The synthesis and characterization of a series of bis-bidentate Schiff base ligands and their coordination complexes with silver(I), copper(I) and zinc(II) d^{10} metal ions†

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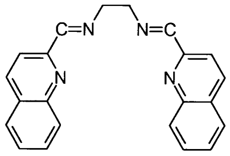
Three bis-bidentate Schiff base ligands **1**, **2** and **3** have been prepared and thoroughly characterized, and their complexation behavior with d^{10} silver, copper and zinc ions was studied. The coordination assembly of Cu(I) and Ag(I) with ligands **1** and **2**, afforded di-nuclear dimeric complexes $[Ag_2(\mathbf{1})_2](ClO_4)_2$ (**1a**), $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1b**), $[Ag_2(\mathbf{2})_2](ClO_4)_2$ (**2a**) and $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2b**), in which the metal ion auxiliaries adopted a pseudo-tetrahedral coordination environment. In these compounds the two ligands wrap around the metal ions in a twisted manner, forming box-like structures. Within these complexes each metal ion binds to two nitrogen sites of one ligand and two N-sites of the other ligand. The metal assisted self-assembly process is complemented by supportive π–π overlap interactions between the aromatic fragments of the assembly. In **1a** and **2a** the two silver ions lie close to one another at 3.1 Å. On the other hand, zinc(II) yields a monomeric crystalline complex with **2**, $[Zn(\mathbf{2})(H_2O)(CH_3CN)](ClO_4)_2$ (**2c**), interacting with four N-donors of the same ligand and complementing its octahedral coordination sphere with molecules of water and acetonitrile. The materials were characterized by UV-VIS, IR, MS, NMR, and X-ray diffraction analysis. Electrochemical behavior of the copper(I) compounds was also examined.

The chemistry of spontaneously self-assembled architectures based on coordination compounds is one of the main aspects of current research in the search after new potentially useful organic–inorganic hybrid materials.[1–4] The methodologies whereby transition metal ions are used as bridging templates to hold together organic ligands in pre-defined patterns within self-assembled oligomeric or polymeric aggregates have been explored by several groups.[5–8] Within this context, it has been shown that the self assembly of oligopyridyl strands with Cu(I) and Ag(I) ions give well organized molecular architectures such as inorganic grids,[9] as well as double-[10–12] and triple-stranded[13–15] metal helicates. Such complexes are of interest for their special functional properties like luminescence,[14a,16] redox activity,[17] molecular switching properties[18] and also potential applications in solar energy conversion schemes.[19] Coordination chemistry of copper(I) complexes with polydentate ligands is particularly relevant to the search for model compounds that can mimic or even ideally duplicate some of the important physical and chemical properties of Cu(I) containing proteins.[20] Self-assembled polymeric Ag(I) complexes are attracting attention because they are readily available, and due to the high diversity in the coordination geometries exhibited by silver(I). It has been shown that Ag(I) can adopt coordination numbers between two and six, and reveal coordination geometries from linear through trigonal to tetrahedral, square planar, trigonal pyramidal and octahedral.[21,22] Furthermore, Ag(I) coordination compounds have been used as drugs and diagnostic agents, which exhibit anti-microbial and anti-cancer activity.[23] Macrocyclic silver(I) complexes are useful also for ^{111}Ag-based radio-immunotherapy.[24] Zinc-containing compounds are useful model compounds for biochemical research, as zinc(II) plays an important role in several zinc-containing metal enzymes such as zinc-peptidases,[25] human carbonic anhydrase[26] and alkalinephosphatase.[27]

Herein we describe the preparations of several bis-bidentate Schiff base ligands with two N,N chelating moieties linked through a spacer. The latter can be either a flexible ethylene fragment as in **1**, a somewhat more spatially constrained –N=C(Ph)–C(Ph)=N– fragment as in **2**, or a rigid 1,4-phenylene unit as in **3**. Ligands **1**–**3** are characterized by a C_2 symmetry. They were designed to contain multiple imino donor nitrogen sites arranged in a converging (towards the center of the molecule) manner, thus promoting the formation of discrete metal–ligand complexes rather than polymeric arrangements. We further report on the coordination behavior of **1** and **2** with Ag(I), Cu(I) and Zn(II) metal ions and a thorough structural characterization of the complexes which form.



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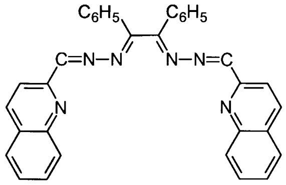

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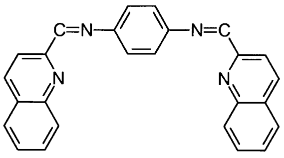

3

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† Electronic supplementary information (ESI) available: Views of the crystal structures of ligands of **1**, **2** and **3**. See http://www.rsc.org/suppdata/nj/b3/b301632c/

Not surprisingly, the most rigid ligand **3** did not form stable complexes with these metal ions, as without conformational flexibility the access to the N-sites in it is somewhat hindered.

Results and discussion

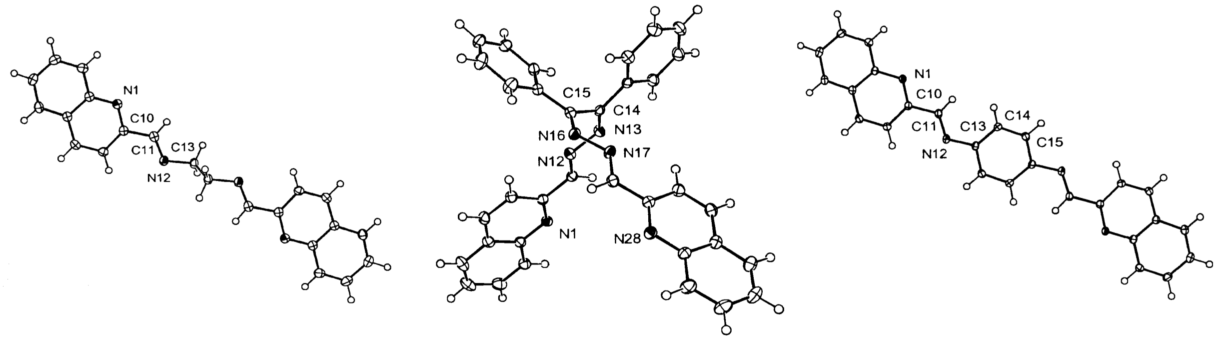
The syntheses of **1**–**3** and of their complexes with metal ions proceeded in high yields and the products were characterized by X-ray crystallography, EI-MS, IR, UV-VIS and NMR spectroscopy as well as by elemental analysis (see Experimental for detailed procedures).

The bis(dipyridyl-diimine) ligand **1**[28] was synthesized by condensing ethylene diamine and 2-quinolinecarboxaldehyde in 1:2 molar ratio in anhydrous methanol. It contains four N-sites suitable to coordinate metal ions, and is conformationally flexible about the central saturated C–C bond. In crystals of the free compound it adopts a fully extended conformation (Fig. 1a), the torsion angle about the N–CH_2–CH_2–N bond being 180.0° (all molecules are located on crystallographic inversion). In the presence of suitable metal ions, **1** can adopt readily a different conformation about this bond (see below) in order to arrange the nitrogen binding sites in a convergent manner and optimize the metal–ligand coordination. Ligand **2** was synthesized by refluxing benzildihydrazone and 2-quinolinecarboxaldehyde in 1:2 molar ratio in anhydrous methanol. It represents a more spatially hindered molecule (Fig. 1b). Due to the steric crowding between the two phenyl groups substituted on the central C14–C15 bond in **2**, the N=C–C=N and C(Ph)–C–C–C(Ph) torsion angles about this bond are 89.45(3) and 83.92°, respectively. Thus the resulting structure consists of two nearly perpendicular, planar and delocalized fragments. The conformational degrees of freedom upon the complex formation with this ligand include a limited flexibility about the central bond and some rotational freedom of the terminal quinoline rings about the C–C bonds, which connect them to the central part of the molecules. The configuration about the C=N bonds in **1** and **2** (as well as in all their complexes) is *trans*, preserving the two sides of the molecule in an extended form. Ligand **3**[29] was prepared by reacting *p*-phenylenediamine with 2-quinolinecarboxaldehyde. It has a rigid planar conformation (Fig. 1c), which allows a limited access to the inner nitrogen sites. Moreover, this conformation prevents formation of chelates upon complexation with metal ions. The size and aromatic nature of the quinoline fragment reveals a high propensity for strong dispersive attractions between the flat molecular surfaces of these rings in the condensed solid phase. This spatial as well as enthalpic element is well expressed in the crystal packing arrangements of the free ligands **1**–**3**, as well as in the crystal structures of the various complexes (see below). For example, π–π stacking interactions between the aromatic 2-quinoline rings (or even larger delocalized fragments) of neighboring molecules has been observed in the crystals of the free ligands (Figs. 1s, 2s, 3s in the supplementary material†). In **2**, face-to-face overlap between the phenyl substituent of one species and the quinoline substituent of another species provides additional stabilizing contribution. Similar interactions are also apparent in the molecular and crystal structures of the metal complexes with **1** and **2** (see below).

Reaction of **1** with $AgClO_4$ in methanol at room temperature in equimolar proportion yields the yellow dinuclear complex $[Ag_2(\mathbf{1})_2](ClO_4)_2$ (**1a**). The bright yellow solvated Ag(I) complex of **2**, $[Ag_2(\mathbf{2})_2](ClO_4)_2{\cdot}CH_2Cl_2$ ($\mathbf{2a}{\cdot}CH_2Cl_2$) was synthesized by refluxing the dichloromethane solution of **2** with $AgClO_4$ in 1:1 molar ratio. The Cu(I) complex of **1** was prepared by reacting **1** with $[Cu(CH_3CN)_4](ClO_4)$ in anhydrous methanol under argon atmosphere in 1:1 ligand-to-metal ratio, to yield $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1b**). The second Cu(I) complex $[Cu_2(\mathbf{2})_2](ClO_4)_2{\cdot}\frac{1}{2}CH_2Cl_2$ ($\mathbf{2b}{\cdot}\frac{1}{2}CH_2Cl_2$) was prepared by the reaction of **2** with $[Cu(CH_3CN)_4](ClO_4)$ in degassed dichloromethane. The red Cu(I) complexes (**1b**) and (**2b**) are stable in air both in the solid state and in solution. The yellow complexes of Ag(I), **1a** and **2a**, are stable in air in the solid state only for about 2–4 weeks; on prolonged exposure to air they turn black. The orange yellow $[Zn(\mathbf{2})(H_2O)(CH_3CN)](ClO_4)_2$ complex **2c** was synthesized by refluxing an equimolar mixture of **2** and hydrated $Zn(ClO_4)_2$ in an ethanol-water (5:1 v/v) mixture and subsequently re-crystallized from acetonitrile-diethyl ether.

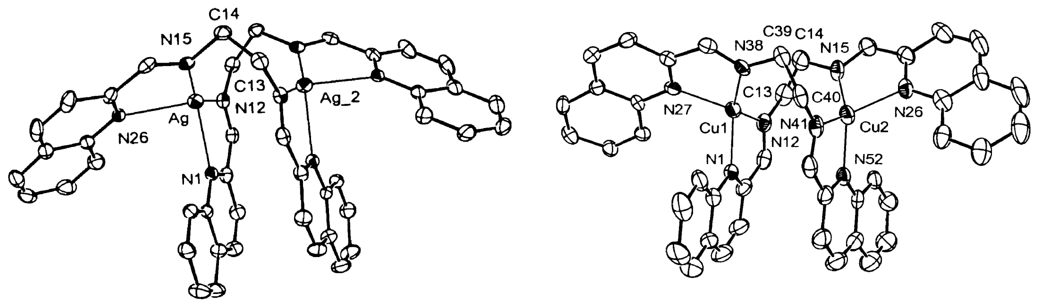
The structure of complex **1a** is shown in Fig. 2a. It consists of a di-nuclear dimer, in which each of the silver ions coordinates to two ligands in a distorted tetrahedral manner. The binding capacity is enhanced by the chelate effect, as all nitrogen sites of the two ligands converge on the silver ions and form four chelating 5-membered rings. The quinoline rings turn with their nitrogen sites inward, and the conformation about the central CH_2–CH_2 bond is changed from 180° in the free ligand to 54.32 and 59.15(8)° in the **1a** complex. The coordination distances are Ag–N1 2.372(2) Å, Ag–N12 2.259(2) Å, Ag–N15 2.221(2) Å and Ag–N26 2.457(2) Å, and the N–Ag–N angles vary from 71.97(8) to 134.90(8)° (the lower limit refers to spatially constrained angles which involve two nitrogens of the same ligand). The two silver ions also interact with one another at 3.3119(4) Å. Noticed is the parallel alignment at close proximity of the two "inner" quinoline groups within **1a**, the distance between their mean planes being 3.33(1) Å. The di-nuclear complex **1a** is characterized by, and is located on, crystallographic twofold symmetry.

In close resemblance, Cu(I) forms a similarly structured dimeric molecular box **1b**, which is sustained by the copper



(a) (b) (c)

Fig. 1 Molecular structures in crystals of the free ligands (a) **1** (located on crystallographic inversion), (b) **2** (the dichloromethane solvent is omitted), and (c) **3** (located on crystallographic inversion; the chloroform solvent is omitted). The thermal displacement parameters are shown by 50% probability ellipsoids.



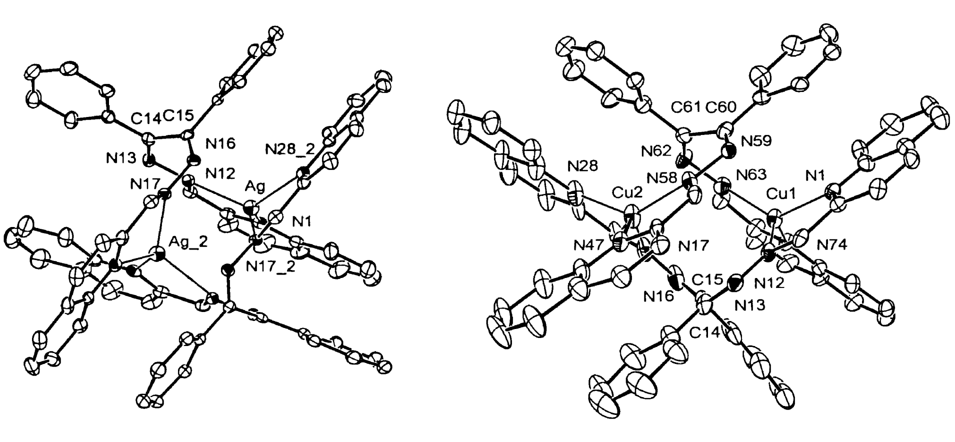
(a) (b)

Fig. 2 Molecular structures of the cationic di-nuclear dimeric complexes of (a) **1a**, and (b) **1b** (only one of the two crystallographically independent units is shown). In (a) the left and right sides of the structure are inter-related by a vertical symmetry axis of twofold rotation (*e.g.*, Ag_2 is related to Ag by the symmetry operation $-x,y,-z-\frac{1}{2}$).

ions (Fig. 2b). It is characterized also by an approximate twofold rotational symmetry (there are two crystallographically independent dimers in the asymmetric unit of **1b**). The respective coordination parameter ranges are Cu–N bonds 1.992–2.081(8) Å and N–Cu–N angles 80.9–133.1(3)°. The shorter metal-to-N distances pool the two smaller ions outward towards the surrounding ligands, which results in larger metal–metal distances within the dimers than in the previous example [$\text{Cu}\cdots\text{Cu}$ = 3.662 and 3.675(4) Å]. In the resulting structure of **1b**, which optimizes the various interactions, the average inter-planar distances between the inner quinoline rings are 3.3 (the dihedral angle between the two planes being 3.7°) and 3.5 Å (dihedral angle between the planes being 11.4°. The N=C–C=N torsion angles about the central bond in the ligands are N=C13–C14=N of 72.1 and 74.2(10)° and N=C39–C40=N of 69.3(7) and 71.1(10)°. The wider torsions in **1b** than in **1a** are associated also with slightly different orientations of the outer quinoline rings with respect to the core of the dimeric entity in the two structures.

Ligand **2** also forms di-nuclear dimeric complexes of C_2 symmetry (crystallographic in **2a** and approximate in **2b**) with the monovalent silver and copper ions. The latter adopt a pseudo-tetrahedral coordination environment tessellating two ligands together in the form of a square supramolecular box (Fig. 3). The geometry of this interlocked entity is affected mostly by the "scissors" shape of the ligand species, which in turn is dictated by the framework torsion about the central carbon–carbon bond. The corresponding N=CH–CH=N angles are 93.21(2)° in **2a** and 99.79(4) and 104.66(4)° in **2b**. In both structures, the metal ions are connected to two of the imino nitrogens of one ligand and two N-sites of another ligand within the dimeric entity. The corresponding coordination parameters in **2a** are within Ag–N = 2.275–2.484(2) Å and N–Ag–N = 70.8–141.3(1)°, the lower angles involving two nitrogens of the same ligand (in the quinoline and the nearby C=N imino fragment). The respective values in **2b** are within Cu–N = 2.015–2.096(6) Å and N–Cu–N 81.4–132.6(3)°. The dimeric aggregates are further stabilized by four pairs of overlapping aryl groups (Fig. 3). The average distances between these two nearly parallel quinoline and phenyl aromatic fragments are 3.45 Å in **2a** and within 3.3–3.5 Å in **2b**. The relatively short metal–metal distance between the silver ions of 3.3145(5) Å in **2a** is indicative of intermetalic interaction, as observed earlier in **1a**. The smaller copper(I) ions in **2b** form shorter coordinative bonds (than the silver ions) to the N-sites of the surrounding ligands, and they do not interact with one another as the observed intramolecular $\text{Cu}\cdots\text{Cu}$ distance in **2b** is only 4.423(2) Å.

The zinc(II) auxiliary was anticipated to exhibit a different coordination behavior than silver(I) and copper(I). First, it was introduced into the reaction with **2** in the form of an octahedral complex $[\text{Zn}(\text{H}_2\text{O})_6]$, a structural property which was carried on into the product. Then, formation of a di-nuclear complex with bivalent cations would be associated with unfavorable electrostatic repulsion. Correspondingly, complex **2c** was found to be a monomeric mono-nuclear, rather than di-nuclear, entity (Fig. 4). To allow a simultaneous coordination of the two inner and the two outer N-sites of the ligand to a single metal ion, the N=C–C=N torsion about the central C14–C15 bond is decreased from nearly 90° (in **2**, **2a** and **2b**) to only 66.18(2)° in the present case. The multi-dentate ligand replaces four of the water molecules in the octahedral coordination sphere of the zinc ion in the starting reagent. Another water is replaced by acetonitrile from the crystallization



(a) (b)

Fig. 3 Molecular structures of the cationic di-nuclear dimeric complexes of (a) **2a**, and (b) **2b**. In (a) the molecule exhibits a crystallographic C_2 symmetry (*e.g.*, Ag_2 is related to Ag by symmetry operation $-x,y,\frac{1}{2}-z$). Note the apparent π–π overlap interaction between the quinoline and phenyl aromatic fragments of these two structures.

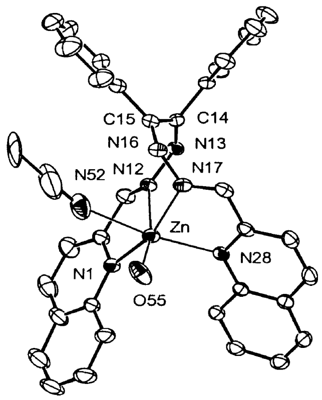


Fig. 4 Molecular structure of the mono-nuclear complex cation of **2c**, with H_2O and CH_3CN co-ligands, showing an approximate octahedral coordination around the metal ion.

solvent, to formulate the $[Zn(\mathbf{2})(H_2O)(CH_3CN)]^{2+}$ entity. The coordination distances in this species are Zn–N(ligand) = 2.105–2.181(3) Å, Zn–(OH_2) = 2.051(3) Å and Zn–N(acetonitrile) = 2.378 (5) Å. The corresponding bond angles between the *cis*-related ligands are within 77.8–114.4(1)°, and those between the *trans*-related moieties are within 157.8–164.0(1)°.

As commonly observed in crystal structures of organic compounds containing aromatic fragments, optimization of π–π stacking interactions is an important factor in determining the intermolecular organization. This should be expected also in the present study, due to the presence of the sizeable quinoline moieties in all compounds. We have shown above already that such interactions affect in many cases the intra-molecular structure of the discrete complexes. Fig. 5 demonstrates that they are also well expressed in the intermolecular organization in these materials, by illustrating three representative crystal structures of complexes **1a**, **2a** and **2c**.

The structural characterizations of the new materials reported in this study are complemented by spectroscopic and electrochemical data:

FT IR spectroscopy

The FT IR spectrum of the ligands **1**, **2** and **3** show characteristic bands at 1557 and 1642 cm^{-1} (for **1**); 1562 and 1614 cm^{-1} (for **2**) and 1559 and 1627 cm^{-1} (for **3**), which we assign to the pyridine ring and imine C=N stretching frequencies respectively. The C=N stretching frequency of the ligand **2** appears at lower energy because it has an extensive conjugative system. In the IR spectrum of (**1a**), (**1b**), (**2a**), (**2b**) and (**2c**) these bands are shifted to higher energies, which agrees with coordination of the metal to the nitrogen donor atoms. The typical strong bands due to the stretching vibrations of the non-coordinated ClO_4^- ions[30] in (**1a**), (**1b**), (**2a**), (**2b**) and (**2c**) appear at the expected regions; 1098 and 621 cm^{-1} (for **1a**), 1098 and 629 cm^{-1} (for **1b**), 1090 and 624 cm^{-1} (for **2a**), 1088 and 630 cm^{-1} (for **2b**) and 1098 and 625 cm^{-1} (for **2c**).

UV-VIS spectroscopy

The absorption spectra of **1** (in methanol); **2** (in dichloromethane) and **3** (in dichlorometane) show intra-ligand charge transfer bands at 290 (ε, 10 260 $M^{-1}cm^{-1}$), 242 nm (ε, 42 710 $M^{-1}cm^{-1}$); 320 (ε, 34 660 $M^{-1}cm^{-1}$), 274 nm (ε,

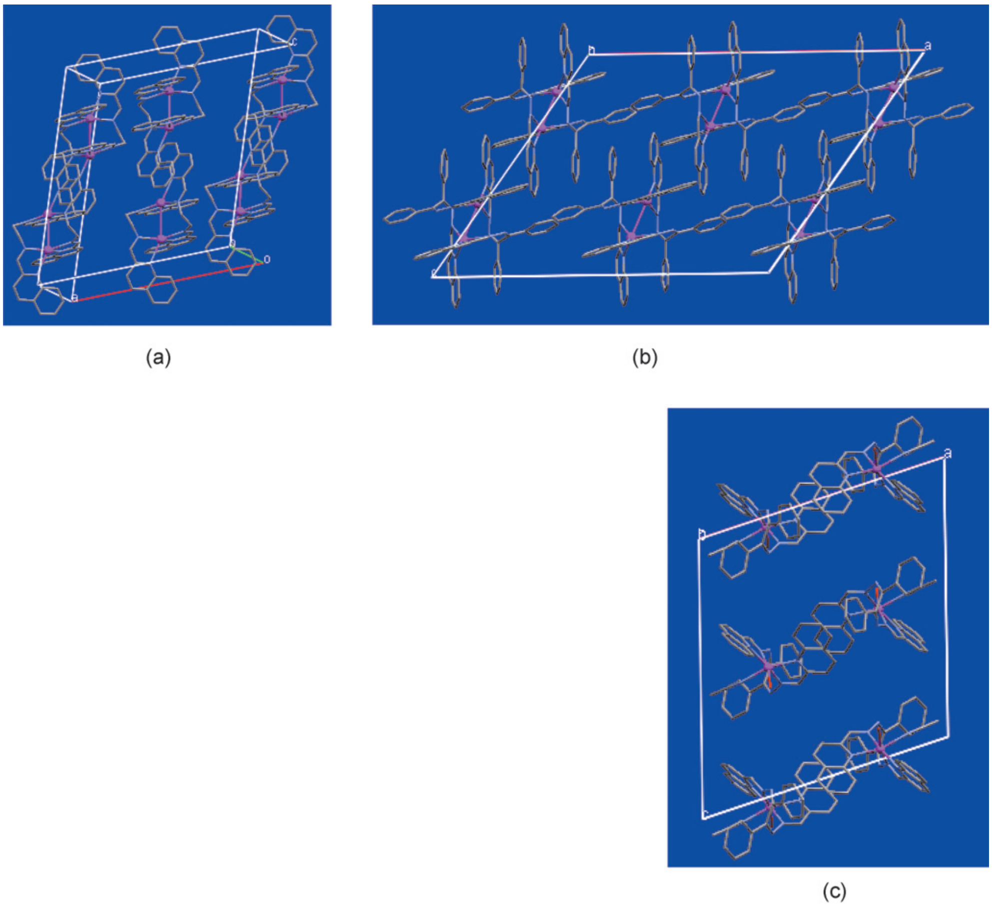


Fig. 5 Crystal structures of (a) **1a**, (b) **2a**, and (c) **2c**, showing the inter-molecular π–π stacking interactions between the quinoline rings of adjacent species. The mean interplanar distances between the overlapping rings are in the range of 3.3–3.5 Å. The counter ions and solvent species are omitted for clarity. The metal ions are denoted by spheres in pink color.

28 100 $M^{-1}cm^{-1}$); 374 (ε, 33 214 $M^{-1}cm^{-1}$) and 294 (ε, 22 660 $M^{-1}cm^{-1}$), respectively. These charge transfer bands appear at 320, 252 nm (for **1a**); 316, 250 nm (for **1b**); 356, 276 nm (for **2a**); 350, 290 nm (for **2b**) and 322, 256 nm (for **2c**). The Cu(I) complexes (**1b**) and (**2b**) display additional broad unstructured band at 532 and 530 nm respectively, which is supposed to be MLCT in origin, and these bands are responsible for the red color of the complexes. All data also demonstrate the coordination of the metal ions to the ligands.

FAB mass spectroscopy

The solution behavior of the coordination complexes is analyzed by fast atom bombardment mass spectrometry (FAB-MS). The FAB-MS spectra of the complexes **1a**, **1b**, **2a** and **2b** in 3-nitrobenzyl as a matrix and dimethylformamide as solvent indicate the di-nuclear species with the highest masses being assigned to $[M_{2:2} - ClO_4]^+$. For the complex **2c** the highest mass observed at $m/z = 740.2$ is assigned to $[M_{1:1} - ClO_4]^+$ (see Experimental section).

NMR spectroscopy

The ^1H and ^{13}C NMR spectra of **1**, **2** and **3** in $CDCl_3$ consist of sharp and well-resolved signals for each of the organic grouping present. The ^1H NMR of **1a** and **1b** are also made up of sharp signals indicative of the single species and the symmetrical nature of the molecule in the solution. In ^{13}C NMR, the C=N carbon atom of **1**, **2** and **3** appear at 163.91, 160.56 and 160.61 ppm respectively.

Cyclic voltammetry

Preliminary data on the electrochemical properties of the di-nuclear copper(I) complexes $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1b**) and $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2b**) were obtained by cyclic voltammetry in dichloromethane at glassy carbon electrode under dry nitrogen atmosphere. Both of the complexes show more or less similar type of quasi-reversible voltammograms with single Cu^{I}–Cu^{II} couple, occurring at $E_{\frac{1}{2}} = 1.28$ and 1.35 V (*vs* Ag/AgCl in 1 M KCl, scan rate 50 mV s^{-1}) for $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1b**) and $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2b**), respectively (Fig. 6). The ΔE_p values of $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1b**) and $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2b**) are 235 and 220 mV, respectively. At higher scan rates the voltammograms become irreversible. The electrode processes can be described by the eqn. (1).

$$[Cu^{II}{}_2L_2]^{4+} + 2e \rightleftharpoons [Cu^{I}{}_2L_2]^{2+} \qquad (1)$$

The high potential of the Cu^{I}–Cu^{II} couple in $[Cu_2(\mathbf{1})_2]ClO_4$ (**1b**) and $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2b**) indicates that **1** and **2** are capable of stabilizing Cu(I) much more than Cu(II). A more thorough investigation of these features, their dependence on the experimental conditions, and nature of the generated products, is however still required. Incidentally, it has not been possible so far to isolate any Cu(II) complexes of **1** and **2**. In this context it should be mentioned that the highest $Cu^{II/I}$ potential hitherto known for any copper complex is 1.55 V *vs* SCE.[31]

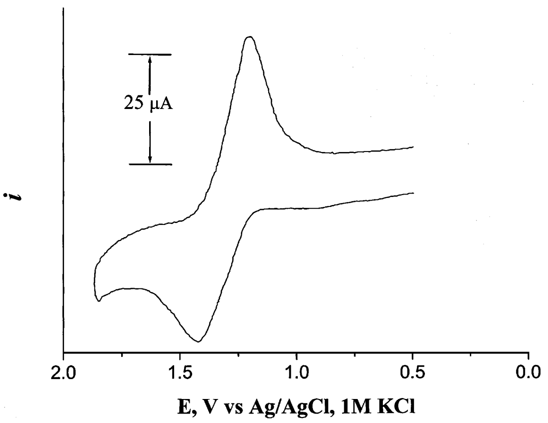


Fig. 6 Cyclic voltammogram of $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2b**) (approximately 10^{-3} M in dichloromethane, 0.2 M Bu_4NClO_4) at a glassy carbon electrode. Scan rate $v = 50$ mV s^{-1}.

Conclusion

Coordination motifs in a series of hybrid organic–inorganic complexes of the Ag(I), Cu(I) and Zn(II) d^{10} ions have been presented employing the inexpensive, easy to prepare bis-bidentate flexible Schiff base ligand **1** and the somewhat more rigid ligand **2**. X-ray single crystal diffraction studies revealed that the silver(I) and copper(I) complexes are di-nuclear, have C_2 symmetry, and adopt molecular box like structures. While the coordination bonds and chelating rings provide the major cohesive force, π–π stacking interactions play also an important role in the metal assisted self-assembling process of these complexes. The bivalent zinc ion afforded as expected a mono-nuclear complex. UV-VIS and FAB-MS data are consistent with the formulation of these species in the solution. The d^{10} metal-ion auxiliaries preserved in this study their commonly observed coordination geometries, *i.e.*, tetrahedral in the case of silver(I) and copper(I) and octahedral in the case of the zinc(II) ion.

The complexation reactions in this study were designed to yield *discrete* molecular hybrid organic–inorganic entities, being based on ligands (*e.g.*, **1** and **2**) with multiple binding sites that are arranged in a converging manner. A slight variation of the ligand design, by substituting the 2-quinolyl(N^1) peripheral group with the 2-quinolyl(N^4) function, places the quinolyl N-sites on the outer surface of the molecular framework (Fig. 7). We have shown that in such case, the divergent disposition of the N-donor sites would promote, with the aid of silver(I) ion auxiliaries, a facile construction of *polymeric* materials.[32]

Experimental

Caution! Perchlorate salts are potentially explosive and should only be handled in small quantities.

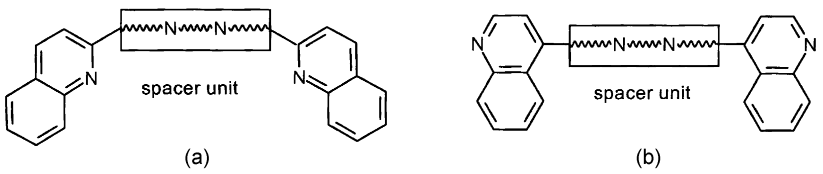


Fig. 7 Ligand design for promoting, in complexation reactions with metal ions, the construction of either discrete (as is this study) or polymeric (as described in ref. 32) hybrid materials, shown in (a) and (b), respectively.

General

The complex $[Cu(CH_3CN)_4]ClO_4$ was synthesized by a reported procedure.[33] All other reagents were procured commercially and used without further purification. Copper was estimated gravimetrically as CuSCN. Microanalyses were performed by Perkin-Elmer 2400II elemental analyzer and CE instruments. The melting points were determined by an electrothermal IA9000 series digital melting point apparatus and are uncorrected. IR spectra (KBr disc) were recorded on a Nicolet Magna-IR spectrophotometer (Series II), UV-VIS spectra on a Shimadzu UV-160A spectrophotometer, ^1H and ^{13}C NMR spectra by a Bruker DPX200 spectrometer and EI and FAB mass spectra on a VG Autospec M-250 instrument. Cyclic voltammetry was performed at room temperature at a planar glassy carbon milli electrode (polished with alumina before measurement) using m-Autolab II with GPES software, version 4.8.5 (EcoChemie, The Netherlands) in purified and anhydrous dichloromethane under dry nitrogen atmosphere in conventional three electrode configurations. Under the experimental conditions employed here, the ferrocene–ferrocenium couple appears at 0.42 V *vs.* Ag/AgCl in 1 M KCl with an ΔE_p of 110 mV at a scan rate of 50 mV s^{-1}.

Syntheses

Ligand **1**. 2.36 g (15 mmol) of 2-quinolinecarboxaldehyde was dissolved in 100 ml of anhydrous methanol. To this yellowish solution 0.5 ml (7.5 mmol) of freshly distilled ethylene diamine was added dropwise with stirring. Then, the reaction mixture was allowed to reflux for 6 h, maintaining dry conditions. The solvent was evaporated under reduced pressure to obtain a yellow semi-solid, which on re-crystallization from diethyl ether gave yellow solid suitable for X-ray analysis. Yield, 1.75 g (69%); mp 128–130 °C. Anal. found (calc. for $C_{22}H_{18}N_4$): C, 77.65 (78.07); H, 5.37 (5.36); N, 16.65 (16.56)%. EI-MS: 338.1 (M^+, 84%); 181.1 ($M^+ - C_{10}H_6NO$, 25%); 169.1 ($M^+/2$, 98%). FTIR/cm^{-1} (KBr): 492 m, 619 m, 748 vs, 840 vs, 868 s, 893 s, 941 m, 971 s, 1015 w, 1030 s, 1108 s, 1142 m, 1206 m, 1280 s, 1321 w, 1382 m, 1432 s, 1461 s, 1500 vs, 1557 s, 1592 vs, 1642 vs (C=N), 2890 m, 3050 m, 3451 vb. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 8.63 (s, 2 H), 8.17 (s, 4 H), 8.11 (d, $J = 4$ Hz, 2 H), 7.83–7.69 (m, 4 H), 7.57 (t, $J = 4$ Hz, 2 H), 4.18 (s, methylene, 4 H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 163.91, 154.52 (quaternary), 147.65 (quaternary), 136.50, 129.70, 129.50, 128.71 (quaternary), 127.63, 127.34, 118.40, 61.43. UV-VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_3OH): 290 (10 260), 242 (42 710)

Ligand **2**. 1.79 g (7.5 mmol) of benzil dihydrazone synthesized by a reported procedure,[34] was dissolved in 150 ml of anhydrous methanol. 2.36 g (15 mmol) of solid 2-quinolinecarboxaldehyde was dissolved with stirring in this colorless solution. The resulting reaction mixture was refluxed for 3 h in a dry atmosphere. After 1 h of reflux, yellow solid began to precipitate out. Then the reaction mixture was cooled to room temperature, kept in air overnight. The yellowish precipitated solid was filtered off, washed with few drops of methanol and dried in air. Yield, 2.40 g (62%); mp 158 °C. Anal. found (calc. for $C_{34}H_{24}N_6$): C, 79.10 (79.04); H, 4.62 (4.69); N, 16.36 (16.27)%. EI-MS: *m/z* 516.2 (M^+, 10%); 258.1 ($M^+/2$, 18%). FTIR/cm^{-1} (KBr): 475 m, 571 w, 590 w, 621 s, 648 m, 678 s, 755 vs, 771 vs, 824 vs, 888 s, split, 961 s, 1015 m, 1133 w, 1162 m, 1182 s, 1201 s, 1322 m, 1373 w, 1422 m, 1447 s, 1505 vs, 1541 s, 1562 s, 1589 s, 1614 vs (C=N), 3056 m, 3441 vb. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 8.70 (s, 2 H), 8.06 (s, 4 H), 8.03–7.97 (m, 6 H), 7.80–7.76 (m, 2 H), 7.57–7.42 (m, 10 H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 165.65 (quaternary), 160.56, 153.48 (quaternary), 147.83 (quaternary), 136.22, 133.70 (quaternary), 131.16, 129.59, 129.53, 128.78, 128.60, 127.90, 127.55, 127.45, 118.99. UV-VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_2Cl_2): 320 (34 660), 274 (28 100). Crystals suitable for X-ray diffraction were obtained by direct diffusion of *n*-hexane into the dichloromethane solution. It crystallizes with one molecule of dichloromethane solvent.

Ligand **3**. 0.81 g (7.5 mmol) of 1,4-phenylenediamine was dissolved in 75 ml anhydrous methanol. To this solution, 2.36 g (15 mmol) of solid 2-quinolinecarboxaldehyde was added and dissolved with stirring. The resulting reaction mixture was refluxed for 4 h maintaining dry conditions. Then, it was cooled to room temperature. Yellowish crystalline solid separated out. It was filtered out, washed with 5 ml of methanol and dried in air. Yield, 1.72 g (78%), mp 163–164 °C. Anal. found (calc. for $C_{26}H_{18}N_4$): C, 80.71 (80.80); H, 4.69 (4.70); N, 16.39 (14.50)%. EI-MS: 386.2 (M^+, 98%), 229.1 ($M^+ - C_{10}H_6NO$, 15%). FTIR/cm^{-1} (KBr): 545 m, 620 s, 673 m, 744 vs, 770 m, split, 821 m, 844 vs, 903 m, 956 m, 1108 s, 1202 vs, 1225 m, 1304 m, 1358 s, 1427 vs, 1455 m, 1500 vs, 1559 s, 1597 s, 1627 vs (C=N), 3460 wb. ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 8.87 (s, 2 H), 8.41–8.22 (m, 8 H), 7.91–7.65 (m, 4 H), 7.79 (d, $J = 4$ Hz, 4 H). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 160.61, 154.58 (quaternary), 147.69 (quaternary), 136.62, 129.71, 129.39, 128.74 (quaternary), 127.67, 127.39, 122.35, 121.19 (quaternary), 118.62. UV-VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_2Cl_2): 374 (33 214), 294 (22 660). Crystallization from direct diffusion of *n*-hexane into chloroform solution of **3** yielded single crystals of the chloroform solvate of **3**.

Complex $[Ag_2(\mathbf{1})_2](ClO_4)_2$ (**1a**). 0.338 g (1 mmol) of **1** was dissolved in 25 ml of methanol. To this solution 0.208 g (1 mmol) of solid $AgClO_4$ was added and dissolved with stirring. Continuous stirring at room temperature for about 3 h yielded a yellow solid. It was filtered off, washed with 5 ml of methanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.350 g (64%). Anal. found (calc. for $C_{22}H_{18}N_4{\cdot}AgClO_4$): C, 48.48 (48.40); H, 3.37 (3.32); N, 10.36 (10.27)%). FAB-MS: *m/z* 990.5 $[(M - ClO_4)^+$ 12.0%]; 890.02 $[(M - ClO_4 - HClO_4)^+$, 8.9%]. FTIR/cm^{-1} (KBr): 481 m, 531 w, 621 vs, 756 s, 775 m, 819 s, 1098 vs, split (ClO_4), 1294 m, 1330 s, 1373 m, 1426 s, 1470 m, 1500 s, 1564 s, 1592 m, 1650 vs (C=N), 2928 w, 3055 m, 3461 vb. ^1H NMR (200 MHz, $(CD_3)_2SO$, TMS): δ 9.02 (s, 2 H), 8.37 (d, $J = 4$ Hz, 2 H), 7.99 (d, $J = 4$ Hz, 2 H), 7.66–7.44 (m, 6 H), 7.37 (d, $J = 4$ Hz, 2 H), 4.44 (s, methylene, 4 H). VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_3OH): 320 (9 875), 252 (36 980). Single crystals suitable for X-ray analysis were grown as acetonitrile solvate by direct diffusion of diethyl ether into an acetonitrile solution of the complex.

Complex $[Cu_2(\mathbf{1})_2](ClO_4)_2$ (**1b**). Solid $[Cu(CH_3CN)_4]ClO_4$ (0.165 g, 0.5 mmol) was added to 30 ml anhydrous degassed methanol solution of 0.17 g (0.5 mmol) of **1** under argon atmosphere and stirred for 1 h maintaining dry conditions. A deep-red compound precipitated out. Then, the solvent was evaporated down to ~10 ml by purging argon to get more crop. It was filtered off, washed with few drops of methanol and dried *in vacuo* over fused $CaCl_2$. Yield, 0.175 g (70%). Anal. found (calc. for $C_{22}H_{18}N_4{\cdot}CuClO_4$): C, 52.59 (52.68); H, 3.68 (3.62); N, 11.19 (11.17); Cu, 12.75 (12.68%). FAB-MS: *m/z* 903.1 $[(M - ClO_4)^+$, 6.1 %]; 802.2 $[(M - ClO_4 - - HClO_4)^+$, 4.2%]. FTIR/cm^{-1} (KBr): 477 m, 589 m, 629 vs, 751 vs, 786 s, 825 vs, 868 vs, 927 s, 996 w, 1098 vs (ClO_4), split, 1225 s, 1260 m, 1295 s, 1323 vs, 1374 m, 1432 s, 1456 m, 1505 vs, 1588 vs, 1648 vs(C=N), 2914 w, 3428 vb. ^1H NMR (200 MHz, $(CD_3)_2SO$, TMS): δ 8.78 (s, 2 H), 8.62 (d, $J = 4$ Hz, 2 H), 8.08 (d, $J = 4$ Hz, 2 H), 7.68–7.47 (m, 6 H), 7.18 (d, $J = 4$ Hz, 2 H), 4.42 (s, methylene, 4 H). UV-VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_3OH): 532 (5 450, per copper), 316 (14 750), 250 (45 260). Single crystals were grown by direct diffusion of diethyl ether into a moderately concentrated methanol solution of the complex. They were found to contain molecules of the methanol and diethyl ether solvent.

Complex $[Ag_2(\mathbf{2})_2](ClO_4)_2$ (**2a**). 0.258 g (0.5 mmol) of **2** was dissolved in 25 ml of dichloromethane. To this yellow solution 0.105 g (0.5 mmol) of solid $AgClO_4$ was added, and the reaction mixture was refluxed for 2 h with stirring and then filtered out. The filtrate was taken in a stoppered tube and *n*-hexane was layered on it. Bright yellow crystals suitable for X-ray analysis deposited after two days. These were taken out by decantation of the remaining solvent and dried *in vacuo* under fused $CaCl_2$ .Yield, 0.275 g (72%). The complex crystallized with one mol of dichloromethane. Anal. found (calc. for $2C_{34}H_{24}N_6{\cdot}2AgClO_4{\cdot}CH_2Cl_2$): C, 54.32 (54.04); H, 3.68 (3.29); N, 11.99 (10.97%). FAB-MS: m/z 1347.6 $[(M_{2:2} - ClO_4)^+$, 2.3%]; 1248.2 $[(M_{2:2} - 2ClO_4)^+$, 6.7%]. FTIR/cm^{-1} (KBr): 478 m, 580 m, 624 vs, 692 s, 756 vs, split, 824 s, 932 m, 981 w, 1090 vs (ClO_4), 1142 s, 1181 m, 1230 w, 1256 m, 1358 s, 1460 s, 1505 vs, 1565 s, 1624 vs (C=N), 3061 m, 3456 vb. VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_2Cl_2): 356 (36 500), 276 (29 680).

Complex $[Cu_2(\mathbf{2})_2](ClO_4)_2$ (**2b**). 0.258 g (0.5 mmol) of **2** was dissolved in 30 ml of anhydrous degassed dichloromethane to which 0.165 g (0.5 mmol) of freshly prepared $[Cu(CH_3CN)_4]ClO_4$ was added under argon atmosphere, to yield a deep red solution. The reaction mixture was stirred for 2 h at room temperature, filtered, and then 15 ml of *n*-hexane was added dropwise to the filtrate. The resulting cloudy solution was kept in the refrigerator for 8 h, after which a red microcrystalline solid was isolated. The solution was filtered out and stored *in vacuo* over fused $CaCl_2$. Yield, 0.210 g (60%). Anal. found (calc. for $2C_{34}H_{24}N_6{\cdot}2CuClO_4{\cdot}\frac{1}{2}CH_2Cl_2$): C, 58.61 (58.67); H, 3.68 (3.53); N, 11.87 (11.99); Cu, 9.15 (9.07)%. FAB-MS: m/z 1259.0 $[(M_{2:2} - ClO_4)^+$, 2.8%]; 1159.8 $[(M_{2:2} - 2ClO_4)^+$, 4.5%]. FTIR/cm^{-1} (KBr): 482 m, 565 w, 590 m, 630 vs, 683 s, 756 vs, 824 s, 863 m, 933 m, 986 w, 1088 vs (ClO_4) 1142 s, 1177 m, 1225 m, 1305 s, 1358 m, 1383 m, 1465 w, 1500 vs, 1520 m, 1564 s, 1622 vs (C=N), 3055 m, 3432 wb. VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_2Cl_2): 530 (5155, per copper), 350 (31 150), 290 (25 380). Single crystals suitable for X-ray analysis were grown by direct diffusion of *n*-hexane into dichloromethane solution of the complex. The complex crystallized in a solvated form with one molecule of CH_2Cl_2 and one molecule of *n*-hexane.

Complex $[Zn(\mathbf{2})(H_2O)(CH_3CN)](ClO_4)_2$ (**2c**). To a 30 ml ethanol–water (5:1 v/v) mixture 0.130 g (0.25 mmol) of **2** and 0.095 g (0.25 mmol) of $Zn(ClO_4)_2{\cdot}6H_2O$ were added and dissolved with stirring. The yellowish reaction mixture was refluxed for 8 h, then cooled to room temperature, and the solvent was removed under reduced pressure to yield a pale yellow solid. It was washed with 5 ml of methanol and dried in air and re-crystallized from acetonitrile–diethyl ether. Yield, 0.110 g (52%). Anal. found [calc. for $C_{34}H_{24}N_6{\cdot}Zn(ClO_4)_2{\cdot}CH_3CN{\cdot}H_2O$]: C, 51.59 (51.45); H, 3.38 (3.48); N, 11.56 (11.67%). FAB-MS: m/z 740.2 $[(M_{1:1} - ClO_4)^+$, 2.1%]; 640.5 $[(M_{1:1} - 2ClO_4)^+$, 6.1%]. FTIR/cm^{-1} (KBr): 492 m, 516 w, 625 vs, 692 s, 771 vs, 834 s, 922 m, 1098 vs (ClO_4), 1216 m, 1290 s, 1333 s, 1373 s, 1436 s, split, 1510 vs, 1570 s, 1628 vs (C=N), 2221 vs, 3065 m, 3465 vb. VIS λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})(CH_3CN): 322 (15 870), 256 (12 190). Single crystals suitable for X-ray analysis were grown by direct diffusion of diethyl ether into an acetonitrile solution of the complex. The complex crystallized with additional 2 mols of acetonitrile and one mol of diethyl ether.

Crystallography

The diffraction measurements were carried out on a Nonius KappaCCD diffractometer, using graphite monochromated MoKα radiation ($\lambda = 0.7107$ Å). The crystalline samples of the analyzed compounds were covered with a thin layer of light oil and freeze-cooled to *ca.* 110 K in order to minimize solvent escape (when included in the crystal), structural disorder and thermal motion effects, and increase the precision of the results. The crystal structures were solved by direct (SHELXS-86, SIR-92)[35,36] and Patterson methods (DIRDIF-96),[37] and refined by full-matrix least-squares on F^2 (SHELXL-97).[38] Intensity data of the metal complexes were routinely corrected for absorption effects. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in idealized positions, and were refined using a riding model with fixed thermal parameters [$U_{ij} = 1.2\ U_{ij}$ (eq.) for the atom to which they are bonded]. The crystal and experimental data for all the compounds are:

1: $C_{22}H_{18}N_4$, $M_r = 338.40$, triclinic, space group $P\bar{1}$, $a = 6.7590(2)$, $b = 7.4030(2)$, $c = 17.3190(5)$ Å, $\alpha = 78{,}267(1)$, $\beta = 87.281(1)$, $\gamma = 85.421(2)°$, $V = 845.34(4)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.399$ g·cm^{-3}, $F(000) = 356$, μ(MoKα) $= 0.081$ mm^{-1}, $2\theta_{max} = 56.5°$, 3868 unique reflections, 235 refined parameters, final $R1 = 0.057$ for 2333 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.103$, $wR2 = 0.167$ and GoF = 1.039 for all 3868 data, $|\Delta\rho|_{max} = 0.34$ e.Å^{-3}. The molecules are located on centers of crystallographic inversion, and the asymmetric unit consists of two half-molecules.

2·CH_2Cl_2 : $C_{34}H_{24}N_6{\cdot}CH_2Cl_2$, $M_r = 601.52$, triclinic, space group $P\bar{1}$, $a = 9.7370(1)$, $b = 11.4350(2)$, $c = 14.9620(3)$ Å, $\alpha = 91.454(1)$, $\beta = 102.707(1)$, $\gamma = 112.455(1)°$, $V = 1490.79(4)$ Å^3, $Z = 2$, $\rho_{calcd.} = 1.340$ g·cm^{-3}, $F(000) = 624$, μ(MoKα) $= 0.254$ mm^{-1}, $2\theta_{max} = 56.5°$, 6977 unique reflections, 388 refined parameters, final $R1 = 0.050$ for 4463 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.099$, $wR2 = 0.143$ and GoF = 1.015 for all 6977 data, $|\Delta\rho|_{max} = 0.60$ e.Å^{-3}.

3·2$CHCl_3$: $C_{26}H_{18}N_4{\cdot}2CHCl_3$, $M_r = 625.18$, triclinic, space group $P\bar{1}$, $a = 6.2340(1)$, $b = 9.3440(2)$, $c = 12.6120(3)$ Å, $\alpha = 70.957(1)$, $\beta = 77.614(1)$, $\gamma = 84.160(2)°$, $V = 677.89(2)$ Å^3, $Z = 1$, $\rho_{calcd.} = 1.531$ g·cm^{-3}, $F(000) = 318$, μ(MoKα) $=$ 0.661 mm^{-1}, $2\theta_{max} = 56.3°$, 3162 unique reflections, 172 refined parameters, final $R1 = 0.031$ for 2712 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.040$, $wR2 = 0.078$ and GoF = 1.032 for all 3162 data, $|\Delta\rho|_{max} = 0.33$ e·Å^{-3}. The ligand molecules are located on centers of crystallographic inversion.

1a·2MeCN: $2(C_{22}H_{18}N_4{\cdot}AgClO_4){\cdot}2CH_3CN$, $M_r = 1173.56$, monoclinic, space group $C2/c$, $a = 18.1870(3)$, $b = 13.8900(2)$, $c = 20.1180(4)$ Å, $\beta = 107.450(1)°$, $V = 4848.3(1)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.608$ g·cm^{-3}, $F(000) = 2368$, μ(MoKα) $=$ 0.98 mm^{-1}, $2\theta_{max} = 55.8°$, 5748 unique reflections, 317 refined parameters, final $R1 = 0.036$ for 4409 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.057$, $wR2 = 0.093$ and GoF = 1.066 for all 5748 data, $|\Delta\rho|_{max} = 0.99$ e·Å^{-3}.

1b·MeOH·$\frac{1}{2}Et_2O$: $2[2(C_{22}H_{18}N_4{\cdot}CuClO_4)]{\cdot}2CH_3OH{\cdot}(C_2H_5)_2O$, $M_r = 2143.78$, monoclinic, space group $P2_1/c$, $a = 11.9300(2)$, $b = 36.5370(5)$, $c = 21.2510(4)$ Å, $\beta = 97.714(5)°$, $V = 9179.2(3)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.551$ g·cm^{-3}, $F(000) = 4408$, μ(MoKα) $= 1.11$ mm^{-1}, $2\theta_{max} = 51.4°$, 15 583 unique reflections, 1196 refined parameters, final $R1 = 0.088$ for 8876 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.157$, $wR2 = 0.269$ and GoF = 1.011 for all 15 583 data, $|\Delta\rho|_{max} = 1.76$ e·Å^{-3}. The asymmetric unit contains two independent species of the di-nuclear complex. The analyzed crystals were characterized by high mosaicity and were diffracting poorly. The diethyl ether and the perchlorate anions were found severely disordered in the crystal lattice even at 110 K, and their structural parameters could not be precisely determined.

2a·2CH_2Cl_2 : $2(C_{34}H_{24}N_6{\cdot}AgClO_4){\cdot}2CH_2Cl_2$, $M_r = 1617.68$, monoclinic, space group $C2/c$, $a = 27.9900(3)$, $b = 12.7400(2)$, $c = 22.6650(3)$ Å, $\beta = 125.802(1)°$, $V = 6557.0(1)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.639$ g·cm^{-3}, $F(000) = 3264$, μ(MoKα) $= 0.91$ mm^{-1}, $2\theta_{max} = 55.8°$, 7695 unique reflections, 442 refined parameters, final $R1 = 0.041$ for 5654 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.071$, $wR2 = 0.103$ and GoF = 1.020 for all 7695 data, $|\Delta\rho|_{max} = 0.72$ e·Å^{-3}.

2b·$CH_2Cl_2{\cdot}C_6H_{14}$: $2(C_{34}H_{24}N_6{\cdot}CuClO_4){\cdot}CH_2Cl_2{\cdot}C_6H_{14}$, $M_r = 1530.26$, monoclinic, space group $P2_1/c$, $a = 12.8350(2)$, $b = 41.4820(7)$, $c = 13.3050(3)$ Å, $\beta = 110.628(1)°$, $V = 6629.7(3)$

Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.533$ g·cm^{-3}, $F(000) = 3152$, $\mu(\text{MoK}\alpha) = 0.87$ mm^{-1}, $2\theta_{\text{max}} = 50.9°$, 11 469 unique reflections, 928 refined parameters, final $R1 = 0.078$ for 6679 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.147$, $wR2 = 0.215$ and GoF = 0.967 for all 11 469 data, $|\Delta\rho|_{\text{max}} = 0.79$ e·Å^{-3}. The analyzed crystals were characterized by high mosaicity and were diffracting poorly. The dichloromethane and the n-hexane solvent were found severely disordered in the crystal lattice even at 110 K, and could not be modeled precisely. One of the perchlorates is partly disordered as well.

2c·$1\frac{1}{2}$MeCN·Et$_2$O: $C_{34}H_{24}N_6 \cdot Zn(ClO_4)_2 \cdot 2\frac{1}{2}CH_3CN \cdot (C_2H_5)_2O \cdot H_2O$, $M_r = 975.63$, monoclinic, space group $P2_1/c$, $a = 18.8160(3)$, $b = 12.6210(2)$, $c = 20.3570(4)$ Å, $\beta = 107.689(1)°$, $V = 4605.8(1)$ Å^3, $Z = 4$, $\rho_{\text{calcd.}} = 1.407$ g·cm^{-3}, $F(000) = 2020$, $\mu(\text{MoK}\alpha) = 0.72$ mm^{-1}, $2\theta_{\text{max}} = 55.8°$, 10 472 unique reflections, 671 refined parameters, final $R1 = 0.068$ for 7343 reflections with $F_o > 4\sigma(F_o)$, $R1 = 0.102$, $wR2 = 0.202$ and GoF = 1.024 for all 10 472 data, $|\Delta\rho|_{\text{max}} = 1.02$ e·Å^{-3}. The acetonitrile and diethyl ether solvent species as well as the perchlorate anions were found partly disordered in the crystal lattice. One of the acetonitriles and the water molecule are coordinated to the zinc ion as well.

The apparent disorder of the solvent and the perchlorate anions in the above structures had only a limited effect on the structural determinations of the metal–ligand entities and their coordination motifs.

CCDC reference numbers 204782–204789. See http://www.rsc.org/suppdata/nj/b3/b301632c/ for crystallographic data in .cif or other electronic format.

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