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7

Structural Diversity on Copper(I) Schiff Base Complexes

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1. Introduction

Azomethines (known as Schiff bases), are perspective materials for wide spectrum of applications, particularly for anion sensor [1], antimicrobial agents [2-4] and nonlinear optical materials [5,6]. There has been considerable interest in some Schiff bases derived from salicylaldehyde because they show photochromism and thermochromism in the solid state [7]. The preparation of these compounds is simple and elegant. Since their discovery by Hugo Schiff in 1864 [8], they are prepared by condensing an active carbonyl compounds (ketone or aldehyde) with an amine, generally in refluxing alcohol [9-15]. Schiff bases are often used as ligands in inorganic chemistry [16-22].
In recent years, there has been a growing interest in the synthesis, characterization and crystal structures of copper(I) Schiff base complexes, not only because they have interesting properties and structural diversity [23-25] but also because they have found important application in catalysis for the coupling of phenylacetylene with halobenzene [26], preparation of supramolecular assemblies [27,28], the design of single and double-stranded architectures [29,30] and the grid complexes [31,32]. Then, Many efforts have been devoted to the design and synthesis of new Schiff base ligands that would be able to control the crystal structure of copper(I) complexes [33-40]. The purpose of this chapter is to present the current status of chemistry of copper(I) Schiff base complexes.

2. Schiff base ligands

Schiff bases are functional groups that contain a carbon-nitrogen double bond (C=N) with the nitrogen atom connected to an aryl or alkyl group, but not hydrogen. They are of the general formula R1R2C=N-R3, where R3 is an aryl or alkyl group that makes the Schiff base a stable imine. Schiff base compounds can be synthesized from an amine and a carbonyl compound by nucleophilic addition, followed by a dehydration to generate an imine [9-15], and are broadly classified as bidnetate and bis-bidentate Schiff bases.

2.1 Bidentate schiff-bases

2.1.1 Symmetric bidentate schiff bases

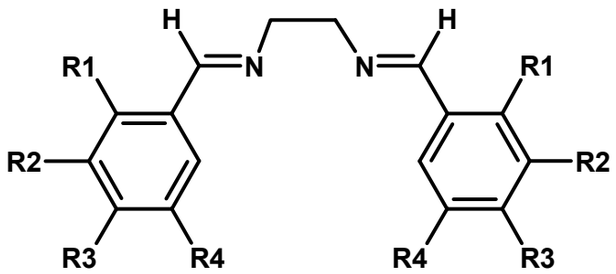
The basic symmetric bidentate Schiff base ligands (Scheme 1) have different R1 and R2 substituents [41-62]. Schiff bases based on aldehydes have hydrogen atom as one of the

substituents (R1) at carbon atom of azomethine group, while second substituent R2 may be an alkyl, an aryl or a heterocyclic group. Schiff bases based on ketones have an alkyl, an aryl or a heterocyclic group in both the substituents at carbon atom of azomethine group, which may be same or different.



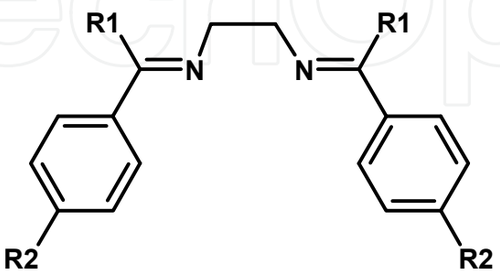
Scheme 1.

The symmetric bidentate Schiff base ligands have two arms connected via a ring, or C-C bond, as for example, shown in Schemes 2-8.



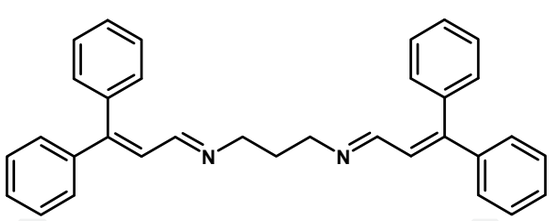
R1 = R2 = R4 = H	R3 = CH_3	L^1 [41]
R1 = H	R2 = R3 = R4 = CH_3O	L^2 [41,42]
R1 = R3 = R4 = H	R2 = CH_3O	L^3 [43]
R1 = R2 = R4 = H	R3 = CH_3O	L^4 [44]
R2 = R3 = R4 = H	R1 = Cl	L^5 [45]
R1 = R2 = R3 = R4 = H		L^6 [46]

Scheme 2.

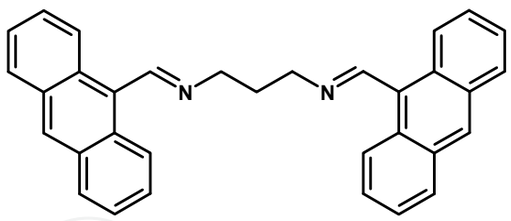


R1 = Ph	R2 = H	L^7 [47]
R1 = CH_3	R2 = Cl	L^8 [48]
R1 = CH_3	R2 = NO_2	L^9 [48]

Scheme 3.

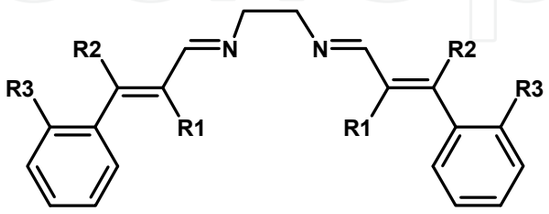


L^{10} [49]

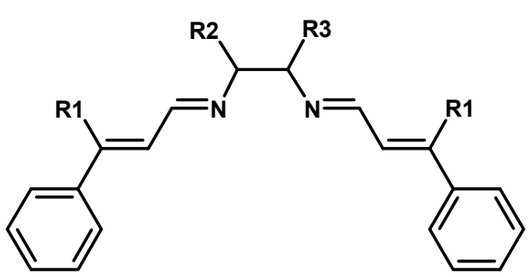


L^{11} [50]

Scheme 4.

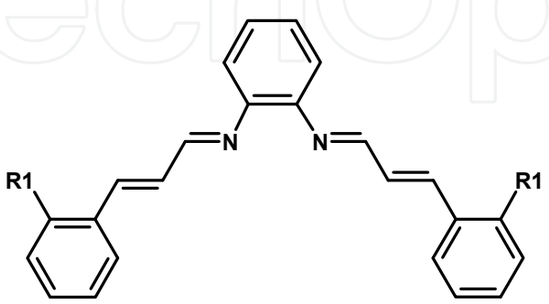


R1 = R2 = R3 = H		L^{12} [51,52]
R1 = R2 = H	$R3 = NO_2$	L^{13} [53]
R1 = R3 = H	R2 = Ph	L^{14} [54,55]
R2 = R3 = H	$R1 = CH_3$	L^{15} [56]



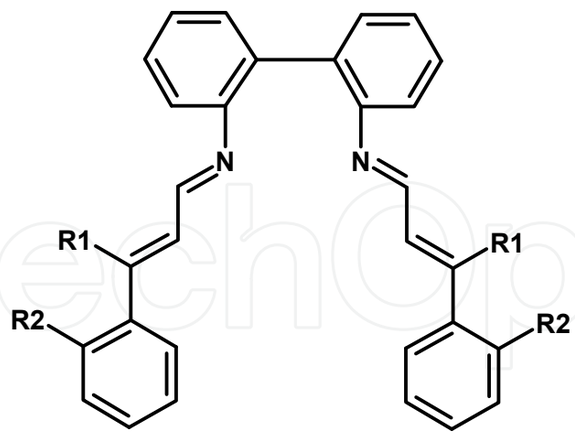
R1 = R2 = H	$R3 = CH_3$	L^{16} [57]
R1 = R2 = R3 = Ph		L^{17} [57]

Scheme 5.



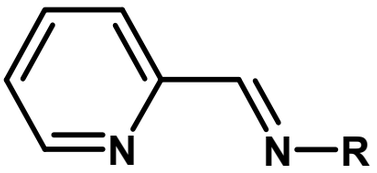
R1 = H	L^{18} [58]
$R1 = NO_2$	L^{19} [59]

Scheme 6.



R1 = Ph , R2 = H L^{20} [60,61] R1 = H, R2 = NO_2 L^{21} [62]

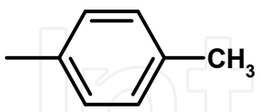
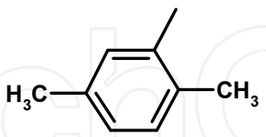
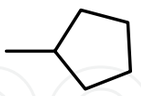
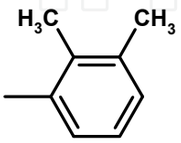
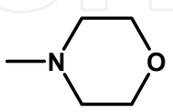
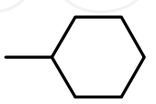
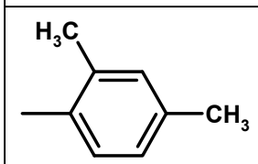
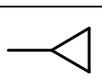
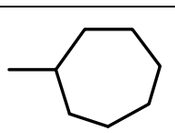
Scheme 7.



Scheme 8.

2.1.2 Asymmetric bidentate schiff bases

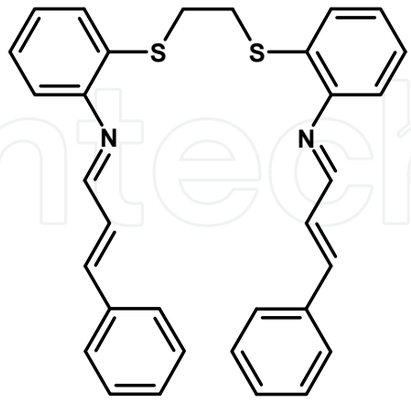
Asymmetric Schiff base ligands (Scheme 9) have been synthesized from an amine and pyridinecarboxaldehyde. They can be classified by different R substituent [6365].

R	L [Ref]	R	L [Ref]	R	L [Ref]
	L^{22} [63]		L^{25} [63]		L^{28} [65]
	L^{23} [63]		L^{26} [64]		L^{29} [65]
	L^{24} [63]		L^{27} [65]		L^{30} [65]

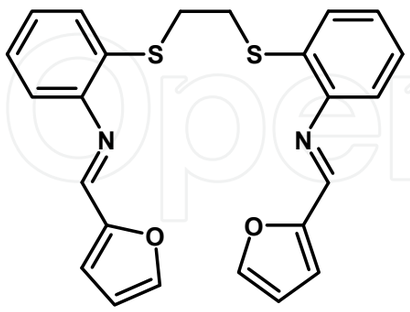
Scheme 9.

2.2 Bis-bidentate schiff-bases

The basic bis-bidentate Schiff base ligands have two arms connected via a ring, or C-C bond, as for example, shown in Schemes 10 – 14 [27-30,32,35-40,66-72].

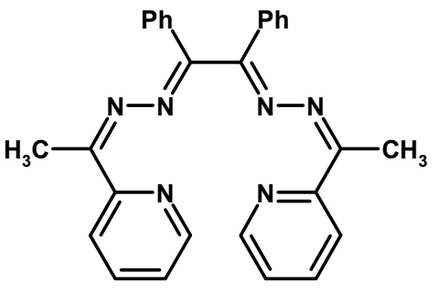


L^{31} [35,66]

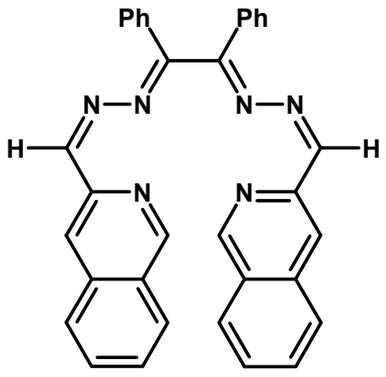


L^{32} [36]

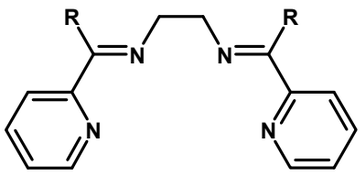
Scheme 10.



L^{33} [29, 67]



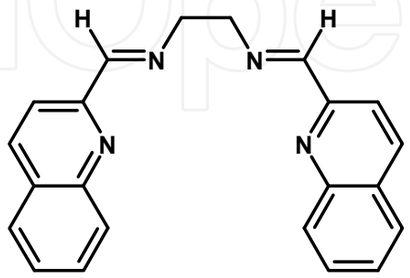
L^{34} [68]



R = H

R = CH_3

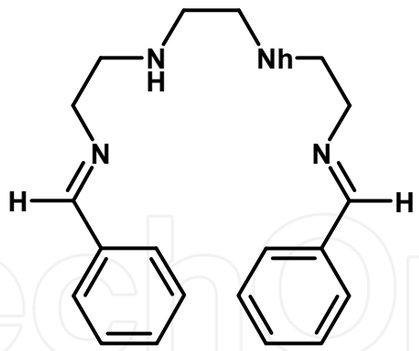
L^{35} [30, 38]



L^{37} [67]

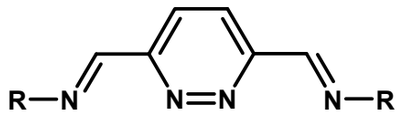
L^{36} [39,69]

Scheme 11.

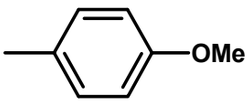
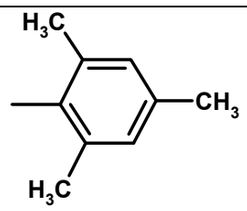
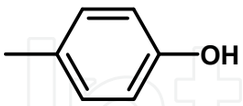
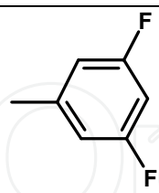
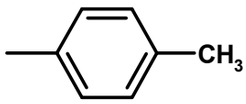
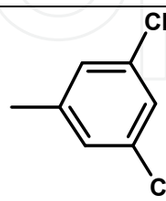
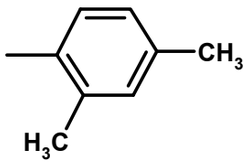
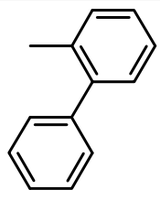


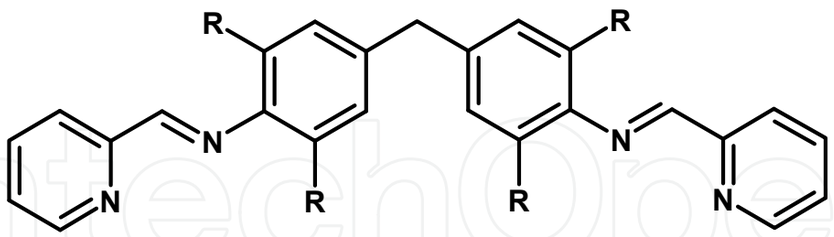
L^{38} [37]

Scheme 12.



Scheme 13 [32].

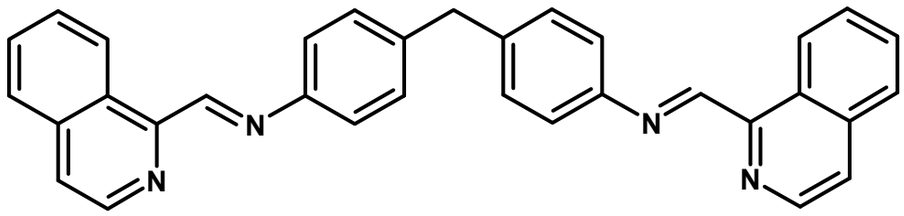
R	L	R	L
	L^{39}		L^{43}
	L^{40}		L^{44}
	L^{41}		L^{45}
	L^{42}		L^{46}



R = H L^{47} [28,70,71]

R = CH_3 L^{48} [72]

R = C_2H_5 L^{49} [27]



L^{50} [40]

Scheme 14.

3. Bonding modes of schiff base ligands

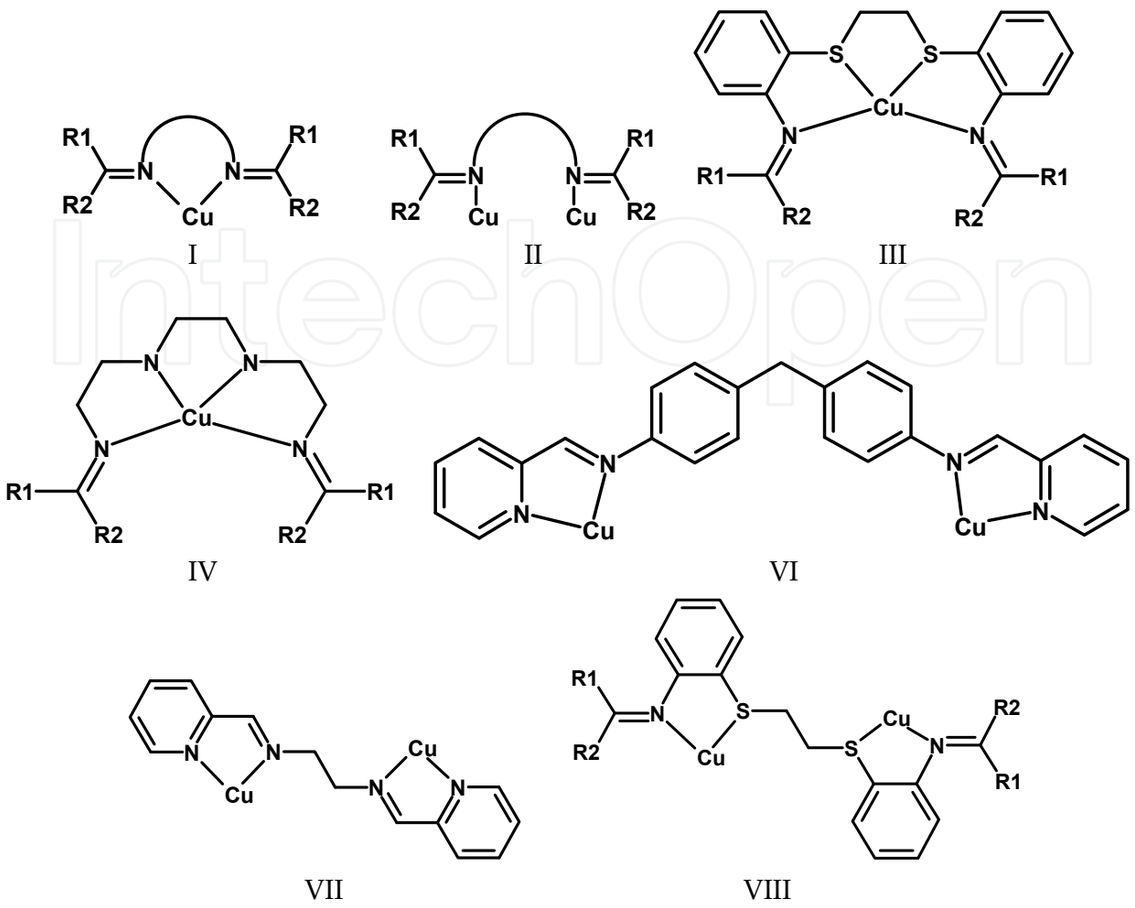
A number of bonding modes have been observed for the Schiff bases in their neutral form. The binding occurs via nitrogen atom of azomethine group in chelating and bridging modes, I - VIII (Scheme 15).

4. Copper(I) schiff base complexes

Copper(I) Schiff base complexes were generally prepared by the reaction of a CuX, where X = halide (Cl^-, Br^-, I^-), pseudohalide (NCS^-, N_3^-), or $[Cu(CH_3CN)_4]Y$ (Y = the non-coordinating anions (ClO_4^-, BPh_4^-) with a suitable Schiff base ligands in an acetonitrile solvent, followed by room temperature stirring under an N_2 or air atmosphere [41-62]. In these complexes, Schiff-bases act as chelating ligands and cause the geometry around the copper(I) atom will be distorted tetrahedral.

Several different crystallization techniques have been used to grow crystals of copper(I) complexes with Schiff base ligands. Some of them are:

1. Slow diffusion of Et_2O into the concentrated solution of complex at room temperature
2. Very slow evaporation of the solvent at ambient temperatures for several days
3. Layering technique
4. Precipitation and re-crystallization from a mixture of solvents

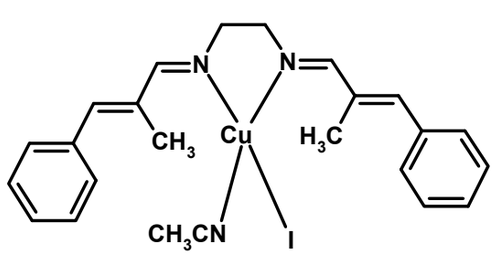


Scheme 15.

4.1 Copper(I) complexes with symmetric bidentate Schiff base ligand

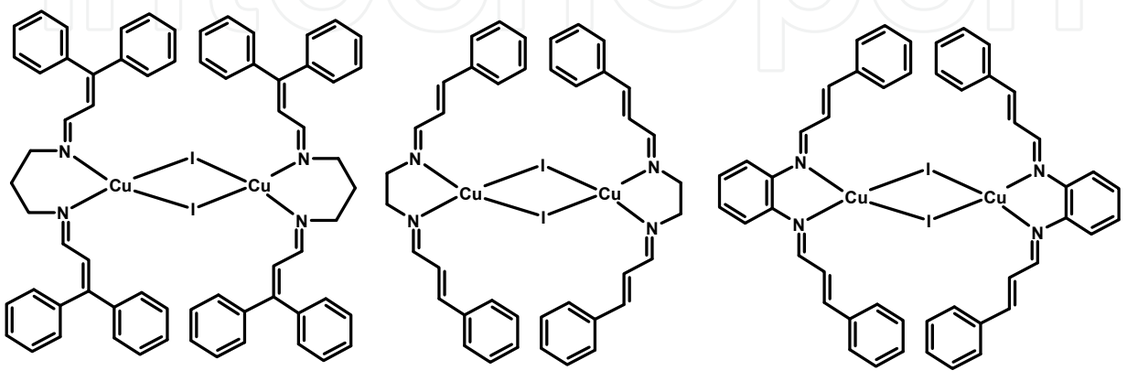
4.1.1 Copper(I) iodide complexes

The reaction of equimolar amounts of $Meca_2en$ (L^{15}) at the presence of copper(I) iodide in acetonitrile at room temperature yielded yellow microcrystalline powder of mononuclear copper(I) complex $Cu(Meca_2en)(CH_3CN)I$ (1) (Scheme 16) [56]. Slow evaporation of the solvent, 1:1 *v/v* chloroform:acetonitrile, at 273 K gave suitable yellow crystals. The coordination geometry around the copper ion is distorted tetrahedron formed by two N atoms from $Meca_2en$, one N atom from acetonitrile and one iodine atom. The $Meca_2en$ acts as a bidentate ligand coordinating *via* two N atoms to the copper.



Scheme 16.

By changing the Schiff base ligand from Meca$_2$en to Phca$_2$pn (L^{10}), ca$_2$en (L^{12}) and ca$_2$ph (L^{18}), dinuclear copper(I) complexes [Cu(Phca$_2$pn)I]$_2$ (2) [49], [Cu(ca$_2$en)I]$_2$ (3) [51] and [Cu(ca$_2$ph)I]$_2$ (4) [58] (Scheme 17) have been prepared. Slow diffusion of diethylether vapour into the concentrated acetonitrile solution at 298 K gave suitable orange crystals (2 and 3), while dark red crystals of complex 4 were obtained at 273 K. The coordination geometry around the copper ion in 2 and 3 is distorted tetrahedron formed by two N atoms from the Schiff base ligand and two iodine substituents. The $Cu^IN_2I_2$ tetrahedra share iodine atoms which therefore double-bridge the neighboring copper(I) ions.



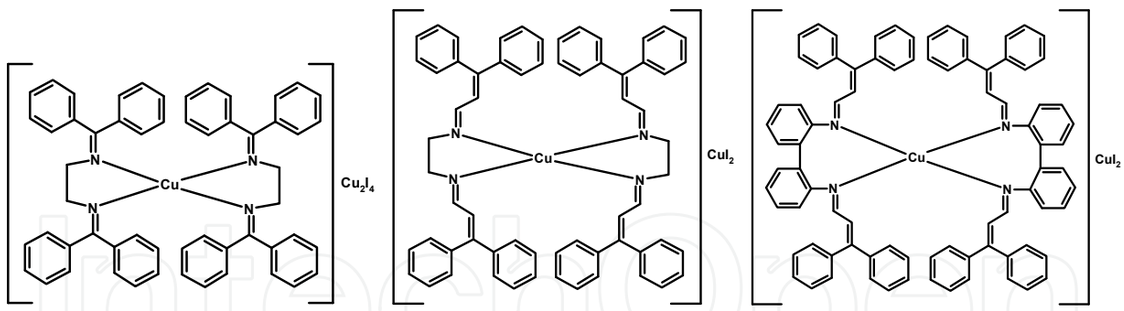
2 3 4

Scheme 17.

However, the chelate N-Cu-N angle in 2 (100.17(12)°) is larger than the corresponding angle in 3 (82.7(3)°), while the I-Cu-I angle in 2 (104.517(17)°) is larger thanthe corresponding one in 3 (119.65(4)°), making the distortion of the tetrahedron considerably larger in (3) because of restricting bite angle of the chelating ligand. The N-Cu-I bond angles range from 100.53(9) to 122.48(9)° in 2 are similar to the corresponding angle in 3 (103.8(2) – 121.8(2)°). The bond distances Cu-I (2.7264(6) Å) and Cu-N (2.055(3) and 2.065(3) Å) in 2 are similar to the corresponding bond distances in 3 (2.6903(14), 2.069(7) and 2.085(7) Å, respectively). The dinuclear unit in these complexes is centrosymmetric with crystallographic center of symmetry located between the two copper(I) ion. The distances between the two copper(I) ions are 3.372(2) Å in 2 and 2.635(2) Å in 3.

The reaction of equimolar amounts of bz$_2$en (L^7), phca$_2$en (L^{14}) and Phca$_2$-dab (L^{17}) at the presence of copper(I) iodide in acetonitrile at room temperature yielded mononuclear copper(I) complexes [Cu(bz$_2$en)][Cu$_2$I$_4$] (6) [47], [Cu(Phca$_2$en)$_2$][I_3^-] (6) [54] and [Cu(Phca$_2$-dab)$_2$][[CuI$_2$] (7) [61] (Scheme 18). Slow diffusion of diethylether vapour into the concentrated acetonitrile-dichloromethane solution for 5, acetonitrile solution for 6 and chloroform solution for 7 at 298 K gave suitable dark red crystals.

The Schiff base ligand Phca$_2$-dab (L^{17}) have two different phenyl rings (the inner and outer phenyl rings) [61]. They play different role in the arrangement of the cations and anions of [Cu(Phca$_2$-dab)$_2$][CuI] (7). As a result, a one-dimensional net of 7 molecules is generated by 4-PE (fourfold phenyl embrace) including Ri rings (Fig. 1a). The Ro rings are not involved in the 4-PE local interactions. The [CuI$_2$]$^-$ anions in the crystal structure are located in the space between Ro rings of the two adjacent cations (Fig. 1b) [61].

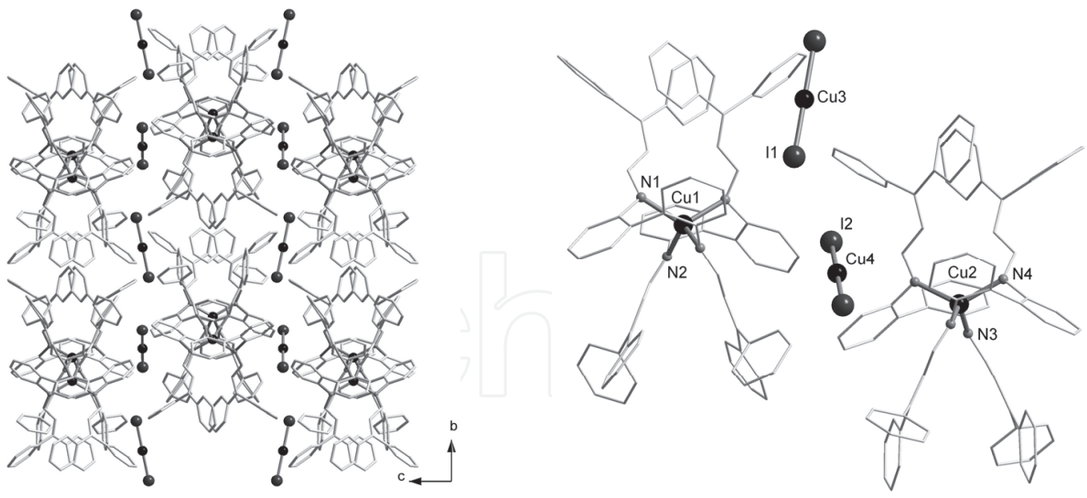


5 6 7

Scheme 18.

The solid-state structure of complexes 5-7 reveals ionic complexes containing a cation of copper(I) ion coordinated to four nitrogen atoms of two Schiff base ligands. The coordination geometry around the copper ion is distorted tetrahedron. The complexes contain anions di-μ-iodo-diiododicuprate(I) for 5, diiodocuprate(I) for 6 and I_3^- for 7.

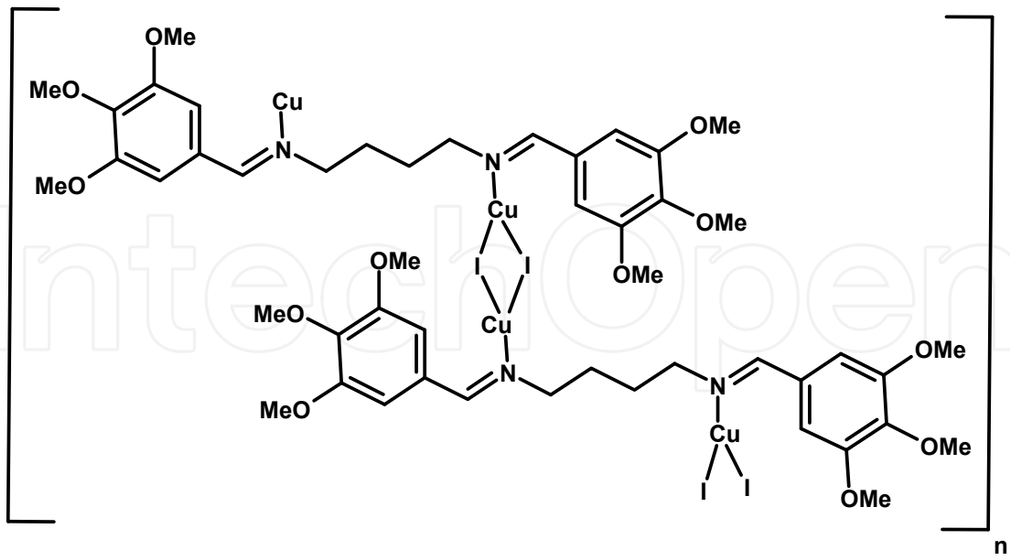
While a tetrahedral geometry might be expected for copper(I) complexes 6 and 7, the coordination sphere around copper(I) in these complexes is distorted by the restricting bite angle of the chelating Schiff base ligand. The average Cu-N bond distance of 2.023 Å in 6 is similar to the corresponding bond distance in 7 (2.035 Å). The chelate N-Cu-N angle in 6 (83.67(11)°) is shorter than similar to the corresponding bond angle in 7 (102.59(15)°).



a b

Fig. 1. a) One-dimensional net of fourfold phenyl embrace (4-PE) in 7. b) Representation of anions (CuI_2) associated with phenyl rings Ro.

The reaction of equimolar amounts of $(3,4,5\text{-MeO-ba})_2$bn (L^{43}) in the presences of copper(I) iodide yields polymeric copper(I) chain complex $[Cu_2(\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)(\mu\text{-}I)_2]_n$ (8) (Scheme 19) [33]. Slow evaporation of the solvent at 273 K gave suitable yellow crystals.



Scheme 19.

The copper(I) atom in 8 is coordinated by two iodine ions and one nitrogen atom from Schiff-base ligand in distorted trigonal planar coordination geometry. In the crystal structure of 8 the $(3,4,5\text{-MeO-ba})_2$bn acts as a bridging ligand with the nitrogen atoms of the two imine functions. This leads to formation of dinuclear $[Cu_2(\mu\text{-}(3,4,5\text{-MeO-ba})_2bn)]$ groups which are bridged by two iodine anions $[(\mu\text{-}I)_2]$ into a neutral 1D-chain copper(I) iodide coordination polymer (Fig. 2).

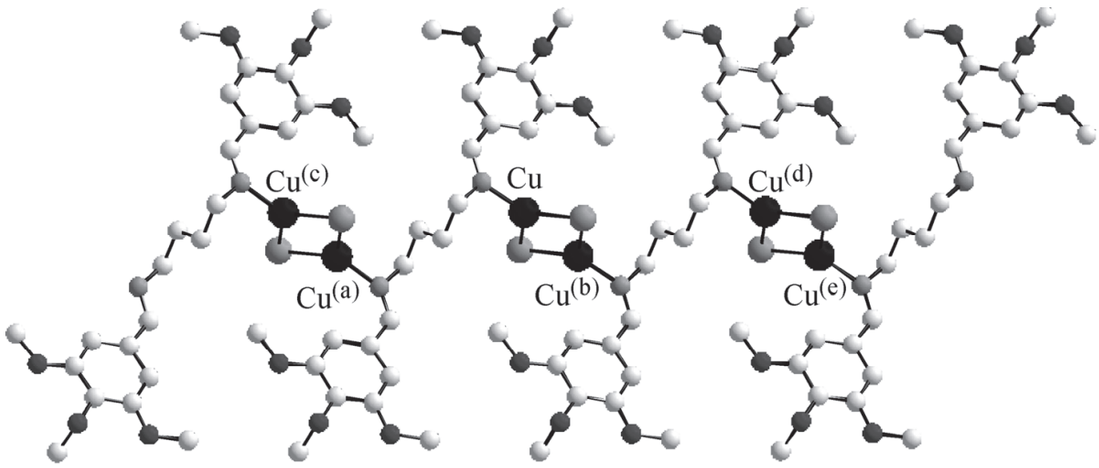
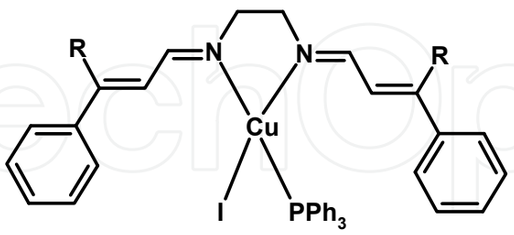


Fig. 2. D-chain of complex 8 running along the [001] direction. Symmetry codes: (a) -x+1,-y,-z+1; (b) -x+1,-y,-z+2

The Cu-N distance 1.9733(19) Å is similar like in other copper(I) complexes [41,43]. The Cu-I distances of 2.5491(4) and 2.5648(3) Å are slightly shorter than those of 2.6650(5) and 2.7393(5) Å in the 1D-chain copper(I) complex $[Cu_2(\mu\text{-}I)_2(PPh_3)_2(4,4'\text{-bpy})]_n$ [73]. The Cu···Cu distance in the Cu-$(\mu\text{-}I)_2$-Cu fragment of 2 is 2.5583(6) Å, i.e. shorter than in other similar Cu-$(\mu\text{-}I)_2$-Cu complexes [73].

The reaction of dinuclear copper(I) complex $[Cu(ca_2en)(I)]_2$ (3) [51] or mononuclear copper(I) complex $[Cu(Phca_2en)_2][I_3^-]$ (6) [54] with PPh_3 in an acetonitrile solution mononuclear copper(I) complex $[Cu(ca_2en)(PPh_3)I]$ (9) [52] and $[Cu(Phca_2en)(PPh_3)I]$ (10) [55] have been prepared (Scheme 20). Slow diffusion of diethylether vapour into the concentrated acetonitrile solution for 9 and 10 at 298 K gave suitable orange crystals.



R = H (9) R = Ph (10)

Scheme 20.

The copper(I) ion in 9 and 10 is coordinated to two N atoms of one Schiff base ligand, one P from PPh_3 and one iodine group in geometry distorted by the restricting bite angle of the chelating ligands. The chelate N-Cu-N angle (81.33(7)°) in 9 is similar to the corresponding bond distance and angle in 10 (2.104 Å and 81.74(5)°). The P-Cu-I angle is 120.964(15) and 115.582(11)° in 9 and 10, respectively, being larger than the tetrahedral values. The Cu-N (2.0915(17), 2.0918(17) Å), Cu-I (2.6469(4) Å) and Cu-P (2.2327(6) Å) bond distances in 9 agree well with the corresponding distances in 10 (2.1129(11), 2.0961(12), 2.6501(2) and 2.2342(4) Å, respectively).

Compounds containing M-PPh_3 moieties are recognized to form multiple phenyl embrance (MPE) as predominant supramolecular motifs [74,75]. In the complex 10, phenyl rings of PPh_3 groups exhibit different conformations that are illustrated in Fig. 3. The Cu-PPh_3 moiety of roughly threefold symmetry forms dimers that are separated from each other 7.270(7) Å, with Cu-P···P angle of 173.61(1)° [55].

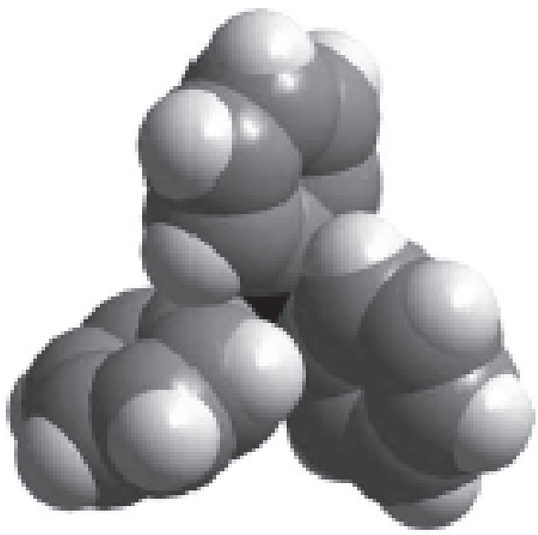
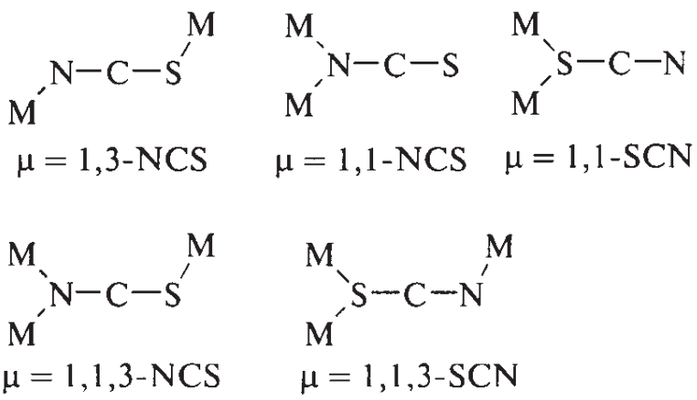


Fig. 3. Conformation of phenyl rings for Cu-PPh_3 moiety viewed along P-M in 10.

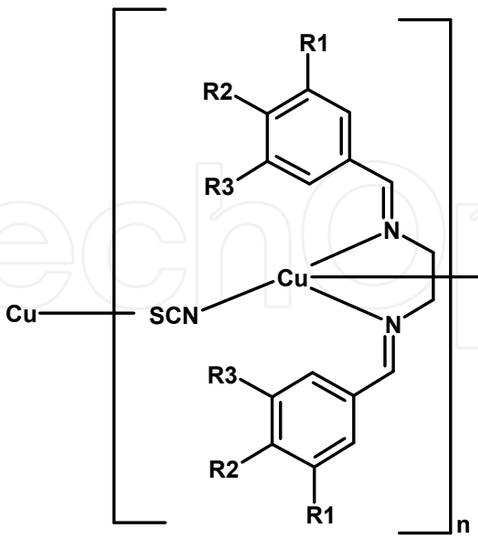
4.1.2 Copper(I) thiocyanate complexes

The pseudohalide NCS^- is known to coordinate to metal ions in both terminal and bridging modes [76,77]. Thiocyanate ion can afford a variety of coordination bridging modes (Scheme 21), such as μ-1,3-NCS, μ-1,1-NCS, μ-1,1-SCN, μ-1,1,3-NCS and μ-1,1,3-SCN, and link one or more transition metal ions to form zero, one-, two- and three-dimensional complexes [76,77].



Scheme 21.

The reaction of bidentate Schiff base ligand (3-Me-ba)$_2$en (L^1), (3,4,5-Meo-ba)$_2$en (L^2) and (2-MeO-ba)$_2$en (L^3) with CuSCN in an acetonitrile, three copper(I) thiocyanate coordination polymers, $[Cu((3\text{-Me-ba})_2en)(SCN)]_n$ (11), $[Cu((3,4,5\text{-MeO-ba})_2en)(SCN)]_n$ (12) and $[Cu((2\text{-MeO-ba})_2en)(SCN)]_n$ (13), with one-dimensional coordination polymer chains (Scheme 22), have been prepared [41,43]. Slow evaporation of the solvent at 273 K gave suitable yellow crystals of 11-13.



R1 = R3 = H, R2 = CH_3 (11) R1 = R2 = R3 = CH_3O (12)
R2 = R3 = H, R1 = CH_3O (13)

Scheme 22.

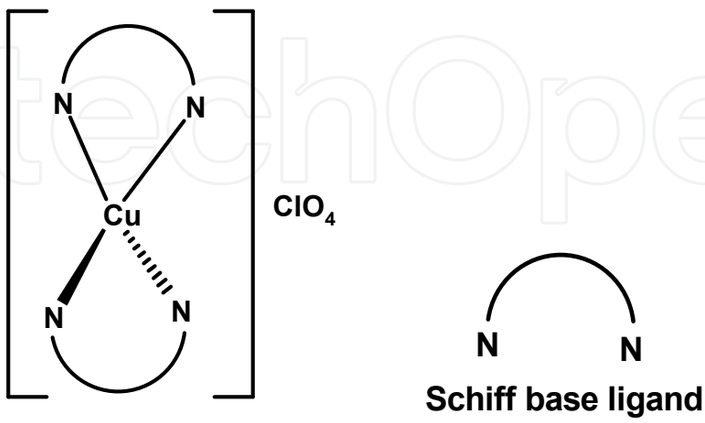
The crystal structures of these complexes have common features. In these complexes distorted tetrahedral coordination at Cu(I) is defined by the two N donor atoms of the Schiff base ligands and the N and S donor atoms of two thiocyanate ligands (Scheme 23). The Schiff base ligands act as chelating ligands while the SCN^- anion acts as a bridging ligand.

In 12, the Cu…Cu separation through the bridging thiocyanate ligand is 5.604 Å. The Cu-S bond length 2.3468(7) Å is greater compared with those of the Cu-N bonds (mean distance 2.06 Å), which causes a significant distortion of the coordination polyhedron around the Cu(I) ion. The values observed for Cu-N and Cu-S distances are comparable with those found in other tetrahedral Cu(I) complexes. Moreover, the Cu-N bond to the bridging SCN group is shorter than Cu-N bonds to the Schiff base ligands. The bridging SCN anion is almost linear with S-C-N bond angle of 179.4(2)°.

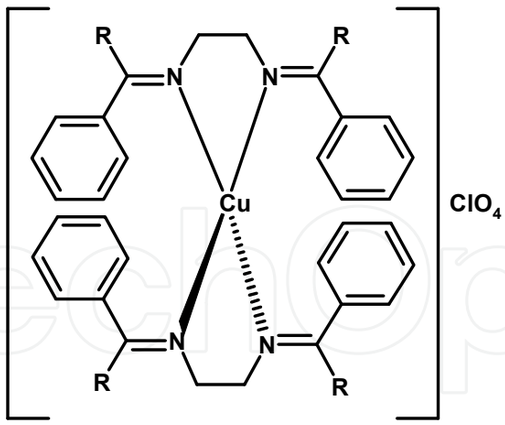
4.1.3 Copper(I) perchlorate complexes

Cu^IN_4 chromophores which exhibit photoluminiscence in solution are known only in copper(I) complexes of substituted 1,10-phenanthrolines and Schiff bases. Many advances in the chemistry of copper(I) complexes have been achieved on four coordinated tetrahedral complexes of the type $[Cu(NN)_2]^+$ or $[Cu(NN)(P)_2]^+$ (Scheme 23), where NN is Schiff base ligand and P is triphenylphosphine [78-80]. These complexes have relatively stable framework and exhibit metal-to-ligand charge transfer transition in the visible region.

The reaction of L^6 and L^7 in the presences of $[Cu(CH_3CN)_4]ClO_4$ (2:1 molar ratio) in degassed methanol under dry N_2 atmosphere, yielded yellow and red precipitates of $[Cu(ba_2en)_2]ClO_4$ (13) and $[Cu(bz_2en)_2]ClO_4$ (14), respectively (Scheme 24). Single crystals of 13 and 14, were grown by slow diffusion of n-hexane into a dilute dichloromethane solution of the complexes [46].



Scheme 23.



R = H (13) R = Ph (14)

Scheme 24.

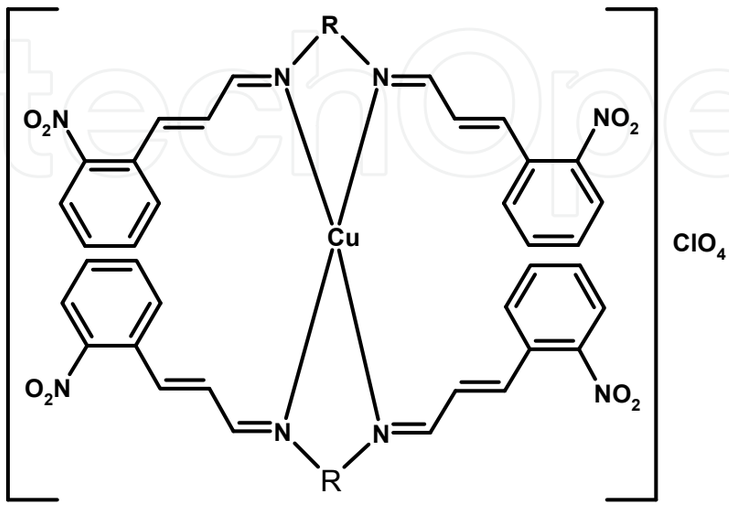
The average bite angle of the ligand (N-Cu-N) in both complexes is 85.3° [46]. In 13, the average Cu-N bond length is 2.073 Å, with an average dihedral angle of 73.1° between the two CuN_2 coordination planes, while the Cu-N bond lengths in 14 are in range from 2.014(4) to 2.183(4) Å, with dihedral angle of 63.9(2)° [46]. Complex 13 shows a quasireversible $Cu^{II/I}$ couple in cyclic voltametery with an $E_{1/2}$ of 0.81 V *vs* SCE, while this couple is much more reversible in complex 14 with an $E_{1/2}$ of 0.66 V *vs* SCE [46]. Interestingly, the emission spectrum of complex 14 shows an additionalband around 550 nm in methanol albeit very weak which is absent in dichloromethane. Both the emissions in 14 in methanol originate from the MLCT state [46].

In recent years, Dehghanpour *et al*. have systematically studied on copper(I) complexes of the type $[Cu(NN)_2]^+$ or $[Cu(NN)(P)^2]^+$ with unconjugated Schiff base ligands [44,48,53,57,59,62]. For example, the reaction of nca^2en (L^{13}) in the presences of $[Cu(CH_3CN)_4]ClO_4$ (2:1 molar ratio) in acetonitrile, yielded orange-red precipitates of $[Cu(nca_2en)_2]ClO_4$ (15) (Scheme 25). Single crystals of 15, were grown by slow diffusion of Et_2O into a concentrated acetonitrile solution of the complex [53]. Complex 15 shows a quasireversible $Cu^{II/I}$ couple in cyclic voltametery with an $E_{1/2}$ of 0.55 V *vs* SCE.

The solid-state structures of complexes 15-17 (Scheme 25) reveal copper(I) ion coordinated to four N atoms of two Schiff base ligands. The coordination geometry around the copper ion is distorted by the restricting bite angle of the chelating ligands. The chelate N-Cu-N angle (84.2(2)°) in 15 is similar to the corresponding bond angle in 16 (82.27(5) and 82.29(9)°) and is shorter than the corresponding bond angle in 17 (99.3(18) and 100.7(18)°). The Cu-N (2.044(3) and 2.020(3) Å) bond distances in 15 agree well with the same distances in 16 (2.035(2), 2.046(2), 2.062(2) and 2.038(2) Å) and in 17 (2.019(4), 2.022(4), 2.041(5) and 2.046(4) Å).

The structure of Schiff base ligands L^2 and L^{11}, are very similarto the ligands reported previously, but the side substitutes are changed to more bulky groups (3 methoxy groups in L^2 and one anthryl group in L^{11}), which is hence expected to exhibit unusual coordination mode with copper(I) ion. The reaction of L^2 in the presence of $[Cu(CH_3CN)_4]ClO_4$ (2:1 molar ratio) in acetonitrile, yielded yellow precipitate of $[Cu((3,4,5\text{-}MeO\text{-}ba)_2en)(CH_3CN)_2]ClO_4$ (18) (Scheme 26). Single crystals of 18 were grown by slow diffusion of Et_2O into an acetonitrile solution of the complex [42]. The copper(I) ion is coordinated by two N atoms from one bidentate Schiff base ligand and two N atoms from two acetonitrile groups. The

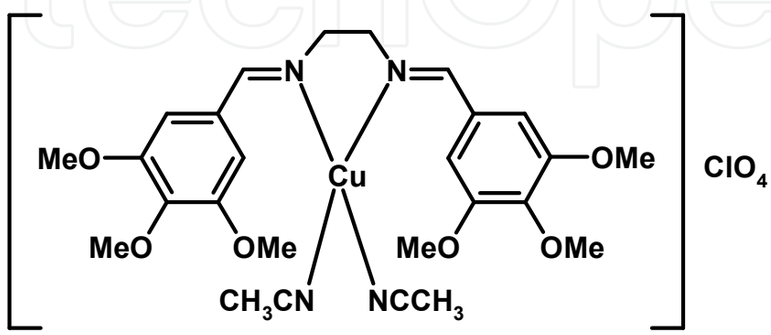
copper atom adopts a tetrahedral geometry. The Cu-N(ligand) distances are 2.076(3) and 2.076(3) Å, and the Cu-N(acetonitrile) distances are 1.964(4) and 1.975(4) Å.



R = -CH_2-CH_2- (15) R = -Ph- (16) R = -Ph-Ph- (17)

Scheme 25.

The reaction of L^{11}, at the presence of $[Cu(CH_3CN)_4]BF_4$ (2:1 molar ratio) in methanol, gave yellow-green precipitates of $[Cu(Anca_2en)_2]BF_4$ (19) (Fig. 4) [50]. Single crystals suitable for X-ray diffraction analysis were grown from a dichloromethane-ethanol (*v/v*, 1/1) solution of complex. The structure of 19 is shown in Fig. 23. In 19 the copper(I) ion is coordinated to three N atoms from two bidentate Schiff base ligands in a distorted trigonal planar geometry. The remaining imine N atom remains uncoordinated. The Cu-N distances are 2.111(3), 1.946(4) and 1.930(3) Å, respectively.



Scheme 26.

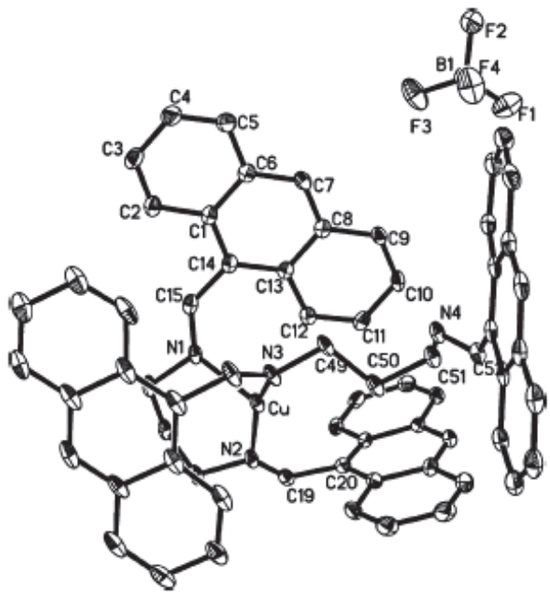
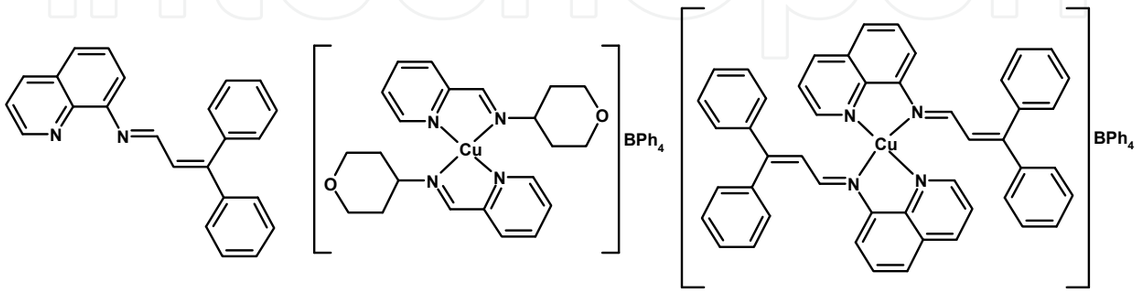


Fig. 4. An ORTEP view of 19, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

Apparently, the coordination pattern of 19 is very different from the copper(I) complexes reported so far [46,47]. In this complex, the bulky anthryl group has larger steric hindrance and may inhibit another imine-N of the second ligand to coordinated with copper(I), resulting in more stable three-coordinated conformation.

4.2 Copper(I) complexes with asymmetric bidentate Schiff base ligand

In recent years, Dehghanpour *et al*. have systematically studied on copper(I) complexes of the type $[Cu(NN)_2]^+$ or $[Cu(NN)(P)_2]^+$ with asymmetric Schiff base ligands [60, 63-65]. For example, the reaction of 4-ampc (L^{26}) (Scheme 9) and dpa-qa (L^{51}) (Scheme 27) in the presences of $[Cu(CH_3CN)_4]BPh_4$ (2:1 molar ratio) in acetonitrile, yielded orange and dark-red precipitates of $[Cu(4\text{-ampc})_2]BPh_4$ (20) [64] (Scheme 27) and $[Cu(dpa\text{-}qa)_2]BPh_4$ (21) [60] (Scheme 27), respectively. Single crystals of 20 and 21, were grown by slow diffusion of Et_2O into a concentrated acetonitrile solution of the complex.



L^{51} [60] 20 21

Scheme 27.

Since no d-d transitions are expected for a d^{10} complex, the UV-Vis bands are assigned to MLCT or ligand-centered π→π* transitions [60]. The absorption spectrum of 21, in $CHCl_3$ reveals a band with a true maximum at 503 nm. This observation is in ag5reement with the higher conjugation in the coordinated dpa-qa [60]. Complex 20 shows a quasireversible $Cu^{II/I}$ couple in cyclic voltametery with an $E_{1/2}$ of 0.47 V *vs* SCE [60].

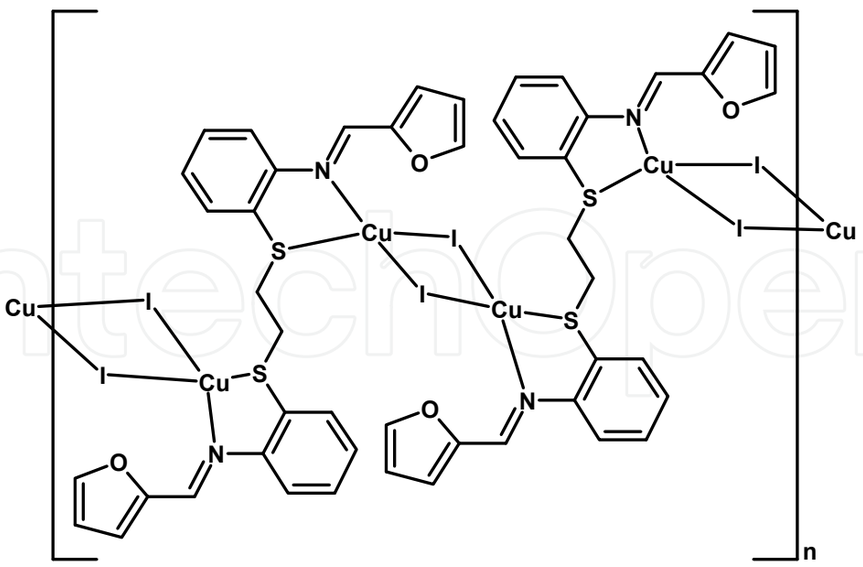
4.3 Copper(I) complexes with symmetric tetradentate Schiff base ligands

Flexible N/S or NN donor ligands have received much attention due to their use in constructing coordination frameworks by self-assembly, and also in investigating the mechanism of supramolecular interactions [81-86]. With flexible ligand, the competition between bridging and chelating coordination modes is an important factor in producing mono, di, and polynuclear metal complexes [81-86].

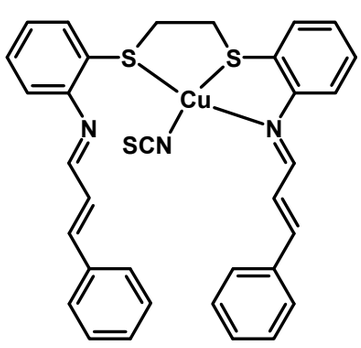
4.3.1 $(NS)_2$ Schiff bases with a flexible spacer

In recent years, Morshedi *et al*. have systematically studied on copper(I) complexes with flexible N/S donor Schiff base ligands [35,36,66]. The tetradentate $(NS)_2$ Schiff bases L^{31} and L^{32} were prepared as reported elsewhere [35,36,66]. The reaction of $(thio)_2$dapte (L^{32}) in the presences of CuI (1:1 molar ratio) in acetonitrile, yielded dark-red precipitates of new one-dimensional copper(I) coordination polymer $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(thio)_2dapte)]_n$ (22) (Scheme 28). Single crystals of 22 were grown by slow evaporation of solvent at room temperature for several days [36]. The solubility of 22 in common organic solvents is very low. Complex 22 crystallizes with the asymmetric unit formed by one copper(I) and one iodine ion located in general positions, and one centrosymmetric organic ligand $(thio)_2$dapte placed in the inversion center (1/2, 1, 1/2). In this complex, the flexible Schiff base ligand $(thio)_2$dapte acts as a bis-chelating ligand through its two iminic nitrogens and two sulfur atoms of ethanedithiolate group, creating the $[Cu_2(\mu\text{-}(thio)_2dapte)]$ dinuclear fragment. Such dinuclear entities are linked to each other by the two iodine anions acting as a doubly μ_2-bridging ligand $[(\mu\text{-}I)_2]$ and forming one-dimensional copper(I) coordination polymer with the general formula $[Cu_2(\mu\text{-}I)_2(\mu\text{-}(thio)_2dapte)]_n$ (22). In this complex, copper(I) ion has a distorted tetrahedral coordination geometry formed by one nitrogen and one sulfur atom from the Schiff base ligand and two iodine substituents, with significantly different bond distances [Cu1-N1 2.073(4), Cu1-S1 2.342(2), Cu1-I1 2.6008(7) and Cu1-$I1^b$ 2.6575(7) Å]. The highly distorted tetrahedral geometry around the copper(I) ion is also due to the small bite angle of the $(thio)_2$dapte bis-chelating ligand. The Cu1···$Cu1^b$ distance of copper atoms connected through the bridging iodine ligands (2.6745(11) Å) is shorter than the corresponding distance of copper atoms connected through the bis-chelating ligand (Cu1···$Cu1^a$ 6.942(1) Å).

By using the bis-chelating Schiff base ligand ca_2dapte [35,66] and at the similar condition to 22, the reaction of ca_2dapte (L^{31}) in the presences of CuSCN (1:1 molar ratio) in acetonitrile under N_2 yielded orange-red precipitates of mononuclear copper(I) complex [Cu(ca_2dapte)(NCS)] (23) (Scheme 29). Single crystals of 23, were grown by slow diffusion of Et_2O vapor into a concentrated solution of complex in acetonitrile at room temperature [66]. In the ^{1}H-NMR spectra of 23, the iminic protons corresponding to the coordinated and non coordinated imine groups appear at 8.95 and 8.97 ppm, respectively (free ligand has 8.14 ppm).



Scheme 28.

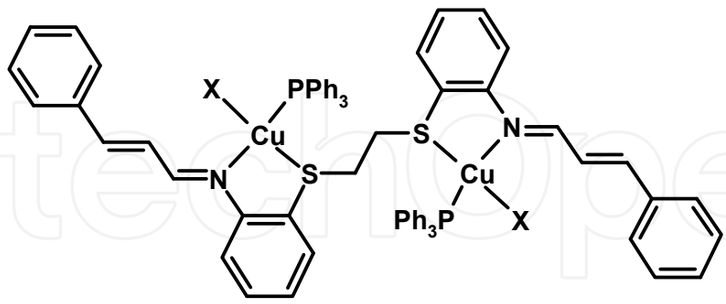


Scheme 29.

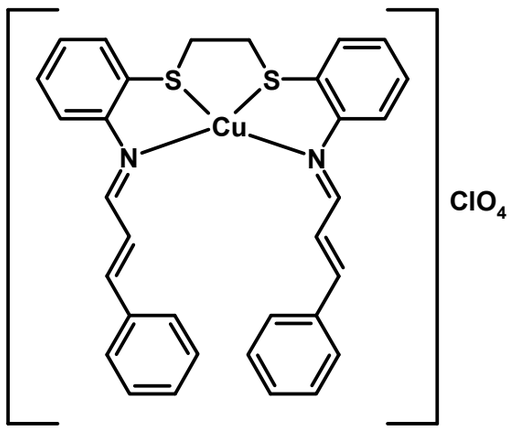
The asymmetric unit of complex 23 contains one copper atom, one NCS^- ligand and a ca_2dapte Schiff base ligand. In this complex, the NCS^- pseudohalide anion acts as a terminal ligand through its nitrogen atom, and ca_2dapte acts as a tridentate ligand coordinated through one N-imino, and two sulfur atoms. The second imino arm is directed away of the copper(I) center. Copper(I) ion has a distorted tetrahedral coordination geometry formed by one nitrogen and two sulfur atom from the Schiff base ligand and one nitrogen from thiocyanate, with significantly different bond distances [Cu-N1 2.064(2), Cu-S1 2.2886(8), Cu-S2 2.3824(7) and Cu-N3 1.903(2) Å] [66]. The high distortion of the coordination tetrahedron is essentially due to the steric requirements of the ca_2dapte bis-chelating ligand leading to strong deviation of the bond angles around the copper(I) ion from ideal tetrahedric values [N-Cu-S, N-Cu-N and S-Cu-S bond angles are in the range 86.2-130.0°] [66].

In the mononuclear copper(I) complex [Cu(ca_2dapte)(NCS)] (23), the N_2S_2 Schiff base ligand ca_2dapte, acts as a tridentate ligand surrounding the copper(I) ion [66]. In [Cu_2(ca_2dapte)(PPh_3)$_2X_2$] (X = I (24) and Br (25)) complexes [35], ca_2dapte acts as two

independent bidentate ligands connected by a flexible bridge (Scheme 30), and in $[Cu(ca_2dapte)]ClO_4$ (26) the ligand is tetradentate surrounding the copper(I) ion [35] (Scheme 30).



X = I (24) X = Br (25)



26

Scheme 30.

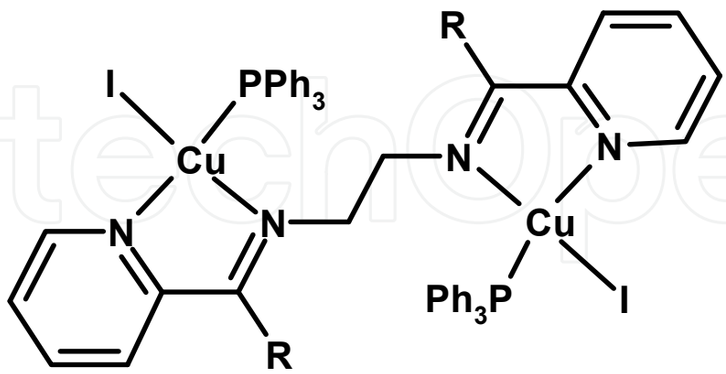
Dinuclear complexes 24 and 25 were prepared by a similar procedure [35]. To a solution of PPh_3 in acetonitrile was added a solution of CuX (X = I (24) and Br (25)) in acetonitrile and the mixture was stirred at room temperature for about 10 min to give a clear solution. Then, the ligand ca_2dapte was added and a clear orange-red solution was obtained. Single crystals of 24 and 25, were grown by slow diffusion of Et_2O vapor into a concentrated solution of complex [35]. These complexes are centrosymmetric dimers with pairs of $Cu(PPh_3)X$ units bridged by ca_2dapte. The solid-state structure of complexes 24 and 25 reveals copper(I) ion coordinated to one N atoms and one sulfur atom of one Schiff base ligand, one P from PPh_3 and one halide group. The central Cu(I)/Cu(Br) ion has a common irregular pseudo-tetrahedral geometry arising from the low intraligand N-Cu-S chelate angles 80.72(8)° in 24 and 80.54(19)° in 25. The P-Cu-X angle is 126.17(3) and 121.41(7)° in 24 and 10, respectively, being larger than the tetrahedral values. In the ^{1}H-NMR spectra of 23 and 24, the iminic protons corresponding to the coordinated imine groups appear as a doublet at 8.41 and 8.33 ppm, respectively (free ligand has 8.14 ppm).

To a solution of $[Cu(CH_3CN)]ClO_4$ in acetonitrile was added, with continuous stirring, a solution of ca_2dapte (L^{31}) in the minimum amount of chloroform at room temperature and

then stirred for 10 min to give a clear dark-red solution. Single crystals of 26, were grown by slow diffusion of Et_2O vapor into a concentrated solution of the complex [35]. There are four similar but independent complex units in the asymmetric unit of 26. In the absence of other coordinating ligands the ca_2dapte acts as a tetradentate ligand. However, [Cu(ca_2dapte)NCS] complex is formed in the presence of NCS [66] causing that the ca_2dapte acts as a tridentate ligand leaving a free site for the NCS to coordinate.
The solid-state structure of complex 26 reveals copper(I) ion coordinated to two N atoms and two sulfur atoms of one Schiff base ligand. The central Cu(I) ion has the common irregular pseudo-tetrahedral geometry arising from the low intraligand N-Cu-S chelate angles 86.55(12) and 86.93(11)° and S-Cu-S chelate angle 93.11(5)°. In the ^{1}H-NMR spectrum of 26, the iminic protons corresponding to the coordinated imine groups appear as a doublet at 8.23 ppm (free ligand has 8.14 ppm).

4.3.2 $(NN')_2$ Schiff bases with a flexible spacer

In this type of complexes, N-donor ligands are mainly focused on Schiff bases containing pyridine group (see L^{35} and L^{36}).
Dinuclear copper(I) complexes were obtained when the ligands with the –C=N- group in *ortho*-position of pyridine ring were used in the synthesis. The reaction of P_2en (L^{35}) [30,38] or $(Mepk)_2$en (L^{36}) [39,69] in the presences of CuI and PPh_3 (1:2:2 molar ratio) in acetonitrile, yielded dark-red or orange precipitates of dinuclear copper(I) complexes [Cu_2I_2(μ-P_2en)(PPh_3)$_2$] (27) or [Cu_2I_2(μ-$(Mepk)_2$en)(PPh_3)$_2$]·$2CH_3CN$ (28). Single crystals of 27 and 28, were grown by slow evaporation of solvent at room temperature for several days [38, 69]. These complexes are centrosymmetric dimers with pairs of Cu(PPh_3)I units bridged by P_2en [38] and $(Mepk)_2$en [69]. The solid-state structure of complexes 27 and 28 reveals copper(I) ion coordinated to two N atoms of one Schiff base ligand, one P from PPh_3 and one iodine group (Scheme 31). The central Cu(I) ion has the common irregular pseudo-tetrahedral coordination geometry arising from the low intraligand N-Cu-N chelate angles 79.40(15)° in 27 and 78.86(10)° in 28. The P-Cu-I angle is 123.11(4) and 119.05(3)° in 27 and 28, respectively, being larger than the ideal tetrahedral values.

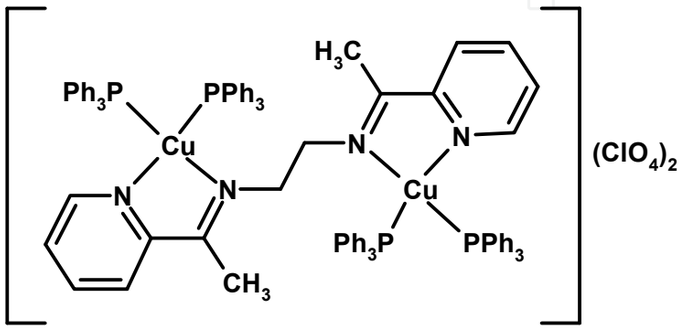


R = H (27) R = CH_3 (28)

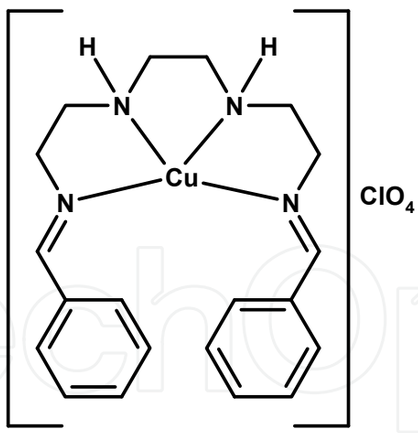
Scheme 31.

The reaction of $(Mepk)_2$en (L^{36}) in the presence of [Cu(CH_3CN)$_4$]ClO_4 and PPh_3 (1:2:4 molar ratio) in acetonitrile yielded yellow precipitates of dinuclear copper(I) complexes [Cu_2(μ-$(Mepk)_2$en)(PPh_3)$_4$]$(ClO_4)_2$·$2CHCl_3$ (29) [39]. Single crystals of 29, were grown by slow

diffusion of Et_2O into the concentrated solution at 273 K for several days [39]. These complexes are centrosymmetric dimers with pairs of $Cu(PPh_3)_2$ units bridged $(Mepk)_2en$. The solid-state structure of complex 29 reveals copper(I) ion coordinated to two N atoms of one Schiff base ligand and two P from two PPh_3 (Scheme 32). The central Cu(I) ion has the common irregular pseudo-tetrahedral geometry arising from the low intraligands N-Cu-N chelate angles 79.4(2)° and the P-Cu-P angle is 118.24(7)°. The N-Cu-P bond angles range from 111 to 120°, i.e. slightly more than in a regular tetrahedron (109.5°). The P-Cu-P angle has opened up due to the steric effect from the bulky PPh_3 ligands. The Cu···Cu' separation distance 7.06(1) Å in 29 is longer than that observed in 27 (6.2577(6) Å) which is also caused by steric effect of PPh_3 ligand and also ClO_4 anions.



Scheme 32.



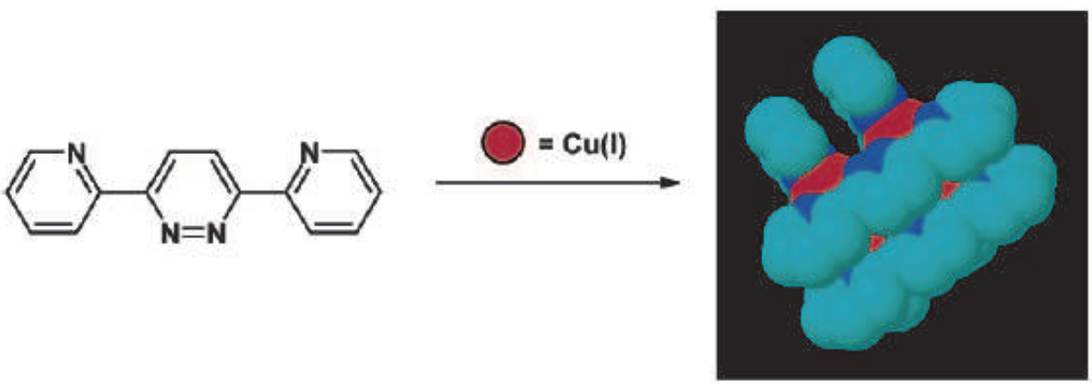
Scheme 33.

The ligand L^{38} is a 2:1 condensate of benzaldehyde and triethylenetetramine (trien). The reaction of ba_2trien in the presences of $[Cu(CH_3CN)_4]ClO_4$ (1:1 molar ratio) in degassed methanol under N_2 atmosphere yielded reddish yellow precipitates of mononuclear copper(I) complexe $[Cu(ba_2trien)]ClO_4$ (30) [37] (Scheme 33). Single crystals of 30, were grown by slow evaporation of dichloromethane-hexane mixture. The N_4 coordination sphere of the copper(I) ion is significantly distorted from tetrahedral due to the steric constraints of the ligand with the $Cu\text{-}N_{imino}$ bond lengths shorter than the $Cu\text{-}N_{amino}$ ones.

The cation has a crystallographic C_2 axis. This complex displays a quasireversible $Cu^{II/I}$ couple with a half-wave potential of 0.12 V *vs*. SCE [37].
Though 30 does not show any emission in methanol at room temperature, at 77 K in methanol glass it displays two very distinct emission bands at 470 and 495 nm together with a faint one at 545 nm. It should be noted that in the rigid matrix at 77 K, methanol coordination to the copper(II) center in the excited state is not operative.

4.4 Copper(I) grid complexes

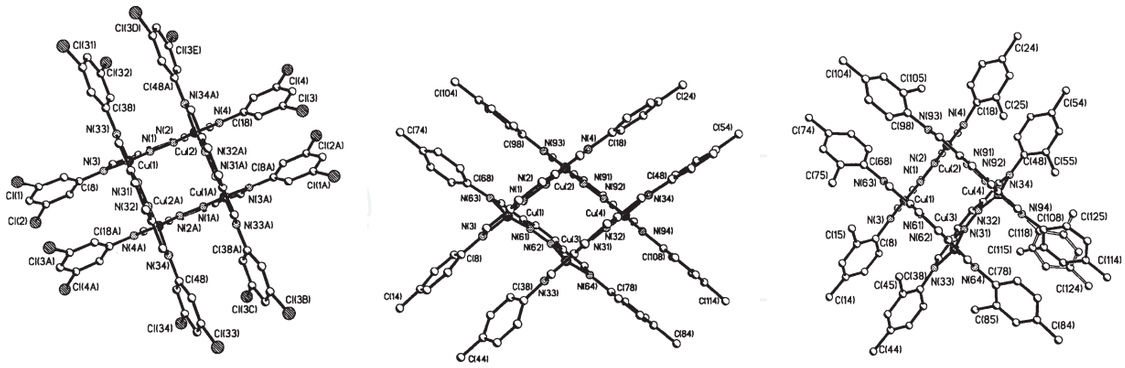
In recent years, grid complexes have been targeted by many researchers as a template to arrange two bidentate ligand binding pockets orthogonal to each other. Brooker *et al*. systematically studied on grid complexes of first transition metal ions that exhibit interesting structural, electrochemical and magnetic properties [31,32, 87-90]. The flat bis-bidentate ligand dppn [3,6-bis(2-pyridiyl)pyridazine] has been used for preparation of copper(I) gridlike complexes in 1992 (Scheme 34) [91]. In recent years, the incorporation of such grid-forming bis-bidentate Schiff base ligands into dppn has been explored (Scheme 13). They have been prepared from the reaction of 3,6-diformylpyridazine and substituted amino-benzenes. It was suggested that these ligands are preorganised to form a tetranuclear [2 × 2] grid complexes with a tetrahedrally coordinated metal ion such as copper(I) and silver(I) [32].



Scheme 34.

For preparation of grid copper(I) complexes, the bis-bidentate Schiff base ligands (Scheme 25) were suspended in pure dry acetone and degassed with nitrogen for 15 min. An equimolar amount of tetrakis(acetonitrile)copper(I) hexaflurophosphate was added and the reaction mixture refluxed under nitrogen for 2h. The diffusion of Et_2O vapour into an acetone solution yielded single crystals of gridelike copper(I) complexes $[Cu_4(L^{45})_4](PF_6)_4$ (31) and $[Cu_4(L^{41})_4](PF_6)_4$ (32) (Fig. 5), while the layering of an acetone solution of the complex on benzene gave single crystals of $[Cu_4(L^{42})_4](PF_6)_4$ (33) (Fig. 5) [32].
While the tetranuclear cations $[Cu_4(L^{45})_4](PF_6)_4$ and $[Cu_4(L^{41})_4](PF_6)_4$ has no crystallographic imposed symmetry, the cation $[Cu_4(L^{45})_4](PF_6)_4$ contains a two-fold rotation axis relating two halves of the grid from the two ligand strands and two copper(I) ions (Fig. 42). In all of the [2 × 2] copper(I) grid complexes, the coordination geometry of the copper(I) centers is a

considerably flattened tetrahedron, formed by four nitrogens from the two Schiff base ligands, with significantly different Cu-N bond distances.



31 32 33

Fig. 5. An ORTEP views of 31-33, showing the atomic numbering scheme. H atoms are omitted for clarity.

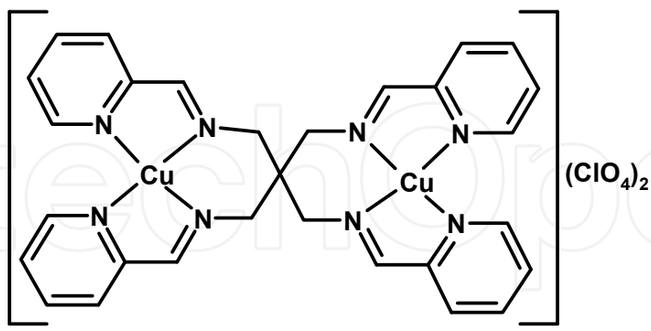
These complexes show multiple reversible redox couples. As anticipated, the $E_{1/2}$ values are observed to vary depending on the electron donating/withdrawing nature of the substituents. Complex 31, with chloro withdrawing sustituents, exhibits a total of four reversible one-electron reduction processes. It is likely that each of these processes involves reduction of one ligand strand which can also be taken as a supporting evidence for the existence of the tetranuclear grid structure. For the two complexes 32 and 33 all of the processes are shifted anodically, and hence the initial portion of the reversible couple is swamped by a strong stripping peak, preventing this fourth process from being resolved [32].

4.5 Double-stranded dinuclear copper(I) helicate complexes

Helicity continues to receive considerable attention as it allows for better understanding of the self-assembly processes involved in supramolecular chemistry [92]. Until now, many examples of both single and double-stranded architectures have now been reported [92]. Studies on inorganic helical complexes containing transition metal ions have attracted much attention recently [27-29,40,67-72]. In these supramolecular self-assembleies, the formation of the helicates can be described as the result of reading molecular information stored in the ligands by metal ions following the coordination algorithm such as tetrahedral. It seems that the self-assembly process of supramolecular helicates is not only controlled by the coordination geometry of metal ions and flexibility of the spacer groups in the ligand, but also influenced by the linkage mode of the spacer group [27-29,40,67-72].

Recently Pal *et al*. have reported a double-stranded, dinuclear, homotopic and neutral copper(I) helicate $[Cu_2(p_2en)_2](ClO_4)_2$ (34) with L^4 [30] (Scheme 35). Copper(I) complex 34 has been obtained by reaction of $p_2$en with $[Cu(CH_3CN)_4]ClO_4$ in equimolar proportion in anhydrous methanol under N_2 atmosphere. This complex is quite stable in solid state as well as in methanol or dichloromethane solution towards aerial oxidation. It is found to be a double-stranded helicate. The N4 coordination sphere around each copper center is distorted tetrahedral, with angles in the range 80.2 – 81.3° (chelate angles) and 116.2 – 136.6° (interligand ones). The Cu-N bond distances are in the range 2.007 – 2.110 Å. For each

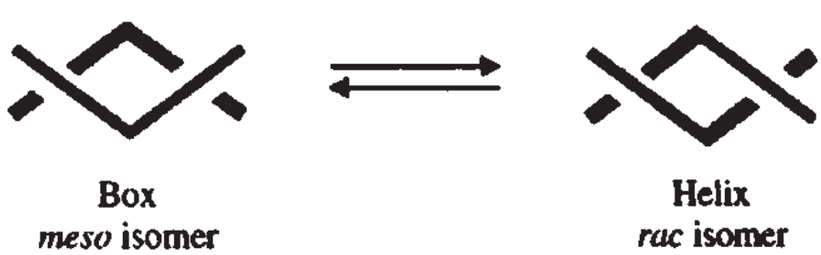
copper, one Cu-N bond is significantly longer than others. The longer bonds are formed by one of the two terminal pyridyl N's.



Scheme 35.

Complex 34 does not exhibit any emission in methanol and dichloromethane at ambient temperature, because coordination of the anion ClO_4 to the copper(II) center generated in the photoexcited state brings about a special type of quenching [30], while copper(I) complex $[Cu_2(p_2en)_2](PF_6)_2$ (35) is as stable as 34 towards aerial oxidation. Upon excitation at 360 or 470 nm, 35 display a single broad emission band with the maxima at 540 nm in methanol at room temperature [30].

In recent years, Hannon *et al*. have systematically studied on helical metallo-supramolecular arrays with multidentate Schiff bas ligands L^{47}–L^{50} [27,28,40,71,72]. For this kind of compounds, the ligand must offer sufficient flexibility for multiple strands to wrap around two or more metal centers, and it should also be sufficiently rigid to impose the same stereochemistry as both metals [27,28]. Non-helical isomers arise when the ligand is too flexible to impose the same stereochemistry at both metal centers [27,28]. For example, while the Schiff base ligand L^{47} is optimal for octahedral metal triple-helix formation [27,28], with tetrahedral metal ions a mixture of double-stranded helices (*rac* isomers) and boxes (*meso* isomers) are formed [27,28] (Scheme 36). These two isomers are in equilibrium in solution and the box is favored enthalpically, while the helix is favored by entropy. Thus at low temperature the box conformation dominates but as the temperature is raised the proportion of helix conformation grows.



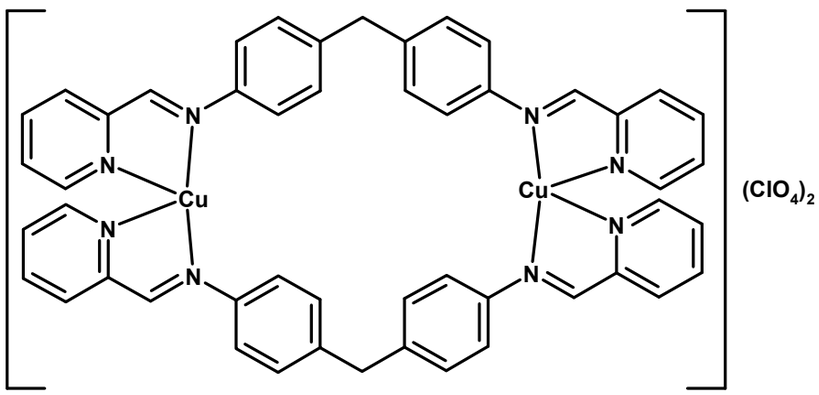
Scheme 36.

Reaction of L^{47} with monocations, such as copper(I), leads to dinuclear double-stranded complexes with 2:2 stoichiometry $[Cu_2L^{47}_2]^{2+}$ (36). In the ^{1}H-NMR spectrum of 36, the central

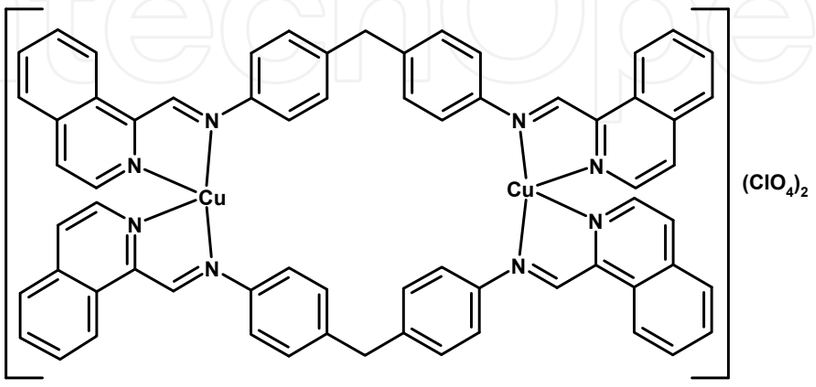
CH_2 protons in the helix can be used to identify the two isomers. The CH_2 protons in the helix are equivalent and thus appear as a singlet resonance, while in the box they are non-equivalent and thus appear as two doublets [28].

Addition of ethyl groups to the central spacer destabilizes the cyclophane configuration so that only $[Cu_2L^{49}{}_2]^{2+}$ (36) helicate isomer is present in solution [70]. This is evident from the ^{1}H-NMR spectrum that reveals single specie at room temperature and low temperature, and the central CH_2 resonance as a single confirming the helical conformation [70]. The double-helicate structure of complex 36 has been further confirmed by crystallography. The double helicate $[Cu_2L^{49}{}_2]^{2+}$ cation represents a dicationic cylinder (Scheme 38) where each copper(I) center bound to two pyridylimine units, one from each ligand. Each ligand bridges two copper(I) centers giving rise to the dinuclear-stranded helicate architecture. In $[Cu_2L^{50}{}_2](BF_4)_2$ (37) each ligand bridges two copper(I) centers giving rise to the dinuclear-stranded helicate architecture (Scheme 37) [70].

^{1}H-NMR spectra of copper(I) complex 37 have been recorded in CD_3NO_2 and CD_3CN solution. In CD_3NO_2 solution at room temperature, two sets of resonance signals are observed consistent with the prersence of two solution species, the *meso*- and *rac*-isomers, and while in CD_3CN solution at room temperature, a singlet set of resonance signals is observed because the ligands exchange is more rapid in this solvent [40].



Scheme 37.



Scheme 38.

5. References

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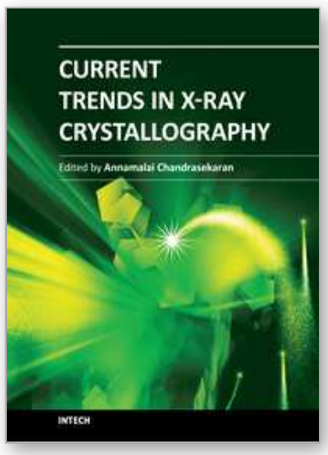
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