



Grid-corner analogues: Synthesis, characterisation and spectroscopic properties of meridional complexes of tridentate NNO Schiff-base ligands

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ABSTRACT

Reactions of the tridentate Schiff-base ligands **HL**¹, **HL**² and **HL**³ formed from pyridine-2-aldehyde and 2-aminophenol plus two of its methoxycarbonyl derivatives, with AgNO₃, [Cu(CH₃CN)₄]PF₆, Cu(NO₃)₂, Co(NO₃)₂ and Zn(NO₃)₂ give complexes of the following types: [Ag(HL)₂]NO₃; (**1a**, **2a**, **3a**); [Cu^{II}(HL)L]PF₆ (**1b**, **2b**, **3b**); [Cu^{II}(HL)L]NO₃ (**1c**, **2c**, **3c**); and [M(HL)L]₂[M(NO₃)₄] where M=Co(II) (**1d**, **2d**, **3d**); or Zn(II) (**1e**, **2e**, **3e**), which in principle define the basic characteristics of the metal sites in certain metallogrids. The complexes have been characterized by spectroscopic techniques and elemental analysis. The solid state structures of complexes **2b** and **2e** have been established by X-ray crystallography.

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1. Introduction

Schiff-base (imine) ligands have been used in the construction of sophisticated metallosupramolecular compounds such as double and triple helicates, grids and coordination polymers, as well as in the preparation of innumerable simple mononuclear complexes [1–7]. Many complexes of Schiff-base ligands with metal ions have been investigated as models for active sites of enzymes [7,8], including DNA-cleavage systems [9,10], and as antibacterial [11–13] and anticancer [14] drugs. They also provide useful magnetic materials [5,15] and have a wide range of catalytic applications, such as in polymerization [8], olefin oxidation [9] and Suzuki-Miyaura coupling [10]. In particular, complexes of metal ions with tetrahedral (e.g. Ag(I)) or octahedral (e.g. Cu(II), Co(II), Fe(II) and Zn(II)) coordination preferences have been found to display important physicochemical properties [1,5,6,11] as well as biological activity [12–15].

Recent progress in supramolecular coordination chemistry allows access to a broad variety of rationally designed transition-metal complexes with interesting physicochemical properties making them attractive in the area of nanoscale materials [16,17]. Of the different structures that may be envisaged, entities with a two-dimensional grid-like structure of metal ions are of special interest since a flat and precise arrangement of an exact number of metal ions suggests an application in high density information storage

and processing technology [6,18]. In order fully understand the uniqueness of grid-type metalloarchitectures it is important to investigate physicochemical properties of mononuclear grid-corner analogues as well as their interactions in the solid state.

The versatility of Schiff-base ligands may be illustrated by the case of the tridentate species **HL**¹ (Fig. 1), which is known to form complexes with Fe(III), Co(III), Ni(II), Zn(II), Cd(II) and lanthanide(III) ions [19–26]. The complexes of Zn(II) and Cd(II) show intense luminescence at room temperature and thus have potential applications as photoactive materials [19] while the Fe(III) and Ni(II) complexes exhibit interesting magnetic properties including photo-induced spin transitions [20] and thermal spin-crossover [21,22]. A solvate of the neutral Ni(II) complex [Ni(**L**¹)₂] forms crystals in which the lattice involves a two-dimensional H-bonding network [23].

Facile variation of the properties of Schiff-base complexes is possible through both introduction of ligand substituents [27] and changes in coordinated co-anions [28,29]. Developing on our earlier work [26], two new additional tridentate Schiff-base ligands, **HL**² and **HL**³ (Fig. 1) containing N,N,O donor-atom sets and related to **HL**¹ were prepared in one-step, high-yielding reactions starting from commercially available 2-pyridinecarboxaldehyde and isomeric 2-aminophenol derivatives (Fig. 1).

These ligands have the same tridentate metal-ion-binding site but different substituent locations. In this paper we describe the synthesis and luminescence properties of the complexes of Zn(II), Co(II), Cu(I), Cu(II) and Ag(I) ions with all three ligands **HL**¹, **HL**² and **HL**³. In addition, we describe some novel aspects of the structural chemistry of the complexes. The principal objective of this work was to characterise the basic properties of constitutive units

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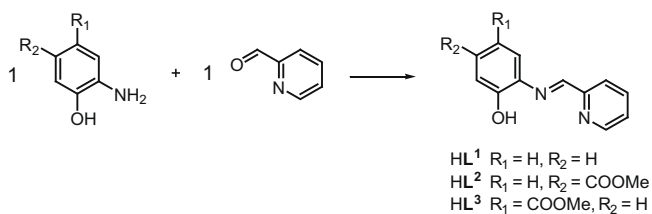


Fig. 1. Synthesis of tridentate Schiff-base ligands HL^{1-3} .

of some particular metallogrids, where the proximity of the metal centres may lead to interactions which significantly modify their properties [6].

2. Results and discussion

The ligands were readily prepared by Schiff-base condensation of equimolar amounts of 2-pyridinecarboxaldehyde and 2-amino-phenol or its 4- and 5-methoxycarbonyl derivatives in absolute ethanol on a multigram scale at room temperature. The combination of 1D and 2D NMR, IR, ESI-MS and elemental analysis techniques established the formation of the desired products. Signals characteristic for the imine proton found in the ^1H NMR spectra (around 8.9 ppm) as well as bands observed in the IR spectrum at 1606 cm^{-1} (HL^2) and 1621 cm^{-1} (HL^3) are consistent with the formation of the imine bond. Additionally, the molecular structure of the ligand HL^2 has been determined by single-crystal X-ray diffraction.

The conformation of the free ligands in solution was established spectroscopically by confirmed by 1D NMR and 2D COSY and NOESY measurements. The NOESY spectrum of ligand HL^2 (Fig. 2) showed the characteristic correlations between protons H_4 – H_2 expected for a *transoid* conformation around the C_{pyr} – C_{imine} single bond. This conformation may be favorable due to the intramolecular hydrogen bonding interaction between OH group from the phenol and N atom from the imine moiety which further stabilize this form of the ligand. The results obtained in solution were confirmed by an X-ray structure determination of the ligand HL^2 in the solid state (see below).

The complexes were all prepared by treating one equivalent of the appropriate metal salt with two equivalents of the Schiff-base ligand in MeCN. Although no additional base was added to the reaction mixtures, all the isolated *bis*(ligand) complexes of M(II) ions contained one ligand in its deprotonated (phenoxo) form. All

complexes were shown to be pure by elemental analysis and their identity verified by spectroscopic measurements. Our initial intention had been to prepare Cu(I) complexes and to see if the preference of this metal ion for coordination geometries other than octahedral and coordination numbers other than 6 might lead to novel stoichiometries and structures but the species isolated without resort to inert-atmosphere procedures all proved to be Cu(II) complexes.

The ESI-MS investigations of all complexes were performed on acetonitrile solutions at approximately 10^{-4} M . For example, the ESI mass spectrum of **3e** showed peaks corresponding to the multiply charged species: m/z (%) = 575 (100) $[\text{Zn}(\text{HL}^3)(\text{L}^3)]^+$, 319 (75) $[\text{Zn}(\text{L}^3)]^+$. These data confirm the presence of the complex **3e** in solution.

2.1. Crystal data for ligand HL^2 and complexes **2b** and **2e**

Single crystals of ligand HL^2 suitable for X-ray crystallography, were obtained by slow evaporation of a chloroform-ethanol solution. The molecular structure of ligand HL^2 is depicted in Fig. 3. The structure shows that the ligand adopts the expected *transoid* conformation around the C_{pyr} – C_{imine} single bond, in agreement with results obtained by NOESY experiments. The hydroxyl group acts as hydrogen bond donor to a N=C unit ($\text{N}\cdots\text{O}$ 2.641 Å and $\text{O}\cdots\text{N}$ 2.164 Å) which further stabilizes that arrangement of the ligand. The configuration about the C=N bond is also *transoid*.

Complexes **2b** and **2e** were originally selected for structural characterisation with the intent of establishing coordination modes for both M(I) and M(II) species in the belief that complex **2b** was a Cu(I) derivative. In fact, the structure determination clearly established **2b** to be a Cu(II) complex containing a cationic unit very similar to that found in the Zn(II) complex **2e**. In both complexes, this Schiff-base-containing unit consists of a centrosymmetric dimer of $[\text{M}(\text{HL}^2)(\text{L}^2)]$ entities connected by very strong and linear $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds between the O-protonated and deprotonated forms of the HL^2 molecule so that the dimer rather strongly resembles a grid with two diagonally opposite metal ions missing (Fig. 6). The distance between oxygen atoms within **2e** is slightly shorter (2.969 Å) than that observed in analogous grid complex (3.133 Å).[6] The greater strength of phenoxide-O as a donor compared to phenol-O is reflected in the bond lengths to Zn of 2.082 and 2.234 Å, respectively. A similar value for the bond length to a phenoxide donor has been found in an Fe(II) grid complex [6].

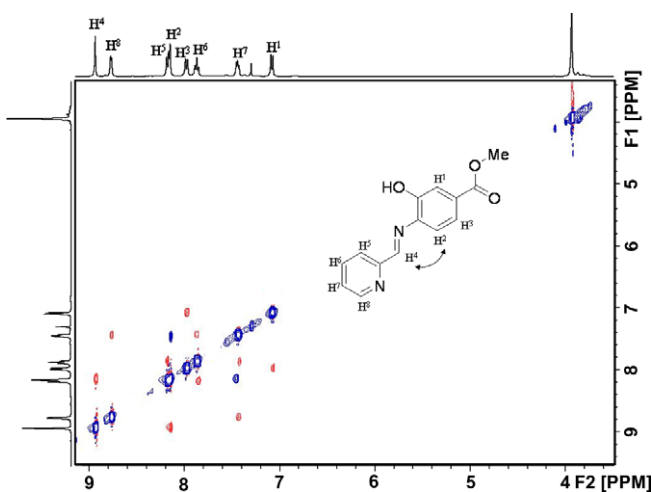


Fig. 2. The NOESY spectrum of ligand HL^2 measured in CDCl_3 .

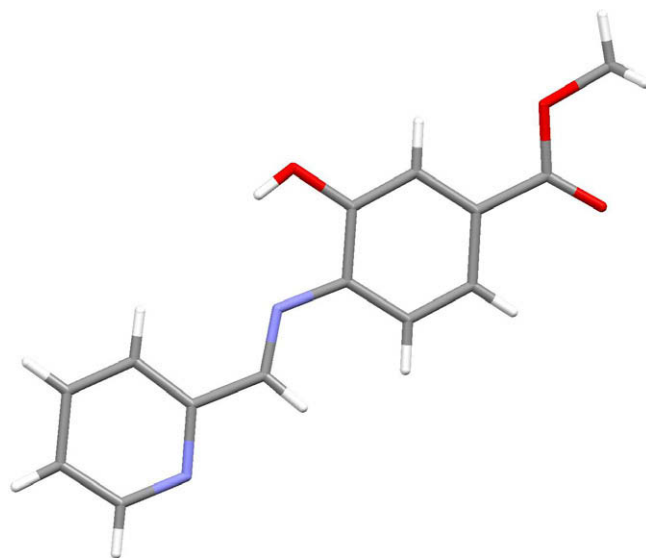


Fig. 3. X-ray crystal structure of ligand HL^2 .

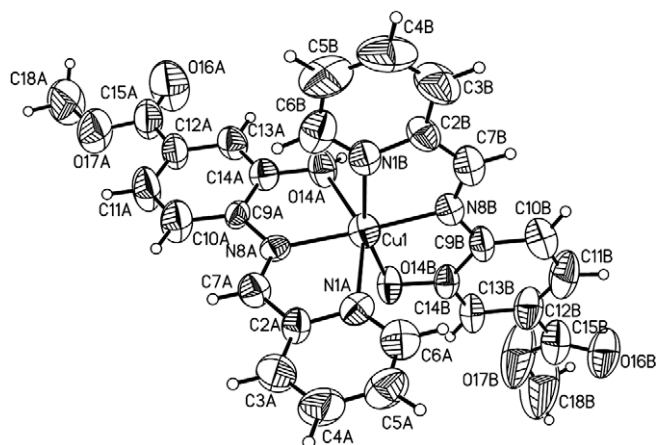


Fig. 4. Perspective view of the cation present in the lattice of complex **2b**; the ellipsoids are drawn at the 50% probability level.

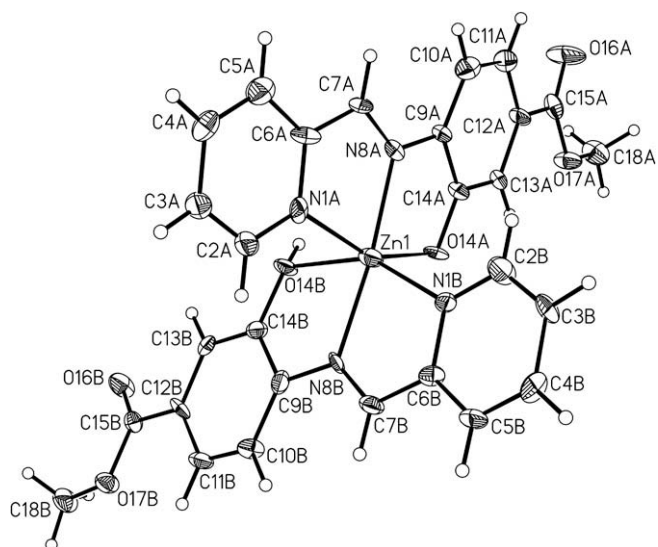


Fig. 5. Perspective view of the cation present in the lattice of complex **2e**; the ellipsoids are drawn at the 50% probability level.

The distances between the oxygen atoms involved in hydrogen bonding interactions are as short as 2.479(6) Å (**2b**) and 2.481(5) Å (**2e**). In the latter case the presence of the hydrogen atom was confirmed by its location in the difference Fourier map and successful refinement; the data for **2b** were of inferior quality and the position of the hydrogen atom involved in the hydrogen bond was calculated. As is often the case for such strong hydrogen bonds, the O–H covalent bond is significantly lengthened, to 1.10(7) Å in **2e**, while the formal H···O contact is very short (1.40(7) Å). The methoxycarbonylphenyl substituents are brought into closely parallel arrays in the dimer, indicating that π -stacking may assist dimer formation, though the ring atom separations (~ 3.6 Å) are quite long. The dimers are centrosymmetric and lie on the twofold axes along [0 0 1] and [0 1 0] directions in **2b** and **2e**, respectively. Figs. 4 and 5 show the “monomers” $[M(\text{HL}^2)(\text{L}^2)]$, and Figs. 6 and 7a and b the hydrogen-bonded dimers.

Both the Schiff-base ligands in both complexes are bound in a tridentate NNO mode, with the phenoxide and phenol donor atoms being distinguished by bond length differences of ~ 0.3 Å for Cu(II) and ~ 0.15 Å for Zn(II), the metal–O(phenoxide) bond being the

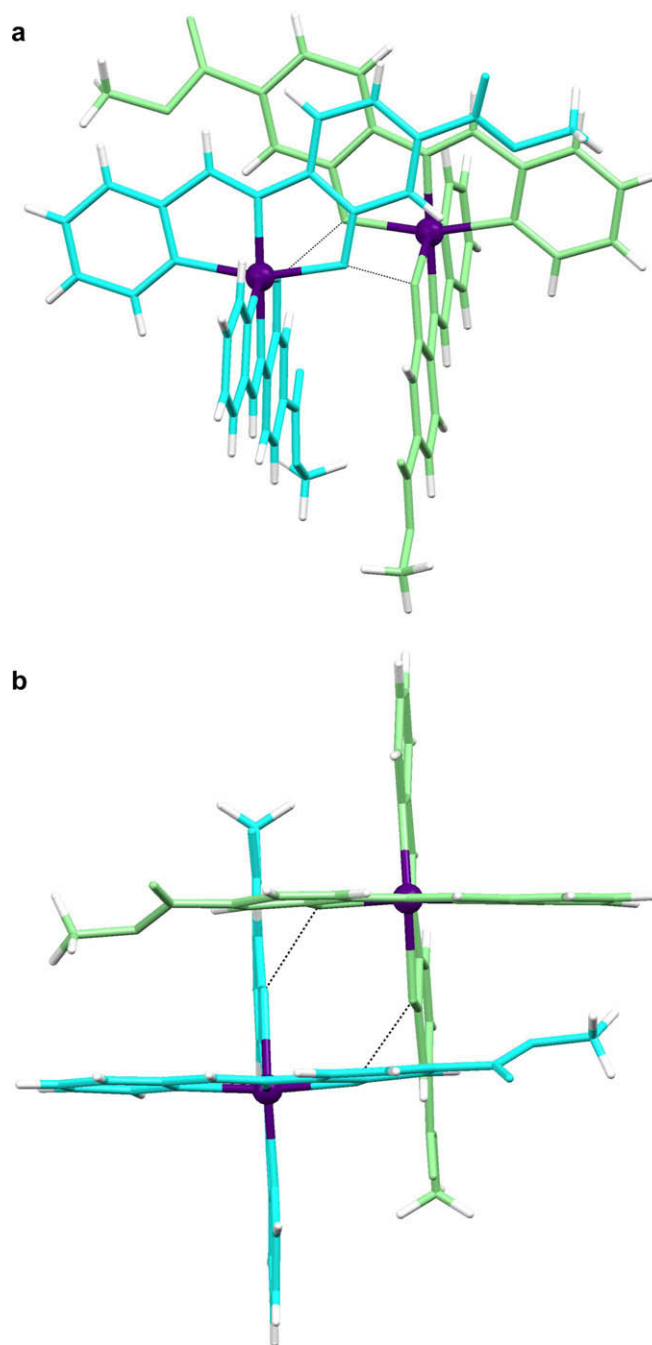


Fig. 6. The hydrogen-bonded centrosymmetric dimer of **2b** – (a) side view; (b) top view.

shorter. The metal ions are therefore six-coordinate and for both the coordination geometry is close to octahedral. The M–O and M–N distances are close to typical values (Table 1). The ligands are close to being planar and the donor atoms coplanar (for instance, the torsion angles N1–C6–C7–N8 and N8–C9–C14–O14 are close to 0°, cf. Table 1), thus enforcing a *bis*(meridional) form of the complexes as found in the analogous grid-type architecture.[6] The dihedral angles between the ring planes are not larger than 9.8(2)°. The ester groups are almost coplanar with the main molecular plane, with the exception of molecule B in **2b**, where the twist angle is almost 25°.

While the counteranion in **2b** is the familiar octahedral $[\text{PF}_6]^-$, in **2e** the counterion is the relatively uncommon $[\text{Zn}(\text{NO}_3)_4]^{2-}$. While with such anions as the latter there is frequently some difficulty in

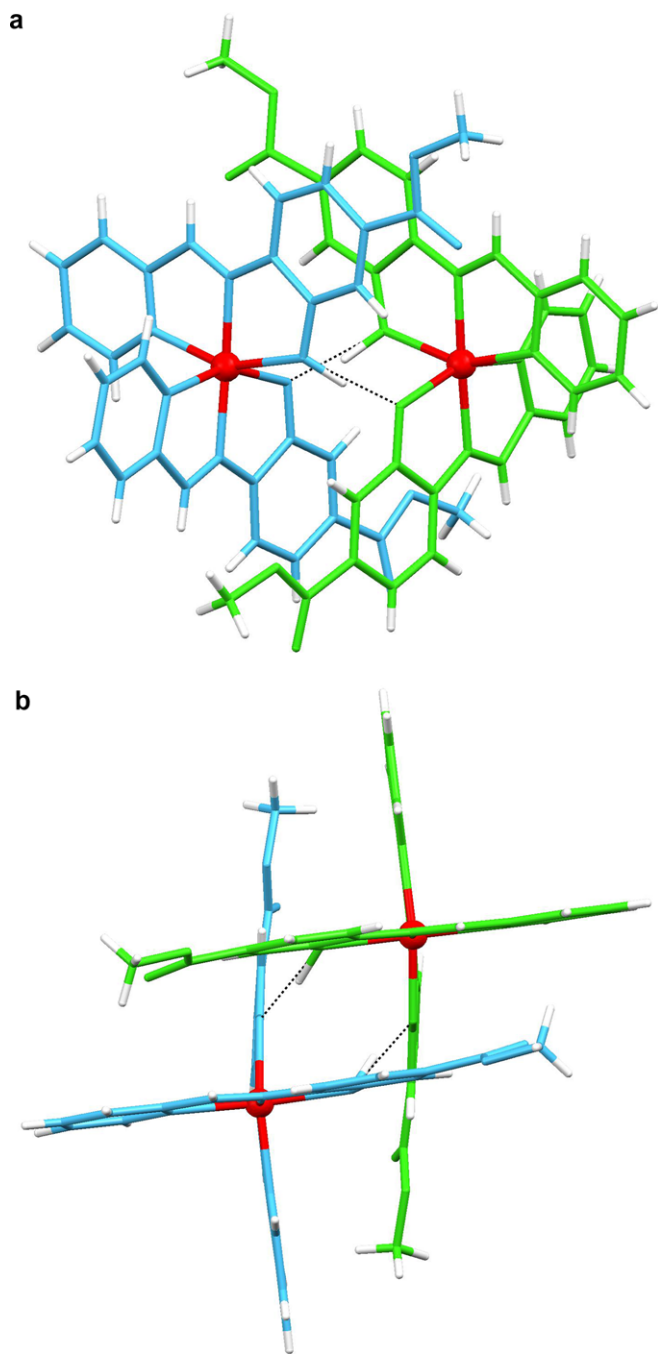


Fig. 7. The hydrogen-bonded centrosymmetric dimer of **2e** – (a) side view; (b) top view.

deciding between descriptions as tetrahedral with nitrate-O atoms singly or in pairs occupying the tetrahedral sites or as 8-coordinate with chelating nitrates, in the present case one oxygen atom from each nitrate is much closer than any other (Table 1), so that a description as a distorted tetrahedral species seems apt.

In the crystal lattice of **2e**, solvent acetonitrile molecules fill the voids created by the packing of the H-bonded dimers and the dianions (Fig. 8); in **2b** there are also voids, which are probably filled by highly disordered solvent molecules but attempts to model the electron density in these voids failed. Some directional C–H···O (and C–H···N(solvent) in **2e**) hydrogen bond-like contacts are also present in the structure and play some, probably secondary, role in the determination of crystal packing.

Table 1
Selected geometrical parameters (Å, °) with s.u.s in parentheses.

	2b (M=Cu)	2e (M=Zn)
M–N1A	2.250(6)	2.170(4)
M–N1B	2.083(6)	2.184(5)
M–N8A	2.019(5)	2.080(4)
M–N8B	1.957(5)	2.088(4)
M–O14A	2.356(4)	2.081(4)
M–O14B	2.023(4)	2.235(4)
N1A–M–N1B	97.1(2)	92.6(2)
N1A–M–N8A	77.4(2)	76.6(2)
N1A–M–N8B	105.1(2)	97.6(2)
N1A–M–O14A	151.2(2)	153.9(2)
N1A–M–O14B	92.4(2)	92.2(2)
N1B–M–N8A	98.3(2)	104.8(2)
N1B–M–N8B	80.1(3)	77.4(2)
N1B–M–O14A	89.2(2)	100.2(2)
N1B–M–O14B	161.0(2)	152.6(2)
N8A–M–N8B	177.2(2)	173.9(2)
N8A–M–O14A	73.9(2)	78.1(1)
N8A–M–O14B	99.8(2)	102.6(2)
N8B–M–O14A	103.6(2)	107.3(2)
N8B–M–O14B	81.6(2)	75.3(2)
O14A–M–O14B	90.4(2)	86.9(1)
N1A–C6A–C7A–N8A	–1.6(9)	0.8(8)
N1B–C6B–C7B–N8B	0.4(9)	1.3(8)
N8A–C9A–C14A–O14A	–2.2(9)	–5.4(8)
N8B–C9B–C14B–O14B	–1.1(9)	–3.1(7)

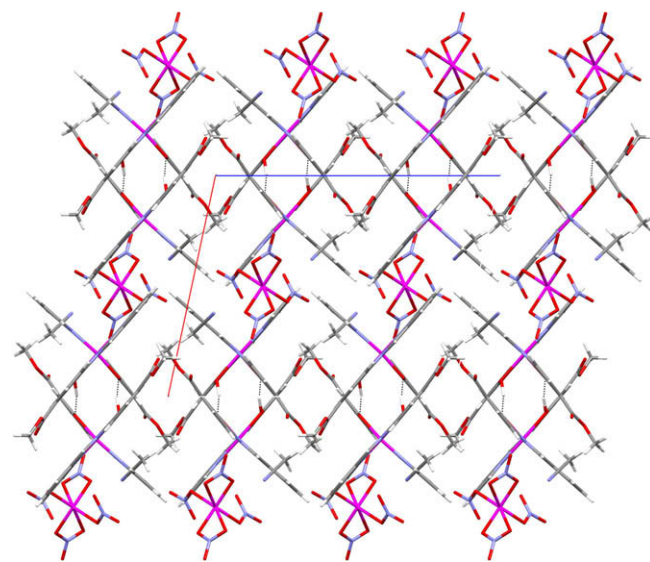


Fig. 8. Crystal packing of **2e** as seen along the *b*-direction.

2.2. Electronic absorption spectra and luminescence properties

All absorption, excitation and emission spectra of the studied compounds were recorded at a concentration of $\sim 5 \times 10^{-5}$ M in acetonitrile solution at room temperature. The electronic spectra of ligands **HL**^{1–3} and **1a–3e** are characterized by intense absorptions at 260–300 nm, less intense bands at ca. 340–360 nm and relatively weak absorptions at ca. 400–530 nm, respectively (Table 2). In the complexes, the stronger absorption bands in 400–530 nm region that are responsible for their yellow, orange and red colours are considered partly due to LMCT or possibly MLCT transitions. [30–32] There is a significant solvent dependence of the ligand spectra and the bands of the ligand **HL**¹, for example, in methanol are bathochromically shifted relative to those in acetonitrile. [19]

Table 2

The absorption and emission data for the studied systems (λ in nm, ϵ in $10^3 \text{ M}^{-1} \text{ cm}^{-1}$).

Compounds	Absorption data	Emission data	
	λ/ϵ	$\lambda_{\text{ex}}/\lambda_{\text{em}}$	$\lambda_{\text{ex}}/\lambda_{\text{em}}$
HL1	256.5/8.5; 284.5/10; 351.5/8.8; 483/0.14;	300/362	
HL2	286.5/18.8; 356.5/10.1; 495.5/0.17;	316/362	
HL3	257.5/23.6; 347.5/9.1; 455.5/0.34;	320/392	
1a	283.5/ 16.1; 350.5/13.6;	300/368	
1b	289/18.0; 340/13.6; 490/5.6	300/374	490/560
1c	300.5/25.1; 493.5/7.3;	300/372	490/560
1d	256.5/25.3; 321/16.2; 525.5/ 6.2;	300/367	
1e	316.5/13.7; 409.5/8.4;	300/366	400/570
2a	277.5/33.8; 303.5/31.9; 353.5/8.4;	315/364	
2b	277.5/28.2; 306/30.2; 501/4.7;	310/370	500/560
2c	305.5/16.3; 338.5/14.4; 506.5/7.9;	314/364	500/560
2d	262/33.8; 324/20.9; 534.5/7.3;	314/370	
2e	321/17.6; 401/10.2;	314/368	460/630
3a	257.5/50.6; 344.5/18.8;	318/394	
3b	257/17.7; 293/20.8; 341/7.5; 473/4.4	322/393	473/560
3c	299.5/41.5; 473/8.7;	318/394	473/560
3d	263.5/11.7; 294.5/23.1; 337/6.0; 507/3.1;	320/400	500/550
3e	301/17.4; 440/2.4;	322/398	440/530

Comparison of the absorption and emission spectra of ligands HL^{1–3} showed that introduction of the methoxycarbonyl substituent in the *para* position of the phenol causes a rather significant difference in shape of the bands of ligand HL³ compared to its structural analogues and a bathochromic shift of the emission band maximum from 362 nm (HL¹, HL²) to 392 nm for HL³ (Fig. 9, Table 2).

The spectra of the complexes (Fig. 10) not only differ from those of their parent ligands but also depend on the metal ion, these aspects reflecting both the fact that the ligand is partially deprotonated in the complexes as well as the presence of the LMCT/MLCT absorptions referred to above.

In the ultra-violet region, the form of the spectra of the M(II) complexes is similar for all. In the visible region, bands in the spectra of complexes with Cu²⁺ and Co²⁺ metal ions appear at much lower energies than those observed for the Zn²⁺ complex, no low-energy LMCT or MLCT transitions being expected in the last case, of course.

As noted earlier, although our initial intention had been to prepare complexes of Cu(I) with all three ligands, the isolated materi-

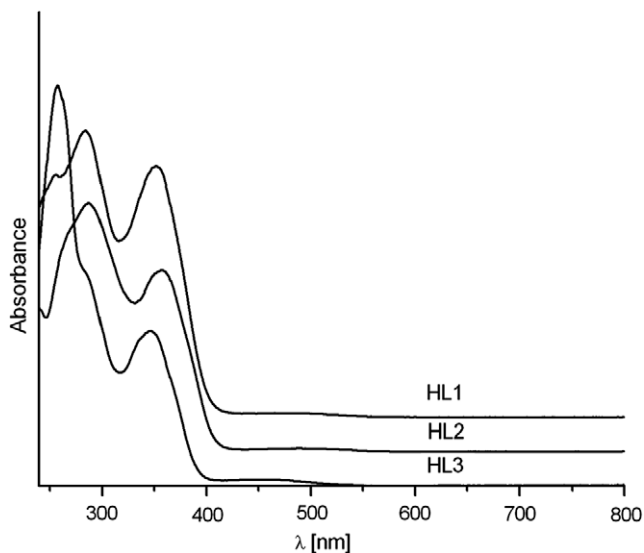


Fig. 9. Electronic absorption spectra of ligands HL¹, HL² and HL³ in CH₃CN at 298 K (The spectra are displaced vertically for clarity).

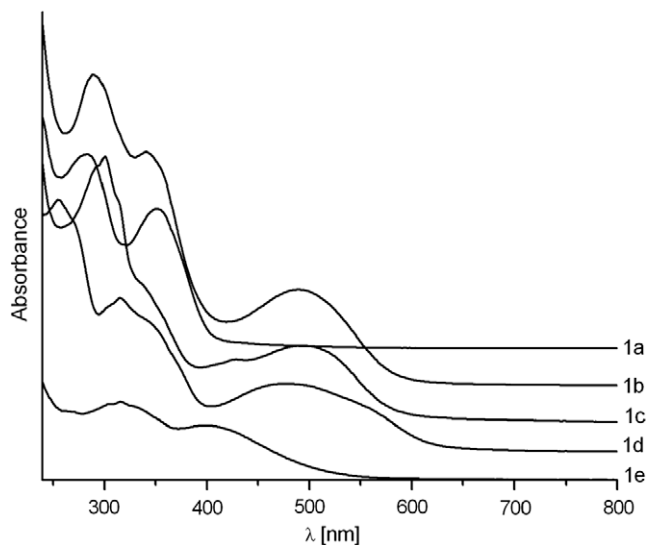


Fig. 10. Absorption spectra of complexes Ag⁺(**1a**), Cu²⁺(**1b, 1c**), Co²⁺(**1d**) and Zn²⁺(**1e**); spectra are taken at concentrations of $5 \times 10^{-5} \text{ M}$ in CH₃CN solution (Again, the spectra are displaced vertically for clarity).

als were paramagnetic and, as shown by the structure determination of complex **2b**, clearly Cu(II) species. Nonetheless, it may be noted that the colour of the solids and the intensity of the absorption bands in the electronic spectra are remarkably similar to those of Cu(I)-bis(phenanthroline) complexes [33]. The complexes do appear to undergo slow decomposition in solution but absorption near 500 nm indicative of the Cu(II) state is retained (Fig. 11).

The excitation and emission spectra of the ligands HL^{1–3} are shown in Fig. 12.

The excitation spectrum of free ligand HL¹ shows one maximum at $\lambda = 296 \text{ nm}$. Excitation maxima for HL² and HL³ are 285, 310 and 260, 315 nm, respectively. HL¹ and HL² display emission bands at $\lambda = 362 \text{ nm}$ while HL³ emits at $\lambda = 392 \text{ nm}$ on UV irradiation. The luminescence data are collected in Table 2.

Under UV irradiation, a single band is seen in the emission spectra of all complexes, with very small red-shifts (Table 2) of the maxima relative to the free ligand (proton complex) band (Fig. 13).

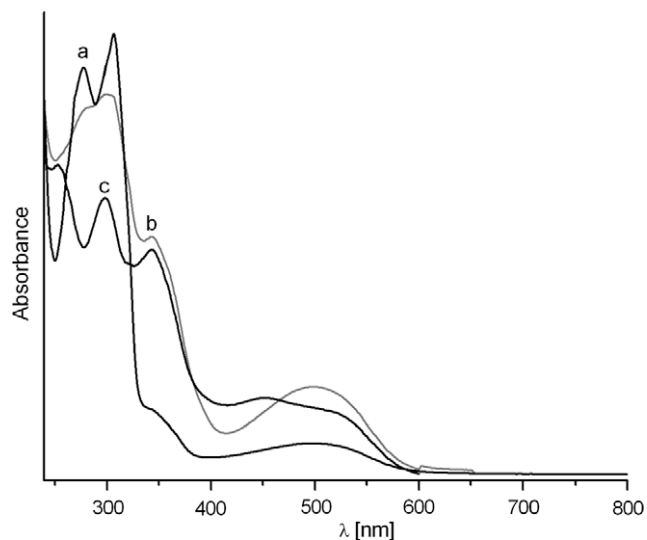


Fig. 11. Absorption spectra of **2b** after preparation (a, black); after one week (b, gray) and **2c** after preparation (c, black).

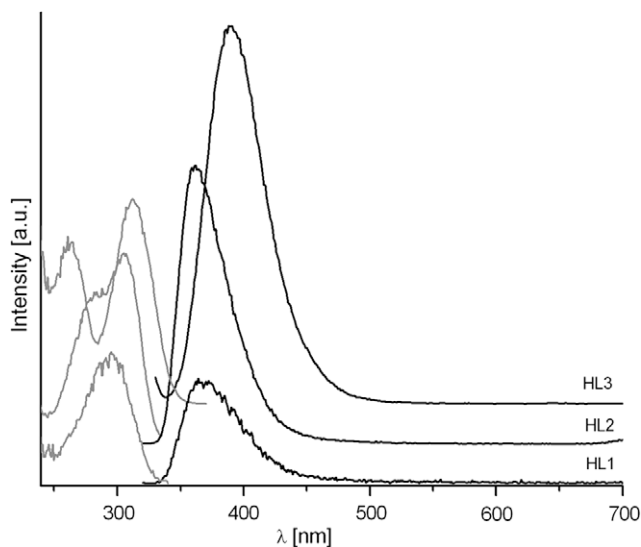


Fig. 12. Excitation (left, gray) and emission (right, black) spectra of ligands HL¹, HL² and HL³ at 5×10^{-3} M (Displaced vertically for clarity).

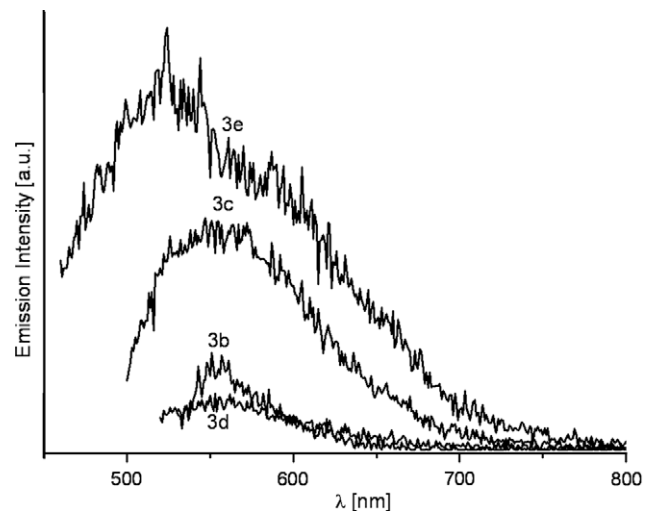


Fig. 14. Emission spectra of **3b**, **3c**, **3d** and **3e**; $\lambda_{\text{ex}} = 473$ nm for **3b** and **3c**, 500 nm for **3d** and 440 nm for **3e**.

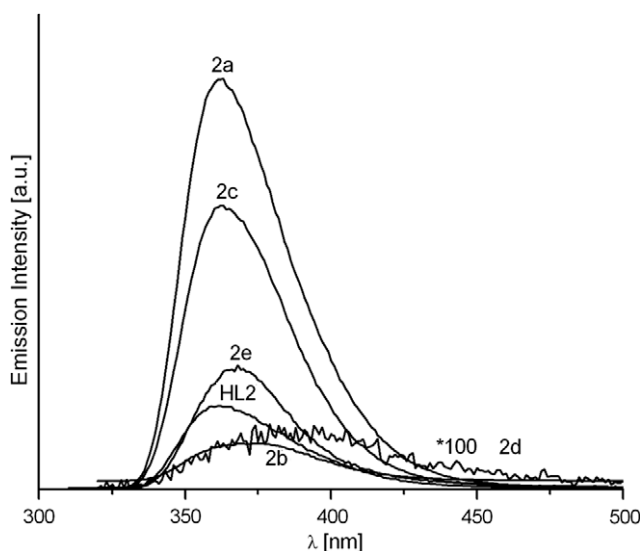


Fig. 13. Emission spectra of compounds HL², **2a**, **2b**, **2c**, **2d** and **2e** taken in acetonitrile solution at 5×10^{-5} M concentration at 298 K under UV excitation (λ_{ex} see Table 2).

This suggests that the emission is mainly a ligand-based one, with the excited state lifetime somewhat dependent upon the nature of the metal ion. The emission of the silver complex (**2a**) is the most intense, while Co(II) (complex **2d**) seems capable of almost completely quenching the emission, these characteristics also being seen with the complexes of ligands HL¹ and HL³.

Excitation of the complexes with visible radiation results in very weak and broad emissions centred near 550 nm (Fig. 14) which give the complexes a green luminescence.

The intensity of the emission bands of **3b** and **3d** is much weaker than that of **3e** and **3c**. Compounds **1d** and **2d** do not display luminescence in this spectral region (Table 2). Changes in the emission intensity of Zn²⁺, Cu²⁺ and Cu⁺ complexes with ligands HL¹ and HL² are identical with those of complexes incorporating ligand HL³.

3. Conclusions

The marked enhancement of ligand acidity that results from coordination is nicely reflected in the present isolation of complexes of deprotonated phenolic Schiff bases without the need to add an exogenous base. That deprotonation is incomplete, so that all M(II) species presently characterised contain one neutral and one anionic tridentate ligand, has interesting consequences in terms of aggregation of the complex cations through H-bonding interactions in the solid state to form centrosymmetric dimers. All these complexes show green fluorescence, the intensity of which depends strongly on the nature of the metal, and it is anticipated from the ease of functionalisation of the Schiff-base ligands that this luminescence should also be susceptible to control through changes in the ligand structure.

Given that early transition metals are typically octahedral and so limit the number of bound tridentate ligands, and hence the number of interaction sites to two, the formation of supramolecular dimers in the present cases can be understood. This indicates that for metals, such as the lanthanides, of higher coordination number, it should be possible to use partial ligand deprotonation to generate aggregates of higher nuclearity, and this is an objective of our continuing work in this area.

Concerning comparison of these mononuclear complexes with related [2 × 2] grids systems [6], marked differences in the electronic spectra are apparent but probably are simply due to the more extensively delocalised nature of the grid ligands, since both the magnetic and structural properties of the simpler complexes do closely match those of the grid sites.

4. Experimental

4.1. General

The metal salts were used without further purification as supplied from Aldrich. Ligand HL¹ (C₁₂H₁₀N₂O) was prepared according to published method [24,34] NMR spectra were run on a Varian Gemini 300 MHz spectrometer and were calibrated against the residual protonated solvent signals (CDCl₃: δ 7.24; CD₃CN: δ 1.94) and are given in ppm. Mass spectra for acetonitrile solutions $\sim 10^{-4}$ M were determined using a Waters Micromass ZQ spectrometer. Sample solutions were introduced into the mass spectrometer source with a syringe pump at a flow rate of

40 $\mu\text{L min}^{-1}$ with a capillary voltage of +3 kV and a desolvation temperature of 300 °C. Source temperature was 120 °C. The cone voltage (V_c) was set to 30 V to allow transmission of ions without fragmentation processes. Scanning was performed from $m/z = 200$ –1000 for 6 s, and 10 scans were summed to obtain the final spectrum. Microanalyses were obtained using a Perkin–Elmer 2400 CHN microanalyzer. IR spectra were obtained with a Perkin–Elmer 580 spectrophotometer and are reported in cm^{-1} . All absorption spectra were recorded with a Shimadzu UVPC 2001 spectrophotometer, between 200 and 600 nm, in 10×10 mm quartz cells using solutions 5×10^{-5} M with respect to the metal ion. Excitation and emission spectra were measured at room temperature on a Perkin–Elmer MPF3 spectrofluorimeter with excitation and emission slits at 10 nm.

4.2. Ligand HL²

To a solution of methyl 2-amino-3-hydroxybenzoate (0.22 g, 1.32 mmol) in EtOH_{abs} (9.5 ml), 2-pyridinecarboxaldehyde (125 μL , 1.30 mmol) was added. The mixture was stirred at r.t. for 24 h, then reduced to dryness. The residue was slurried with Et₂O to remove any unreacted materials, giving the product as a light brown solid. Yield: 290 mg (1.13 mmol, 86%) ¹H NMR (300 MHz, CDCl₃): $\delta = 9.83$ (s, 1H, OH), 8.93 (s, 1H, H–C=N), 8.76 (d, 1H, $J = 4.8$ Hz), 8.18 (m, 2H), 7.98 (d, 1H, $J = 8.4$ Hz), 7.86 (t, 1H, $J = 7.6$ Hz), 7.43 (t, 1H, $J = 5.2$ Hz), 7.08 (d, 1H, $J = 8.4$ Hz), 3.92 (s, 3H, OMe) ppm. IR (KBr): $\bar{\nu} = 3378$ (OH), 3051 (CH arom), 3010 (CH imin), 2950 (CH₃), 1713 (C=O), 1606 (CN), 1585 (py), 1566 (py), 1500 (py), 1467 (py), 1450 (py), 1438 (py), 1310 (py), 1295 (py), 1278 (py), 1213 (CO), 1154 (py), 1117 (py), 875 (OH), 783 (py), 766 (py), 744 (py), 582 (py), 512 (py) cm^{-1} . FAB-MS: $m/z = 257.08$ (M⁺, 100). Anal. Calc. for (C₁₄H₁₂N₂O₃) (256.26): C, 65.62; H, 4.72; N, 10.93. Found C, 65.58; H, 4.75; N, 10.90%.

4.3. Ligand HL³

To a solution of methyl 3-amino-4-hydroxybenzoate (0.19 g, 1.14 mmol) in EtOH_{abs} (8 ml), 2-pyridinecarboxaldehyde (110 μL , 1.14 mmol) was added. The mixture was stirred at r.t. for 24 h, then reduced to dryness. The residue was slurried with Et₂O to remove any unreacted materials, giving the product as a light brown solid. Yield: 194 mg (0.75 mmol, 68%). ¹H NMR (300 MHz, CDCl₃): $\delta = 10.02$ (s, 1H, OH), 8.90 (s, 1H, H–C=N), 8.73 (d, 1H, $J = 4.8$ Hz), 8.16 (d, 1H, $J = 8.0$ Hz), 8.11 (d, 1H, $J = 2.0$ Hz), 7.95 (t, 1H, $J = 6.8$ Hz), 7.82 (t, 1H, $J = 6.4$ Hz), 7.41 (s, 1H), 7.05 (d, 1H, $J = 8.8$ Hz), 3.89 (s, 3H, OMe) ppm. IR (KBr): $\bar{\nu} = 3397$ (OH), 3067 (CH arom), 3019 (CH imin), 2951 (CH₃), 1713 (C=O), 1621 (CN), 1600 (py), 1576 (py), 1567 (py), 1506 (py), 1479 (py), 1455 (py), 1429 (py), 1299 (py), 1281 (py), 1235 (CO), 1184 (py), 1173 (py), 1097 (py), 865 (OH), 780 (py), 761 (py), 743 (py), 589 (py), 510 (py) cm^{-1} . FAB-MS: $m/z = 257.08$ (M⁺, 100). Anal. Calc. for (C₁₄H₁₂N₂O₃) (256.26): C, 65.62; H, 4.72; N, 10.93. Found: C, 65.57; H, 4.73; N, 10.95%.

4.4. Ag(I) complex (1a)

A mixture of AgNO₃ (7.0 mg, 41.5 μmol) and ligand HL¹ (16.4 mg, 83 μmol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The yellow complex **1a** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS: $m/z = 503$ (10) [Ag(HL¹)₂]⁺, 305 (100) [Ag(HL¹)]⁺. ¹H NMR (300 MHz, CD₃CN): $\delta = 10.00$ (s, 1H, OH), 8.85 (s, 1H, H–C=N), 8.67 (d, 1H, $J = 4.9$ Hz), 8.10 (t, 2H, $J = 1.9$ Hz), 7.63 (d, 1H, $J = 2.1$ Hz), 7.61 (t, 1H, $J = 1.4$ Hz), 7.38 (d, 1H, $J = 1.4$ Hz), 7.19 (t, 1H, $J = 1.4$ Hz), 6.96 (d, 1H, $J = 6.7$ Hz), 6.67 (t,

1H, $J = 6.6$ Hz) ppm. IR (KBr): $\bar{\nu} = 3349$ (OH), 3051 (CH arom), 3018 (CH imin), 1623 (CN), 1588 (py), 1564 (py), 1489 (py), 1472 (py), 1457 (py), 1437 (py), 1384 (NO₃⁻), 1303 (py), 1180 (py), 1151 (py), 858 (OH), 792 (NO₃⁻), 778 (py), 744 (py), 581 (py), 511 (py) cm^{-1} . Anal. Calc. for [Ag(HL¹)₂][NO₃] (566.31): C, 50.90; H, 3.56; N, 12.37. Found: C, 50.92; H, 3.54; N, 12.40%.

4.5. Cu(II) complex (1b)

A mixture of [Cu(CH₃CN)₄][PF₆] (12.6 mg, 33.8 μmol) and ligand HL¹ (13.5 mg, 68.2 μmol) in CH₃CN (10 mL) was stirred at room temperature for 24 h under the normal atmosphere. The red-brown complex **1b** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS: $m/z = 459$ (100) [Cu(HL¹)(L¹)]⁺, 260 (30) [Cu(L¹)]⁺. IR (KBr): $\bar{\nu} = 3373$ (OH), 3057 (CH arom), 2961 (CH imin), 1653 (CN), 1587 (py), 1569 (py), 1551 (py), 1482 (py), 1458 (py), 1300 (py), 1272 (py), 1188 (py), 1148 (py), 840 (PF₆⁻), 775 (py), 745 (py), 557 (py) cm^{-1} . Anal. Calc. for [Cu(HL¹)(L¹)]PF₆ (604.95): C, 47.65; H, 3.33; N, 9.26. Found: C, 47.70; H, 3.30; N, 9.27%.

4.6. Cu(II) complex (1c)

A mixture of Cu(NO₃)₂·6H₂O (10.3 mg, 37.0 μmol) and ligand HL¹ (14.7 mg, 74.0 μmol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The red-brown complex **1c** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS(+) $m/z = 456$ (20) [Cu(HL¹)(L¹)]⁺, 260 (100) [Cu(L¹)]⁺. IR (KBr): $\bar{\nu} = 3378$ (OH), 3071 (CH arom), 3021 (CH imin), 1634 (CN), 1587 (py), 1569 (py), 1547 (py), 1482 (py), 1460 (py), 1384 (NO₃⁻), 1300 (py), 1273 (py), 1187 (py), 1149 (py), 863 (OH), 809 (NO₃⁻), 767 (py), 588 (py), 515 (py) cm^{-1} . Anal. Calc. for [Cu(HL¹)(L¹)](NO₃) (520.98): C, 55.33; H, 3.68; N, 13.44. Found: C, 55.38; H, 3.70; N, 13.40%.

4.7. Co(II) complex (1d)

A mixture of Co(NO₃)₂·6H₂O (11.8 mg, 4.05 μmol) and ligand HL¹ (16.0 mg, 81 μmol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The red complex **1d** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS(+): $m/z = 453$ (100) [Co(HL¹)(L¹)]⁺. ESI-MS(-): $m/z = 243$ (60) [Co(NO₃)₃]⁻, 153 (40) [Co(NO₃)₄]²⁻. IR (KBr): $\bar{\nu} = 3362$ (OH), 3067 (CH arom), 3029 (CH imin), 1719 (NO₃⁻), 1636 (CN), 1604 (py), 1585 (py), 1565 (py), 1544 (py), 1478 (py), 1420 (NO₃⁻), 1385 (NO₃⁻), 1315 (NO₃⁻), 1299 (py), 1274 (py), 1190 (py), 1142 (py), 862 (OH), 813 (NO₃⁻), 764 (py), 746 (py), 550 (py), 515 (py) cm^{-1} . Anal. Calc. for [Co(HL¹)(L¹)₂][Co(NO₃)₄] (1215.69): C, 47.42; H, 3.15; N, 13.83. Found: C, 47.44; H, 3.12; N, 13.84%.

4.8. Zn(II) complex (1e)

A mixture of Zn(NO₃)₂·6H₂O (9.6 mg, 32 μmol) and ligand HL¹ (12.8 mg, 64 μmol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The orange complex **1e** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS(+): $m/z = 459$ (80) [Zn(HL¹)(L¹)]⁺, 261 (65) [Zn(L¹)]⁺. ESI-MS(-): $m/z = 250$ (100) [Zn(NO₃)₃]⁻, 198 (20) [Zn(NO₃)₄]²⁻·2CH₃CN. ¹H NMR (300 MHz, CD₃CN): $\delta = 10.00$ (s, 1H, OH), 9.00 (s, 1H, H–C=N), 8.80 (d, 1H, $J = 5.2$ Hz), 7.95 (d, 1H, $J = 7.7$ Hz), 7.64 (d, 1H, $J = 1.6$ Hz), 7.61 (t, 1H, $J = 2.2$ Hz), 7.15 (m,

2H, $J = 8.2$ Hz), 6.94 (d, 1H, $J = 6.9$ Hz), 6.88 (t, 1H, $J = 8.5$ Hz) ppm. IR (KBr): $\bar{\nu} = 3357$ (OH), 3063 (CH arom), 3029 (CH imin), 1631 (CN), 1596 (py), 1569 (py), 1554 (py), 1482 (py), 1465 (py), 1420 (NO₃⁻), 1385 (NO₃⁻), 1372 (NO₃⁻), 1315 (NO₃⁻), 1300 (py), 1277 (py), 1154 (py), 863 (OH), 803 (NO₃⁻), 777 (py), 746 (py), 588 (py) cm⁻¹. Anal. Calc. for [Zn(HL¹)(L¹)₂][Zn(NO₃)₄] \cdot 2CH₃CN (1312.09): C, 47.42; H, 3.37; N, 14.89. Found: C, 47.50; H, 3.37; N, 14.85%.

4.9. Ag(I) complex (2a)

A mixture of AgNO₃ (4.4 mg, 26 μ mol) and ligand HL² (13.4 mg, 52 μ mol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The yellow complex **2a** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS: $m/z = 621$ (70) [Ag(HL²)₂]⁺, 363 (40) [Ag(HL²)]⁺. ¹H NMR (300 MHz, CD₃CN): $\delta = 10.00$ (s, 1H, OH), 8.79 (m, 2H, $J = 4.4$ Hz), 8.24 (d, 1H, $J = 7.1$ Hz), 7.95 (t, 1H, $J = 8.8$ Hz), 7.64 (t, 1H, $J = 3.0$ Hz), 7.38 (d, 1H, $J = 8.2$ Hz), 7.30 (s, 1H), 6.68 (d, 1H, $J = 8.2$ Hz), 3.85 (s, 3H, OCH₃) ppm. IR (KBr) $\bar{\nu} = 3340$ (OH), 3103 (CH arom), 2951 (CH imin), 2924 (CH₃), 1707 (C=O), 1605 (CN), 1529 (py), 1490 (py), 1437 (py), 1384 (NO₃⁻), 1295 (py), 1227 (CO), 1097 (py), 890 (OH), 796 (NO₃⁻), 766 (py), 747 (py), 580 (py) cm⁻¹. Anal. Calc. for [Ag(HL²)₂][NO₃] (682.39): C, 49.28; H, 3.54; N, 10.26. Found: C, 49.30; H, 3.55; N, 10.25%.

4.10. Cu(II) complex (2b)

A mixture of [Cu(CH₃CN)₄][PF₆] (7.1 mg, 19 μ mol) and ligand HL² (9.7 mg, 38 μ mol) in CH₃CN (10 mL) was stirred at room temperature for 24 h under the normal atmosphere. The brown-red complex **2b** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS: m/z (%) = 574 (70) [Cu(HL²)(L²)]⁺, 319 (80) [Cu(L²)]⁺. IR (KBr) $\bar{\nu} = 3378$ (OH), 3077 (CH arom), 3040 (CH imin), 2952 (CH₃), 1724 (C=O), 1602 (CN), 1588 (py), 1567 (py), 1481 (py), 1438 (py), 1307 (py), 1295 (py), 1226 (CO), 1158 (py), 1127 (py), 877 (OH), 847 (PF₆⁻), 778 (py), 767 (py), 747 (py), 559 (py), 516 (py) cm⁻¹. Anal. Calc. for [Cu(HL²)(L²)][PF₆] (721.02): C, 46.64; H, 3.36; N, 7.77. Found: C, 46.62; H, 3.30; N, 7.77%.

4.11. Cu(II) complex (2c)

A mixture of Cu(NO₃)₂ \cdot 6H₂O (7.4 mg, 27.0 μ mol) and ligand HL² (13.7 mg, 54.0 μ mol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The dark red complex **2c** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS: m/z (%) = 572 (30) [Cu(HL²)(L²)]⁺, 318 (100) [Cu(L²)]⁺. IR (KBr): $\bar{\nu} = 3368$ (OH), 3068 (CH arom), 3023 (CH imin), 2955 (CH₃), 1716 (C=O), 1645 (CN), 1569 (py), 1537 (py), 1482 (py), 1465 (py), 1384 (NO₃⁻), 1301 (py), 1289 (py), 1264 (py), 1233 (CO), 1117 (py), 894 (OH), 797 (NO₃⁻), 780 (py), 768 (py), 747 (py), 518 (py) cm⁻¹. Anal. Calc. for [Cu(HL²)(L²)][NO₃] (637.06): C, 52.79; H, 3.64; N, 10.99. Found: C, 52.80; H, 3.63; N, 11.00%.

4.12. Co(II) complex (2d)

A mixture of Co(NO₃)₂ \cdot 6H₂O (7.5 mg, 26 μ mol) and ligand HL² (13.2 mg, 52 μ mol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The red complex **2d** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition

of ether. ESI-MS(+): $m/z = 569$ (100) [Co(HL²)(L²)]⁺. ESI-MS(-): $m/z = 245$ (35) [Co(NO₃)₃]⁻, 153 (20) [Co(NO₃)₄]²⁻. IR (KBr): $\bar{\nu} = 3405$ (OH), 3068 (CH arom), 3006 (CH imin), 2950 (CH₃), 1715 (C=O), 1606 (CN), 1580 (py), 1565 (py), 1515 (py), 1461 (py), 1437 (NO₃⁻), 1417 (NO₃⁻), 1385 (NO₃⁻), 1310 (NO₃⁻), 1289 (py), 1227 (CO), 1188 (py), 1160 (py), 886 (OH), 800 (NO₃⁻), 768 (py), 746 (py), 580 (py), 512 (py) cm⁻¹. Anal. Calc. for [Co(HL²)(L²)₂][Co(NO₃)₄] (1447.83): C, 46.46; H, 3.20; N, 11.61. Found: C, 46.43; H, 3.24; N, 11.60%.

4.13. Zn(II) complex (2e)

A mixture of Zn(NO₃)₂ \cdot 6H₂O (9.6 mg, 30 μ mol) and ligand HL² (15.5 mg, 60 μ mol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The orange complex **2e** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS(+): $m/z = 575$ (10) [Zn(HL²)(L²)]⁺, 319 (75) [Zn(L²)]⁺, 257 (10) [H₂L²]⁺. ESI-MS(-): $m/z = 156$ (50) [Zn(NO₃)₄]²⁻. ¹H NMR (300 MHz, CD₃CN): $\delta = 10.01$ (s, 1H, OH), 8.97 (s, 1H, H-C=N), 8.96 (d, 1H, $J = 1.2$ Hz), 8.17 (d, 1H, $J = 2.0$ Hz), 8.00 (t, 1H, $J = 6.0$ Hz), 7.51 (d, 1H, $J = 1.2$ Hz), 7.49 (m, 2H, $J = 2.4$ Hz), 7.38 (d, 1H, $J = 2.0$ Hz), 3.90 (s, 3H, OCH₃) ppm. IR (KBr): $\bar{\nu} = 3333$ (OH), 3065 (CH arom), 3026 (CH imin), 2951 (CH₃), 1716 (C=O), 1616 (CN), 1595 (py), 1569 (py), 1480 (py), 1440 (NO₃⁻), 1384 (NO₃⁻), 1310 (NO₃⁻), 1290 (py), 1229 (CO), 1157 (py), 1125 (py), 896 (OH), 795 (NO₃⁻), 778 (py), 766 (py), 747 (py), 538 (py), 514 (py) cm⁻¹. Anal. Calc. for [Zn(HL²)(L²)₂][Zn(NO₃)₄](CH₃CN)₂ (1549.31): C, 46.51; H, 3.38; N, 12.66. Found: C, 46.50; H, 3.40; N, 12.65%.

4.14. Ag(I) complex (3a)

A mixture of AgNO₃ (3.3 mg, 19 μ mol) and ligand HL³ (9.8 mg, 38 μ mol) in CH₃CN (10 mL) was stirred at room temperature for 24 h. The yellow complex **3a** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS: $m/z = 619$ (10) [Ag(HL³)₂]⁺, 364 (40) [Ag(HL³)]⁺. ¹H NMR (300 MHz, CD₃CN): $\delta = 10.01$ (s, 1H, OH), 8.98 (s, 1H, H-C=N), 8.79 (d, 1H, $J = 4.9$ Hz), 8.69 (d, 1H, $J = 4.7$ Hz), 8.01 (d, 1H, $J = 3.8$ Hz), 7.97 (t, 1H, $J = 8.8$ Hz), 7.87 (t, 1H, $J = 7.4$ Hz), 7.35 (s, 1H), 7.03 (d, 1H, $J = 8.2$ Hz), 3.85 (s, 3H, OCH₃) ppm. IR (KBr): $\bar{\nu} = 3360$ (OH), 3082 (CH arom), 3017 (CH imin), 2951 (CH₃), 1704 (C=O), 1620 (CN), 1592 (py), 1567 (py), 1512 (py), 1474 (py), 1434 (py), 1384 (NO₃⁻), 1289 (py), 1274 (py), 1228 (CO), 1165 (py), 1132 (py), 1102 (py), 883 (OH), 800 (NO₃⁻), 780 (py), 763 (py), 745 (py), 508 (py) cm⁻¹. Anal. Calc. for [Ag(HL³)₂][NO₃] (682.39): C, 49.28; H, 3.54; N, 10.26. Found: C, 49.31; H, 3.53; N, 10.27%.

4.15. Cu(II) complex (3b)

A mixture of [Cu(CH₃CN)₄][PF₆] (9.6 mg, 26 μ mol) and ligand HL³ (13.3 mg, 52 μ mol) in CH₃CN (10 mL) was stirred at room temperature for 24 h under the normal atmosphere. The brown complex **3b** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH₃CN by the gradual addition of ether. ESI-MS m/z (%) = 574 (70) [Cu(HL³)(L³)]⁺, 319 (20) [Cu(L³)]⁺. IR (KBr) $\bar{\nu} = 3399$ (OH), 3060 (CH arom), 3028 (CH imin), 2953 (CH₃), 1710 (C=O), 1592 (py), 1566 (py), 1493 (py), 1471 (py), 1432 (py), 1295 (py), 1235 (CO), 1194 (py), 1121 (py), 880 (OH), 852 (PF₆⁻), 765 (py), 740 (py), 557 (py), 510 (py) cm⁻¹. Anal. Calc. for [Cu(HL³)(L³)][PF₆] (721.02): C, 46.64; H, 3.36; N, 7.77. Found: C, 46.63; H, 3.33; N, 7.75%.

4.16. Cu(II) complex (3c)

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.1 mg, 18 μmol) and ligand HL^3 (9.3 mg, 36 μmol) in CH_3CN (10 mL) was stirred at room temperature for 24 h. The dark red complex **3c** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether. ESI-MS(+): m/z (%) = 572 (100) $[\text{Cu}(\text{HL}^3)(\text{L}^3)]^+$, 318 (40) $[\text{Cu}(\text{L}^3)]^+$. IR (KBr): $\bar{\nu}$ = 3392 (OH), 3071 (CH arom), 3026 (CH imin), 2951 (CH_3), 1710 (C=O), 1653 (CN), 1592 (py), 1567 (py), 1491 (py), 1384 (NO_3^-), 1294 (py), 1234 (CO), 1195 (py), 1158 (py), 1119 (py), 879 (OH), 813 (NO_3^-), 766 (py), 749 (py), 572 (py), 512 (py) cm^{-1} . Anal. Calc. for $[\text{Cu}(\text{HL}^3)(\text{L}^3)](\text{NO}_3)$ (637.06): C, 52.79; H, 3.64; N, 10.99. Found: C, 52.82; H, 3.67; N, 11.03%.

4.17. Co(II) complex (3d)

A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.3 mg, 15 μmol) and ligand HL^3 (7.5 mg, 30 μmol) in CH_3CN (10 mL) was stirred at room temperature for 24 h. The red complex **3d** was isolated in quantitative yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether. ESI-MS(+): m/z = 569 (100) $[\text{Co}(\text{HL}^3)(\text{L}^3)]^+$. ESI-MS(-): m/z = 245 (40) $[\text{Co}(\text{NO}_3)_3]^-$, 174 (20) $[\text{Co}(\text{NO}_3)_4]^{2-}$ - CH_3CN . IR (KBr) $\bar{\nu}$ = 3361 (OH), 3065 (CH arom), 3038 (CH imin), 2949 (CH_3), 1708 (C=O), 1643 (py), 1596 (py), 1584 (py), 1562 (py), 1545 (py), 1488 (py), 1468 (py), 1436 (NO_3^-), 1384 (NO_3^-), 1315 (NO_3^-), 1294 (py), 1283 (py), 1229 (CO), 1195 (py), 1164 (py), 879 (OH), 806 (NO_3^-), 782 (py), 764 (py), 730 (py), 552 (py), 514 (py) cm^{-1} . Anal. Calc. for $[\text{Co}(\text{HL}^2)(\text{L}^2)]_2[\text{Co}(\text{NO}_3)_4](\text{CH}_3\text{CN})$ (1488.10): C, 46.79; H, 3.32; N, 12.23. Found: C, 46.75; H, 3.36; N, 12.23%.

4.18. Zn(II) complex (3e)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.8 mg, 16 μmol) and ligand HL^3 (7.8 mg, 31 μmol) in CH_3CN (10 mL) was stirred at room temperature for 24 h. The orange complex **3e** was isolated in quantitative

yield by evaporation of the solvent and recrystallisation of the residue from the minimum volume of CH_3CN by the gradual addition of ether. ESI-MS(+): m/z = 575 (100) $[\text{Zn}(\text{HL}^3)(\text{L}^3)]^+$, 319 (75) $[\text{Zn}(\text{L}^3)]^+$. ESI-MS(-): m/z (%) = 255 (10) $[\text{Zn}(\text{NO}_3)_3]^-$, 157 (50) $[\text{Zn}(\text{NO}_3)_4]^{2-}$. ^1H NMR (300 MHz, CD_3CN): δ = 10.00 (s, 1H, OH), 9.10 (s, 1H, H-C=N), 8.94 (d, 1H, J = 7.1 Hz), 8.17 (m, 3H, J = 8.0 Hz), 7.45 (s, 1H), 7.41 (t, 1H, J = 8.2 Hz), 6.88 (d, 1H, J = 8.0 Hz), 3.84 (s, 3H, OCH_3) ppm. IR (KBr) $\bar{\nu}$ = 3385 (OH), 3063 (CH arom), 3029 (CH imin), 2957 (CH_3), 1704 (C=O), 1596 (py), 1567 (py), 1497 (py), 1473 (py), 1459 (py), 1436 (py), 1385 (NO_3^-), 1371 (NO_3^-), 1310 (NO_3^-), 1294 (py), 1271 (py), 1251 (py), 1222 (CO), 885 (OH), 814 (NO_3^-), 772 (py), 560 (py), 529 (py), 509 (py) cm^{-1} . Anal. Calc. for $[\text{Zn}(\text{HL}^3)(\text{L}^3)]_2[\text{Zn}(\text{NO}_3)_4]$ (1467.20): C, 45.84; H, 3.16; N, 11.46. Found: C, 45.80; H, 3.12; N, 11.45%.

5. Crystal structure determinations of ligand HL^2 and complexes **2b** and **2e**

Very small yellow needles were obtained by slow evaporation of chloroform-ethanol solutions (ligand HL^2) whereas red (**2b**) and yellow (**2e**) plates of both complexes were obtained by slow diffusion of hexane into methanol (**2b**) and toluene into acetonitrile (**2e**) solutions. Data were collected at room temperature (ligand HL^2 , **2b**) and at 100(1)K (**2e**) by ω -scan technique in the θ range 2–25° on a KUMA KM4CCD four-circle diffractometer with CCD detector, using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Accurate cell parameters were determined by a least-squares fit of 2941 (HL^2), 3009 (**2b**), and 3507 (**2e**) reflections of highest intensity, chosen from the whole experiments. Data were corrected for Lorentz-polarization effects and for absorption [35]. The structures were solved by direct methods with SHELXS-97 [36] and refined with SHELXL-97 [36]. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located at calculated positions and refined as 'riding model' with their isotropic thermal parameters set at 1.2 times the U_{eq} 's of the appropriate carrier atom. Some weak restraints were applied to the displacement parameters of selected atoms in **2e**. Crystallographic data for both complexes are listed in Table 3.

Table 3
Crystal data, data collection and structure refinement.

Compound	2b	2e	HL^2
Formula	$\text{C}_{28}\text{H}_{23}\text{CuN}_4\text{O}_6 \cdot \text{PF}_6$	$\text{C}_{56}\text{H}_{46}\text{N}_8\text{O}_{12}\text{Zn}_2 \cdot \text{N}_4\text{O}_{12}\text{Zn} \cdot 2(\text{C}_2\text{H}_3\text{N})$	$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$
Formula weight	720.01	1549.27	256.26
Crystal system	tetragonal	monoclinic	monoclinic
Space group	$I4_1/a$	$P2/c$	$P2/c$
a (Å)	17.3773(11)	14.0283(14)	10.9316(11)
b (Å)	17.3773(11)	13.4342(13)	6.4808(4)
c (Å)	43.731(5)	17.6518(14)	17.5367(16)
β (°)	90	102.111(7)	93.946(4)
V (Å ³)	13205.5(19)	3252.6(5)	1239.4(18)
Z	16	2	4
D_x (g cm ⁻³)	1.45	1.58	1.373
μ (mm ⁻¹)	0.79	1.19	0.098
Crystal size (mm)	0.15 × 0.15 × 0.02	0.15 × 0.15 × 0.1	0.3 × 0.3 × 0.3
θ range (°)	2–25	2–25	1–27
hkl range	$-20 \leq h \leq 20$ $-20 \leq k \leq 9$ $-51 \leq l \leq 52$	$-16 \leq h \leq 14$ $-15 \leq k \leq 15$ $-20 \leq l \leq 19$	$-14 \leq h \leq 14$ $-7 \leq k \leq 8$ $-22 \leq l \leq 22$
Reflections::			
Measured	36352	18870	4543
Unique (R_{int})	5823 (0.24)	5730 (0.10)	2797 (0.10)
With $I > 2\sigma(I)$	1664	2961	1090
Number of parameters	417	460	175
$R(F)$	0.064	0.062	0.054
$wR(F^2)$	0.108	0.109	0.116
Goodness of fit	0.93	1.09	0.90
max/min $\Delta\rho$ (e Å ⁻³)	0.47/−0.36	1.25/−0.60	0.20/−0.20

Supplementary data

CCDC 715917 (2b), 715918 (2e) and 730367 (HL2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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