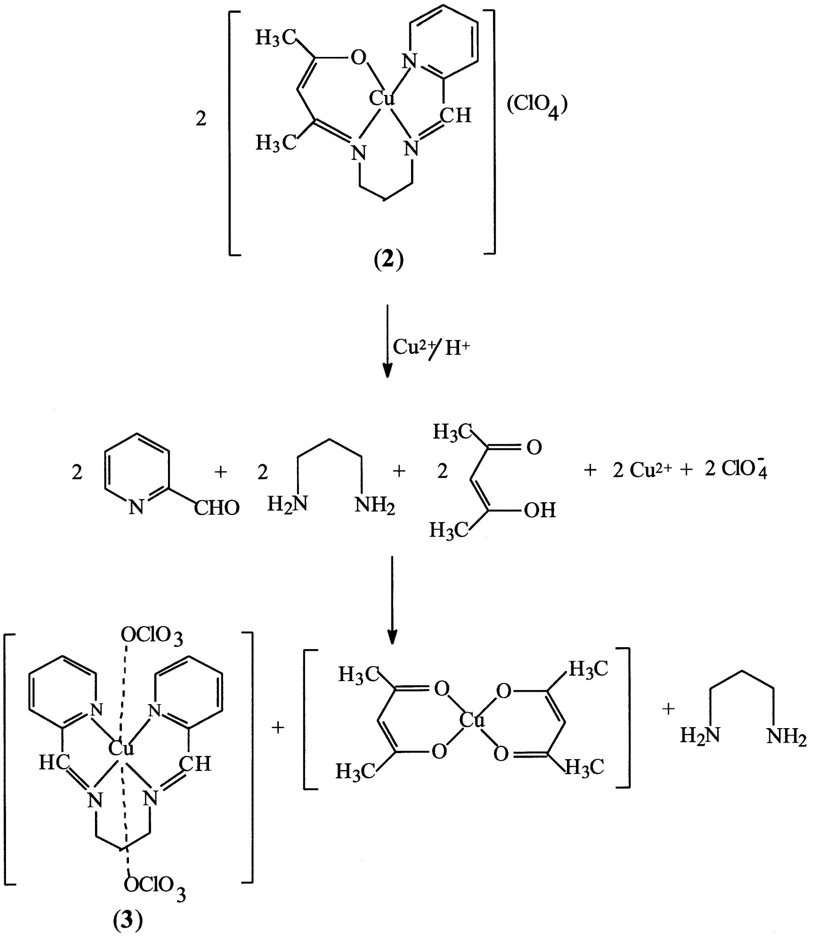


Fig. 5. Stacking of the molecules of complex **2** along the *a*-axis.

It is well known that Schiff bases are subject to hydrolysis in acidic or basic conditions to reform the constituent carbonyl and amine precursors [21]. The hydrolysis of compound **2** is believed to follow the similar path as proposed by Bermijo et al. [7] However, the Mn(III) acetylacetonato complex was not isolated by this group. The isolation of the $Cu(acac)_2$ in our study substantiate the formation of the constituents in the initial stage. From Scheme 2 although it is apparent that there is an excess of Cu(II) (0.005 g, added for hydrolysis) and diamine left in the solution, we were unable to isolate any Cu(II) diamine complex.

It is to be mentioned here that no rearrangement was observed for HL^1 under similar conditions either during synthesis or in the presence of Cu(II) ion. The susceptibility of the complex with HL^2 towards hydrolysis can be attributed to the steric strain imparted to the system by the presence of two adjacent six-membered chelate rings (vide crystal structures, Section 3.3).



Scheme 2.

4. Conclusion

In the present study we first noticed that Cu(II) can also catalyse the unsymmetrical to symmetrical rearrangement of the tetradentate Schiff base ligand and the rearrangement can take place with ligand which is complexed with metal ion in the presence of some free Cu(II) or H^+ ions. The nature of the ligand is also very important. Rearrangement was observed with complex **2** where the chelate rings around the copper ion were under more strain in comparison to complex **1** where no such rearrangement was observed during the study.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC Nos. 179038 (complex **1**), 179837 (complex **2**), 179039 (complex **3**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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