Polyhedron 67 (2014) 181–190

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Copper(II) complexes with tridentate N_2O donor Schiff bases: Modulation of crystalline architectures through supramolecular interactions

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ARTICLE INFO

Article history:
Received 10 May 2013
Accepted 4 August 2013
Available online 20 August 2013

Keywords:
Copper(II)
Schiff base
Crystal structure
Supramolecular interaction

ABSTRACT

Three mononuclear copper(II) complexes, $[Cu(L^1)(DMF)]ClO_4$ (**1**), $[Cu(L^2)(DMSO)]ClO_4$ (**2**) and $[CuL^3(NCO)]$ (**3**) (where HL^1 {2-[(2-methylamino-ethylimino)-methyl]-4-nitro-phenol}, HL^2 {2-[(2-ethylamino-ethylimino)-methyl]-4-nitro-phenol} and HL^3 {2-[(2-(dimethylamino)ethylimino)methyl]-4-nitrophenol} are tridentate Schiff-base ligands), have been synthesized and characterized by elemental analysis, IR and UV–Vis spectroscopy and single-crystal X-ray diffraction studies. All the complexes are square planar. Complex **1** crystallizes in the triclinic space group, $P\bar{1}$, with cell dimensions $a = 8.0396(2)$, $b = 9.0892(2)$, $c = 12.9977(3)$ Å, $\alpha = 85.591(1)°$, $\beta = 84.198(1)°$ and $\gamma = 76.423(1)°$, whereas complex **2** crystallizes in the orthorhombic space group, Pbca with cell dimensions $a = 8.4615(4)$, $b = 17.2708(11)$ and $c = 25.8517(12)$ Å. Complex **3** crystallizes in the monoclinic space group, $P2_1/n$ with cell dimensions $a = 6.9550(3)$, $b = 13.2257(7)$, $c = 14.7755(6)$ Å and $\beta = 102.697(3)°$. Both HL^1 and HL^2 are capable of forming H bonds due to the presence of H atoms in their amine groups. On the other hand, HL^3 cannot form H-bonds. The weak forces like H-bonding, lone pair$\cdots\pi$ and $\pi\cdots\pi$ interactions lead to various supramolecular architectures in the complexes.

1. Introduction

Supramolecular systems based on coordination compounds have received much attention because of their potential uses as sensors, probes, photonic devices, catalysts and in host–guest chemistry [1–7]. A significant number of supramolecular coordination complexes have been synthesized in the recent years [8–12]. The most commonly used approach for engineering the crystal structure of such complexes employ non-covalent intermolecular forces (hydrogen bonding, aromatic ring stacking etc.) [13–17]. This approach has produced pre-designed 2D or 3D supramolecular architectures. However, although there have been a great deal of reports on supramolecular systems, it still remains a challenging task to explore several compounds with different topological networks.

The ease of synthesis, stability under various conditions, structural versatility and several applications of Schiff bases in catalysis, in designing molecular ferromagnets, in biological modeling applications and in preparing liquid crystals have attracted the attention of coordination chemists towards this class of ligands [18–23]. The salen type Schiff bases, prepared from the condensation of a diamine with salicylaldehyde or its derivatives in a 1:2 M ratio, are very popular now-a-days, to prepare phenoxo bridged poly nuclear complexes [24,25]. N_2O donor tridentate Schiff bases may also easily be prepared on refluxing N-substituted diamines with salicylaldehyde or its derivatives [26]. The ligands can then be used to form complexes with several transition metals [27–30]. In the present work, we have used three N_2O donor Schiff bases by the condensation of 5-nitro salicylaldehyde with three different N-substituted diamines; N-methyl-1,2-diaminoethane, N,N-dimethyl-1,2-diaminoethane and N-ethyl-1,2-diaminoethane, to prepare three new copper(II) complexes. Copper(II) assumes a square planar geometry in each of the three complexes. In the present work, we would like to explore the supramolecular interactions in these three complexes and in some related ones, retrieved from CSD. The complexes form various supramolecular architectures via H-bonding, $\pi\cdots\pi$, C–H$\cdots\pi$, N–H$\cdots\pi$, lone pair$\cdots\pi$ and anion$\cdots\pi$ interactions.

Herein, we report the syntheses, structural features, spectroscopic characterization and X-ray crystal structures of three new complexes of copper(II). Different crystalline architectures are obtained via various supramolecular interactions, like H bonding, $\pi\cdots\pi$ and lone pair$\cdots\pi$ interactions.

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http://dx.doi.org/10.1016/j.poly.2013.08.037

2. Experimental

2.1. Materials

All reagents were of commercially available, reagent grade and were used without further purification.

Caution!!! Although no problem was encountered in this work, perchlorate salts containing organic ligands are potentially explosive. Only a small amount of the material should be prepared and handled with care.

2.2. Preparations

2.2.1. Preparation of [Cu(L^1)(DMF)]ClO$_4$ (**1**)

The tridentate Schiff base 2-[(2-methylamino-ethylimino)-methyl]-4-nitro-phenol (HL^1) was synthesized by refluxing 5-nitrosalicylaldehyde (170 mg, 1 mmol) and N-methyl-1,2-diaminoethane (0.1 ml, 1 mmol) in methanol (20 ml) for 1 h. The ligand was not isolated. It was used directly for the preparation of complex **1**. A methanol solution of $Cu(ClO_4)_2.6H_2O$ (370 mg, 1 mmol) was added to the methanol solution of the ligand and refluxed for 1 h to give a deep green solution. This solution was cooled and kept for a few days to get green crystalline compound, which was collected by filtration. Deep green single crystals, suitable for X-ray diffraction, were obtained after few weeks by slow evaporation of a DMF solution of this green compound in open atmosphere.

Yield: 270 mg (59%). *Anal.* Calc. for $C_{13}H_{19}ClCuN_4O_8$: C, 34.07; H, 4.18; N, 12.22. Found: C, 34.0; H, 4.0; N, 12.1%. IR (KBr, cm^{-1}): 1648 ($\nu_{C=N}$), 1100 (ν_{ClO4}), 1313 (ν_{NO2}), UV–Vis, λ_{max} (nm) (ε_{max}, (dm^3 mol^{-1} cm^{-1})) (acetonitrile): 601 (8.9×10^1), 358 (1.9×10^4), 250 (2.2×10^4). Magnetic moment: 1.70 BM.

2.2.2. Preparation of [Cu(L^2)(DMSO)]ClO$_4$ (**2**)

The tridentate Schiff base 2-[(2-ethylamino-ethylimino)-methyl]-4-nitro-phenol (HL^2) was prepared by following a similar procedure as that of HL^1, except that here we used N-ethyl-1,2-diaminoethane (0.1 ml, 1 mmol) instead of N-methyl-1,2-diaminoethane. The ligand was not isolated. A methanol solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (370 mg, 1 mmol) was added to the methanol solution of the ligand and refluxed for 1 h to give a deep green solution. This solution was cooled and kept for a few days to get green crystalline compound, which was collected by filtration. Deep green single crystals, suitable for X-ray diffraction, were obtained after few days by slow evaporation of a DMSO solution of this green compound in open atmosphere.

Yield: 300 mg (63%). *Anal.* Calc. for $C_{13}H_{20}ClCuN_3O_8S$: C, 32.71; H, 4.22; N, 8.80. Found: C, 32.6; H, 4.1; N, 8.6%. IR (KBr, cm^{-1}): 1651 ($\nu_{C=N}$), 1112 (ν_{ClO4}), 1313 (ν_{NO2}), UV–Vis, λ_{max} (nm) (ε_{max}, (dm^3 mol^{-1} cm^{-1})) (acetonitrile): 580 (2.7×10^2), 362 (2.5×10^4), 252 (2.6×10^4). Magnetic moment: 1.71 BM.

2.2.3. Preparation of [CuL^3(NCO)] (**3**)

The tridentate Schiff base 2-[(2-(dimethylamino)ethylimino)methyl]-4-nitrophenol (HL^3) was prepared by following a similar procedure to that of HL^1, except that here we used N,N-dimethyl-1,2-diaminoethane (0.1 ml, 1 mmol) instead of N-methyl-1,2-diaminoethane. The ligand was not isolated. A methanol solution of $Cu(OAc)_2{\cdot}H_2O$ (199.6 mg, 1 mmol) was then added to the methanol solution of the ligand and refluxed for 1 h to give a deep green solution. An aqueous solution of NaOCN (65 mg, 1 mmol) was added to it and refluxed again for an additional hour to obtain a deep green precipitate. The precipitate was collected by filtration. Single crystals, suitable for X-ray diffraction, were obtained after several days on slow evaporation of the DMF solution of this green precipitate in open atmosphere.

Yield: 210 mg (61%). *Anal.* Calc. for $C_{12}H_{14}CuN_4O_4$: C, 42.17; H, 4.13; N, 16.39. Found: C, 42.0; H, 4.1; N, 16.2%. IR (KBr, cm^{-1}): 1641 ($\nu_{C=N}$), 1317 (ν_{NO2}), 2231 ($\nu_{NCO)}$, UV–Vis, λ_{max} (nm) (ε_{max}, (dm^3 mol^{-1} cm^{-1})) (acetonitrile): 641 (8.1×10^1), 365 (1.1×10^4), 251 (1.2×10^4). Magnetic moment: 1.75 BM.

2.3. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) of the complexes were performed on a Perkin–Elmer 240 °C elemental analyzer. Infrared spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin–Elmer FT-IR spectrum two spectrophotometer. Electronic spectra in acetonitrile (900–200 nm) were recorded on a Jasco V-630 UV–Vis spectrophotometer. Fluorescence spectra were obtained on HORIBA Jobin Yvon FluoroMax-P spectrophotometer at room temperature. 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. X-ray crystallography

A single crystal of complex **1** having suitable dimensions was used for data collection by means of a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELX-97 package [31]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on the atoms to which they were attached. Empirical absorption corrections were carried out with the ABSPACK program [32].

Single crystals of **2** and **3** of suitable dimensions were mounted in inert oil and transferred to the cold gas stream of the cooling device. Data were collected at 100 K on a STOE IPDS 2T diffractometer using graphite monochromated Mo Kα radiation and were

Table 1
Crystal data and refinement details of complexes **1–3**.

	1	**2**	**3**
Formula	$C_{13}H_{19}ClCuN_4O_8$	$C_{13}H_{20}ClCuN_3O_8S$	$C_{12}H_{14}CuN_4O_4$
Formula weight	458.32	477.37	341.81
T (K)	293	100	100
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$Pbca$	$P2_1/n$
a (Å)	8.0396(2)	8.4615(4)	6.9550(3)
b (Å)	9.0892(2)	17.2708(11)	13.2257(7)
c (Å)	12.9977(3)	25.8517(12)	14.7755(6)
α (°)	85.591(1)	90	90
β (°)	84.198(1)	90	102.697(3)
γ (°)	76.423(1)	90	90
Z	2	8	4
D_{calc} (g cm^{-3})	1.660	1.679	1.712
μ (mm^{-1})	1.386	1.455	1.670
$F(000)$	470	1960	700
Total reflections	16119	28649	10017
Unique reflections	6283	4007	2799
Observed data[$I > 2\sigma(I)$]	4177	2153	2099
Number of parameters	244	256	192
R_{int}	0.019	0.071	0.048
R_1, wR_2 (all data)	0.0498, 0.1099	0.1321, 0.0689,	0.0407, 0.0618
R_1, wR_2 [$I > 2\sigma(I)$]	0.0370, 0.1040	0.0400, 0.0513	0.0272, 0.0602

corrected for absorption effects using multiscanned reflections. Non hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Programs used: `sir` 2011 [33], SHELXL-97 [34], DIAMOND [35], ORTEP [36], STOE IPDS2 [37] and MERCURY [38] software. The crystallographic and refinement data are summarized in Table 1.

3. Results and discussion

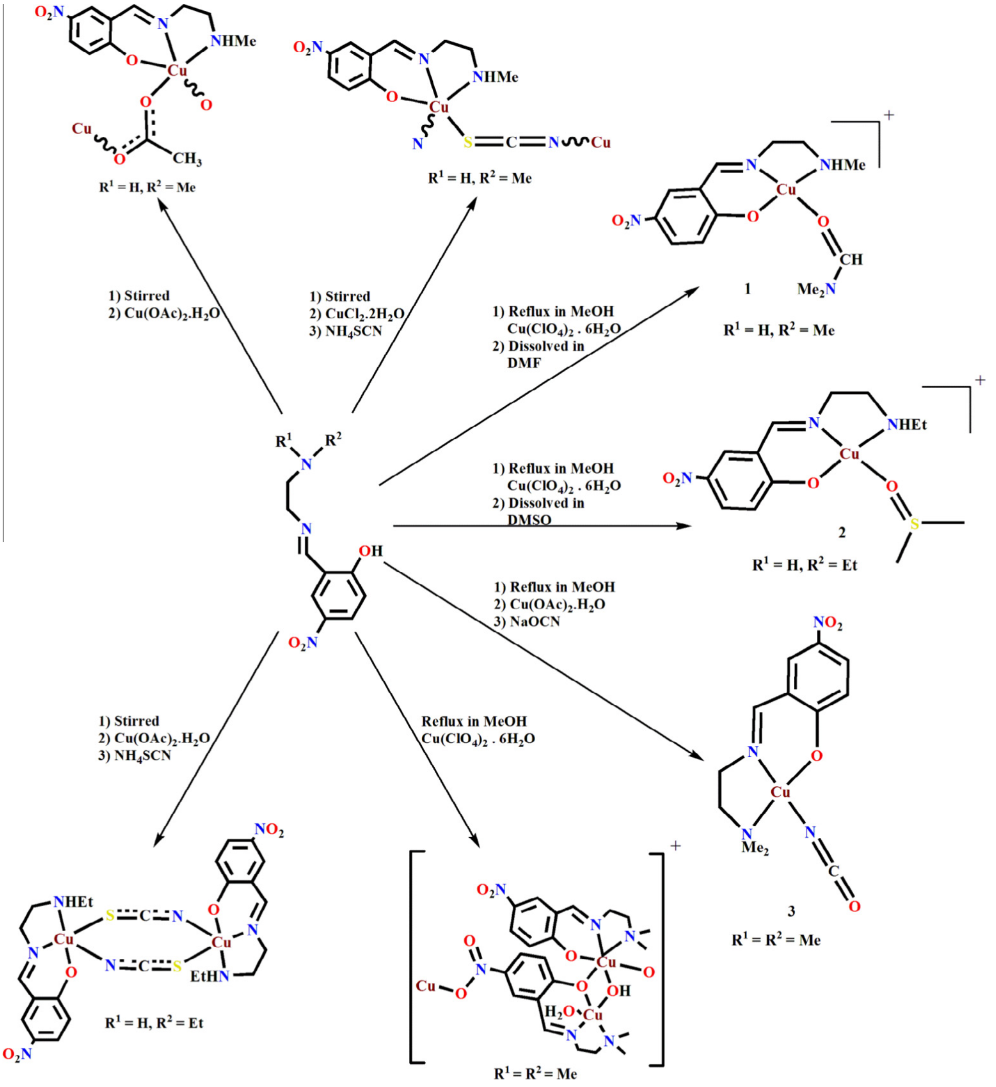
3.1. Synthesis of the Cu(II) complexes

The tridentate Schiff-base ligands HL^1, HL^2 and HL^3 were synthesized by the condensation of N-methyl-1,2-diaminoethane, N-ethyl-1,2-diaminoethane and N,N-dimethyl-1,2-diaminoethane with 5-nitrosalicylaldehyde in a 1:1 M ratio separately, following the literature method [26]. Addition of copper(II) perchlorate to the methanol solution of HL^1 produced a deep green solution. The compound separated from the methanol solution was dissolved in DMF. Single crystals of **1**, suitable for X-ray diffraction, were grown from it. Use of copper(II) acetate could not produce complex **1**, instead an acetate bridged polymeric copper(II) complex, $[CuL^1(CH_3COO)]_n$, was formed, the structure of which was reported by a different group [39]. Addition of ammonium thiocyanate to the methanol solution of **1** produced a thiocyanato bridged polymeric copper(II) complex, $[CuL^1(\mu\text{-}1,3\text{-}NCS)]_n$, the structure of which was already reported in the literature [40]. The addition of copper(II) perchlorate into the methanol solution of HL^2 produced a deep green solution. The compound that separated from the methanol solution was dissolved in DMF to get suitable single crystals of **2**. Addition of ammonium thiocyanate into the methanol solution of **2** produced a double thiocyanato bridged dimeric copper(II) complex, $[Cu_2(L^2)_2(\mu\text{-}1,3\text{-}NCS)_2]$, which was reported earlier [41]. Addition of copper(II) acetate into the methanol solution of HL^3, followed by the addition of NaOCN produced the monomeric complex **3**. Use of copper(II) perchlorate produced a novel polymeric copper(II) complex, in which the potential tridentate ligand acted as a tetradentate ligand with the participation of the nitro oxygen in coordination. We have already reported the structure of this complex [26]. The formation of all the complexes is shown in Scheme 1.

3.2. Description of the structures

3.2.1. $[Cu(L^1)(DMF)]ClO_4$ (1)

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of a discrete $[Cu(L^1)(DMF)]^+$ cation and a perchlorate anion. A perspective view of the complex is shown in Fig 1. The copper ion, Cu(1), is bound to three coordinating atoms {the



Scheme 1. Formation of the complexes **1**, **2** and **3**.

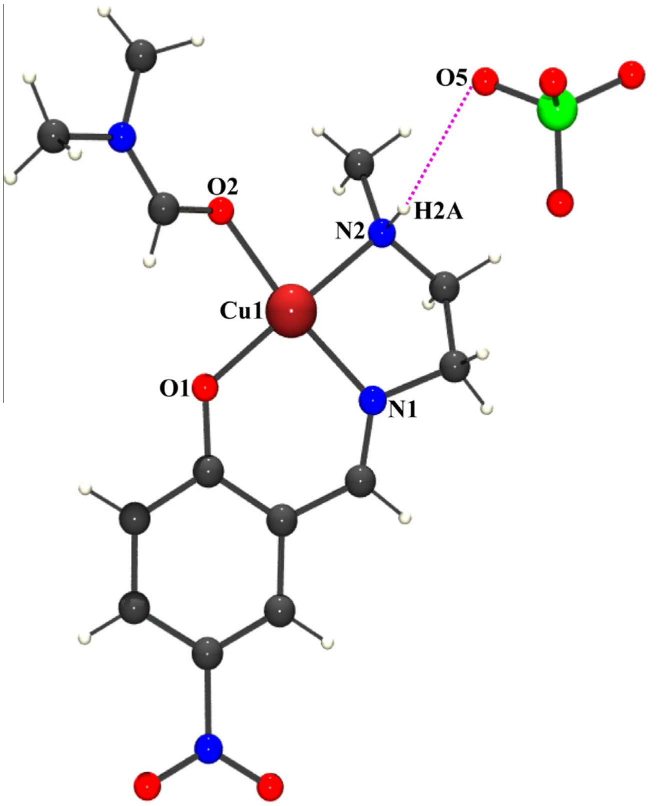


Fig. 1. Perspective view of complex **1**. Broken line (pink) represents the hydrogen bond. (Colour online.)

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

	1	**2**	**3**
Cu(1)–O(1)	1.895(2)	1.913(3)	–
Cu(1)–O(2)	1.958(2)	–	–
Cu(1)–O(4)	–	1.970(2)	1.929(2)
Cu(1)–N(1)	1.931(2)	2.014(3)	1.933(2)
Cu(1)–N(2)	2.005(2)	–	2.069(2)
Cu(1)–N(4)	–	1.935(3)	1.908(2)
O(1)–Cu(1)–O(2)	90.72(6)	–	–
O(1)–Cu(1)–O(4)	–	88.66(10)	–
O(1)–Cu(1)–N(1)	93.86(7)	174.07(13)	–
O(1)–Cu(1)–N(2)	178.54(7)	–	–
O(1)–Cu(1)–N(4)	–	92.63(12)	–
O(2)–Cu(1)–N(1)	168.37(7)	–	–
O(4)–Cu(1)–N(1)	–	93.57(11)	92.07(7)
O(4)–Cu(1)–N(2)	–	–	172.53(7)
O(4)–Cu(1)–N(4)	–	178.64(12)	91.73(7)
O(2)–Cu(1)–N(2)	90.49(7)	–	–
N(1)–Cu(1)–N(2)	85.11(7)	–	–
N(1)–Cu(1)–N(2)	–	–	84.37(8)
N(1)–Cu(1)–N(4)	–	85.11(13)	173.09(8)
N(2)–Cu(1)–N(4)	–	–	92.50(8)

Table 3
Hydrogen bond distances (Å) and angles (°) of complexes **1** and **2**.

Complex	D–H···A	D–H	D···A	H···A	∠D–H···A
1	N(2)–H(2A)···O(5)	0.91	3.129(4)	2.40	137
2	N(1)–H(1A)···O(8)	0.93	3.230(4)	2.35	159

D, Donor; A, Acceptor; H, Hydrogen.

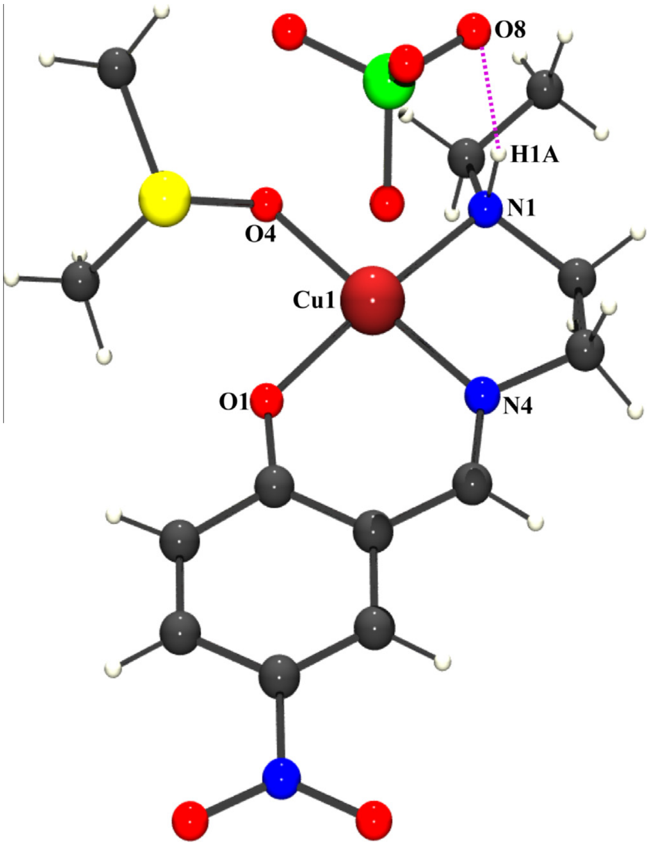


Fig. 2. Perspective view of complex **2**. Broken line (pink) represents the hydrogen bond. (Colour online.)

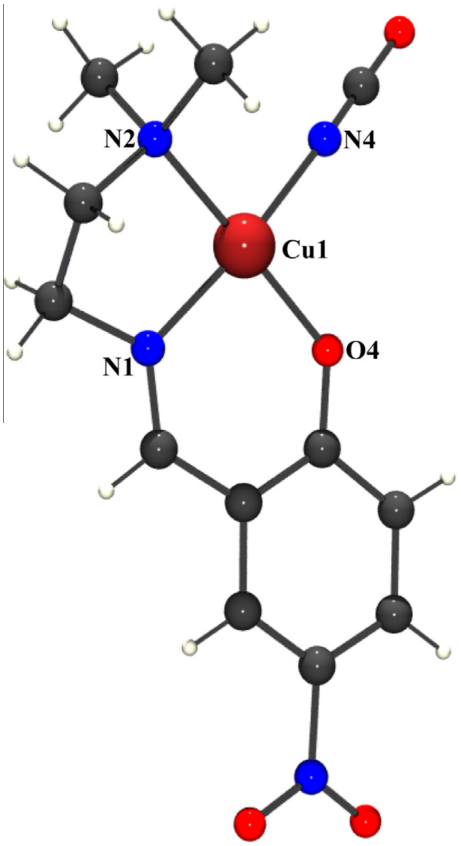


Fig. 3. Perspective view of complex **3**.

oxygen atom O(1), imine nitrogen atom N(1), and amine nitrogen atom N(2)} from the chelating deprotonated Schiff base ligand and one oxygen atom, O(2), from a DMF molecule. The sum of the different angles around copper(II) is 360.18°, indicating a slightly distorted square-planar geometry around the copper(II) center. This deviation of the equatorial plane from planarity also manifests itself in the trans angles {O(1)–Cu(1)–N(2) and O(2)–Cu(1)–N(1)} which are 178.54(7)° and 168.37(7)°. The deviations of coordinating atoms O(1), O(2), N(1) and N(2) from the least-square mean plane passing through them are −0.0977(16), 0.0970(16), 0.1006(17) and −0.0999(17) Å respectively, and that of the copper(II) center from the same plane is −0.0829(3) Å. The Cu–N_{imine} distance {1.9313(17) Å} is shorter than the Cu–N_{amine} {2.0046(18) Å} distance, as observed in similar systems [42]. The closest conformation of the five-membered chelate ring Cu(1)–N(1)–C(8)–C(9)–N(2) is envelope, with puckering parameters $q(2) = 0.416(2)$ Å and $\phi(2) = 283.1(2)°$ [43]. Selected bond lengths and bond angles are summarized in Table 2.

The H(2A) atom, attached to N(2), of the Schiff base forms a strong H bond with the O(5) atom of a neighboring perchlorate anion (Fig. 1). Details of the H-bonding are given in Table 3.

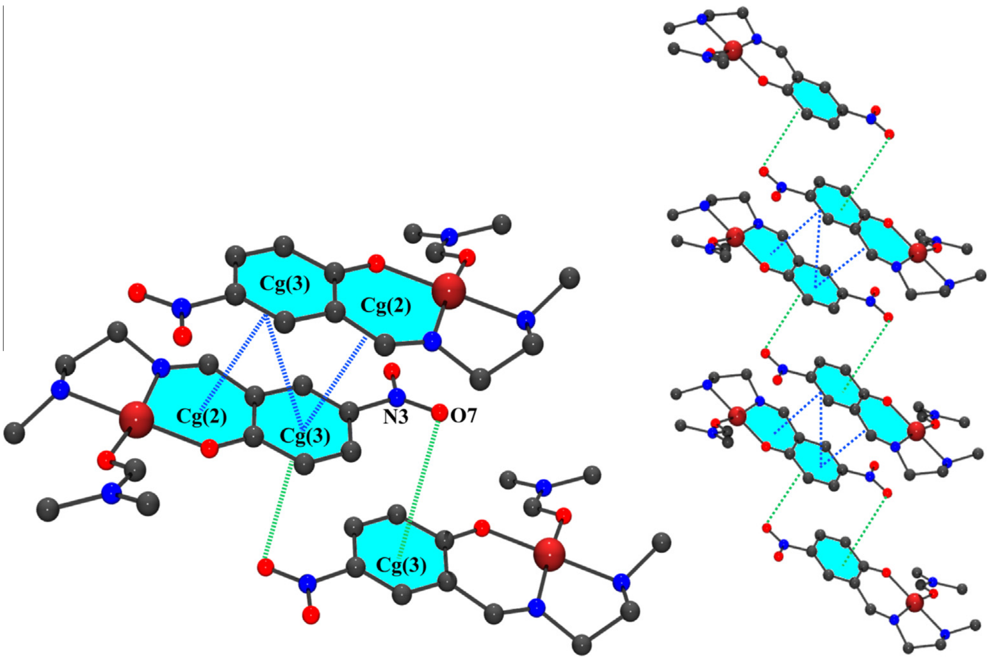
3.2.2. [Cu(L^2)(DMSO)]ClO_4 (**2**)

Complex **2** crystallizes as blue prism blocks in the orthorhombic space group Pbca. The structure determination reveals that it has a very similar molecular structure as that of complex **1**. A perspective view of the complex is shown in Fig. 2. Selected bond lengths and angles are summarized in Table 2. The copper ion, Cu(1), is bound to three coordinating atoms {the phenoxo oxygen atom O(1), imine nitrogen atom N(4), and amine nitrogen atom N(1)} from the chelating deprotonated Schiff base $(L^2)^-$ and one oxygen atom, O(4), from a DMSO molecule. The sum of the different angles

Table 4
Geometrical parameters (Å, °) for the lone pair···π interaction of complex **1**.

Complex	Y–X(I)···Cg(J)	X···C(g)	Y···C(g)	Y–X···C(g)	X–Perp	Symmetry
1	N(3)–O(7)···Cg(3)	3.802(3)	3.887(3)	84.90(16)	-3.602	-x,2-y,2-z

Cg(3) = centre of gravity of ring [C(1)–C(2)–C(3)–C(4)–C(5)–C(6)].



(i) (ii)

Fig. 4. (i) The lone pair···π (green) and π···π (blue) interactions highlighted in complex **1**. (ii) One-dimensional assembly of monomeric units of **1** via lone pair···π/π···π interactions. (Colour online.)

Table 5
Geometrical parameters (Å, °) for the π···stacking moieties involved in the π···π interactions for complexes **1** and **2**.

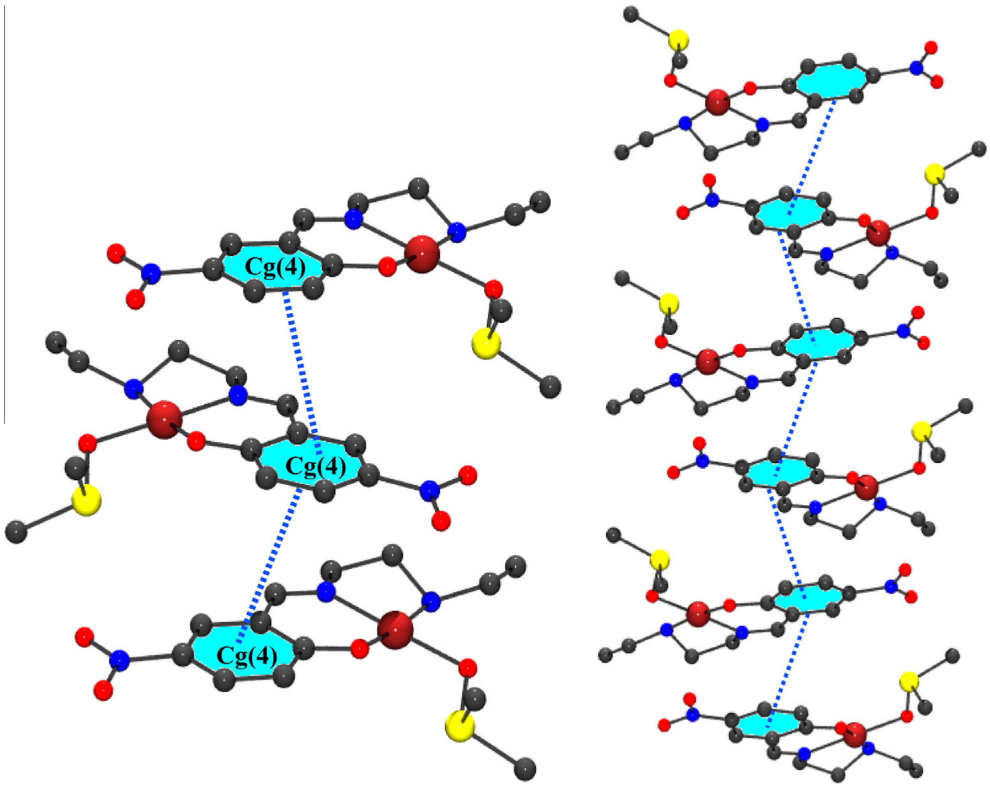
Complex	Rings I–J	Rc[a]	R1v[b]	R2v[c]	α	β	γ	Symmetry
1	Cg(2)–Cg(3)	3.6570(11)	3.3271(8)	3.3443(9)	1.37(9)	23.9	24.5	1 − x, 2 − y, 2 − z
	Cg(3)–Cg(3)	3.6317(14)	3.3691(9)	3.3690(9)	0	21.9	21.9	1 − x, 2 − y, 2 − z
2	Cg(4)–Cg(4)	4.400(2)	−3.2549(15)	3.2614(15)	0	42.2	42.3	1/2 + x, y, 3/2 − z

[a] Centroid distance between ring I and ring J.

[b] Vertical distance from ring centroid I to ring J.

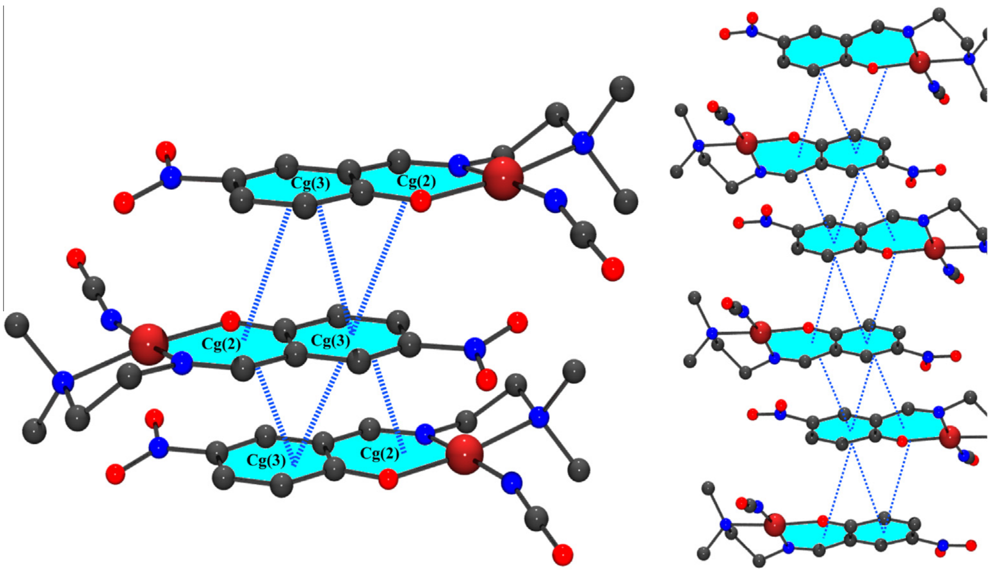
[c] Vertical distance from ring centroid J to ring I. α = dihedral angle between planes I and J (°); β = angle Cg(I) → Cg(J) or Cg(I) → Me vector and normal to plane I (°); γ = angle Cg(I) → Cg(J) vector and normal to plane J (°). Cg(2) = centre of gravity of the ring [Cu(1)–O(1)–C(1)–C(6)–C(7)–N(1)]; Cg(3) = centre of gravity of the ring [C(1)–C(2)–C(3)–C(4)–C(5)–C(6)] for complex **1** and Cg(4) = centre of gravity of the ring [C(6)–C(7)–C(8)–C(9)–C(10)–C(11)] for complex **2**.

around copper(II) is 359.97°, indicating a slightly distorted square-planar geometry around the copper(II) center. This deviation from planarity of the equatorial plane also manifests itself in the trans angles {O(1)–Cu(1)–N(1) and O(4)–Cu(1)–N(4)}, which are 174.07(13)° and 178.64(12)°. The deviations of the coordinating atoms O(1), O(4), N(1) and N(4) from the least-square mean plane passing through them are −0.044(3), 0.043(2), −0.043(3) and 0.045(3) Å respectively,and that of the copper(II) center from the same plane is 0.050(5) Å. The Cu–N_{imine} distance {1.935(3) Å} is shorter than the Cu–N_{amine} {2.014(3) Å} distance, as also observed in similar systems [42]. The closest conformation of the five-mem-



(i) (ii)

Fig. 5. (i) The π···π (blue) interactions highlighted in complex **2**. (ii) One-dimensional assembly of monomeric units of **2** via π···π interactions. (Colour online.)



(i) (ii)

Fig. 6. (i) The π···π (blue) interactions highlighted in complex **3**. (ii) One-dimensional assembly of monomeric units of **3** via π···π interactions. (Colour online.)

Table 6
Geometrical parameters (Å, °) for the π···stacking moieties involved in the π···π interactions for complex **3**.

Complex	Rings I–J	Rc[a]	R1v[b]	R2v[c]	α	β	γ	Symmetry
3	Cg(2)–Cg(3)	3.5870(12)	−3.2750(7)	3.2492(9)	2.04(9)	25.1	24.1	1 − *x*, −*y*, 1 − *z*
	Cg(2)–Cg(3)	3.9905(12)	3.2848(7)	3.2248(9)	2.04(9)	36.1	34.6	2 − *x*, −*y*, 1 − *z*
	Cg(3)–Cg(3)	3.4779(13)	−3.2966(9)	3.2966(9)	0	18.6	18.6	1 − *x*, −*y*, 1 − *z*
	Cg(3)–Cg(3)	4.0433(13)	3.2632(9)	3.2632(9)	0	36.2	36.2	2 − *x*, −*y*, 1 − *z*

[a] Centroid distance between ring I and ring J.
[b] Vertical distance from ring centroid I to ring J.
[c] Vertical distance from ring centroid J to ring I. α = Dihedral angle between planes I and J (°); β = angle Cg(I) → Cg(J) or Cg(I) → Me vector and normal to plane I (°); γ = angle Cg(I) → Cg(J) vector and normal to plane J (°). Cg(2) = centre of gravity of the ring [Cu(1)–O(4)–C(3)–C(2)–C(1)–N(1)]; Cg(3) = centre of gravity of the ring [C(2)–C(3)–C(4)–C(5)–C(6)–C(7)].

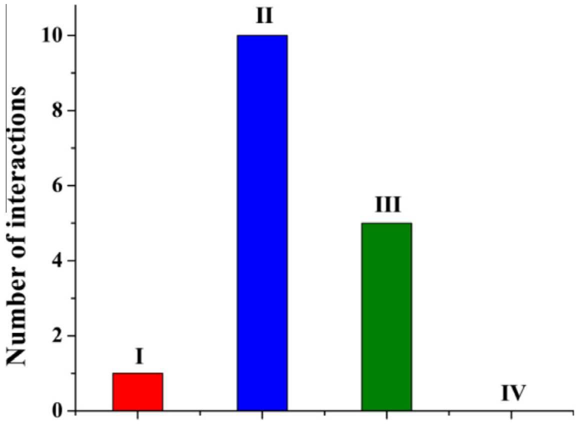


Fig. 7. Histogram showing the number of structures with certain interactions in the copper(II) complexes with N-methyl-1,2-diaminoethane based N_2O donor tridentate Schiff bases: (I) C–H···π interactions, (II) π···π interactions, (III) lone pair···π interactions and (IV) anion···π interactions.

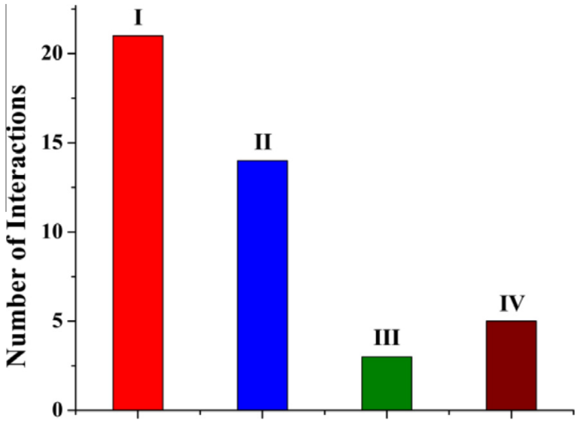


Fig. 8. Histogram showing the number of structures with certain interactions in copper(II) complexes with N-ethyl-1,2-diaminoethane based N_2O donor tridentate Schiff bases: (I) C–H···π interactions, (II) π···π interactions, (III) lone pair···π interactions and (IV) anion···π interactions.

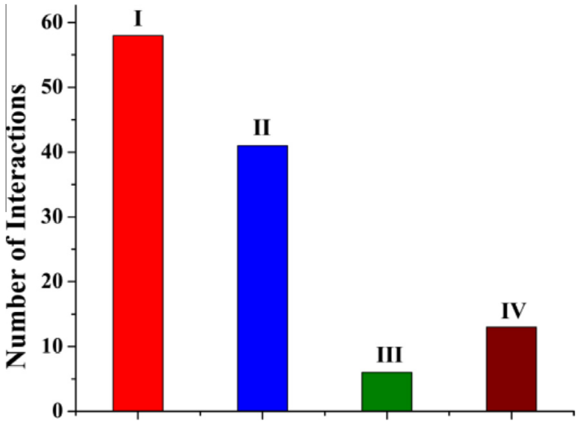


Fig. 9. Histogram showing the number of structures with certain interactions in copper(II) complexes with N,N-dimethyl-1,2-diaminoethane based N_2O donor tridentate Schiff bases: (I) C–H···π interactions, (II) π···π interactions, (III) lone pair···π interactions and (IV) anion···π interactions.

bered chelate ring Cu(1)–N(1)–C(2)–C(3)–N(4) is envelope, with puckering parameters *q*(2) = 0.377(8) Å and *ϕ*(2) = 258.8(7)° [43].

There is a strong H bond between H(1A) (attached to N(1) of the Schiff base) and O(8) of a neighboring perchlorate anion (Fig. 2). Details of the H-bonding are given in Table 3.

3.2.3. [CuL^3(NCO)] (3)

Complex **3** crystallizes in the monoclinic space group $P2_1/n$. Fig. 3 shows a perspective view of the monomeric copper(II) complex, [CuL^3(NCO)]. The central copper atom, Cu(1), is coordinated equatorially by one amine nitrogen atom, N(2), one imine nitrogen atom, N(1) and one oxygen atom, O(4), of the tridentate Schiff base ligand and a nitrogen atom, N(4), of the cyanate ligand to form a square planar structure. The trans angles are found to be 172.53(7)° {O(4)–Cu(1)–N(2)} and 173.09(8)° {N(1)–Cu(1)–N(4)}. Deviations of the coordinating atoms N(1), N(2), N(4) and O(4) from the least-square mean plane passing through them are −0.1088(15), 0.105(2), −0.102(2) and 0.1061(14) Å respectively, and that of the copper atom from the same plane is −0.0054(3) Å. In the equatorial plane, the Cu–N_{imine} distance (1.9326 Å) is shorter than the Cu–N_{amine} (2.0694 Å) distance, as observed in similar systems [42]. The five-membered chelate ring formed by the diamine with Cu(1), {Cu(1)–N(1)–C(8)–C(9)–N(2)}, is twisted on C(8)–C(9) with puckering parameters *q*(2) = 0.424(2) Å; *ϕ*(2) = 270.1(2)° [43]. Significant bond distances and angles are given in Table 2. There are no significant H-bonding interactions in complex **3**.

3.3. π···π, C–H···π, N–H···π, lone pair···π and anion···π interactions

In complex **1**, the non-coordinating oxygen atom, O(7), makes a lone pair···π contact (Table 4) with the phenyl ring C(1)/C(2)/C(3)/C(4)/C(5)/C(6) of symmetry −*x*, 2 − *y*, 2 − *z*, with the angle α = N(3)–O(7)···Cg(3) = 84.90(16)° and distance N(3)···Cg(3) = 3.887(3) Å, where Cg(3) is the centroid of the above mentioned ring. The formation of a supramolecular 1D chain (Fig. 4) is ensured mainly by two additional π···π interactions (Table 5). Firstly, the chelating ring Cu(1)/O(1)/C(1)/C(6)/C(7)/N(1)} is stacked over the phenyl ring, C(1)/C(2)/C(3)/C(4)/C(5)/C(6)} of a neighboring molecule of symmetry 1 − *x*, 2 − *y*, 2 − *z* and secondly the phenyl ring,

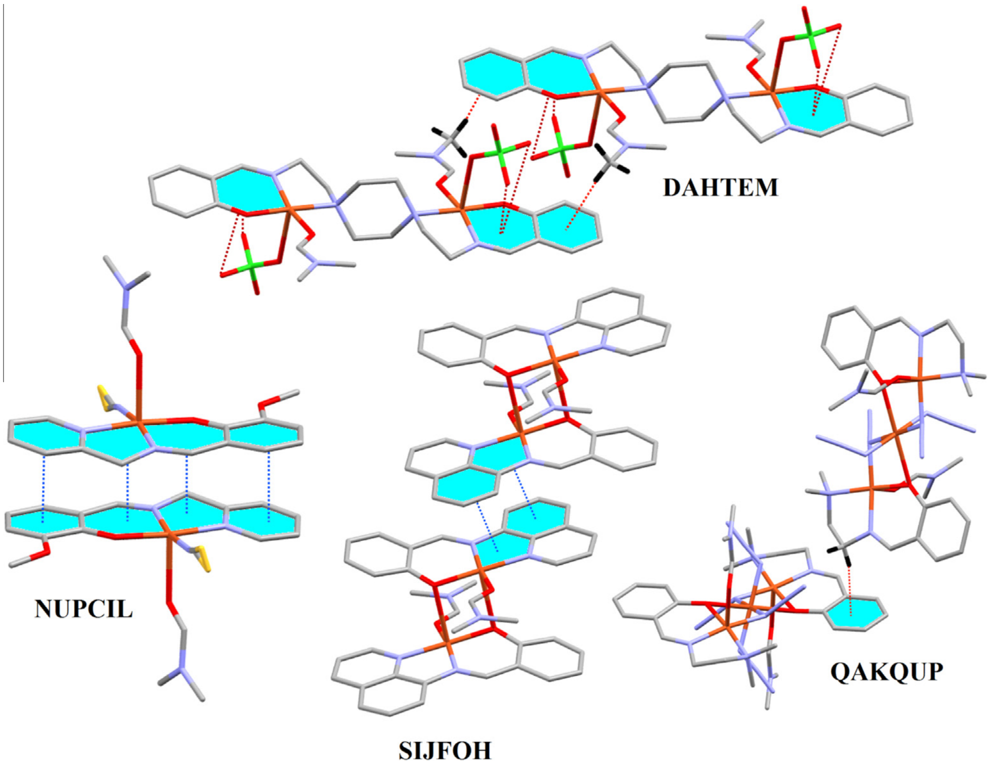


Fig. 10. Some related X-ray structures retrieved from the CSD exhibiting C–H$\cdots\pi$, $\pi\cdots\pi$ and anion$\cdots\pi$ interactions.

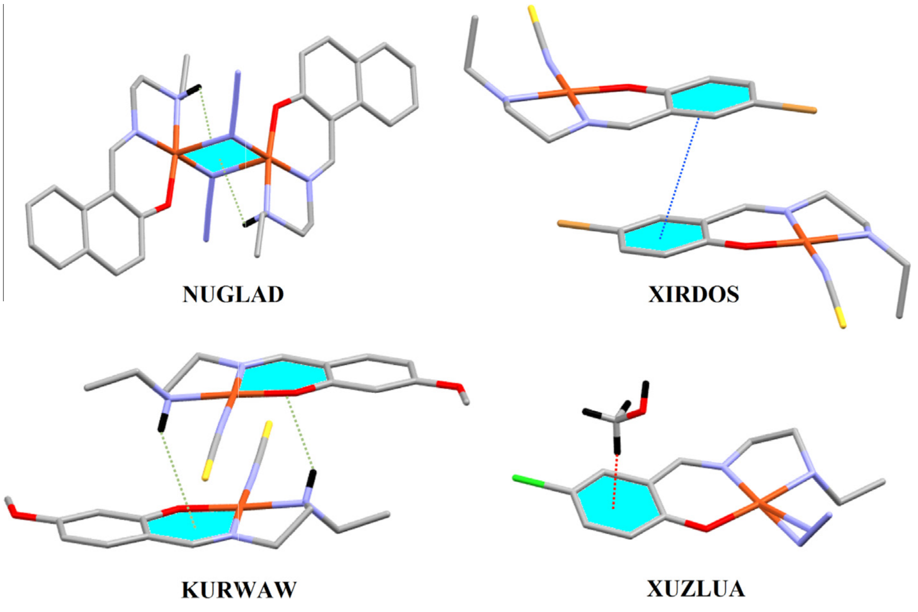


Fig. 11. Some related X-ray structures retrieved from the CSD exhibiting N–H$\cdots\pi$, C–H$\cdots\pi$ and $\pi\cdots\pi$ interactions.

C(1)/C(2)/C(3)/C(4)/C(5)/C(6) of the host complex is stacked over the same neighboring phenyl ring of symmetry $1-x$, $2-y$, $2-z$ to give rise to a second $\pi\cdots\pi$ interaction. These coupled lone pair$\cdots\pi$ and $\pi\cdots\pi$ interactions within the monomeric units add stability to the formation of the supramolecular architecture.

A one-dimensional supramolecular chain (Fig. 5) is formed in complex **2** by face-to-face $\pi\cdots\pi$ stacking between a phenyl ring, C(6)/C(7)/C(8)/C(9)/C(10)/C(11), of the host molecule with a symmetry related $(1/2+x, y, 3/2-z)$ phenyl ring of a neighboring molecule (Table 5).

The formation of a supramolecular one dimentional chain in complex **3** (Fig. 6) is ensured by four basic face-to-face $\pi\cdots\pi$ stacks (Table 6). The first $\pi\cdots\pi$ interaction occurs between the chelate ring Cu(1)/O(4)/C(3)/C(2)/C(1)/N(1) and the phenyl ring C(2)/C(3)/C(4)/C(5)/C(6)/C(7) of symmetry $1-x$, $-y$, $1-z$ of a neighboring molecule. The second $\pi\cdots\pi$ interaction occurs between the chelate ring Cu(1)/O(4)/C(3)/C(2)/C(1)/N(1) and the phenyl ring C(2)/C(3)/C(4)/C(5)/C(6)/C(7) of symmetry $2-x$, $-y$, $1-z$. Finally the third and fourth $\pi\cdots\pi$ interactions occur between the host phenyl ring C(2)/C(3)/C(4)/C(5)/C(6)/C(7) and two neighboring

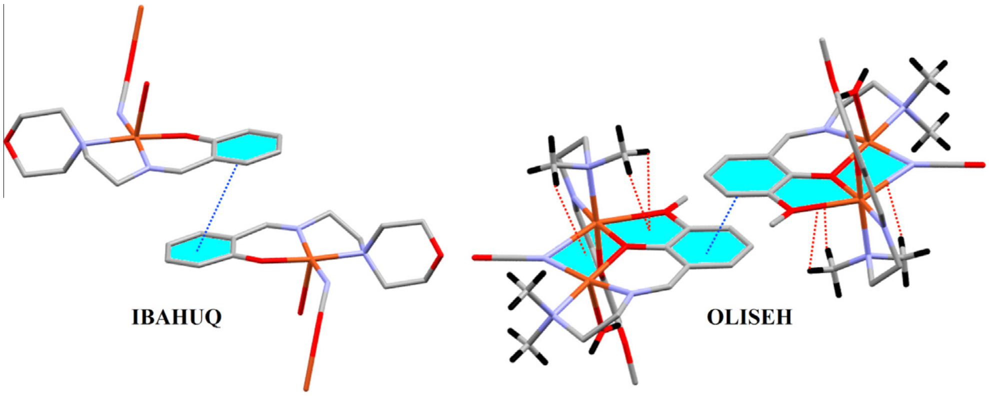


Fig. 12. Some related X-ray structures retrieved from the CSD exhibiting C–H···π and π···π interactions.

Table 7
Photophysical data for complexes **1**–**3**.

Complex	Excitation (nm)	Emission (nm)
1	350	413
2	350	424
3	350	423

identical phenyl rings, one at the top face {symmetry code 1 − *x*, −*y*, 1 − *z*} and the other at the bottom face {symmetry code 2 − *x*, −*y*, 1 − *z*}. These coupled π···π interactions within the monomeric units enhance the stability of the supramolecular architecture.

We would like to compare the supramolecular interactions of these three complexes with other copper(II) complexes with N,N,O donor Schiff bases, reported earlier. In doing so, we have searched the database thoroughly to find the possible supramolecular interactions in the related copper(II) complexes. We considered those Schiff bases which are formed by the condensation of (i) N-methyl ethylenediamine, (ii) N-ethyl ethylenediamine or (iii) N,N-dimethyl ethylenediamine with salicyaldehyde or its derivatives (CSD search as the Supplementary material). We have checked the possibilities of all types of supramolecular interactions (e.g. CH···π, π···π, anion···π, lone pair···π etc.) in those copper(II) complexes. The results are given as histograms for all the complexes (Figs. 7–9). It is difficult to rationalize the trend in supramolecular interactions in different complexes, but the database suggests that CH···π interactions are observed in a maximum number of complexes with N-ethyl and N,N-dimethyl ethylenedimine based Schiff bases and π···π interactions are maximum in N-methyl ethylenedimine based Schiff bases. The details of these interactions are given in the Supplementary information (Tables S1, S2 and S3). Some related X-ray structures retrieved from the CSD exhibiting C–H···π, N–H···π, π···π and anion···π interactions are shown in Figs. 10–12.

3.4. IR, electronic spectra, luminescence study and magnetic moments

Bands corresponding to the C=N (azomethine) stretching vibrations appear in the range 1641–1651 cm^{-1} in the IR spectra of all the three complexes, as also observed in similar systems [44]. The absorption bands due to the perchlorate anion appear at around 1100 cm^{-1} for complexes **1** and **2** [45]. Intense bands for complexes **1**–**3** appear within 1313–1317 cm^{-1}, which may be attributed to NO_2 vibrations [46]. The IR spectrum of **3** shows an intense absorption band at 2231 cm^{-1} corresponding to the NCO ligand [47].

The electronic spectra of all the complexes in acetonitrile were recorded in the range 200–1000 nm. The intense absorption bands at short wavelengths, around 360 nm, may be assigned to ligand to metal ion charge transfer bands (LMCT). The absorptions around 600 nm may be assigned to d–d transitions. The positions of these bands are consistent with the observed square planar geometries around the copper(II) centres [25]. Complexes **1**–**3** exhibit luminescence in acetonitrile medium. The luminescence data are listed in Table 7 (without solvent correction). These are assigned to intraligand $^1(\pi–\pi^*)$ fluorescence [48].

Room temperature magnetic susceptibility measurements for complexes **1**, **2** and **3** showed that they have magnetic moments close to 1.73 BM, as expected for the discrete magnetically non-coupled spin-only value for copper(II), as was observed in similar systems [49–51].

4. Conclusions

In the present paper, we report the synthesis and characterization of three new copper(II) complexes with three different tridentate Schiff bases, HL^1, HL^2 and HL^3. In each of the three complexes, the copper(II) center assumes a square planar geometry. The tridentate Schiff bases occupy three coordinating positions. The fourth coordination site is occupied by DMF in **1**, DMSO in **2** and cyanate in complex **3**. Both the Schiff bases HL^1 and HL^2 are capable of forming H bonds due to the presence of hydrogen atoms attached to the amine N atoms. These H atoms form strong H bonds with perchlorate ions. The supramolecular architecture of complex **1** involves H bonding, π···π and lone pair···π interactions whereas in the case of complex **2**, H bonding and π···π interactions are responsible for the supramolecular architecture. The Schiff base HL^3 is not capable of forming H bonds and therefore only π···π interactions are responsible for the formation of the supramolecular architecture.

Acknowledgments

This work was supported by the DST, India, under FAST Track Scheme (Order No. SR/FT/CS-118/2010, dated 15/02/2012). We are thankful to Mr. Ramesh Chandra Santra and Dr. Saurabh Das, Department of Chemistry, Jadavpur University, India for providing facilities for the UV–Vis spectral studies.

Appendix A. Supplementary data

CCDC 935114, 935314 and 935313 contains the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.08.037.

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