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Quaterpyridine Ligands Forming Helical Complexes of Mono- and Dinuclear (Helicate) Forms

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The dimethylquaterpyridine ligand **L1** reacts with Cu^I and Ag^I to give dinuclear complexes of "helicate" form, in which the metals are in an approximate tetrahedral coordination, whereas reactions with Co^{II} and Zn^{II} provide mononuclear complexes, in which the metals are apparently six-coordinate with markedly distorted octahedral coordination, and the ligand retains a helical conformation. Oxidation of the methyl substituents of **L1** into carboxylic acid groups, followed by esterification, gives ligand **L2**, which also forms a dinuclear Cu^I helicate and a mononuclear Co^{II} complex; one of the ester groups appears to be involved in complexation in the latter. All the complexes were characterised by single-crystal X-ray structure determinations.

Introduction

Helicity in inorganic systems has a historical significance extending back to the recognition of the enantiomeric forms of quartz and fundamental studies of the optical activity of tris(chelate) octahedral complexes.[1,2] The recognition of the double-stranded helical structure of DNA[3] provided a new stimulus in this area for the development of DNA analogues based on double and higher helices formed by metal-ion complexation; such complexes, of nuclearity two or greater, are named "helicates".[4–7] Interest in helicates has in fact increased in recent times because of the wide variety of potential applications in areas such as asymmetric catalysis,[8] medicinal chemistry,[9] nonlinear optical materials,[10] and possible uses in systems displaying controlled molecular motions.[11]

One of the important attributes of artificial helical systems is the enormous variety of chemical structures that can be incorporated within the ligands and the subtlety of the interplay between metal-ion coordination preferences and the donor-atom array of the ligand.[4–7,12] In general, the use of homotopic N-donor ligands and metal ions in self-assembly processes has attracted much attention for the design and synthesis of novel functional materials;[13–15] one report of particular promise is that of the development of transistors incorporating complexes containing Co^{II} bonded to polypyridine ligands.[16] There is, of course, very extensive literature concerning polypyridine ligands and their complexes,[17–19] but a relatively infrequently investigated area of this work, despite its significance in the development of helicate chemistry,[4c,20] is that concerning quaterpyridine ligands.[21] Thus, in the present work, we present an extension of this field through the characterisation, in the solid state and solution, of complexes of Co^{II}, Cu^I, Zn^{II} and Ag^I with 6,6′′′-dimethyl-2,2′;6′,2′′;6′′,2′′′-quaterpyridine, **L1**, and of Co^{II} and Cu^I with **L2**, a derivative of **L1** in which both methyl groups have been oxidised to ethoxycarbonyl units. The focus largely upon d^{10} metal ions for this initial work was a consequence of our interest in the evidence for the varied biological activity of their complexes.[22] Although all the complexes proved to contain the ligand in a helical form, only the Cu^I and Ag^I species, being dinuclear rather than mononuculear as with Co^{II} and Zn^{II}, can be classified as helicates. An interesting issue with the Co^{II} and Zn^{II} complexes is whether they should be considered to contain six- or seven-coordinate metal ions. Although there are close similarities to the results obtained with other quaterpyridine derivatives,[21] in particular with regard to the influence of substituents on the conformation and hence the coordinating tendencies of the ligands,[20,21] the 6,6′′′ substituents in the present systems produce some significant points of difference.

Results and Discussion

Synthesis and Characterisation of Ligands L1 and L2

Metal-catalysed coupling reactions of halopyridines and their derivatives are a long-established means of synthesis

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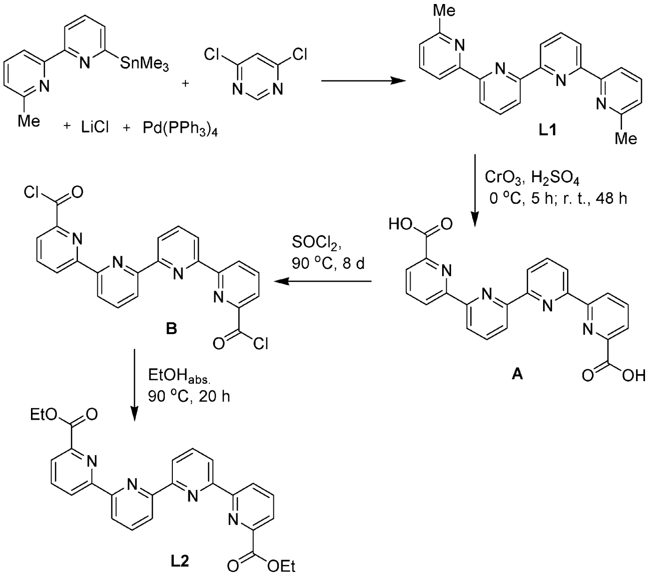
of polypyridines, including quaterpyridines, though milder and more selective procedures have been more recently developed.[19,21] In the present case, quaterpyridine **L1** was obtained as a side product of a Stille coupling reaction,[23] as outlined in Scheme 1.



Scheme 1. Reaction scheme for the synthesis of ligands **L1** and **L2**.

2-(6-Methylpyridin-2-yl)-6-(trimethylstannyl)pyridine[24] was treated with 4,6-dichloropyrimidine under Pd^0 catalysis to obtain compound **L1** in 24% yield. The main product of this reaction was 4,6-bis[6-(6-methylpyridin-2-yl)pyridin-2-yl]pyrimidine.[24] Treatment of **L1** with CrO_3 in concentrated H_2SO_4 gave diacid **A** in 26% yield. Acid **A** is insoluble in most organic solvents but slightly soluble in DMSO. Compound **A** was converted into diacid dichloride **B** upon refluxing in $SOCl_2$, and the product was pure enough to be used in further transformations without purification. When **B** was treated with EtOH at reflux, ligand **L2** was obtained in 39% yield by simple crystallisation. Elemental analyses and mass spectra were consistent with the formulations given for **L1** and **L2**, and their NMR spectra clearly demonstrated their twofold symmetry.

Synthesis and Characterisation of Metal-Ion Complexes of L1 and L2

Although an ultimate objective of the synthesis of **L2** was to obtain a bis(tridentate) ligand possibly best suited to the formation of oligonuclear lanthanide-ion complexes,[25] our initial focus was the establishment of the basic coordination chemistry of both **L1** and **L2** with transition-metal ions. Previous studies of quaterpyridine ligands and their complexation by transition-metal ions[20,21,26] showed that the 2,2′;6′,2′′;6′′,2′′′-quaterpyridine isomer and its derivatives tend to give mononuclear complexes with metal ions favouring octahedral or square-planar coordination geometry and dinuclear helicate species with metals favouring tetrahedral coordination. These gross expectations are confirmed by the present studies of solid-state structures determined by X-ray crystallography (detailed below). However, there are various features of the structures that appear to depend upon the particular substitution pattern seen in **L1** and **L2**. In solution, although it is clear that the complexes presently isolated are of relatively high stability in that some form of complexation is retained even at 10^{-5} M, the exact nature of the equilibria involved remains to be established.

Although it is possible for a quaterpyridine ligand to adopt a (strained) planar conformation with all N-donor sites oriented internally, the geometry of the resultant donor-atom array is not compatible with regular octahedral or square-planar coordination commonly found with first-row transition-metal ions, and indeed, in known cases,[21] binding of quaterpyridines to formally six-coordinate metal ions is associated with major distortions from octahedral symmetry. An alternative binding mode, possibly influenced by substituent dispositions,[20] is one in which the ligand is twisted out of planarity and acts as a bis(bidentate) ligand towards two metal ions (and not one). When the metal ion is one that can adopt essentially tetrahedral four-coordination, a second twisted ligand can complete the coordination spheres to give a helicate, as observed for complexes **1**, **2** and **7**.

Dinuclear Helicates of Cu^I and Ag^I

Reactions at room temperature in an acetonitrile/dichloromethane mixture with the use of ligands **L1** and **L2** and tetrakis(acetonitrile)copper(I) hexafluorophosphate or silver(I) tetrafluoroborate produced quantitatively and selectively double-stranded dinuclear helicates $[Cu_2(\mathbf{L1})_2](PF_6)_2$ (**1**) $[Cu_2(\mathbf{L2})_2]$ $(PF_6)_2$ (**7**) and $[Ag_2(\mathbf{L1})_2](BF_4)_2$ (**2**). Elemental analysis and IR and NMR spectroscopy were consistent with the composition and structure defined by the X-ray diffraction measurements (Table 1; and see below), although the ^1H NMR spectra do not exclude the possible presence of simpler species of twofold symmetry in solution. However, each mass spectrum displayed a peak unambiguously assigned to the molecular cations $[Cu_2(\mathbf{L1})_2]^{2+}$- ($m/z$ = 401), $[Ag_2(\mathbf{L1})_2]^{2+}$ (m/z = 445) and $[Cu_2(\mathbf{L2})_2]^{2+}$($m/z$ = 517). In all cases, the metal ion shows a strongly distorted but essentially flattened-tetrahedral coordination geometry (Table 1).

Because the helicates crystallised in the present work were all prepared from racemic ligands, it is possible for the complexes to crystallise in two forms: either one where individual crystals contain but a single enantiomer (a "racemic mixture") or another where both enantiomers are present in the one lattice (a "racemic compound").[2] In fact, **1** appears to crystallise as a racemic mixture, as the crystal chosen for structural examination contained but one enantiomer, arbitrarily shown as the right-handed species in Figure 1.

The high symmetry of the lattice formed by the complex is clearly evident viewed down the *c* axis (Figure 2), where

Table 1. Selected geometrical parameters (bond lengths, Å; bond angles, °). N4 (max) means the maximum deviation from the N_4 plane of the ligand; the following rows are deviations from this plane.

	1 (Cu)	**2** (Ag)	**3A** (Co)	**3B** (Co)	**4** (Co)	**5** (Zn)	**6** (Zn)	**7** (Cu)	**8** (Co)
M–N1	2.0139(9)	2.335(3)	2.254(2)	2.225(2)	2.420(2)	2.451(2)	2.490(5)	2.023(5)	2.218(3)
M–N8	2.0383(9)	2.377(3)	2.097(2)	2.092(2)	2.125(2)	2.135(3)	2.167(5)	2.046(5)	2.164(4)
M–N14	2.0383(9)	2.377(3)	2.095(2)	2.092(2)	2.108(2)	2.118(3)	2.160(5)	2.046(5)	2.143(3)
M–N20	2.0139(9)	2.335(3)	2.237(2)	2.224(2)	2.360(2)	2.383(3)	2.454(5)	2.023(5)	2.428(3)
M–O1w			2.117(2)	2.105(2)	2.073(2)	2.010(2)	2.010(4)		
M–O2w			2.087(2)	2.127(2)		2.019(2)			
M–Cl					2.3168(7)		2.280(2)		
M–F									2.083(3)
M–N(CH_3CN)									2.094(4)
M–O(ester)									2.423(3)
N4 (max)	0.844(1)	0.723(2)	0.179(1)	0.181(1)	0.042(1)	0.067(2)	0.019(3)	0.831(4)	0.168(2)
N4–M			0.028(1)	0.021(1)	0.163(1)	0.023(1)	0.163(3)	0.153(4)	–0.033(2)
N4–O1w			–2.071(2)	–2.053(2)	–1.845(2)	–1.832(3)	–1.678(5)		
N4–O2w			2.084(2)	2.138(2)		1.950(3)			
N4–Cl					–2.444(1)		2.339(4)		
N4–F (BF_4)									2.028(4)
N4–N(CH_3CN)									–2.125(5)
A/D	74.99(3)	58.34(11)	27.90(9)	26.38(6)	14.57(11)	18.58(6)	5.4(4)	69.1(2)	31.2(2)

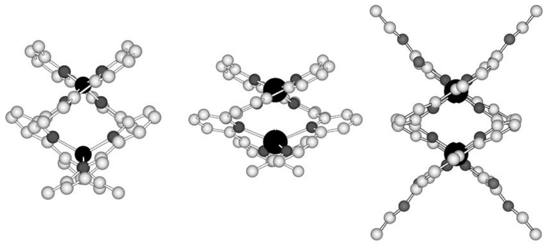

1 **2** **7**

Figure 1. The cations present in complexes **1**, **2** and **7** arbitrarily shown in a common right-handed helical form.

the cations, alternating with some of the hexafluorophosphate anions, lie in columns parallel to the *c* axis hexagonally surrounding channels filled with the remaining anions.

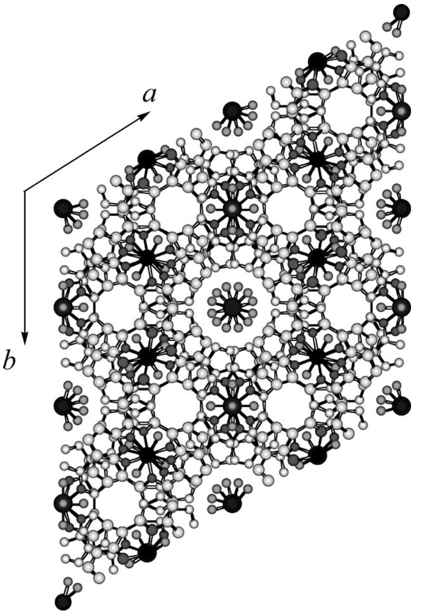


Figure 2. A partial view of the lattice of **1** down c.

Other smaller channels appear to be empty. Overall, every cation is fairly well insulated from contacts with another through a sheath of surrounding anions, and although it appears in the given projection that partial overlap of aromatic quaterpyridine occurs, the cations in adjacent columns are in fact staggered, so that the only short intercolumn contacts are CH_3···C(aromatic) at 3.43 Å. These methyl groups also make long contacts (3.78 Å) to F of the anions interposing between the cation. The cations in different columns are bridged by interactions involving the anions in the large channel, and the contacts of 3.42–3.50 Å are of a geometry such that it appears that both CH···F and F···π interactions[27] occur. The cations themselves form relatively squat units with Cu···Cu 3.795(*x*) Å; this length expressed as the distance between the midpoints of the vectors linking methyl groups at each extremity along the Cu···Cu axis is 8.023(*x*) Å and is ≈8.8 Å wide.

In contrast, with nearly all these points, the structure of Ag^I complex **2** shows the cations to be flattened so that Ag···Ag is short [3.125(*x*) Å], and the cation length [6.660(*x*) Å] is considerably less than their width (≈9.9 Å). These dimensions may reflect the influence of "argentophilic" interactions, which have been argued to be of importance in related Ag^I helicates,[11] though here they do not appear to produce intermolecular contacts; the shortest intercation Ag···Ag distance is 4.853(*x*) Å. Nonetheless, the cations do lie in columns without intervening anions, and the closest contacts between cations in these columns is hydrophobic CH_3···CH_3 [3.627(*x*) Å], though CH_3···N contacts are only slightly longer [3.677(*x*) Å]. Within a given column, all cations are of the same chirality but columns of alternating chirality lie side by side to form racemic sheets parallel to the *bc* plane and they are separated by tetrafluoroborate anions and acetonitrile molecules so that **2** is indeed a racemic compound (an alternative view is that homochiral sheets including anions and solvent lie parallel to the *ab* plane and the cation chirality alternates from one sheet to the next). As in **1**, there is little evidence of aromatic–aromatic interactions[28] within or between cation columns (with any contacts being few and >3.6 Å). Any stacking would appear to be intramolecular, though the shortening of the metal–metal distance in **2** is associated only with an increase in the number of contacts, and the mean aromatic-plane separations are little different from those in **1**. As with $[PF_6]^-$ in **1**, the $[BF_4]^-$ anion in **2** appears to be involved in a multitude of contacts (here, more difficult to define because of disorder) that organise the lattice. The CH_3CN molecules are also involved in numerous contacts.

Aside from its ethoxycarbonyl substituents, the cation present in **7** is very similar to that in **1**. It is slightly flattened [Cu···Cu 3.690(x) Å, length (ignoring the ester groups) 7.842(x) Å, width ≈8.93 Å], but again the cations form homochiral columns that are parallel to the *b* axis and the cations are separated by hexafluorophosphate anions. Unlike **1** and like **2**, however, columns of alternating chirality lie side by side in sheets (parallel to the *ab* plane) separated by sheets of water molecules, so that **7** is another racemic compound (Figure 3). The anions again appear to be involved in numerous interactions with the cations both within and between columns, and the axial F atoms make contacts of 3.59 Å to the carbonyl carbon atom, whereas each equatorial F makes at least one contact as short as 3.38 Å to an aromatic carbon atom. Perhaps as a consequence of their opposite chirality, adjacent columns interpenetrate to a greater extent so that, in this case, there appears to be evidence of intercolumn stacking interactions, with numerous contacts between 3.4–3.5 Å. If these are the factors responsible for the adoption of a centrosymmetric space group by crystals of **7**, then it may be that the resolution of helicates can be controlled by the size of the anion relative to that of the cation.

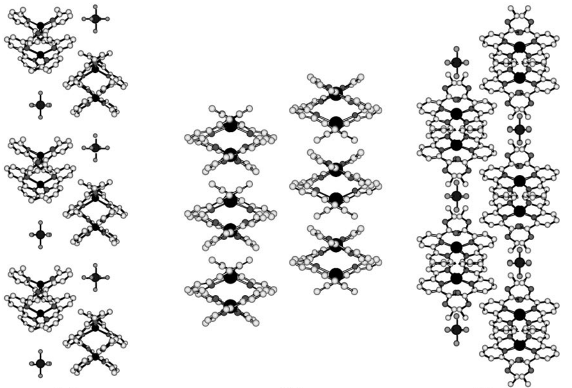


Figure 3. Partial views of cation columns (perpendicular to the column axes) found in: (a) complex **1**, where the cations are all of the same chirality and hexafluorophosphate anions lie between each pair along the axis; (b) complex **2**, where anions do not separate the cations and adjacent columns are of opposite chirality; and (c) complex **7**, where again anions separate the cations in columns but adjacent columns are of opposite chirality.

Mononuclear Complexes of Co^{II} and Zn^{II}

The labile metal ions Co^{II} and Zn^{II} appeared also to react readily with ligands **L1** and **L2** to give, here, mononuclear complexes isolable in essentially quantitative yields. In the case of Co^{II}, there was no evidence of any oxidation to Co^{III} species under the conditions of synthesis. Various salts (Cl^-, $CF_3SO_3^-$, BF_4^-) were used, often as mixtures, both with a view to finding crystals best suited to diffraction measurements[29] and to evaluating any anion effects. The crystal-structure determinations (Table 1), discussed in detail below, show that the anions have no marked influences on the form of the bound ligand, which is nonplanar and perceptibly helical in all cases. The solution ^1H NMR spectra of both the Zn^{II} complexes of **L1** isolated (i.e., **5** and **6**) are identical and indicate that the bound ligand has twofold symmetry. This symmetry is expected if both unidentate ligands in solid **6** are replaced by solvent molecules, but could also be consistent with rapid exchange between species where but one methyl group at a time is engaged in agostic interaction with the metal (see below).

Once again, the gross features of the solid-state structures presently determined (Table 1) are consistent with those of other quaterpyridine complex structures in the literature.[20,21] As noted above, the basic structure of the ligand is incompatible with a truly square-planar MN_4 array, and it might well be asked if addition of a unidentate ligand L in the same plane as that of the four N atoms could give rise to a seven-coordinate $MN_4(L)S_2$ (S = solvent) species.[30] Although Co^{III}, which is not known to form seven-coordinate species, forms $[Co(quaterpyridine)(SO_3)(OH_2)]^+$ containing an essentially square-planar CoN_4 unit,[31] the question as to whether larger M^{II} metals (such as Co^{II}) can form seven-coordinate species becomes more pertinent. Nonetheless, there is no evidence in the current structural literature for involvement of another ligand in the plane of the quaterpyridine N donors.

Structure determination of the two Co^{II} complexes (i.e., **3**, Figure 4; **4**, Figure 5) of ligand **L1** show evidence of strain in the coordination in the sense that there are small but significant differences between the two close-to-planar CoN_4 units (even between the two nonequivalent entities in the one lattice of **3**) and that there are large distortions from true octahedral symmetry in the CoN_4O_2 and $CoN_4O(Cl)$ entities, respectively.

In both, perhaps as a result of repulsive interactions between the methyl substituents, the ligand is nonplanar and in fact helical in form, which means of course that the complexes are chiral and that crystallisation as a racemic mixture or a racemic compound is possible. The space groups found show that both crystals must contain both enantiomers, that is, that the solids are racemic compounds.

In the case of **3**, the helicity of the bound ligand is quite marked, and within the lattice, homochiral chains of cations involving partial π-stacking overlaps can be discerned, though there are also chains of cations of alternating chirality where partial π-stacking overlaps again occur. Perhaps more importantly, heterochiral pairs of cations are linked

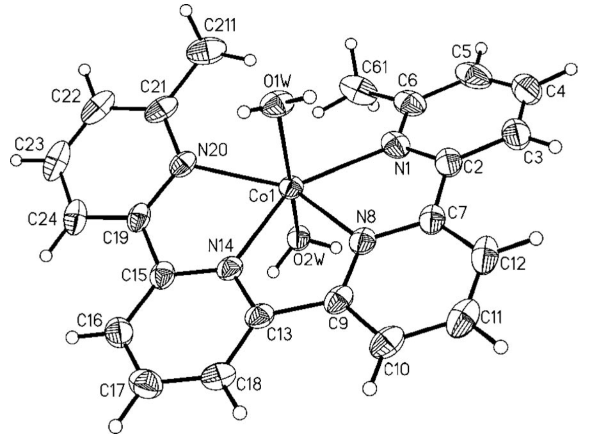


Figure 4. Perspective view of complex **3**; ellipsoids are drawn at the 50% probability level.

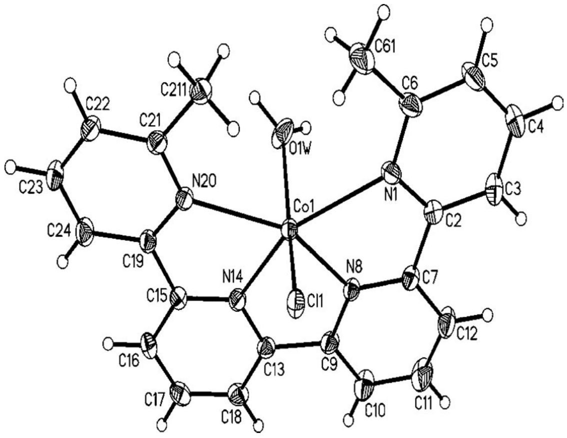


Figure 5. Perspective view of complex **4**; ellipsoids are drawn at the 50% probability level.

by H-bonding interactions involving the aqua ligands and the tetrafluoroborate anions.

In **4**, the helicity is less marked than that in **3** and involves only a slight twisting of the terminal rings. It appears that cations of the same chirality interlock to a significant extent through π stacking, whereas cations of opposite chirality are bridged by H-bonding involving the aqua ligands and tetrafluoroborate; the latter are less extensive than those in **3** because of the fact that one axial ligand is chloride and not water. In both **3** and **4**, the methyl groups lie at significantly different distances form the metal ion and it is conceivable that this could be indicative of an agostic interaction[32] between Co and one methyl group to make the metal seven coordinate in a pentagonal bipyramidal array. However, the distortions of the metal-ion donor-atom environment, particularly the bending of the O–Co–O and O–Co–Cl axes, could also be taken as indicative of a change from octahedral towards tetrahedral MN_2O_2 [or $MN_2O(Cl)$] binding, and observations on the Zn^{II} complexes of **L1** appear to support this interpretation.

Unsurprisingly, the structures of Zn^{II} complexes **5** (Figure 6) and **6** (Figure 7) closely resemble those of Co complexes **3** and **4**, respectively, and the dimensions of the MN_4 entities in particular are very similar (thus ensuring that the $Zn\cdots CH_3$ distances are very close to those of $Co\cdots CH_3$).

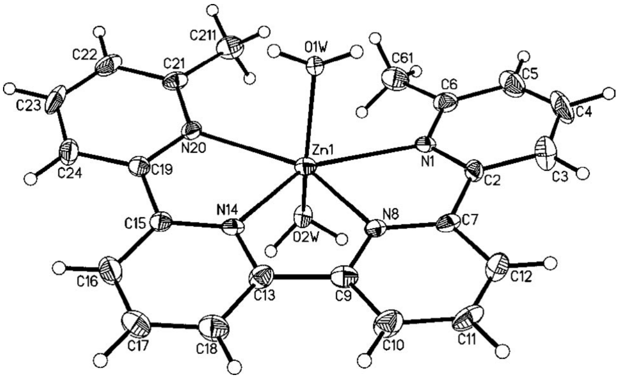


Figure 6. Perspective view of complex **5**; ellipsoids are drawn at the 50% probability level.

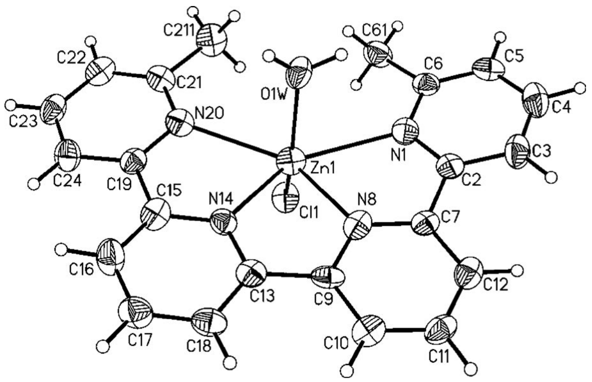
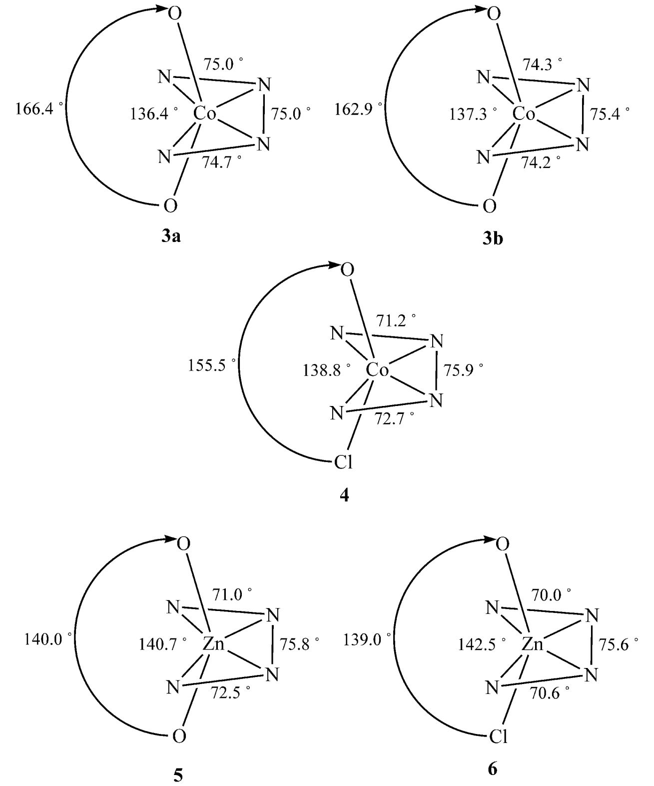


Figure 7. Perspective view of complex **6**; ellipsoids are drawn at the 50% probability level.

Where they do differ significantly is in the O–Zn–O and O–Zn–Cl angles of 140.0 and 139.0°, respectively, and the corresponding O–Co–O and O–Co–Cl angles are 166.3 and 155.5° (Figure 8). Thus, the Zn^{II} complexes can be said to show a much more marked distortion towards tetrahedral binding than their Co analogues, and because this is associated with a negligible change in $M\cdots CH_3$ distances, it is possible that agostic interactions are of no significance.

As with the Co^{II} complexes, helicity of the quaterpyridine is more obvious in diaqua complex **5** than in chloro–aqua complex **6**, though various features of both lattices can be associated with the chirality of the cations, and both solids are racemic compounds. Thus, a view of the lattice of **5** down the *a* axis shows pairs of cations that actually form columns parallel to the *a* axis. Enantiomer pairs within these columns interpenetrate through π stacking so that each half column is homochiral and its cations are all linked by double H-bond bridges involving the aqua ligands and triflate anions. In the lattice of **6**, a view down the *a* axis again can be interpreted in terms of pairs of cations forming columns parallel to the axis. Again, each half column is homochiral, with an infinite π-stacking array involving overlap of entities of alternating chirality, in such a way



3a **3b**

4

5 **6**

Figure 8. Bond angles within the primary coordination spheres of complexes **3**–**6** (bond lengths are given in Table 1). Note that for a pentagonal-planar ML_5 unit, the ideal bond angle would be 72°.

that aqua ligands alternate in projection from one face to the opposite of the column. Triflate anions then again form double H-bond bridges with these aqua ligands, necessarily resulting here in links between columns and in fact between cations of opposite chirality.

Within this context, the structure found for the Co^{II} complex **8** of **L2** is of particular significance (Figure 9). Despite different coligands and the conversion of the quaterpyridine methyl groups to ethoxycarbonyl units, the CoN_4 unit is very similar to that in **3** and **4**, and the ligand again is helical.

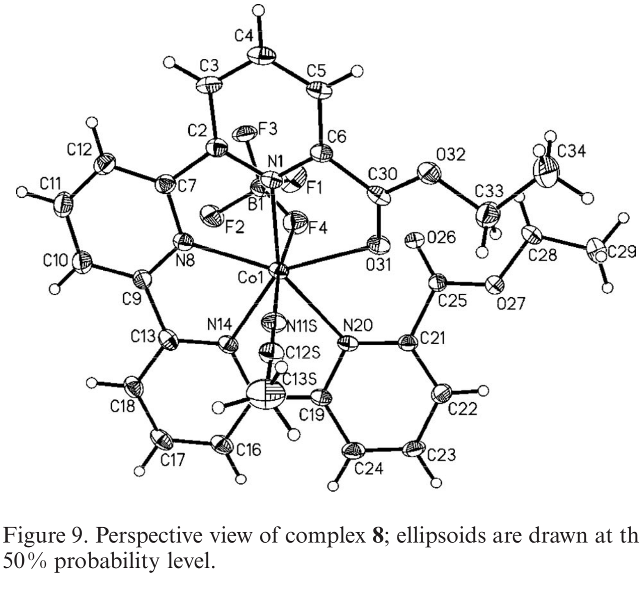


Figure 9. Perspective view of complex **8**; ellipsoids are drawn at the 50% probability level.

In the view of the lattice down the *c* axis, it is possible to discern pairs of cations forming columns (parallel to the *c* axis) in which centrosymmetric pairs appear to be bridged by reciprocal $CH_3\cdots\pi$ interactions involving the coordinated acetonitrile ligands, which thus gives a basic structure similar to those of Zn^{II} complexes **5** and **6**. However, the F–Co–N axis is much closer to linearity (171.9°) than in any of the complexes of **L1**, and it is clear that the Co^{II} ion forms a seventh bond to one carbonyl O atom of the ester groups, so that the coordination geometry can be described as that of a pentagonal bipyramid, which is not an unexpected arrangement for Co^{II}.[30] Thus, it would appear possible that agostic interactions giving seven-coordination occur within the complexes of **L1**, though additional experimental and theoretical work may be necessary to resolve the issue of when seven coordination may become preferred over a distortion towards tetrahedral four coordination (Figure 10).

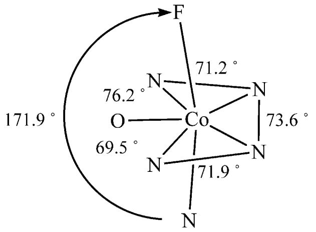


Figure 10. The near-pentagonal bipyramidal geometry of the coordination sphere in **8**.

Electronic Absorption Spectra and Luminescence Properties

All absorption and emission spectra of ligands **L1** and **L2** and their metal complexes were recorded at concentrations of 5×10^{-5} M in acetonitrile solution at room temperature. Although it is obvious from the colour of these solutions that the ligand remains bound to the metals, the stability constants are unknown, and it is possible that at 10^{-5} M, considerable dissociation of the species characterised in the solid state occurs.

The electronic absorption spectra in the UV region showed bands typical for $\pi\rightarrow\pi^*$ ligand-based transitions (Table 2, Figure 11). In the case of Cu^I complexes **1** and **7**, weaker broad bands observed at 450.0 and 446.8 nm are assigned to MLCT electronic transitions.[33] Ligands **L1** and **L2** and metal complexes **1**, **2**, **3**, **5**, **7** and **8** showed broad luminescence bands centred around 370 nm when irradiated by UV light (λ_{ex} = absorption band maximum). This suggests that the emission is mainly ligand based. **L1** and **L2** displayed broad emission bands at λ_{max} = 359 and 349 nm (λ_{ex} = 290 nm), respectively. The emission band maxima are redshifted by 19, 5, 8, 10, 10 and 18 nm for the solutions of compounds **1** (λ_{em} = 378 nm, λ_{ex} = 290 nm), **2** (λ_{em} = 364 nm, λ_{ex} = 300 nm), **3** (λ_{em} = 367 nm, λ_{ex} =

300 nm) **5** (λ_{em} = 369 nm, λ_{ex} = 296 nm), **7** (λ_{em} = 359 nm, λ_{ex} = 290 nm) and **8** (λ_{em} = 367 nm, λ_{ex} = 280 nm), respectively, relative to those of free **L1** and **L2**. These shifts are similar to those reported for complexes of 1,3,5-tris[*p*-(2,2′-dipyridylamino)phenyl]benzene and 2,2′bis(4,6-pyrimidinediyl)pyridine-6,6′-diethyl diamide with Zn^{II} ion[34] and significantly different from the emission maxima observed for the complexes formed from Zn^{II} and 4,6-bis(2′′,2′-bipyrid-6′-yl)-2-phenylpyrimidine[35] and between Ag^{I} and a pyridyl pendant-arm macrocyclic ligand.[36]

Table 2. The absorption maxima (λ_{max}, nm) and extinction coefficients (ε, $\times 10^4$ M^{-1} cm^{-1}; in parentheses) for studied compounds.

Compd.		π→π*
L1		252.0 (1.7), 292.5 (2.5)
L2		254.0 (2.1), 289.0 (2.4)
1	450.0 (0.25)[a]	252.0 (1.4), 291.0 (1.6)
2		299.0 (3.0), 315.0 (2.6)
3		303.5 (2.7), 340.0 (1.6)
4		302.5 (3.2), 339.0 (1.6)
5		266.0 (1.6), 296.0 (2.5), 305.0 (3.0), 343.5 (2.1)
7	446.8 (0.12)[a]	250.4 (4.1), 290.6 (5.0),
8		250.4 (2.3), 282.6 (2.2), 299.6 (2.4), 337.4 (0.9)

[a] MLCT electronic transitions.[33]

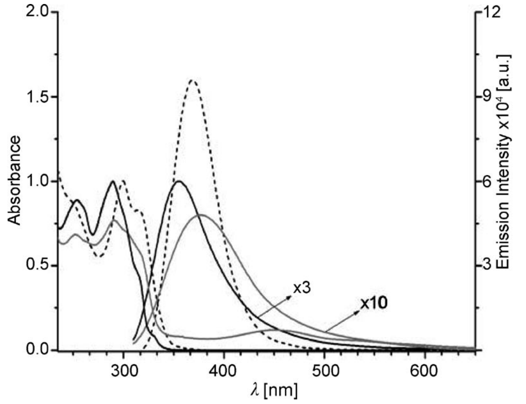


Figure 11. UV/Vis absorption and luminescence spectra of **L1** (solid, black), **1** (gray) and **2** (dash, black), in acetonitrile (1×10^{-5} M) at 298 K.

For compounds **1**, **3**, **7** and **8**, the intensity of the emission bands was much weaker than that of free **L1** and **L2** at the same concentration, which indicates that the Cu^{I} and Co^{II} ions partially quench the emission from **L1** and **L2**. The ligand-based luminescence intensity of compounds **1** and **3** was about four and three times lower than that of **L1** and for compounds **7** and **8** it was two times lower than that of **L2**. However, the intensity of the emission bands of **2** and **5** is much greater than that of the bands of **L1**. The Ag^{I} and Zn^{II} ions enhance the luminescence 5- and 20-fold, respectively. The quenching of emission **L1** and **L2** by Co^{II} and Cu^{I} is probably due to radiationless deactivation of the ligand-centred levels through low-energy charge transfer and MLCT excited states, whereas enhancement in the emission of Zn^{II} and Ag^{I} complexes is related to the rigidity of these complexes, which decreases the radiationless deactivation in comparison to the free ligands.[35] The quenching of luminescence in solution at room temperature by Co^{II} ions but retention in Ag^{I}, Cu^{I} and Zn^{II} complexes similar to the present ones has been previously observed.[33–37]

Conclusions

Quaterpyridine would appear to be a ligand rather delicately poised to enforce various coordination geometries on a metal ion. As shown by the present and other work,[20,21] substitution on the basic ligand framework can offer some degree of control of its coordination preferences. Given the ease of functionalisation at the 6,6′′′-positions illustrated by the present work and the possibility of coordinating the pendent species produced, presumably in a labile manner reflecting the ease of conversion between six- and seven-coordination, mononuclear complexes of such quaterpyridines may have various applications in catalysis. We are currently investigating the degree and selectivity of activation of the ester group in complex **8**.

Experimental Section

General: The metal salts were used without further purification as supplied from Aldrich. NMR spectra were obtained with a Varian Gemini 300 MHz spectrometer and were calibrated against the residual protonated solvent signals ($CDCl_3$: δ = 7.24 ppm; [D$_6$]-DMSO: δ = 2.50 ppm; CD_3CN: δ = 1.94 ppm) and are given in ppm. Mass spectra for acetonitrile solutions $\approx 10^{-4}$ M were determined by 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 µL 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 to 1000 for 6 s, and 10 scans were summed to obtain the final spectrum. Microanalyses were obtained by using a Perkin–Elmer 2400 CHN microanalyser. 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 by using 10^{-5} M solutions with respect to the metal ion. Excitation and emission spectra were measured at room temperature with a Perkin–Elmer MPF3 spectrofluorimeter with excitation and emission slits at 10 nm.

Ligand L1: To a mixture of 2-(6-methylpyridin-2-yl)-6-(trimethylstannyl)pyridine (1.541 g, 4.8 mmol), 4,6-dichloropyrimidine (0.276 g, 1.9 mmol), LiCl (0.500 g, 11.8 mmol) and $Pd(PPh_3)_4$ (0.100 g, 0.1 mmol) was gradually added degassed toluene (25mL) by syringe under an argon atmosphere. The reaction mixture was stirred and heated at reflux for 24 h, and then the toluene was evaporated under reduced pressure. The residue was purified by column chromatography on alumina (dichloromethane/hexane, 7:3) to afford 0.146 g (24%) of compound **L1**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, *J* = 7.6 Hz, 2 H), 8.46 (t, *J* = 7.6 Hz, 2 H), 7.98 (t, *J* = 7.6 Hz, 2 H), 7.76 (d, *J* = 7.6 Hz, 2 H), 7.41 (d, *J* = 7.6 Hz, 2 H), 7.22 (d, *J* = 7.5 Hz, 2 H), 2.67 (s, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.68, 157.85, 155.68, 155.58, 137.71, 137.03, 123.29, 121.00, 120.87, 118.17, 29.62 ppm. IR (KBr): $\tilde{\nu}$ = 3054, 2918, 1615, 1567, 1465, 1369, 1267, 1113, 1075, 994, 903, 829, 781, 641, 634, 420 cm^{-1}. MS (FAB): *m*/*z* (%) = 339.3 (100) $[M]^+$. UV/Vis (CH_3Cl): λ = 251, 292.5 nm. $C_{22}H_{18}N_4$ (338.41): calcd. C 78.08, H 5.36, N 16.56; found C 78.02, H 5.37, N 16.51.

A: Product **L1** (0.167 g, 0.49 mmol) was added to concentrated H_2SO_4 (10 mL) and cooled to 0 °C with stirring in an ice bath. Chromium(VI) oxide (0.296 g, 49 mmol) was then added in 0.1-g portions to the stirred solution of **2** at a rate that maintained the reaction temperature below 3 °C. When the addition of CrO_3 was complete (about 5 h), the mixture was stirred for 48 h at room temperature. The viscous reaction solution was then poured onto excess crushed ice and stirred for 2 h. The precipitate was isolated by suction filtration, washed with distilled water and air dried to yield 0.050 g (26%) of **A**. ^1H NMR (300 MHz, $[D_6]DMSO$): δ = 12.50 (s, 2 H, OH), 8.95 (d, *J* = 5.6 Hz, 2 H), 8.25 (d, *J* = 4.7 Hz, 4 H), 8.07 (m, *J* = 4.7 Hz, 4 H), 7.57 (t, *J* = 5.6 Hz, 2 H) ppm. $C_{22}H_{14}N_4O_4$ (398.37): calcd. C 66.33, H 3.54, N 14.06; found C 66.57, H 3.42, N 14.13.

B: Compound **A** (0.050 g, 0.125 mmol) was heated at reflux for 8 d in thionyl chloride (15 mL), and the solvent was then evaporated under reduced pressure. Crude **B** was used immediately for the subsequent synthesis of diester **L2**.

Ligand L2: EtOH (30 mL) was added to **B**, and the resulting mixture was heated at reflux for 20 h and then cooled to room temperature. The volume was then reduced to 8 mL under reduced pressure, and the mixture was cooled in an ice bath. The crystalline solid that precipitated was collected by suction filtration, washed with a small quantity of ice-cold EtOH and air dried to yield 0.022 g (39%) of **L2** as a white powder. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.88 (d, *J* = 8.1 Hz, 2 H), 8.71 (d, *J* = 7.8 Hz, 2 H), 8.67 (d, *J* = 8.1 Hz, 2 H), 8.19 (d, *J* = 7.8 Hz, 2 H), 8.06 (t, *J* = 8.1 Hz, 2 H), 8.05 (t, *J* = 7.8 Hz, 2 H), 4.56 (q, *J* = 7.2 Hz, 4 H), 1.55 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.36, 156.39, 155.29, 154.48, 147.81, 137.97, 137.81, 125.00, 124.21, 121.72, 121.54, 61.90, 14.34 ppm. IR (KBr): $\tilde{\nu}$ = 3456, 3060, 2982, 2929, 2008, 1855, 1736, 1706, 1578, 1566, 1463, 1432, 1370, 1269, 1134, 1070, 993, 806, 765, 687, 637, 418 cm^{-1}. MS (FAB): *m*/*z* (%) = 456 (100) [**L2** + H]. MS (ESI): *m*/*z* (%) = 493 (50) $[K(\mathbf{L2})]^+$, 478 (100) $[Na(\mathbf{L2})]^+$, 456 (5) $[H(\mathbf{L2})]^+$. $C_{26}H_{22}N_4O_4$ (454.48): calcd. C 68.71, H 4.88, N 12.33; found C 67.26, H 4.52, N 11.53.

Cu^I Complex 1: A mixture of $[Cu(CH_3CN)_4]PF_6$ (6.4 mg, 17 µmol) and ligand **L1** (5.8 mg, 17 µmol) in CH_3CN/CH_2Cl_2 (1:1, 10 mL) was stirred at room temperature for 48 h. The solvent was evaporated under reduced pressure to give quantitative yield of **1** as a purple powder. ^1H NMR (300 MHz, CD_3CN): δ = 7.91 (m, *J* = 6.6 Hz, 4 H), 7.77 (t, *J* = 7.8 Hz, 4 H), 7.57 (d, *J* = 8.1 Hz, 2 H), 7.29 (d, *J* = 6.3 Hz, 2 H), 2.35 (s, 6 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3420, 3115, 3083, 2924, 2854, 1997, 1734, 1653, 1605, 1595, 1571, 1564, 1472, 1450, 1420, 1388, 1334, 1256, 1173, 1108, 1015, 908, 840, 787, 751, 737, 654, 634, 556, 434 cm^{-1}. MS (ESI): *m*/*z* (%) = 401 (100) $[Cu_2(\mathbf{L1})_2]^{2+}$. $[Cu_2(\mathbf{L1})_2](PF_6)_2$ (1093.84): calcd. C 48.31, H 3.32, N 10.24; found C 48.30, H 3.39, N 10.24.

Ag^I Complex 2: A solution of ligand **L1** (8.1 mg, 24 µmol) and $AgBF_4$ (4.7 mg, 24 µmol) in CH_3CN/CH_2Cl_2 (1:1, 10 mL) was stirred at room temperature for 48 h. Colourless complex **2** was isolated in quantitative yield by evaporation of the solvent. ^1H NMR (300 MHz, CD_3CN): δ = 8.00 (m, *J* = 2.2 Hz, 4 H), 7.85 (t, *J* = 7.6 Hz, 4 H), 7.78 (d, *J* = 7.8 Hz, 2 H), 7.20 (d, *J* = 7.3 Hz, 2 H), 2.17 (s, 6 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2924, 2009, 1734, 1595, 1568, 1467, 1439, 1380, 1299, 1269, 1252, 1177, 1112, 1084, 1009, 829, 781, 738, 641, 533, 420 cm^{-1}. MS (ESI): *m*/*z* (%) = 445 (100) $[Ag_2(\mathbf{L1})_2]^+$. $Ag_2(\mathbf{L1})_2(BF_4)_2{\cdot}2CH_3CN$ (1148.28): calcd. C 50.21, H 3.69, N 12.20; found C 49.98, H 3.60, N 12.25.

Co^{II} Complex 3: A mixture of $Co(BF_4)_2{\cdot}6H_2O$ (4.53 mg, 13.3 µmol) and **L1** (4.5 mg, 13.3 µmol) in CH_3CN/CH_2Cl_2 (1:1, 10 mL) was stirred at room temperature for 48 h. Pale-pink complex **3** was isolated in quantitative yield by evaporation of the solvent. IR (KBr): $\tilde{\nu}$ = 3438, 3109, 2925, 2854, 1714, 1653, 1605, 1578, 1489, 1472, 1420, 1378, 1273, 1248, 1195, 1084, 1020, 837, 792, 768, 740, 653, 522, 482, 438 cm^{-1}. MS (ESI): *m*/*z* (%) = 199 (100) $[Co(\mathbf{L1})]^{2+}$. $Co(\mathbf{L1})(BF_4)_2{\cdot}2H_2O$ (606.99): calcd. C 43.53, H 3.65, N 9.23; found C 44.88, H 3.49, N 9.25.

Co^{II} Complex 4: A solution of ligand **L1** (9.7 mg, 28 µmol), $Co(BF_4)_2{\cdot}6H_2O$ (3.3 mg, 14 µmol) and $CoCl_2{\cdot}6H_2O$ in CH_3CN/CH_2Cl_2 (1:1, 10 mL) was stirred at room temperature for 48 h. The solvent was evaporated under reduced pressure to give quantitative yield of **4** as a yellow powder. IR (KBr): $\tilde{\nu}$ = 3448, 3110, 2927, 2854, 1715, 1657, 1608, 1579, 1492, 1470, 1409, 1377, 1270, 1243, 1190, 1079, 1025, 838, 796, 766, 741, 653, 520, 481, 436 cm^{-1}. MS (ESI): *m*/*z* (%) = 199 (100) $[Co(\mathbf{L1})]^{2+}$. $Co(\mathbf{L1})(BF_4)Cl{\cdot}H_2O$ (537.61): calcd. C 49.15, H 3.75, N 10.42; found C 49.88, H 3.49, N 10.25.

Zn^{II} Complex 5: A solution of ligand **L1** (8.1 mg, 24 µmol) and $Zn(CF_3SO_3)_2$ (8.7 mg, 24 µmol) in CH_3CN/CH_2Cl_2 (1:1, 10 mL) was stirred at room temperature for 48 h. White complex **5** was isolated in quantitative yield by evaporation of the solvent. ^1H NMR (300 MHz, CD_3CN): δ = 8.6 (d, *J* = 8.7 Hz, 2 H), 8.5 (d, *J* = 7.0 Hz, 2 H), 8.1 (t, *J* = 5.5 Hz, 4 H), 7.6 (d, *J* = 7.6 Hz, 2 H), 7.5 (d, *J* = 6.6 Hz, 2 H), 2.0 (s, 6 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3339, 3106, 2924, 2852, 2002, 1662, 1600, 1579, 1487, 1470, 1452, 1378, 1287, 1252, 1167, 1110, 1031, 825, 794, 760, 635, 572, 515, 437 cm^{-1}. MS (ESI): *m*/*z* (%) = 551 (80) $[Zn(\mathbf{L1})(CF_3SO_3)]^+$, 201 (100) $[Zn(\mathbf{L1})]^{2+}$. $Zn(\mathbf{L1})(CF_3SO_3)_2{\cdot}2H_2O$ (737.95): calcd. C 39.06, H 3.00, N 7.59, S 8.69; found C 39.63, H 3.25, N 7.68, S = 8.55.

Zn^{II} Complex 6: A solution of ligand **L1** (16 mg, 47.2 µmol), $Zn(CF_3SO_3)_2$ (8.6 mg, 23.6 µmol) and $ZnCl_2$ (3.2 mg, 23.6 µmol) in CH_3CN/CH_2Cl_2 (1:1, 10 mL) was stirred at room temperature for 48 h. Colourless complex **6** was isolated in quantitative yield by evaporation of the solvent. ^1H NMR (300 MHz, CD_3CN): δ = 8.6 (d, *J* = 8.7 Hz, 2 H), 8.5 (d, *J* = 7.0 Hz, 2 H), 8.1 (t, *J* = 5.5 Hz, 4 H), 7.6 (d, *J* = 7.6 Hz, 2 H), 7.5 (d, *J* = 6.6 Hz, 2 H), 2.0 (s, 6 H, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3341, 3108, 2920, 2851, 2012, 1672, 1601, 1578, 1488, 1470, 1452, 1378, 1286, 1253, 1168, 1111, 1032, 823, 790, 763, 630, 571, 514, 427 cm^{-1}. MS (ESI): *m*/*z* (%) = 551 (80) $[Zn(\mathbf{L1})(CF_3SO_3)]^+$, 437 (20) $[Zn(\mathbf{L1})Cl]^+$, 201 (100) $[Zn(\mathbf{L1})]^{2+}$. $Zn(\mathbf{L1})(CF_3SO_3)Cl{\cdot}H_2O$ (606.31): calcd. C 45.56, H 3.32, N 9.24, S 5.29; found C 45.63, H 3.25, N 9.68, S 5.11.

Cu^I Complex 7: A mixture of $[Cu(CH_3CN)_4]PF_6$ (5 mg, 13 µmol) and ligand **L2** (6 mg, 13 µmol) in acetonitrile (3 mL) was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure to give quantitative yield of **7** as a dark-brown powder. ^1H NMR (300 MHz, CD_3CN): δ = 8.23 (d, *J* = 6.6 Hz, 2 H), 8.16 (t, *J* = 7.4 Hz, 2 H), 8.02 (d, *J* = 6.0 Hz, 2 H), 7.98 (d, *J* = 7.3 Hz, 2 H), 7.85 (t, *J* = 7.6 Hz, 2 H) 7.58 (d, *J* = 6.7 Hz, 2 H) 3.72 (q, *J* = 7.2 Hz, 4 H) 1.95 (t, *J* = 2.4 Hz, 6 H) ppm. IR (KBr): $\tilde{\nu}$ = 3364, 3194, 2924, 2852, 2006, 1732, 1660, 1633, 1594, 1572, 1469, 1432, 1368, 1291, 1250, 1191, 1153, 1021, 844, 807, 765, 687, 637, 557, 419 cm^{-1}. MS (ESI): *m*/*z* (%) = 517 (100) $[Cu_2(\mathbf{L2})_2]^{2+}$. $[Cu_2(\mathbf{L2})_2](PF_6)_2{\cdot}7H_2O$ (1324.09): calcd. C 47.17, H 4.42, N 8.46; found C 47.28, H 4.47, N 8.57.

Co^{II} Complex 8: To ligand **L2** (6 mg, 13 µmol) in CH_3CN (3 mL) was added $Co(BF_4)_2{\cdot}6H_2O$ (2.25 mg, 6.5 µmol) and $Co(NO_3)_2{\cdot}6H_2O$ (1.89 mg, 6.5 µmol). The mixture was stirred at room temperature for 24 h. Pale-pink complex **8** was isolated in quantitative yield by evaporation of the solvent. IR (KBr): $\tilde{\nu}$ = 3360, 3160, 2982, 2929, 2009, 1749, 1736, 1706, 1578, 1566, 1463, 1432, 1383, 1370, 1269, 1134, 1070, 993, 824, 806, 765, 687, 637, 418 cm^{-1}. MS (ESI): *m*/*z* (%) = 257 (100) [Co(**L2**)]$^{2+}$. Co(**L2**)$(BF_4)_2{\cdot}2CH_3CN$ (810.19): calcd. C 47.44, H 3.86, N 12.10; found C 47.25, H 3.84, N 12.17.

Crystal Structure Determination of Complexes: Data were collected at 100 (**1**, **3**–**6**), 200 (**7**, **8**) and 295 K (**2**) by the ω-scan technique in the θ range of 2–30° with a KUMA KM4CCD four-circle diffractometer equipped with a CCD detector[38] by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Accurate cell parameters were determined by the least-squares fit of 3335, 7179, 5946, 4280, 6215, 7125, 3250 and 2940 reflections (for complexes **1**–**8**) of highest intensity chosen from the complete dataset. Data were corrected for Lorentz-polarization effects and for absorp-

Table 3. Crystal data, data collection and structure refinement.

	1	2	3	4
Formula	$C_{44}H_{36}Cu_2N_8{\cdot}2PF_6$	$C_{44}H_{36}Ag_2N_8{\cdot}2(BF_4){\cdot}2(C_2H_3N)$	$C_{22}H_{22}CoN_4O_2{\cdot}2BF_4$	$C_{22}H_{20}ClCoN_4O{\cdot}BF_4$
Formula weight	1093.84	1148.28	606.99	537.61
Crystal system	hexagonal	monoclinic	monoclinic	monoclinic
Space group	$P6_222$	$C2/c$	$P2_1/n$	$P2_1/c$
a [Å]	14.850(1)	29.6191(18)	19.3185(4)	12.3042(8)
b [Å]	14.850(1)	7.9784(8)	14.4729(2)	10.9333(6)
c [Å]	16.963(1)	22.9286(12)	19.3243(4)	16.3813(9)
α [°]	90	90	90	90
β [°]	90	116.086(5)	113.349(2)	95.829(5)
γ [°]	120	90	90	90
V [Å^3]	3239.6(4)	4866.4(7)	4960.51(18)	2192.3(2)
Z	3	4	8	4
D_x [g cm^{-3}]	1.68	1.57	1.63	1.63
F(000)	1656	2304	2456	1092
μ [mm^{-1}]	1.16	0.88	0.78	0.96
Crystal size [mm]	0.5,0.4,0.15	0.6,0.2,0.2	0.3,0.2,0.1	0.3,0.2,0.1
Θ range [°]	3–30	2.7–26.0	2.3–29.8	2.7–29.2
Reflections:				
Collected	30611	19643	49032	10975
Unique (R_{int})	2965 (0.016)	4777 (0.036)	12861 (0.032)	4953 (0.022)
Final R(F) [$I > 3\sigma(I)$]	0.019	0.046	0.043	0.038
Final $wR(F^2)$ [$I > 3\sigma(I)$]	0.051	0.128	0.101	0.099
Goodness of fit	1.04	1.07	1.07	1.08
Max/min $\Delta\rho$ [e Å^{-3}]	0.20/–0.48	2.04/–0.75	1.08/–0.67	1.58/–0.57

Table 4. Crystal data, data collection and structure refinement.

	5	6	7	8
Formula	$C_{22}H_{22}N_4O_2Zn{\cdot}2CF_3O_3S$	$C_{22}H_{20}ClN_4OZn{\cdot}CF_3O_3S$	$C_{52}H_{44}Cu_2N_8O_8{\cdot}7(H_2O){\cdot}PF_6$	$C_{28}H_{25}BCoF_4N_5O_4{\cdot}BF_4{\cdot}2(C_2H_3N)$
Formula weight	737.95	606.31	1307.11	810.19
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Ibam*	$P\bar{1}$
a [Å]	8.4897(13)	9.376(2)	15.117(3)	11.652(2)
b [Å]	12.322(2)	11.256(3)	16.090(3)	12.482(2)
c [Å]	15.069(3)	12.313(3)	25.965(5)	14.551(3)
α [°]	71.677(15)	80.185(19)	90	72.07(2)
β [°]	82.866(14)	79.12(2)	90	68.07(2)
γ [°]	77.478(14)	89.343(19)	90	88.10(2)
V [Å^3]	1458.2(5)	1257.2(5)	6315(2)	1859.8(6)
Z	2	2	4	2
D_x [g cm^{-3}]	1.68	1.60	1.38	1.45
F(000)	748	616	2692	826
μ [mm^{-1}]	1.08	1.23	0.78	0.55
Crystal size [mm]	0.15,0.1,0.1	0.15,0.1,0.1	0.3,0.2,0.1	0.6,0.15,0.1
Θ range [°]	2.6–29.7	2.9–25.0	1.9–25.0	1.9–25.0
Reflections:				
Collected	15048	9913	16022	11640
Unique (R_{int})	7373 (0.059)	4402 (0.114)	2826 (0.095)	5993 (0.046)
Final R(F) [$I > 3\sigma(I)$]	0.050	0.069	0.089	0.058
Final $wR(F^2)$ [$I > 3\sigma(I)$]	0.079	0.146	0.223	0.136
Goodness of fit	0.94	1.05	1.84	1.07
Max/min $\Delta\rho$ [e Å^{-3}]	0.85/–0.73	0.70/–0.90	0.93/–0.83	0.55/–0.48

tion.[38] The structures were solved by direct methods with SIR-92[39] and refined with SHELXL-97.[40] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms in **1** were found in difference Fourier maps and isotropically refined. In all other compounds, hydrogen atoms from water molecules were found in the difference Fourier maps, and all others were placed at calculated positions, then refined by using a riding model with their isotropic thermal parameters set to 1.2 (1.5 for methyl groups) times the $U_{\text{eq.}}$ of the appropriate carrier atom. In the structures of **2**, **3** and **8**, some of the anions were found disordered; the alternative positions for the atoms were determined and refined with weak constraints. In **7**, the residual electron density around the mirror plane was interpreted as the layer of disordered water molecules (isotropically refined). No attempts were made to determine the positions of hydrogen atoms of these water molecules. Relevant crystal data and refinement details are listed in Tables 3 and 4. CCDC-673685, -673686, -673687, -673688, -673689, -673690, -673691 and -673692 (for complexes **1**–**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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