The Coordination Chemistry of 3,3′-Diamino-2,2′-bipyridine and Its Dication: Exploring the Role of the Amino Groups by X-ray Crystallography

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The synthesis and structural chemistry of a series of new divalent transition metal complexes of the bis-bidentate ligand 3,3′-diamino-2,2′-bipyridine (**L1**) and its dication $\mathbf{L1H_2}$ are described. Ligand **L1** reacts with salts of divalent transition metals to afford the (1:1) metal-ligand complexes (**2a**–**2d**) as well as the tris complexes (**3a**–**3f**). All complexes were fully characterised by spectroscopic methods and the following compounds $[Cu(\mathbf{L1})Cl_2]_2$ (**2a**), $[Cu(\mathbf{L1})(OAc)_2]$ (**2b**), $[Zn(\mathbf{L1})_3][OTf]_2$ (**3a**), and $[Zn(\mathbf{L1})_3][ZnCl_4]$ (**3e** and **3f**) were structurally characterised. Results from single crystal X-ray diffraction measurements indicate that formation of an intramolecular hydrogen bond between the two amino groups allows the ligand to coordinate divalent metal ions through their diimine binding sites. Furthermore, the structure of compound **2a** reveals that it crystallises as a dimer in which each copper ion is bound to two pyridine nitrogen atoms and two chloride ions in a distorted square planar arrangement, with a long axial contact from a neighbouring amino group completing the approximately square-pyramidal geometry at Cu^{II}. Complexation of this ligand in acidic conditions afforded the compound $[Cu(\mathbf{L1H_2})Cl_4]$ (**4**), as well as the two salts $[\mathbf{L1H_2}][CuCl_4]$ (**5a**) and $[\mathbf{L1H_2}][ZnCl_4]$ (**5b**). All three compounds have been structurally characterised and results indicate that the dication ($\mathbf{L1H_2}$) displays a different coordination preference for the chelation of metal ions. In all three cases, both of the heterocyclic N atoms of the ligand are protonated, thus preventing chelation to the metal ion, although for compound **4** crystallographic studies reveal that the two amino functionalities coordinate the copper(II) ion.

Introduction

The construction of multicomponent molecular systems represents an important first step in the development of novel molecular and supramolecular systems for catalysis, light-to-energy conversion, and molecule-based devices. For systems in which the components are transition metal ions, the emphasis lies in the design of the bridging ligands as well as on the choice of the metal ions. Consequently, the careful choice of bridging ligands, as suitable linkers for transition metal ions in a wide variety of oxidation states, is currently viewed as a critical element in successful design. One of the simplest but most widely used organic linkers is the bidentate ligand 2,2′-bipyridine. In recent years, this ligand has been incorporated into a huge diversity of supramolecular inorganic architectures including helices, ladders, grids and chains.[1] Furthermore, chemical modification of the 2,2′-bipyridine ligand by the introduction of additional functionality at the 4-, 5- and 6-positions is well-known, and the coordination chemistry of these compounds has been actively explored. In contrast, however, much fewer 3,3′-disubstituted bipyridines are available and the coordination chemistry of only a small number of such compounds has been studied. This is primarily due to the expectation that van der Waals repulsions between large substituents in the 3,3′-positions could prevent the pyridine rings from adopting a near *cis*-coplanar conformation, rendering them unfavourable ligands for chelation. Nevertheless, small substituents in the 3 and 3′ positions such as methyl groups,[2] carboxylic acids,[3,4] and methyl esters[5] have all been reported not to inhibit the binding of a metal ion to the diimine binding site, despite the fact that the pyridine rings in these systems are indeed displaced from co-planarity by 30−35°. Furthermore, in the early 1980's Rebek et al. were able to successfully exploit the 3,3′-substitution positions for the preparation of a novel crown ether derivative which bound transition metal ions at the diimine site, or alkali metal ions at the crown ether.[6]

Dinuclear complexes in which the metal fragments are joined by an appropriate bridging organic ligand have been of particular interest with a view to the preparation of vari-

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ous types of organometallic frameworks. Indeed, the dual coordinating ability of the oxalate ion (ox = $C_2O_4^{2-}$) has made it a particularly versatile bridging species for the controlled self-assembly of one-, two- and three-dimensional inorganic architectures.[7] Along these lines, with a view to prepare novel coordination polymers, we have recently turned our attention to study the coordination behaviour of the potentially ambidentate ligand 3,3′-diamino-2,2′-bipyridine (**L1**). This ligand has two possible modes for binding namely, symmetric and asymmetric (Figure 1).

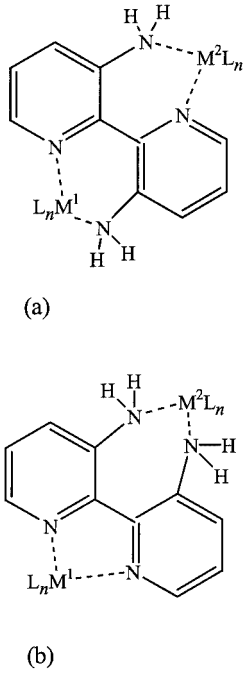


Figure 1. Potential symmetric (a) and asymmetric (b) binding modes of ligand **L1**

Since only one coordination compound incorporating ligand **L1** has been previously characterised by X-ray crystallography,[8] we have primarily set out to investigate the coordination chemistry of this compound and determine: (i) which pair of nitrogen atoms are preferred for coordination, (ii) whether the second pair of nitrogen atoms can contribute to the coordination in any way, and (iii) to what degree the substituents influence the angle between the planes of the pyridine rings.

Results and Discussion

Ligand Synthesis

The synthesis of **L1** has been achieved by two independent routes. The first method involves the preparation of 3,3′-dinitro-2,2′-bipyridine following the Ullman coupling procedure, first described by MacBride et al.[9] This was then followed by a reduction step to afford ligand **L1**. Unfortunately, the reaction conditions described by MacBride proved to be problematic, giving poor yields of a very insoluble material that was difficult to purify. After carefully monitoring the progress of the reaction, we found that it was only necessary to heat the reaction mixture for 2.5 h (cf. 15 h in the original literature).[8] The warm reaction mixture could then be poured directly into water and filtered immediately, washing with concentrated ammonia solution. This process essentially removes any insoluble impurities on the sinter, and the product which precipitates from the filtrate on cooling is easily extracted into hot dioxane, giving 3,3′-dinitro-2,2′-bipyridine in good yield. This compound is then readily reduced with Sn^{II}/HCl to afford ligand **L1**. Since the initial preparation of the dinitro precursor proved to be problematic, a second route to **L1** was also investigated. This involves the Ullman coupling of 3-acetylamino-2-chloropyridine following the route of Kaczmarek et al.,[10] followed by acidic hydrolysis to afford **L1** in substantially improved yields.

Syntheses of Metal Complexes of L1

An overview of the prepared metal complexes is provided in Scheme 1.

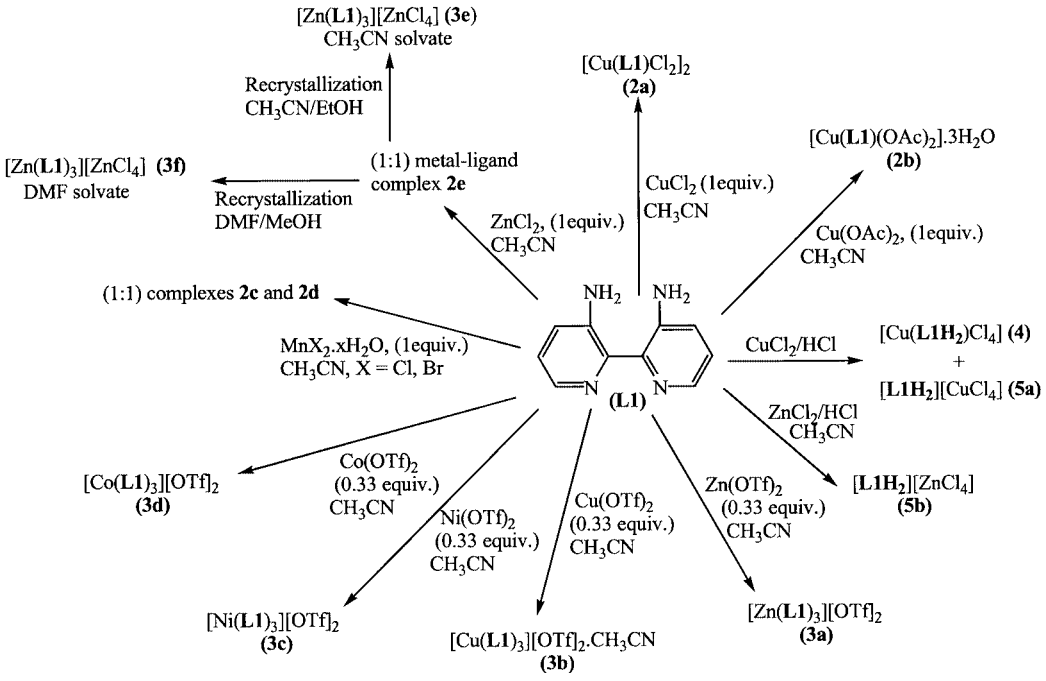
The complexation reactions can be divided up into three classes: (i) binding to metal salts through the diimine nitrogens, (ii) tris complexation by binding to the diimine nitrogens, and (iii) binding of the bis-protonated ligand $\mathbf{L1H_2}$ to a metal through the amino groups. The first class involves reaction of an acetonitrile solution of the ligand **L1** with one equivalent of a salt of a divalent metal, M^{II} = Cu, Mn, Zn. This afforded a range of complexes with 1:1 ligand-to-metal ratios, namely compounds **2a**−**2e**. From the microanalysis data of complex **2a**, we could deduce that ligand **L1** forms a 1:1 complex with copper(II) chloride, although the crystal structure later revealed that **2a** actually crystallises as an unusual 2:2 centrosymmetric complex of ligand **L1** and copper(II) chloride (Figure 2a).

The ligand **L1** binds copper through the diimine coordination site, and dimers are formed by a pair of bonds from neighbouring amino groups.

Copper(II) acetate forms a variety of structures with unsubstituted 2,2′-bipyridine. The formation of multinuclear systems containing two or three copper ions,[11,12,13] polymers[14] and a mononuclear cation[15] $[Cu(bipy)_2(acetate)]^+$ are facilitated by the possibility of acetate either acting as a bidentate ligand, or using one oxygen atom to bridge two metal centres. To determine in our case whether or not the amino groups of 3,3′-diamino-2,2′-bipyridine would also contribute to the coordination of the copper ion, complex **2b** was prepared and its structure determined by X-ray crystallography. The molecular structure of **2b** is shown in Figure 3.

The diimine binding site of the bipyridine together with two acetate ligands are bound to the copper ion, thus enabling us to conclude that the amino groups are not involved in coordination to the copper ion when the bidentate acetate ligands can each provide two donor atoms.

Reactions of ligand **L1** with manganese(II) chloride or manganese(II) bromide also gave compounds with 1:1 metal-to-ligand ratios, although crystals suitable for single crystal X-ray diffraction could not be grown to-date. Never-



Scheme 1. An overview of the coordination chemistry of **L1**

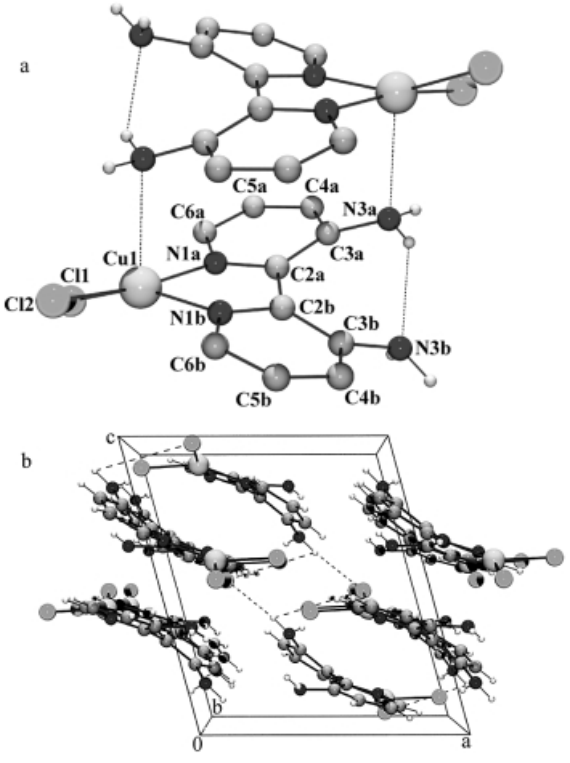


Figure 2. a) The dimeric structure of **2a**; selected distances [Å] and angles [°]: N(1A)−Cu 1.998(2), N(1B)−Cu 2.105(3), N(3A′)−Cu 2.625(3) (dotted line), Cl(1)−Cu 2.2565(10), Cl(2)−Cu 2.2880(8); N(1A)−Cu−N(1B) 80.94(10), N(1A)−Cu−Cl(1) 94.50(8), N(1A)−Cu−Cl(2) 169.32(8), N(1B)−Cu−Cl(1) 156.29(8), N(1B)−Cu−Cl(2) 94.84(7), Cl(1)−Cu−Cl(2) 93.20(3), N(1A)−Cu−N(3A′) 86.04(7), N(1B)−Cu−N(3A′) 91.62(8), Cl(1)−Cu−N(3A′) 111.36(10), Cl(2)−Cu−N(3A′) 84.27(8); b) The molecular packing arrangement for **2a**; dashed lines indicate the intermolecular hydrogen bond between H(31B) and a neighbouring chlorine atom H(31B)···Cl = 2.47 Å

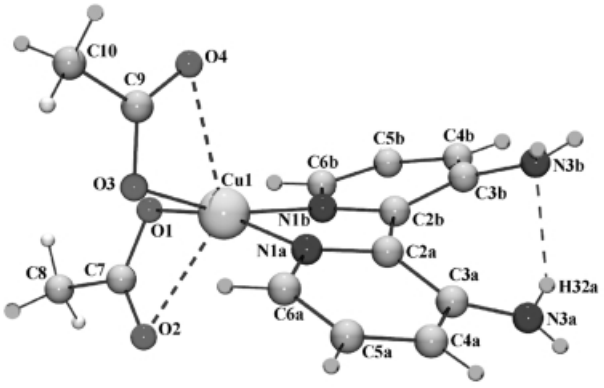


Figure 3. Molecular structure of **2b**; selected distances [Å] and angles [°]: N(1A)−Cu 1.969(5), N(1B)−Cu 1.985(5), O(1)−Cu 1.961(4), O(2)−Cu 2.616(5), O(3)−Cu 1.959(5), O(4)−Cu 2.571(6); N(1A)−Cu−N(1B) 82.05(19), N(1A)−Cu−O(1) 164.72(19), N(1A)−Cu−O(2) 110.77(17), N(1A)−Cu−O(3) 93.6(2), N(1A)−Cu−O(4) 100.45(20), N(1B)−Cu−O(1) 95.6(2), N(1B)−Cu−O(2) 104.93(18), N(1B)−Cu−O(3) 162.85(19), N(1B)−Cu−O(4) 108.32(19), O(1)−Cu−O(2) 55.10(16), O(1)−Cu−O(3) 92.9(2), O(1)−Cu−O(4) 94.64(19), O(2)−Cu−O(3) 92.14(18), O(2)−Cu−O(4) 136.85(18), O(3)−Cu−O(4) 55.99(18)

theless, we would expect the manganese(II) to favour an octahedral coordination, which could be completed by bridging halides in a similar manner to the salt formed between manganese(II) chloride and 2,2′-bipyridine, in which both chlorides bridge two neighbouring Mn^{II} ions.[16] Reactions of ligand **L1** with one equivalent of zinc(II) chloride in acetonitrile yielded complex **2e** whose chemical analysis suggested a 1:1 ratio of ligand to metal salt. These results parallel the reaction of unsubstituted 2,2′-bipyridine with zinc(II) chloride which forms a simple four-coordinate 1:1 complex.[17] In contrast, X-ray diffraction studies showed

that crystals grown from an acetonitrile/ethanol solution of the 1:1 complex **2e** belong to the second class of coordination compounds, i.e. that **3e** is the Zn^{2+} tris complex of **L1** with a tetrachlorozincate counterion. Similarly, crystals grown from **2e** in DMF/methanol were shown by X-ray crystallography to be a DMF solvate **3f** whose asymmetric unit contains three tris complexes each hydrogen bonded to one DMF solvent molecule. The closely related tris complex **3a** was prepared by reaction of zinc(II) triflate with three equivalents of **L1**. From these observations we can conclude that compound **2e** can readily rearrange in solution to afford a tris complex. Reaction of three equivalents of ligand **L1** with copper(II), nickel(II) or cobalt(II) triflates afforded the second series of 3:1 compounds, namely the tris complexes **3b**−**3d**.

Under acidic conditions it is reasonable to expect the coordination chemistry of ligand **L1** to change significantly as the more basic pair of nitrogens is protonated. Judging from the pK_b's of aniline (4.6) and pyridine (5.0) the amino nitrogen atoms would be expected to be slightly more basic; however, the crystalline salts of 3-aminopyridine are protonated on the ring nitrogen atom.[18,19] The pK_b's of the two nitrogen sites are probably quite similar. If the amino groups are protonated, metal ion binding at the diimine site may be disfavoured since there would be repulsions between the two positively charged ammonium groups in the 3- and 3′ positions. Protonation of the ring nitrogen atoms would leave open the possibility of metal ion binding to the amino groups, forming a less favourable seven-membered chelate ring.

Reaction of **L1** with copper(II) chloride in dilute hydrochloric acid yielded a third class of compound, namely complex **4**. In this case, both heterocyclic nitrogen atoms are protonated preventing coordination to the copper and, as a consequence, the two amino groups and four chloride ions are bound to the Cu^{II} completing an octahedral coordination sphere (Figure 4).

On one occasion, isomeric red crystals were also isolated from the preparation of **4**. X-ray crystallography showed that this compound was the tetrachlorocopper(II) salt of the 3,3′-diamino-2,2′-bipyridinediium dication **5a** (Figure 5). The only compound isolated from the reaction of ligand **L1** with zinc(II) chloride in a hydrochloric acid/acetonitrile mixture was shown by X-ray methods to be the corresponding tetrachlorozinc(II) salt **5b** (Figure 5).

Our findings clearly show that the pyridine rings are the favoured binding sites for coordination to divalent transition metal ions. However, by controlling the pH of the reaction mixture, it is possible to coordinate metal ions through the diamino functionality. In theory this ligand can adopt either an asymmetric or symmetric bridging mode for coordination, although the latter mode of binding has not been observed for this ligand to-date. This is in contrast to the closely related ligand 3,3′-dihydroxy-2,2′-bipyridine, which binds Ru^{II} as a mononucleating ligand through its diimine sites as well as in a symmetric "turned-around" mode presenting two N,O-donor sites to two Ru^{II} ions in an ambidentate manner.[20] For both the dihydroxy and the

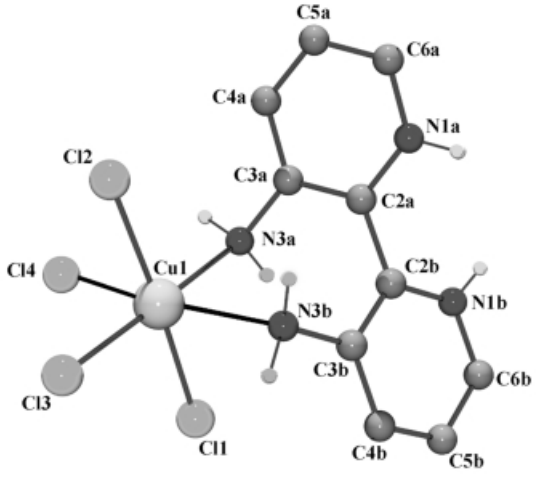
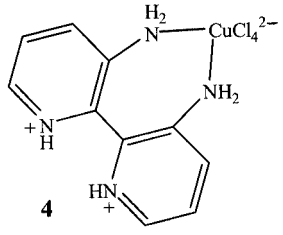


Figure 4. Molecular structure of **4**; selected distances [Å] and angles [°]: N(3A)−Cu 2.120(4), N(3B)−Cu 2.467(4), Cl(1)−Cu 2.299(2), Cl(2)−Cu 2.284(2), Cl(3)−Cu 2.3047(15), Cl(4)−Cu 3.079(2); N(3A)−Cu−N(3B) 84.3(2), N(3A)−Cu−Cl(1) 89.62(13), N(3A)−Cu−Cl(2) 88.91(13), N(3A)−Cu−Cl(3) 178.54(13), N(3A)−Cu−Cl(4) 79.03(12), N(3B)−Cu−Cl(1) 86.63(11), N(3B)−Cu−Cl(2) 100.67(11), N(3B)−Cu−Cl(3) 95.71(11), N(3B)−Cu−Cl(4) 161.43(11), Cl(1)−Cu−Cl(2) 172.37(6), Cl(1)−Cu−Cl(3) 91.84(5), Cl(1)−Cu−Cl(4) 85.23(5), Cl(2)−Cu−Cl(3) 89.67(5), Cl(2)−Cu−Cl(4) 87.14(5), Cl(3)−Cu−Cl(4) 101.21(5)



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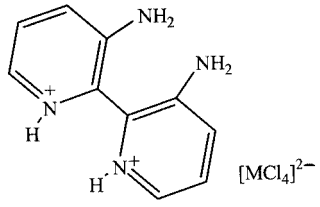


5a M = Cu
5b M = Zn

Figure 5. Compounds **4**, **5a**, and **5b**

diaminobipyridine ligands, the asymmetric mode of binding is unfavourable for dual chelation due to the fact that coordination through the diimine binding site requires an essentially planar arrangement of the two pyridine rings, whereas chelation through the diamino or dihydroxy groups requires it to be substantially twisted. As a consequence, the flexibility of the ligand is limited by the coordination requirements

of the first binding site. In this respect the bipyridine and phenanthroline families of molecules differ quite considerably. The dual chelating ability of the dipyridocatecholate (dpcat) ligand was first reported in 1975 by Balch et al.,[21] and during recent years Ward et al. have prepared dinuclear ruthenium(II) complexes of the ambidentate bridging ligand phenanthroline-5,6-diimine (pdi).[22] In this system coordination through the diamino groups of the bridging ligand is accomplished by their oxidation to the diimine state with the loss of two hydrogen atoms. Complexation by the diaminobipyridine ligand in this manner is highly unlikely since oxidation of the diamino groups would in this case occur at the expense of losing the aromaticity in both of its pyridine rings.

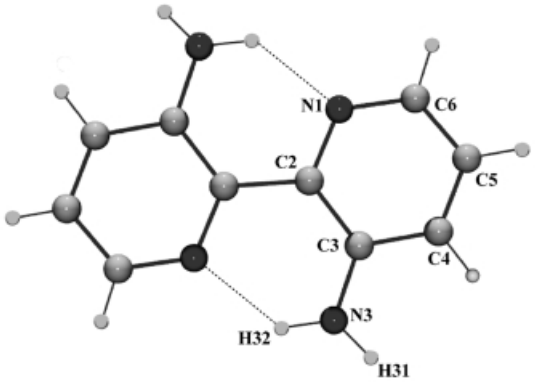


Figure 6. The molecular structure of **L1**; the dotted lines indicate the pair of intramolecular H bonds (N−H···N = 1.948 Å)

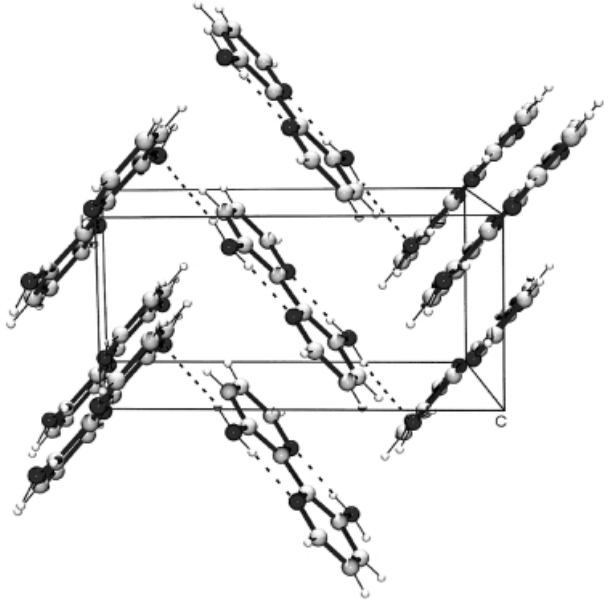


Figure 7. Molecular packing arrangement for **L1**; intra- and intermolecular H-bonding interactions are indicated by dashed lines

X-ray Structural Studies

The X-ray crystal structure of the free ligand **L1** (Figure 6) shows that the free ligand is held in a centrosymmetric *trans* conformation via a pair of intramolecular hydrogen bonds between an amino hydrogen atom and the heterocyclic nitrogen atom of the opposite ring [N−H···N = 1.948(18) Å, N−H···N = 132.7(14)°].

The molecules are packed so that the second amino hydrogen atom can participate in an intermolecular hydrogen bond to the amino N atom of another molecule, with an N···H bond length of 2.40(2) Å, and close to linear bonding at the hydrogen [N−H···N = 168.5(15)°] (Figure 7). This interaction leads to a slight pyramidalisation of the amino nitrogen atom as indicated by the sum of bond angles around nitrogen (352.5°), which enables the lone-pair electron density to participate in the intermolecular hydrogen

Table 1. Bond lengths and angles of 3,3′-diamino-2,2′-bipyridine in compounds **L1**, **2a**, **4**, **5a** and **5b**

Bond length [Å]	**L1**	**2a**[a]	**4**[a]	**5a**[a]	**5b**[a]
N(1)−C(2)	1.3502(15)	1.360(4)	1.361(6)	1.352(5)	1.374(8)
		1.374(4)	1.351(6)	1.368(5)	1.360(8)
N(1)−C(6)	1.3320(17)	1.348(4)	1.316(7)	1.324(6)	1.323(8)
		1.332(4)	1.329(7)	1.329(5)	1.330(8)
C(2)−C(3)	1.4241(18)	1.417(4)	1.388(7)	1.406(5)	1.396(8)
		1.404(4)	1.395(7)	1.402(6)	1.400(8)
N(3)−C(3)	1.3728(17)	1.387(4)	1.419(6)	1.364(4)	1.350(9)
		1.387(4)	1.384(6)	1.341(6)	1.369(8)
C(3)−C(4)	1.3984(19)	1.415(5)	1.386(7)	1.397(6)	1.392(8)
		1.403(5)	1.404(7)	1.411(6)	1.414(8)
C(4)−C(5)	1.364(2)	1.351(5)	1.383(7)	1.378(7)	1.376(9)
		1.371(5)	1.380(7)	1.373(6)	1.383(10)
C(5)−C(6)	1.375(2)	1.395(5)	1.393(8)	1.382(7)	1.376(9)
		1.388(5)	1.391(7)	1.383(7)	1.366(10)
C(2)−C(2′)	1.485(2)	1.481(4)	1.480(7)	1.465(5)	1.477(8)
Bond angle [°]					
C(2)−N(1)−C(6)	120.77(11)	121.5(3)	123.9(5)	124.6(4)	124.1(5)
		120.3(3)	123.7(5)	124.6(4)	123.6(5)
N(1)−C(2)−C(3)	119.86(11)	119.7(3)	119.5(4)	118.8(4)	118.5(5)
		119.6(3)	120.1(4)	118.7(4)	118.5(5)
N(1)−C(2)−C(2′)	116.47(13)	113.5(2)	118.9(4)	117.7(4)	116. 1(5)
		113.1(3)	118.4(4)	116.9(4)	116.8(5)
C(3)−C(2)−C(2′)	123.67(14)	126.7(3)	121.6(4)	123.5(4)	125.1(6)
		127.3(3)	121.3(4)	124.3(4)	124.7(5)
N(3)−C(3)−C(2)	123.95(12)	124.3(3)	119.9(4)	121.3(4)	122.4(6)
		123.2(3)	119.7(4)	122.7(4)	120.7(5)
N(3)−C(3)−C(4)	118.73(12)	118.5(3)	122.2(5)	121.6(4)	119.9(6)
		118.8(3)	123.4(5)	120.3(4)	121.5(6)
C(2)−C(3)−C(4)	117.29(12)	116.8(3)	117.8(5)	117.1(4)	117.7(6)
		118.0(3)	116.8(5)	117.0(4)	117.7(6)
C(3)−C(4)−C(5)	121.28(13)	121.5(3)	120.7(5)	121.0(4)	121.1(6)
		120.8(3)	121.0(5)	121.3(4)	120.2(6)
C(4)−C(5)−C(6)	118.30(13)	119.1(3)	119.6(5)	119.8(4)	120.1(6)
		118.1(3)	119.6(5)	120.1(4)	119.6(6)
N(1)−C(6)−C(5)	122.48(13)	120.6(3)	118.4(5)	118.4(4)	118.6(6)
		122.4(3)	118.6(5)	118.3(4)	119.9(6)

[a] $R1 = (F_0 - F_c)/F_0$; $wR2 = \{[w(F_0^2 - F_c^2)^2]/(F_0^2)^2]\}^{1/2}$.

Table 2. Selected molecular geometry of **L1** and its dication in complexes **2a**, **2b**, **3a**, **3e**, **4** and in salts **5a** and **5b**

Compound	**2a**	**2b**	**3a**	**3e**	**4**	**5a**	**5b**
N(3A)−H(32A) [Å]	0.78(4)	0.92(8)	0.93(6)	1.01(13)	−	−	−
H(32A)···N(3B) [Å]	2.19(4)	2.07(8)	1.97(6)	2.05(14)	−	−	−
N(3A)−H(32A)···N(3B) [°]	136(4)	135(7)	149(5)	136(11)	−	−	−
Angle between best planes of heterocyclic rings [°]	24.4(1)	28.9(2)	31.3(2) 35.3(2)	37.4(4) 37.8(4)	68.4(1)	54.5(1)	53.0(3)
Deviation of N(3A) from best plane of ring A [°]	0.374(3)	0.22(1)	0.245(4)	0.234(9)	0.072(4)	0.115(4)	0.033(7)
Deviation of N(3B) from best plane of ring B [°]	0.176(3)	0.26(1)	0.152(4)	0.133(8)	0.019(4)	0.072(5)	0.139(6)

bond. Each pyridine ring is planar, but the amino nitrogen atom is displaced to one side of this plane by 0.061(1) Å and its two hydrogen atoms are displaced by −0.12 and −0.15 Å to the other side. The molecular geometry of the pyridine rings is summarised in Table 1. In comparison with the similar *trans* conformation also adopted by 2,2′-bipyridine in the solid state,[23] differences are observed in the geometry of the pyridine rings.

For ligand **L1**, the C(2)−C(3) bond is slightly longer 1.4241(18) Å [cf. 1.394(2) for bipy] and the exocyclic C(3)−C(2)−C(2′) angle is widened from to 121.2(1)° to 123.67(14)°. This is accompanied by a consequent contraction of the endocyclic angle at C(2) by 2.7° to 119.86(11)° and an increase in the endocyclic angle at N(1) by 3.5° to 120.77(11)°. The amino group is displaced away from the opposite pyridine ring by 2.6° in the plane of the molecule. These effects enable the molecule to optimise its hydrogen bonding interactions.

The crystal structures of complexes of **L1** with copper(II) chloride (**2a**) and copper(II) acetate (**2b**), the tris complexes of **L1** with zinc(II) (**3a**, **3e** and **3f**), the complex of the dication of **L1** with copper(II) chloride (**4**) and two salts of the dication of **L1** are described. The molecular geometry of the pyridine rings for selected compounds is summarised in Table 1. Intramolecular hydrogen bonding interactions as well as the conformational geometry for ligand **L1** are listed in Table 2.

[Cu(L1)Cl$_2$]$_2$ (2a)

Remarkably, complex **2a** crystallises as a 2:2 centrosymmetric complex of ligand **L1** and copper(II) chloride (Figure 2a). The Cu^{II} metal ion adopts a near square-pyramidal geometry with two pyridine nitrogen atoms and two chloride ions bound in a distorted square-planar arrangement with angles between neighbouring atoms at copper in the range 80.9(1) to 94.8(1)°. A long axial contact from an amino nitrogen of a neighbouring bipyridine molecule to the copper metal [Cu···NH$_2$ = 2.625(3) Å] completes the five-coordinate geometry. The Cu^{II} is displaced out of the best planes of each pyridine ring by 0.482(1) and 0.468(1) Å, respectively, and the angle between the [Cl(1), Cl(2), Cu] plane and the [N(1A), N(1B), Cu] plane is 25.1(1)°. As shown in Figure 2a, these molecules are arranged in dimers as a consequence of a pair of long axial contacts between a copper ion and an amino nitrogen atom belonging to the opposite half of the dimer. A coordinating amino group approaches one face of the copper ion at angles to the other four ligating atoms in the range of 84−111°, leaving the opposite face of the copper ion exposed. The shortest contact from this face is intermolecular to a pyridine ring and is 3.785(4) and 3.626(4) Å for Cu···C(3A) of ring A and Cu···C(4A) of ring B, respectively. An intramolecular hydrogen bond [N···H = 2.19(4) Å, N···H−N = 136(3)°] leads to the best planes of the two attached pyridine rings lying at only 24.4(1)° to each other (Table 2). There is a slight folding of pyridine ring A about the C(3A)···C(6A) vector, and a slight folding of ring B about the C(2B)···C(5B) vector. This folding serves to displace the amino groups out of the best planes of their respective pyridine rings in opposite directions: N(3A) is displaced towards the copper ion to which it binds by 0.374(3) Å, while N(3B) is displaced by only 0.174(3) Å in the opposite direction. The bonding geometries at C(3A) and C(3B) remain planar. Small in-plane angular displacements of the C−N bonds at C(3A) and C(3B) in the range of 2−3° contribute to increase the distance between the amino groups, as observed in the structure of the free ligand. The molecules are packed such that there is an intermolecular hydrogen bond between H(31B) and a neighbouring chlorine atom [H(31B)···Cl = 2.47 Å] (Figure 2b). Two types of 1:1 complexes with copper(II) chloride have been reported for the unsubstituted 2,2′-bipyridine ligand.[24] The first complex is comprised of long chains in which the octahedrally bound copper(II) ions are linked by bridging chloride ions. The second complex contains a pentacoordinate Cu^{II} ion with only one bridging chloride linking adjacent metal centres. The two Cu−N bond lengths in complex **2a** [1.998(2) and 2.015(3) Å] are slightly shorter than those in the 1:1 complexes of bipyridine with copper(II) [2.026(5)−2.079(3) Å]. In contrast, the 1:1 complex of copper(II) chloride with 5,5′-diamino-2,2′-bipyridine adopts a tetracoordinate structure with even shorter Cu−N bond lengths of 1.981(1) Å.[25] Interestingly, a derivative of 3-amino-2,2′-bipyridine-6-carboxylate is reported to bind copper(II) through both a deprotonated amino group, a pyridine nitrogen and a carboxylate group.[26]

[Cu(L1)(OAc)$_2$]·3H$_2$O (2b)

To determine whether the amino groups of 3,3′-diamino-2,2′-bipyridine would still contribute to the coordination of the copper ion, the structure of the hydrated 1:1 complex **2b** with copper(II) acetate was determined by X-ray crystallography (Figure 3). The bipyridine binds to copper

through its pyridine nitrogen atoms [Cu(1)−N(3A) = 1.969(5), Cu(1)−N(3B) = 1.985(5) Å] and two acetate ligands coordinate in a bidentate manner to complete a distorted octahedral geometry. Both acetates form one short bond to copper [Cu(1)−O(1) = 1.961(4), Cu(1)−O(3) = 1.959(5) Å]. However, in contrast to **2a**, the acetate ligands make a second pair of longer contacts [Cu(1)−O(2) = 2.616(5), Cu(1)−O (4) = 2.571(6) Å] to the copper from above and below the equatorial plane. The bite angles of each acetate at the copper metal are 55.1(2) and 56.0(2)°, respectively. This mode of binding is very similar to that of the single acetate moiety in the perchlorate and tetrafluoroborate salts of the acetato-bis-bipyridinecopper(II) cation, which contain one short Cu−O bond [2.031(5) and 1.980(4) Å] and a longer Cu··O contact [2.648(5) and 2.785(5) Å].[14] The structures of the acetate ligands in **2b** are asymmetric, with longer C−O bonds [1.268(8) and 1.272(7) Å] to the oxygens which bind more tightly to the copper than for the other pair of oxygens [1.238(9) and 1.236(7) Å].

In analogy with complex **2a**, the two pyridine rings are connected by an intramolecular hydrogen bond that links the two amino groups (Table 2). The angle between the planes of the two pyridine rings is 28.9(2)° and each amino nitrogen atom is displaced by similar amounts from the plane of its attached pyridine ring, namely by 0.22(1) Å for N(3A) and 0.26(1) Å for N(3B). This serves to orient the amino groups away from each other and differs from the more asymmetric disposition of amino groups in **2a**, where one amino group coordinates the copper ion. The asymmetric unit contains two well-ordered water molecules, one of which is hydrogen bonded to an acetate oxygen O(1) and an amino hydrogen H(31B) from different molecules in the crystal structure as well as to the second water molecule.

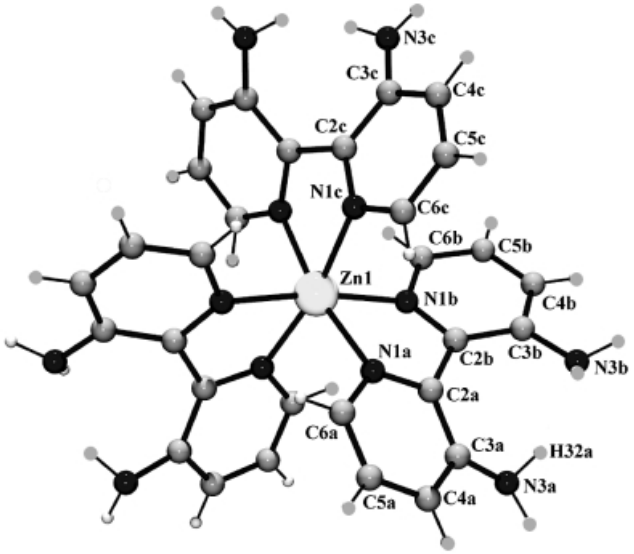


Figure 8. Molecular structure of **3a**; selected distances [Å] and angles [°]: N(1A)−Cu 2.160(3), N(1B)−Cu 2.132(3), N(1C)−Cu 2.164(3); N(1A)−Cu−N(1B) 76.1(1), N(1A)−Cu−N(1C) 169.2(1), N(1A)−Cu−N(1A′), 91.2(2), N(1A)−Cu−N(1B′) 97.9(1), N(1A)−Cu−N(1C′) 96.5(1), N(1B)−Cu−N(1C) 95.3(1), N(1B)−Cu−N(1B′) 171.5(2), N(1B)−Cu−N(1C′) 91.3, N(1C)−Cu−N(1C′) 76.9(2)

The second water molecule lies in a channel that runs through the crystal parallel to the *c* axis that contains an additional, disordered water molecule.

[Zn(L1)$_3$][CF$_3$SO$_3$]$_2$ (3a), [Zn(L1)$_3$][ZnCl$_4$]·CH$_3$CN (3e) and [Zn(L1y)$_3$][ZnCl$_4$]·DMF (3f)

The structures of the cations in all three compounds are very similar. The molecular structure of **3a** is shown in Figure 8. (NB The structures of **3a** and **3e** were solved in space groups which require the cation to lie on twofold axes, thus only one-and-a-half ligand molecules are crystallographically unique. However, the bisected ligand does not exactly conform to this twofold axis due to the asymmetry expected in the arrangement of the amino groups, where one must hydrogen bond to the other).

In all complexes three bipyridine ligands bind the zinc(II) metal through their diimine binding sites, and the cations are all octahedral with Zn−N bond lengths in the range 2.132(3)−2.164(3) Å and bond angles around the Zn^{2+} in the range 76.1(1)−97.9(1)°. The Zn−N bond lengths fall within the range typical for Zn^{2+}tris(bipyridine) complexes (2.133−2.166 Å).[27−29]

[Cu(L1H$_2$)Cl$_4$] (4)

Reaction of **L1** with copper(II) chloride in dilute hydrochloric acid yielded complex **4,** which was characterised by X-ray crystallography. The molecular structure is shown in Figure 4. Both heterocyclic nitrogen atoms are protonated and the two amino groups, which together with four additional chloride ligands complete the charge balance, are bound to the copper ion, giving an octahedral coordination sphere around the Cu^{II} ion. The endocyclic bond angles at both pyridinyl nitrogen atoms show the expected widening by 2−3° relative to the free ligand **L1** due to protonation. The Cu^{II} metal ion shows the expected Jahn−Teller distortion, namely the C−N and C−Cl bonds along one axis are longer than other similar bonds in the complex. The N(3B)−Cu bond [2.467(4) Å] is 0.35 Å longer than the N(3A)−Cu bond [2.120(4) Å], although both are shorter than the pair of bonds from amino nitrogens to coppers in the 2:2 complex **2a**. Both amino groups show a tetrahedral bonding geometry, indicative of the binding interactions between nitrogen and copper. The 1,6-bite angle of the diamino groups at the copper metal is 84.2(1)°. The molecule achieves this mode of coordination by increasing the angle between the best planes of the two pyridinium rings to 68.4(1)° from the *cis* coplanar arrangement. The amino nitrogen atoms are nearly coplanar with their pyridine rings, in contrast to the complexed neutral ligand. The two C−NH_2 bond lengths are different; this bond is longer [1.419(6) vs. 1.384(6) Å] for the amino group which binds the copper more tightly, since the nitrogen lone pair is less available for conjugation with the pyridine ring. Indeed, the shorter bond is similar in length to those in the unbound dication in **5a** and **5b**, suggesting that this amino group only binds weakly to the copper. The molecules are packed in such a way that there are intermolecular hydrogen bonds

between all six nitrogen-bonded hydrogen atoms and neighbouring chloride ions in the range of 2.24−2.67 Å.

Only a few structurally characterised examples of 2,2′-diaminobiaryl systems binding in this way have been reported in the chemical literature. 2,2′-Diaminobiphenyl and 1,2-diaminocyclohexane bind platinum(II) chloride[30] and two molecules of 2,2′-diamino-6,6′-dimethylbiphenyl bind to rhodium(III) chloride[31] with bite angles for the diamino groups at the metal atom in the 87−89° range. Several complexes of the 3-aminopyridinium cation coordinated through the amino groups to copper(II) have been reported and provide a useful comparison.[32,33] For these complexes, the Cu−N distances are in the range 2.043−2.071 Å, similar to the shorter of the Cu−N bonds in **4**, and the C−NH_2 bond lengths are in the range 1.400−1.432 Å, similar to the C(3A)−N(3A) bond length in **4**.

[L1H$_2$][CuCl$_4$] (5a) and [L1H$_2$][ZnCl$_4$] (5b)

The molecular structure of the zinc salt **5b** is presented in Figure 9. The geometry and conformation of the dication in both compounds is very similar, however the geometry of the anion in the former is intermediate between tetrahedral and square planar, whereas in the latter it is tetrahedral.

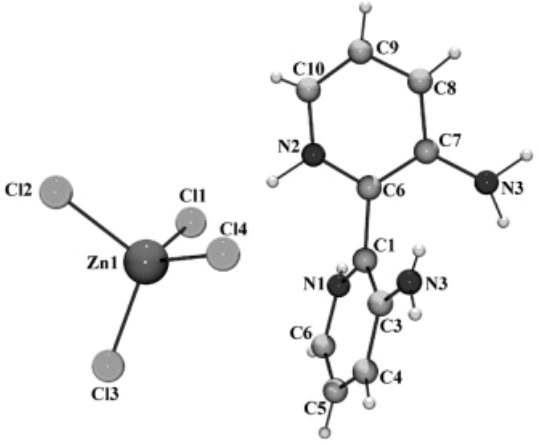


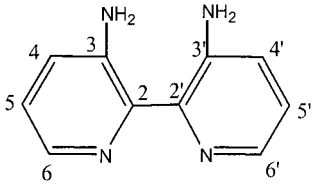
Figure 9. Molecular structure of **5b**

Protonation of the ring diimine nitrogens leads to widening of the endocyclic ring angles at these heteroatoms in the range of 123.6(5)−124.6(4)°. The best planes of the pyridinium rings lie at 54.5(1)° and 53.0(3)° from the *cis* coplanar arrangement, which serves to separate the amino nitrogen atoms at van der Waals distances of 3.063(6) Å and 3.023(9) Å. The shortest N···H separations between the two amino groups are ca. 2.7 Å, although the positions of the hydrogen atoms determined from these room temperature measurements are not very accurate. In contrast to the complexed dication in **4**, the bonding geometries at the amino nitrogen atoms are in most cases nearer to planar (the average sum of bond angles at the amino N are in the range 347−360°). The bonds between the amino nitrogen atoms and the pyridine rings are in the range 1.341(6)−1.369(8) Å (Table 1), and are shorter than in 3-aminopyridine (1.384 Å).[34] This is in accordance with the expected increase in π-overlap between each amino group's lone pair and the positively charged heterocyclic ring. The corresponding bond lengths in the complexed dication **4** are ca. 0.4 Å longer than in **5a** and **5b** since the nitrogen atoms' lone pairs are utilised in forming dative bonds.

NMR Spectroscopy

All NMR spectra were measured in [D_6]DMSO for consistency. The ^{1}H NMR chemical shifts for selected compounds are shown in Table 3.

Table 3. ^{1}H NMR spectroscopic data for selected compounds containing **L1**



Compound	Solvent	H6, H6′	H5, H5′	H4, H4′
Free ligand (**L1**)	[D_6]DMSO	7.76	7.02	7.02
L1·2HCl	[D_6]DMSO	8.09	7.60	7.65
(**L1**H$_2$)[ZnCl$_4$] (**5b**)	[D_6]DMSO	8.07	7.55	7.55
[Dichloro(**L1**)zinc(II)] (**2e**)	[D_6]DMSO	7.80 (br)	7.04 (br)	7.14 (br)
[Zn(**L1**)$_3$][ZnCl$_4$] (**3e**)	[D_6]DMSO	7.84	7.05	7.14
[Zn(**L1**)$_3$][CF_3SO_3]$_2$ (**3a**)	[D_6]DMSO	7.62	7.16	7.40

In comparison with the free ligand **L1**, the positive charge resulting from protonation of both rings causes a downfield shift of the aromatic protons since they are now more deshielded than in **L1**. The protons in the 4- and 5-positions are shifted by approximately 0.6 ppm whereas the H-6 protons are shifted to a lesser degree by 0.3 ppm. These shifts are observed for both the HCl salt as well as compound **5b**. For the tris-zinc compound **3a**, complexation causes a small upfield shift of the protons in the 6-position, since there is a small diamagnetic interaction of the ring current with the metal ion resulting in a shielding effect of the protons α to the metal centre. The protons in the 4- and 5-positions are deshielded slightly (0.1−0.4 ppm) with respect to the free ligand **L1**. Interestingly, the ^{1}H NMR spectrum for the 1:1 complex **2e** is very broad, indicating an exchange process, and has similar chemical shifts to a solution of the tetrachlorozincate salt of the tris-zinc complex **3e**. It is notable that the ^{1}H NMR spectrum of the latter differs from that of **3a**, the triflate salt of the tris-zinc complex, which would not be expected to be involved in any exchange processes. Crystalline **3e** was initially grown from solutions of **2e**, thus it seems that the two chlorides and ligand **L1** bound to zinc in **2e** are exchanging between zinc ions.

Conclusion

Substitution at the 3,3′-positions does not prevent coordination to the pyridine rings. Compound **L1** behaves as a bidentate ligand coordinating metal ions preferentially through the nitrogen atoms of the pyridine rings. Furthermore, this ligand displays an unusual pH-dependent coordination chemistry, enabling the diamino group to participate in the coordination chemistry when both pyridine nitrogens are protonated. The second mode of binding, namely the symmetrical bridging mode, has not been observed for this ligand to-date. Attempts to prepare dinuclear complexes with ligand **L1** acting as an asymmetric bridge have so far been unsuccessful. This is most probably due to the fact that the asymmetric bridging mode is sterically difficult for divalent metal ions since chelation through the diamino functionality requires the ligand to be substantially more twisted. The above findings lead us to conclude that this ligand is not particularly well suited for linking metal ions for the assembly of coordination polymers. Tris-bipyridine complexes of selected paramagnetic ions do, however, display the phenomenon of spin-crossover. As a consequence, the preparation and magnetic studies of further derivatives of **L1** are currently in progress.[35]

Experimental Section

General: 3-Amino-2-chloropyridine, copper bronze (99%) and tin(II) chloride (98%) were purchased from Aldrich. 2-Chloro-3-nitropyridine (97%), DMF (99.8% over molecular sieves) and dioxane (99.5%) were purchased from Fluka. Solvents were dried before use. NMR spectra were measured on a JEOL GX 270 spectrometer (270 MHz for ^{1}H and 67.8 MHz for ^{13}C) using tetramethylsilane (TMS) as standard, and measured in ppm downfield from TMS, or on a Bruker AC-300 spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C) and calibrated against the deuterated solvent. Chemical shifts δ are given in ppm and coupling constants (*J*) are given in Hz. IR spectra were recorded on an ATI Mattson Genesis Series FT-IR or a Perkin−Elmer Spectrum One FT-IR spectrophotometer as liquid films, nujol mulls or KBr pellets. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre and at the University of Berne. Microanalyses were performed at the Analytical Centre, University of Kent, UK, and at the University of Fribourg, Switzerland. Flash chromatography was performed on 40−63 silica gel (Merck).

Synthesis of 3,3′-Diamino-2,2′-bipyridine (L1)

Method A: 2-Chloro-3-nitropyridine (2.00 g, 12.62 mmol) was reacted with freshly activated copper bronze (2.00 g) in dry DMF (40 mL) at 150 °C under nitrogen for 2.5 h.[8] After 2 h TLC (SiO_2, CH_2Cl_2) indicated that the starting material had been consumed. The resulting mixture was poured into water (40 mL), the solid filtered immediately and then washed with concentrated ammonia (2 × 20 mL). The remaining solid was then extracted into boiling dioxane (2 × 150 mL), stirring for about 20 min each time. After evaporating the combined extracts to dryness, the solid was recrystallised from ethanol to give 3,3′-dinitro-2,2′-bipyridine as a yellow solid (yield 1.16 g, 73%). M.p. 205−206 °C. ^{1}H NMR ($CDCl_3$): δ = 8.87 (dd, $J_{6,5}$ = 4.7 Hz, $J_{6,4}$ = 1.7 Hz, 2 H, 6-,6′-H), 8.58 (dd, $J_{4,5}$ = 8.4 Hz, $J_{4,6}$ = 1.5 Hz, 2 H, 4-,4′-H), 7.65 (m, 2 H, 5-,5′-H). ^{13}C NMR ($CDCl_3$): δ = 152.9 (6-,6′-C), 150.7 (2-,2′C), 144.0 (3-,3′-C), 133.1 (4-,4′-C), 124.6 (5-,5′-C). IR (KBr pellet): $\tilde{\nu}$ = 3084, 1590, 1561, 1534, 1440, 1417, 1366, 1048, 1038, 865, 855, 821, 790, 751, 621, 529 cm^{-1}. The dinitro product (0.8 g, 3.25 mmol) was added to a solution of tin(II) chloride dihydrate (5.6 g, 29.5 mmol) in conc. HCl (32%, 14 mL).[7] The solution was refluxed for 0.5 h, to give a yellow solution (**Important:** *do not let the solution cool, otherwise a green insoluble solid precipitates out of solution*). After adjustment of the pH to 12−13 with a solution of NaOH, the solution was extracted with chloroform, and the solvents evaporated to give **L1** as a yellow solid. (yield 0.5 g, 86%). Single crystals suitable for X-ray diffraction were grown from ethyl acetate by slow evaporation of the solvent at room temperature. M.p. 133−134 °C. ^{1}H NMR ($CDCl_3$): δ = 7.96 (dd, $J_{6,5}$ = 7.0 Hz, $J_{6,4}$ = 3.0 Hz, 2 H, 6,6′-H), 7.02 (m, 4 H, 5,5′-H and 4,4′-H), 6.27 (br. s, 4 H, 2 × NH_2). ^{13}C NMR ($CDCl_3$): δ = 143.8 (3,3′-C), 140.6 (2,2′-C), 135.7 (6,6′-C), 123.9 (4,4′-C), 122.9 (5,5′-C). IR (KBr): $\tilde{\nu}$ = 3354, 3221, 2925, 2855, 1586, 1548, 1444, 1430, 1316, 1269, 1149, 1060, 1024, 796, 729, 638 cm^{-1}.

Method B: Freshly distilled acetic anhydride (200 mL, 2.02 mol) was added to 2-chloro-3-aminopyridine (20.0 g, 0.156 mol) and the solution left to stir overnight. The excess acetic acid and acetic anhydride were both removed by distillation under reduced pressure. On cooling in ice the remaining oil produced an off-white solid which was recrystallised from toluene to give 3-acetylamino-2-chloropyridine (20.1 g, 74.0%) as white crystals, M.p. 89 °C. Activated copper bronze (18 g, 0.283 mol) was added to a solution of 3-acetylamino-2-chloropyridine (20.0 g, 0.117 mol) in dry DMF (100 mL) under nitrogen.[9] This mixture was then heated at 110 °C until TLC (SiO_2,ethyl acetate) showed the absence of starting material (3−4 h). After cooling, water (20 mL) was added and the solution filtered. The filter cake was washed with more water (20 mL), ammonium hydroxide (40 mL, 0.88 grav) and finally more water (20 mL). The cake was allowed to dry fully in a desiccator. The desired solid was then extracted with dichloromethane (5 × 200 mL) and the solvents evaporated to give crude 3,3′-diacetylamino-2,2′-bipyridine (yield 12.2 g, 76.6%). M.p. 230°C (dec.) (ref.[9] 225−226 °C), ^{1}H NMR ($CDCl_3$): δ = 9.13 (dd, $J_{4,5}$ = 8.5 Hz, $J_{4,6}$ = 1.7 Hz, 2 H, 4,4′-H), 8.35 (dd, $J_{6,5}$ = 5.9 Hz, $J_{6,4}$ = 1.5 Hz, 2 H, 6,6′-H), 7.36 (dd, $J_{5,6}$ = 13.1 Hz, $J_{5,4}$ = 4.5 Hz, 2 H, 5,5′-H), 2.20 (s, 6 H, 2 × -CH_3). ^{13}C NMR ($CDCl_3$): δ = 169.2 (C=O), 141.7 (2,2′-C), 140.3 (6,6′-C), 136.5 (4,4′-C), 129.8 (3,3′-C), 123.9 (5,5′-C), 25.4 (2 × -CH_3). IR (KBr): $\tilde{\nu}$ = 3344 (N−H str), 1691 (C=O str) cm^{-1}. This crude product (12.0 g, 44.4 mmol) was added to concentrated HCl (50 mL) and the mixture refluxed for 30 min. After cooling in ice, concentrated ammonium hydroxide was added (80 mL, 0.88 grav) to give bright yellow crystals of pure **L1** (yield 8.03 g, 95.2%).

3,3′-Diamino-2,2′-bipyridinediium Dichloride: A 2 M solution of HCl (10 mL) was added to ligand **L1** (1.0 g, 4.4 mmol) and the solution stirred for 24 h. The desired salt was precipitated from the solution by the dropwise addition of acetonitrile to give a bright yellow, amorphous solid which was washed with water and dried (yield 0.89 g, 63.9%). M.p. 181 °C (dec.), ^{1}H NMR (D_2O): δ = 8.20 (dd, $J_{6,5}$ = 5.2 Hz, $J_{6,4}$ = 1.2 Hz, 2 H, 6,6′-H), 8.01 (dd, $J_{4,5}$ = 8.9 Hz, $J_{4,6}$ = 5.4 Hz, 2 H, 4,4′-H), 7.90 (dd, $J_{5,4}$ = 8.9 Hz, $J_{5,6}$ = 5.4 Hz, 2 H, 5,5′-H). ^{13}C NMR (D_2O): δ = 146.7 (6,6′-C), 133.1 (4,4′-C), 132.9 (2,2′-C), 129.0 (5,5′-C), 122.1 (3,3′-C) IR (KBr

disc): $\tilde{\nu}$ = 3378−3207 (N−H str), 2958 (C−H, arom. str), 2631 (N^+−H str), 1546 (C=N, arom. str) cm^{-1}.

Tetrachlorobis(3,3′-diamino-2,2′-bipyridine)dicopper(II) (2a): Equimolar amounts of ligand **L1** (0.30 g) and copper(II) chloride dihydrate (0.22 g) were stirred together in acetonitrile overnight. The resulting precipitate was filtered, dried and recrystallised from water to give single crystals of **2a** as green blocks (yield 0.49 g, 97%). M.p 266−267 °C. $C_{10}H_{10}Cl_2CuN_4$ (320.7): calcd. C: 37.5, H 3.1, N 17.5; found C 37.3, H 3.1, N 17.9. IR (Nujol): $\tilde{\nu}$ = 3345, 3305, 3218, 1643, 1633, 1590, 1581, 1330, 1313, 1267, 1230, 1201, 1149, 1076, 1064, 944, 904, 823, 798,723, 713, 686 cm^{-1}.

Diacetato(3,3′-diamino-2,2′-bipyridine)copper(II)·3H_2O (2b): Following the above procedure for **2a**, reaction of ligand **L1** (0.30 g) and copper(II) acetate hydrate (0.32 g) yielded a solid which was collected, dried and recrystallised from aqueous ethanol to afford single crystals of **2b** as dark green prisms (yield 0.55 g, 93%). M.p. 212−214 °C. $C_{14}H_{16}N_4O_4Cu{\cdot}3H_2O$ (421.9): calcd. C 39.8, H 5.2, N 13.3; found C 40.0, H 4.8, N 13.5. IR (Nujol): $\tilde{\nu}$ = 3491, 3415, 3329, 3173, 1639, 1579, 1279, 1245, 1156, 1051, 1012, 922, 815, 799, 667 cm^{-1}.

Catena-dichloro(3,3′-diamino-2,2′-bipyridine)manganese(II) (2c): Reaction of **L1** (0.30 g) with manganese(II) chloride tetrahydrate (0.32 g) as for **2a** gave a dark crystalline solid tentatively assigned as **2c** (yield 0.41 g, 82%). M.p. > 330 °C. $C_{10}H_{10}Cl_2MnN_4$ (312.1): calcd. C 38.5, H 3.3, N 18.0; found C 38.3, H 3.2, N 17.7. IR (Nujol): $\tilde{\nu}$ = 3440, 3392, 3334, 3305, 3205, 1735**,** 1615, 1593, 1295, 1242, 1159, 1025, 952, 918, 817, 786, 770, 734 cm^{-1}.

Catena-dibromo(3,3′-diamino-2,2′-bipyridine)manganese(II) (2d): Reaction of **L1** (0.30 g) with manganese(II) bromide hexahydrate (0.52 g) as for **2a** gave a black solid tentatively assigned as **2d** (yield 0.47 g, 73%). M.p. dec. 280 °C. $C_{10}H_{10}Br_2MnN_4$ (401.0): calcd. C 30.0, H 2.5, N 14.0; found C 29.9, H 2.5, N 13.7. IR (Nujol): $\tilde{\nu}$ = 3330, 3301, 3203, 1712, 1627, 1589, 1314, 1263, 1207, 1156, 1012, 972, 839, 801, 737 cm^{-1}.

Tris(3,3′-diamino-2,2′-bipyridine)zinc(II) Trifluoromethanesulfonate (3a): Reaction of an acetonitrile solution of **L1** (0.56 g, 3.0 mmol) with zinc(II) trifluoromethanesulfonate tetrahydrate (0.41 g, 1.0 mmol) following the procedure as for **2a** afforded yellow single crystals of **3a** after recrystallisation from water (yield 0.84 g, 91%). M.p. 308 °C. $C_{32}H_{30}F_6N_{12}O_6S_2Zn$ (922.2): calcd. C 41.7, H 3.3, N 18.2; found C 41.3, H 3.1, N 18.5. ^{1}H NMR ([D_6]DMSO): δ = 7.84 (br. d, J = 3.4 Hz, 6 H, 3 × 6-,6′-H), 7.26 (dd, $J_{4,5}$ = 7.9 Hz, $J_{4,6}$ = 1.3 Hz, 6 H, 3 × 4-,4′-H), 7.16 (dd, $J_{4,5}$ = 8.1 Hz, $J_{5,6}$ = 4.6 Hz, 6 H, 3 × 5-,5′-H). ^{13}C NMR ([D_6]DMSO): δ = 144.1 (3,3′-C), 138.0 (2,2′-C), 135.2 (6,6′-C), 124.5 (4,4′-C), 123.2 (5,5′-C). IR (Nujol): $\tilde{\nu}$ = 3373, 3331, 3208, 1642, 1630, 1584, 1332, 1258, 1237, 1224, 1165, 1152, 1029, 804, 726, 706, 641 cm^{-1}.

Tris(3,3′-diamino-2,2′-bipyridine)copper(II) Trifluoromethanesulfonate (3b): Copper(II) trifluoromethanesulfonate (0.65 g, 1.79 mmol) was added to solution of **L1** (1.0 g, 5.38 mmol) in acetonitrile (25 mL) and stirred for 10 min. Standing overnight produced ruby red crystals of **3b** as its acetonitrile solvate (yield 0.90 g, 54%). M.p. 249 °C. $C_{32}H_{30}CuF_6N_{12}O_6S_2{\cdot}CH_3CN$ (961.7): calcd. C 42.5, H 3.5, N 18.9, Cu 6.6; found C 42.2, H 3.3, N 19.2, Cu 6.5. IR (Nujol): $\tilde{\nu}$ = 3376, 2960, 1638, 1590, 1264, 1168, 1032, 804, 724, 638 cm^{-1}.

Tris(3,3′-diamino-2,2′-bipyridine)nickel(II) Trifluoromethanesulfonate (3c): Reaction of an acetonitrile solution of **L1** (0.56 g, 3.0 mmol) with nickel(II) trifluoromethanesulfonate pentahydrate (0.41 g, 1.0 mmol) following the procedure as for **2a** gave pale-yellow single crystals of **3c** after recrystallisation from water (yield 0.89 g, 98%). M.p. 336 °C (dec.). $C_{32}H_{30}F_6N_{12}NiO_6S_2$ (915.5): calcd. C 42.0, H 3.3, N 18.4; found C 41.9, H 3.3, N 18.6. IR (Nujol): $\tilde{\nu}$ = 3369, 3331, 3209, 1643, 1632, 1590, 1257, 1234, 1165, 1028, 803, 641 cm^{-1}.

Tris(3,3′-diamino-2,2′-bipyridine)cobalt(II) Trifluoromethanesulfonate (3d): Reaction of an acetonitrile solution of **L1** (0.56 g, 3.0 mmol) with cobalt(II) trifluoromethanesulfonate tetrahydrate (0.41 g,1.0 mmol) gave dark-red single crystals of **3d** after recrystallisation from water (yield 0.82 g, 97%). M.p. 330 °C (dec. starts at 300 °C). $C_{32}H_{30}CoF_6N_{12}O_6S_2$ (915.7): calcd. C 42.0, H 3.3, N 18.4; found C 41.9, H 3.1, N 18.7. IR (Nujol): $\tilde{\nu}$ = 3372, 3330, 3209, 1642, 1602, 1590, 1258, 1235, 1224, 1165, 1029, 803, 724, 641 cm^{-1}.

Dichloro(3,3′-diamino-2,2′-bipyridine)zinc(II) (2e): Ligand **L1** (0.15 g, 0.81 mmol) was stirred with dry zinc(II) chloride (0.11 g, 0.81 mmol) in acetonitrile (10 mL) overnight. A fine, bright-yellow precipitate and was separated from the solution by centrifugation, and dried under vacuum to give **2e** (yield 0.22 g, 86%). M.p. > 310 °C. $C_{10}H_{10}Cl_2N_4Zn$ (322.5): calcd. C 37.24, H 3.13, N 17.37; found C 37.50, H 3.13, N 17.23. ^{1}H NMR ([D_6]DMSO): δ = 7.80 (br., 2 H, 6,6′-H), 7.14 (br., 2 H, 4,4′-H) 7.04 (br., 2 H, 5,5′-H), 7.00 (br., 4 H, 2 × NH_2). ^{13}C NMR ([D_6]DMSO): δ = 144.4 (3,3′-C), 139.0 (2,2′-C), 134.1 (6,6′-C), 123.1 (4,4′-C), 122.9 (5,5′-C). IR (KBr pellet): $\tilde{\nu}$ = 3409, 3327, 3234, 1638, 1626, 1593, 1583, 1467, 1440, 1344, 1331, 1271, 1248, 1203, 1157, 1102, 1075, 806, 773, 726, 710, 650, 594 cm^{-1}.

Tris(3,3′-diamino-2,2′-bipyridine)zinc(II) Tetrachlorozincate(II) (3e) and Its DMF Solvate (3f)

Slow evaporation of a 1:1 ethanol/acetonitrile mixture of the 1:1 complex **2e** yielded single crystals which were characterised by X-ray crystallography to be the tris complex **3e**. M.p > 310 °C. ^{1}H NMR ([D_6]DMSO): δ = 7.84 (dd, $J_{6,5}$ = 4.2 Hz, $J_{6,4}$ = 1.5 Hz, 6 H, 3 × 6,6′-H), 7.14 (dd, $J_{4,5}$ = 8.2 Hz, $J_{4,6}$ = 1.5 Hz, 6 H, 3 × 4,4′-H), 7.05 (dd, $J_{5,4}$ = 8.2 Hz, $J_{5,6}$ = 4.2 Hz, 6 H, 3 × 5,5′-H), 6.97 (br., 12 H, 6 × NH_2). IR (KBr pellet): $\tilde{\nu}$ = 3514, 3327, 3214, 2925, 1945, 1634, 1588, 1465, 1445, 1321, 1270, 1242, 1206, 1152, 1101, 1076, 1022, 875, 883, 806, 732, 707, 639, 589 cm^{-1}. A second set of crystals were grown by diffusion of methanol into a DMF solution of **2e**. The crystals were characterised as being compound **3f**, a DMF solvate of **3e**. M.p. 335−338 °C. ^{1}H NMR ([D_6]DMSO): δ = 7.84 (dd, $J_{6,5}$ = 4.2 Hz, $J_{6,4}$ = 1.5 Hz, 6 H 3 × 6,6′-H), 7.14 (dd, $J_{4,5}$ = 8.2 Hz, $J_{4,6}$ = 1.5 Hz, 6 H, 3 × 4,4′-H), 7.05 (dd, $J_{5,4}$ = 8.2 Hz, $J_{5,6}$ = 4.2 Hz, 6 H, 3 × 5,5′-H), 6.97 (br., 12 H, 6 × NH_2). ^{13}C NMR ([D_6]DMSO): δ = 144.39 (3,3′-C), 138.84 (2,2′-C), 134.43 (6,6′-C), 123.49 (4,4′-C), 123.04 (5,5′-C). IR (Nujol): $\tilde{\nu}$ = 3401, 3331, 3191, 1634, 1588, 1325, 1270, 1242, 1206, 1155, 1102, 1075, 806, 726, 707, 640 cm^{-1}.

3,3′-Diamino-2,2′-bipyridinium Tetrachlorocuprate(II) (4): Copper(II) chloride dihydrate (0.45 g) dissolved in 1 M HCl (5 mL) was added to a solution of **L1** (0.50 g) in acetonitrile (5 mL) and stirred for 30 min. The resulting green precipitate was collected by filtration. A second batch of green solid crystallised out of the filtrate and was collected affording compound **4** in an overall yield of 0.57 g (54%). M.p. 290−291°C. $C_{10}H_{12}Cl_4CuN_4$ (393.6): calcd. C 29.6, H 3.0, N 13.8, Cu 16.1; found C 29.7, H 3.0, N 14.2, Cu 15.7. IR (Nujol): $\tilde{\nu}$ = 3346, 3295, 3215, 1634, 1586, 1582, 1330, 1314, 1266, 1229, 1200, 1150, 904, 819, 799, 714, 684, 648 cm^{-1}.

3,3′-Diamino-2,2′-bipyridinium Tetrachlorocuprate(II) (5a): On one occasion a few red crystals were isolated on evaporation of the

above filtrate. These crystals were carefully separated from the green crystals and characterised by X-ray crystallography as being **5a**, the salt of the diprotonated ligand **L1**. M.p > 300°C. $C_{10}H_{12}Cl_4CuN_4$ (393.6): calcd. C 29.6, H 3.0, N 13.8, Cu 16.1.%; found C 29.6, H 3.0, N 14.2, Cu 15.9.

3,3′-Diamino-2,2′-bipyridinium Tetrachlorozincate(II) (5b): Aqueous HCl (10 mL, 4.77 M) was added to a solution of **L1** (150 mg) in acetonitrile (10 mL). Zinc(II) chloride (110 mg) was then added and the reaction mixture was stirred overnight. The volume of the resulting yellow solution was reduced until a solid started to precipitate. The product was then filtered, washed with ether and dried under vacuum to give **5b** (yield 0.23 g, 72%). M.p. > 310 °C. $C_{10}H_{12}Cl_4N_4Zn$ (395.4): calcd. C 30.4, H 3.1, N 14.2; found C 30.5, H 3.1, N 13.9. ^{1}H NMR ([D$_6$]DMSO): δ = 8.07 (dd, $J_{6,5}$ = 4.3 Hz, $J_{6,4}$ = 1.3 Hz, 2 H, 6,6′-H), 7.55 (m, 4 H, 4,4′-H, 5,5′-H), 3.76 (br., 6 H, 2 × NH_2, 2 × NH). ^{13}C NMR ([D$_6$]DMSO): δ = 145.4 (3,3′-C), 132.6 (6,6′-C), 128.8 (2,2′-C) 128.6 (4, 4′-C), 126.9 (5,5′-C). IR (KBr): $\tilde{\nu}$ = 3436, 3352, 3313, 3199, 3067, 2908, 1640, 1630, 1619, 1561, 1553, 1471, 1384, 1300, 1165, 1154, 945, 806, 785 cm^{-1}.

X-ray Structure Determinations: All crystal data are summarised in Table 4 and 5 unless otherwise stated. Data were collected with Mo-K_α radiation (λ = 0.71073 Å) using a graphite monochromator with the exception of compounds **L1** and **3e**, which were collected with Cu-K_α radiation (λ = 1.54178 Å). Structure solution was performed by Patterson or direct methods using SHELXS-97.[36] Refinement: Full-matrix least-squares on F^2 (SHELXL-97)[36] all non-hydrogen positions found and refined with anisotropic temperature factors. Hydrogen atoms were located from Fourier distance maps and refined isotropically. Graphics are drawn with the WINGX package for windows.[37]

CCDC-173203−173211 (**L1, 2a, 2b, 3a, 4, 5a, 5b, 3e, 3f**, respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Table 4. Crystal data for ligand **L1** together with complexes **2a**, **2b**, **4**, **5a**, **5b**

	L1	**2a**	**2b**	**4**	**5a**	**5b**
Empirical formula	$C_{10}H_{10}N_4$	$C_{20}H_{20}Cl_4Cu_4N_8$	$C_{14}H_{22}CuN_4O_7$	$C_{10}H_{12}Cl_4CuN_4$	$C_{10}H_{12}Cl_4CuN_4$	$C_{10}H_{12}Cl_4N_4Zn$
M (g mol^{-1})	186.2	641.4	421.9	393.6	393.6	395.4
Crystal size [mm]	0.38 × 0.30 × 0.19	0.2 × 0.10 × 0.10	0.49 × 0.42 × 0.30	0.28 × 0.20 × 0.18	0.08 × 0.25 × 0.40	0.45 × 0.25 × 0.05
Crystal description	blocks	blocks	blocks	Blocks	plates	plates
Crystal colour	yellow	green	dark blue	green	green	yellow
T [K]	293(2)	150(2)	293(2)	150(2)	293(3)	153(2)
Diffractometer	STOE AED2	Enraf Nonius Fast	STOE AED2	Enraf Nonius Fast	Enraf Nonius CAD4	STOE IPDS
2θ range [°]	13−119	4−51	4−51	5−50	4−50	5.4−52
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P2_1/a$	$Pna2_1$	$P\bar{1}$
a [Å]	7.7896(7)	10.110(2)	18.819(4)	10.926(3)	17.457(9)	7.4417(11)
b [Å]	5.3100(4)	10.08122(9)	13.326(6)	8.214(1)	7.486(7)	7.6257(10)
c [Å]	11.0474(8)	11.6522(1)	15.950(3)	15.890(3)	11.213(3)	13.5058(18)
α [°]	90	90	90	90	90	85.071(16)
β [°]	100.594	105.18(2)	112.82(1)	104.37(2)	90	78.467(16)
γ [°]	90	90	90	90	90	85.088(17)
V [Å]^3	449.16(6)	1146.3(3)	3687.0(19)	1381.4(5)	1461.8(5)	746.34(18)
Z	2	2	8	4	4	2
$D_{calcd.}$ [gcm^{-3}]	1.38	1.86	1.46	1.89	1.78	1.76
μ [$^{-1}$]	7.1	23.5	12.2	23.4	22.3	23.5
Absorption correction	−	DIFABS	−	DIFABS	PSI SCANS	DIFABS
Min/max transmission	−	0.72/0.89	−	0.65/0.86	0.60/0.86	0.62/0.88
Measured reflections	2618	4854	3647	5122	1685	5313
Unique reflect. for Refinement (R_{int})	660	1766	3422	2033	1685	2702
Observed reflections [$I > 2\sigma(I)$]	633	1633	2478	1223	1462	2036
Max/minΔρ [e·Å^{-3}]	0.13/-0.10	0.55/-0.63	0.79/-0.51	0.57/-0.50	0.64/-0.38	1.09/-1.70
$R1$ [$I > 2\sigma(I)$][a]	0.035	0.038	0.069	0.034	0.026	0.073
$wR2$ (all reflections)	0.097	0.095	0.15	0.093		0.18
GOF on F^2 [b]	0.66	1.09	1.19	0.46	1.81	0.95

[a] $R1 = (F_o - F_c)/F_o$; $wR2 = \{[w(F_o^2 - F_c^2)^2]/(F_o^2)^2]\}^{1/2}$. [b] GOF = $\{[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$; $w = 1/[\sigma 2(F_o^2) + (aP)^2 + bP$, where $P = [\max(F_o^2$ or $0 + 2F_c^2]/3$.

Table 5. Crystal data for the 3:1 Complexes **3a**, **3e, and 3f**

	3a	**3e**	**3f**
Empirical formula	$C_{32}H_{30}F_6N_{12}O_6S_2Zn$	$C_{32}H_{33}Cl_4N_{13}Zn_2$	$C_{33}H_{37}Cl_4N_{13}OZn_2$
M (g mol^{-1})	922.19	872.3	904.30
Crystal size [mm]	0.24 × 0.16 × 0.16	0.38 × 0.30 × 0.11	0.5 × 0.5 × 0.5
Crystal description	blocks	blocks	blocks
Crystal colour	yellow	yellow	yellow
T [K]	150(2)	293(3)	153(2)
Diffractometer	Enraf Nonius FAST	STOE AED2	STOE IPDS
Scan type 2θ range [°]	4-50	8-120	4-51
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	$C222_1$	$Ama2$	$Pna2_1$
a [Å]	11.829(2)	21.721(8)	21.2015(10)
b [Å]	14.7536(7)	11.633(2)	11.7334(6)
c [Å]	21.581(5)	15.104(5)	45.956(3)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	90	90	90
V [Å]^3	3766.3(2)	3816(2)	11486.2(11)
Z	4	4	12
$D_{calcd.}$ [gcm^{-3}]	1.63	1.52	1.57
μ [$^{-1}$]	8.5	44.8	15.8
Absorption correction	DIFABS	Psi scans	DIFABS
Min/max transmission	0.98/0.82	0.432/0.192	0.860/0.547
Measured reflections	6681	2974	30716
Unique reflect. for Refinement (R_{int})	2884	1505	16544
Observed reflections [$I > 2\sigma(I)$]	2632	1423	12055
Max/minΔρ [e·Å^{-3}]	0.42/−0.33	0.47/−0.31	0.535/−0.480
$R1$/$wR2$ [$I > 2\sigma(I)$][a]	0.036	0.037	0.040
$R1$/$wR2$ (all reflections)	0.085	0.096	0.102
GOF on F^2[b]	1.070	1.05	0.952

[a] $R1 = (F_o - F_c)/F_o$; $wR2 = \{[w(F_o^2 - F_c^2)^2]/(F_o^2)^2]\}^{1/2}$. [b] GOF $= \{[F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. $w = 1/[\sigma 2(F_o^2) + (aP)^2 + bP$ where $P = [\max(F_o^2$ or $0 + 2F_c^2]/3$.

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