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Probing the reactivity of a 2,2′-bipyridyl-3,3′-bis-imine ligand by X-ray crystallography†

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The reactivity of a Schiff-base bis-imine ligand **3** is probed by X-ray diffraction studies. Its susceptibility to hydrolysis, oxidation and nucleophilic addition reactions is demonstrated by the isolation of the methanol adduct **4** and two diazapene heterocycles **5** and **6**. This reactivity is also reflected in the molecular structures of two coordination complexes isolated by the reaction of **3** with $M(hfac)_2$ salts, to afford [Cu(**5**)-(hfac)(tfa)] (**8**) and [Zn(**6**)$(hfac)_2$] (**9**).

Introduction

2,2′-Bipyridine ligands have been widely employed in the field of supramolecular chemistry due to their highly predictable coordination chemistry, ease of functionalization and redox stabilities of their resulting complexes.[1] Substitutions at the 4-, 5- and 6-positions of the bipyridine framework have been actively investigated over the last three decades, resulting in a wide range of new derivatives that find applications in macromolecular chemistry,[2] catalysis,[3] molecular recognition,[4] and optoelectronics.[5] In addition, this family of ligands has been incorporated into the structures of molecular sensors,[6] metal organic frameworks[7] and luminescent devices.[8] In contrast, exploitation of the 3- and 3′-positions for the preparation of new derivatives has been much less well explored. In part this is due to the inherent twisting of the bipyridine framework from planarity when including substituents in both 3 and 3′-positions which may inhibit the conventional *N*,*N*′-bipyridine coordination mode. Whilst substitution at the 3 and 3′ positions is synthetically challenging, a range of 3,3′-derivatives have now been reported including the 3,3′-dimethyl,[9a] 3,3′-dinitro,[9b] 3,3′-dicarboxylate,[9c] 3,3′-diester,[9d] 3,3′-dihydroxy[9e] and 3,3′-diarylphosphoryl[9f]-2,2′-bipyridine derivatives, as well as 3,3′-diamino-2,2′-bipyridine, **1**.[10] All these derivatives have been shown to chelate to metal ions through the pyridine nitrogen atoms albeit with twists of 20–40° about the inter-pyridine bond arising from the 3,3′-substitution. Applications of such derivatives to catalysis,[11] and sensing[12] have been developed, and progress has recently been made in methods for benzylic substitution at the 3,3′-positions on the $Ru(bipy)_2$ complex of a 3,3′-bis-hydroxymethylene derivative.[13] Construction of a crown ether between the 3,3′-positions has led to systems which bind two different metal ions,[14] and thus modulation of properties in the presence of a second cation, *e.g.* selectivity of the initial binding or luminescent properties. In our previous studies on the coordination chemistry of the diamino ligand **1** we demonstrated that the amino groups form an internal hydrogen bond, and coordination takes places preferentially through the pyridyl nitrogen atoms, although one or both amino groups participate in the complex with $CuCl_2$ depending on the pH of the reaction mixture.[10] Synthetic developments on **1** have included attachment to an analyte by ring closure with a ketone link[15] and unsymmetrical acylations leading to chiral helical fibres and organogels.[16]

In more recent work we shifted focus to exploit the amine functionality of **1** to access new families of polynuclear complexes that include first row transition metal complexes of the 2,2′-bipyridyl carboxamide ligand **2**.[17] Extending this approach we also targeted the preparation and study of the bis-imine ligand **3**.[18] Schiff-base ligands are widely employed in the field of coordination chemistry since they are easily

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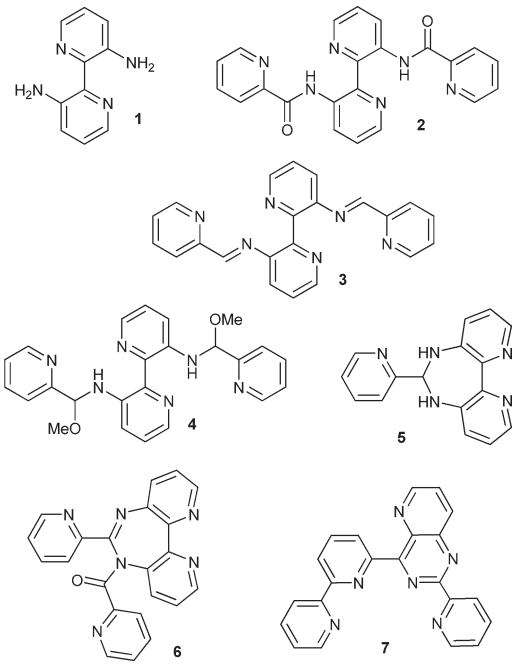
prepared from readily available starting materials and can incorporate N and/or O donors that can often result in compounds capable of binding metal ions in a multidentate manner.[19]



The Schiff-base condensation reaction is a facile way of introducing suitable substituents into the 3,3′-positions of the bipyridine enabling the steric and electronic features of the ligand to be tuned systematically. In a previous communication we reported the synthesis and metal catalysed rearrangement of **3** to the quaterpyridine-type ligand **7**.[18] In this more recent study, we present a more complete picture of the reactivity of **3** in which two electron deficient pyridine rings are linked *via* an imine bridge to the 3,3′-positions of a 2,2′-bipyridine framework. We show that **3** readily undergoes a nucleophilic attack by water followed by an intramolecular cyclization reaction to afford diazapene ligands, both in the absence and presence of Lewis acidic transition metal ions.

Experimental section

General considerations

All experiments were performed under a nitrogen atmosphere unless stated otherwise. Dry solvents were obtained from a Puresolve PS MD-4 solvent purification system. 3,3′-Diamino-2,2′-bipyridine **1** and the Schiff-base bis-imine ligand **3** were synthesized following the methods described previously.[10,18] All chemicals were commercially available and used as received, unless otherwise stated.

Physical measurements

NMR spectra were recorded on a Bruker Avance AV 600 Digital NMR spectrometer with a 14.1 Tesla Ultrashield Plus magnet. Samples for IR were pressed as KBr pellets and their spectra were recorded using a ThermoMattson RS-1 FT-IR. EI and FAB mass spectra were obtained using a Kratos Concept 1S High Resolution E/B mass spectrometer. Samples for elemental analysis were obtained from Atlantic Microlab.

Synthesis

***E*,*E*-*N*3,*N*3′-Bis-(2-pyridylmethylene)-(2,2′-bipyridine)-3,3′ diamine, (3).**[18]. m.p.$_{dec.}$ 80–81 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ_H = 8.71 (dd, J = 4.7, 1.2 Hz, 2H), 8.51 (d, J = 4.7 Hz, 2H), 8.34 (s, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.69 (dd, J = 7.8, 1.2 Hz, 2H), 7.47 (dd, J = 7.8, 1.2 Hz, 2H), 7.43 (dd, J = 7.8, 4.6 Hz, 2H), 7.30 (dd, J = 7.8, 4.7 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C = 162.3, 154.1, 151.5, 149.4, 147.5, 146.1, 136.7, 125.7, 125.3, 124.1, 121.6; FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3053, 1630, 1566, 1501, 1458, 1418, 1401, 1224, 1188, 993, 879, 797, 756, 622; HRMS (EI): m/z = 364.1435, $C_{22}H_{16}N_6$ requires 364.1436. Elemental analysis (%): calculated for $C_{22}H_{16}N_6$: C, 72.50; H, 4.43; N, 23.07; found C, 71.97; H, 4.43; N, 23.43%.

***Meso*-3,3′-di(α-methoxypyrid-2-ylmethylamino)-2,2′-bipyridine, (4).** Addition of dry MeOH (3 mL) to **3** (10 mg) followed by slow evaporation of the solvent under nitrogen afforded a few single crystals of the *meso* stereoisomer of **4** which were characterized by X-ray crystallography. FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3300, 3053, 1566, 1501, 1458, 1418, 1401, 1224, 1188, 1110, 993, 879, 797, 756, 622; MS (FAB m/z) 428 (100%); elemental analysis (%): calculated for $C_{24}H_{24}N_6O_2$: C, 67.27; H, 5.65; N, 19.61; found C, 67.42; H, 5.60; N, 19.37%.

6-(Pyridin-2-yl)-6,7-dihydro-5*H*-dipyrido[3,2-*d*:2′,3′*f*][1,3] diazepine, (5). Compound **3** (20 mg, 0.05 mmol) was dissolved in wet acetonitrile (5 mL) and the flask was left exposed to the air. After 1 week slow evaporation of the solvent afforded colourless plates of the diazepine heterocycle **5**. Yield: 8 mg, 53%. MS (FAB m/z) 275 (100%); FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3070, 1634, 1575, 1456, 1270, 1200, 800, 755, 706, 655; elemental analysis (%): calculated for $C_{16}H_{13}N_5$: C, 69.80; H, 4.76; N, 25.44; found C, 69.92; H, 4.53; N, 25.70%.

[Cu(5)(hfac)(tfa)], (8). Cu(hfac)$_2$·nH$_2$O (0.248 g, 0.500 mmol) was added to a solution of **3** (0.182 g, 0.500 mmol) in MeCN (5 mL). The mixture was stirred for 0.5 h after which time a yellow precipitate was formed. The complex was collected by filtration and washed with Et_2O to afford **8** as a yellow solid. Yield: 150 mg (45%). FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3321, 1664, 1598, 1549, 1528, 1497, 1470, 1427, 1337, 1260, 1201, 1144, 1085, 801, 667, 583; MS (FAB m/z) 545 [Cu(**5**)(hfac)]H$^+$; UV-Vis (MeOH, nm, ε/M^{-1} cm^{-1}) 240 (6800), 280 (5000), 420 (18 500) nm; elemental analysis (%): calculated for $C_{23}H_{14}CuF_9N_5O_4$: C, 41.92; H, 2.14; N, 10.63; found C, 41.51; H, 2.24; N, 10.37%. Suitable crystals of **8** for X-ray diffraction were grown after a few days *via* the slow evaporation of acetonitrile.

[Zn(6)(hfac)$_2$], (9). Zn(hfac)$_2$·2H$_2$O (0.516 g, 1.00 mmol) was added to a solution of **3** (0.364 g, 1.00 mmol) in MeOH (5 mL). The mixture was stirred for 0.5 h and then heated to 60 °C overnight. The solvent was removed and the residue was dissolved in CH_2Cl_2 (3 mL) and slowly dropped into cold *n*-pentane (30 mL) at 0 °C. The resulting yellow precipitate

was collected by filtration and washed with cold *n*-pentane to afford **9** as a yellow solid. Yield: 453 mg (52%). MS (FAB *m*/*z*) 545; FT-IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3320, 2359, 1670, 1650, 1590, 1526, 1501, 1460, 1428, 1257, 1200, 1144, 1095, 802, 725, 665, 582; elemental analysis (%): calculated for $C_{32}H_{16}F_{12}N_6O_5Zn$: C, 44.8; H, 1.88; N, 9.80; found C, 44.73; H, 1.78; N, 9.72%. Suitable single crystals for X-ray diffraction were grown after a couple of weeks *via* the slow evaporation of an acetonitrile solution.

X-Ray crystallography

Single crystals of compounds **3** and **5** were mounted on a cryoloop with paratone oil and examined on a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryostream low temperature device. Data were measured at 150(2) K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and the APEX-II software.[20] Final cell constants were determined from full least squares refinement of all observed reflections. The data were corrected for absorption (SADABS).[21] Single crystals of **4** as well as complexes **8** and **9** were collected at 173 K on a STOE Mark II-Image Plate Diffraction System equipped with a two-circle goniometer and using graphite-monochromated Mo-Kα radiation. The data were corrected for absorption (in PLATON).[22] For all compounds, the structures were solved by direct methods with SHELXS[23] and refined by full-matrix least-squares on F^2 with SHELXL-97.[23] Hydrogen atoms were placed in calculated positions and refined as riding atoms using SHELXL default parameters. Crystallographic data for ligands **3**–**5** and complexes **8** and **9** are summarized in Table 1. In the case of **4** and **8** there was evidence for disorder. In this respect the centrosymmetrically related pyridyl rings in **4** were modelled over two orientations (1 : 1) related to each other by a rotation of 32° about the C2–C5 axis of the ring, and the CF_3 group of trifluoroacetate in complex **9** was modelled with two orientations (4 : 1) about the C–CF_3 bond. All compounds have been submitted to the Cambridge structural database and have been allocated the following numbers. CCDC 972052–972056.

Computational studies

Single point DFT calculations were undertaken on the structure of **3** determined by X-ray diffraction using the Pople[24] 6-311G* basis set and B3LYP[25] functional within Jaguar.[26]

Results and discussion

Synthesis and reactivity of the 2,2′-bipyridyl bis-imine ligand, 3

The bipyridyl bis-imine ligand **3** was prepared by refluxing one equivalent of 3,3′-diamino-2,2′-bipyridine **1** with two equivalents of 2-formylpyridine in toluene and removal of water using a Dean Stark, over a five day period.[18] The ^{1}H and ^{13}C NMR spectra of **3** show characteristic ^{1}H and ^{13}C resonances at 8.34 and 162.3 ppm, respectively, consistent with the presence of an imine functionality. An intense band in the IR spectrum at 1630 cm^{-1} is assigned to the C=N str of the bis-imine, shifted to slightly lower frequencies due to its conjugation with the pyridyl ring. The high resolution (EI) mass spectrum of $\mathbf{L_3}$ is consistent with its molecular structure showing a parent ion peak at *m*/*z* = 364.1435, in good agreement with the calculated value of 364.1436 for $C_{22}H_{16}N_6$. Single crystals suitable for X-ray diffraction were grown from a saturated THF solution at −40 °C. The ligand crystallizes in the monoclinic space group $P2_1/c$ with one independent molecule in the asymmetric unit. The two rings of the bipyridine molecule lie at 64.26(8)° from the *cis*-coplanar conformation. The best planes of the unit containing a terminal pyridine and imine group lie at 51.8(8)° and 56.59(8)° to the plane of the bipyridyl pyridine ring to which they are attached. In the crystal, molecules are

Table 1 Crystallographic data

Compound reference	3	4	5	8	9
Chemical formula	$C_{22}H_{16}N_6$	$C_{24}H_{24}N_6O_2$	$C_{16}H_{13}N_5$	$C_{23}H_{14}CuF_9N_5O_4$	$C_{32}H_{16}F_{12}N_6O_5Zn$
Formula mass	364.41	428.49	275.31	658.93	857.88
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
a/Å	10.9614(6)	4.9022(6)	9.8020(15)	8.2407(9)	9.5227(8)
b/Å	20.1743(11)	13.8842(15)	11.0335(17)	10.3017(11)	12.9131(11)
c/Å	8.7356(5)	15.385(2)	12.7221(15)	15.4495(16)	13.7732(11)
α/°	90.00	90.00	87.172(7)	103.709(12)	80.759(10)
β/°	101.490(3)	99.095(16)	84.520(7)	98.082(12)	80.757(10)
γ/°	90.00	90.00	85.678(7)	101.143(13)	84.987(10)
Unit cell volume/Å^3	1893.06(18)	1034.0(2)	1364.5(3)	1226.0(2)	1646.7(2)
Temperature/K	150(2)	173(2)	150(2)	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	2	4	2	2
No. of reflections measured	29 931	1884	14 185	9628	10 520
No. of independent reflections	4286	1884	6646	4451	5992
R_{int}	0.0466	0.0792	0.0534	0.0508	0.0498
Final R_1 values ($I > 2\sigma(I)$)	0.0529	0.0352	0.0556	0.0422	0.0465
Final w$R(F^2)$ values ($I > 2\sigma(I)$)	0.0994	0.0728	0.1106	0.1056	0.1089
Final R_1 values (all data)	0.0869	0.0774	0.1273	0.0661	0.0831
Final w$R(F^2)$ values (all data)	0.1110	0.0833	0.1393	0.1305	0.1291

linked by a pair of long C(17)–H···N(5) formyl-type contacts (2.53 Å) involving the pyridine N and imine CH groups forming inversion dimers (Fig. 1).

These dimers pack in a herringbone manner and are connected within a stack *via* contacts involving a Ar–H to the π-system of a neighbouring molecule such that C–H(1)···π = 2.86 Å (Fig. 2, green dashed lines).

The reactivity of the imine groups towards nucleophilic species is demonstrated by the product **4**, obtained after recrystallization of **3** from dry methanol. In this respect, single crystals of cyclized **4** were characterized by X-ray diffraction which reveals that a methanol molecule has added across each of the bis-imine bonds (Fig. 3). This is supported by the IR spectrum that reveals an NH str at 3300 cm^{-1} that shifted to lower frequencies as a consequence of its participation in H-bonding interactions, *vide infra*. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ and sits on a crystallographic centre of symmetry. Both of the outer pyridine rings are disordered between two orientations related by a 32° rotation about the 2C–5C vector of the ring. The molecule is almost planar with the exception of the two methoxy groups which adopt axial positions and are located *trans* with respect to each other. The bipyridine rings adopt a *trans* conformation stabilized by two hydrogen bonds from each NH group (Fig. 3a). The amino hydrogen atom was located in the difference Fourier map and its position corresponds to approximate planar bonding geometry at nitrogen.

The first hydrogen bond is to a bipyridine N atom, with a N(3)···H(2) bond length of 1.81(3) Å and a N(3)···H(2)–N(2) angle of 140(2)°, similar to the intramolecular hydrogen bonding interactions present in the structure of 3,3′-diamino-2,2′-bipyridine **1**.[10] The second hydrogen bond is to the disordered terminal pyridine ring (N(1A)···H(2): 2.20(3) Å, N(1A)···H(2)–N(2): 102.84(2)° and N(1B)···H(2): 2.40(3) Å, N(1B)···H(2)–N(2): 99.70(2)°) but with much less favourable geometry at H. The torsion angle about the NH–C–O–CH_3 system is 60.3°, similar to that found in seven related systems,[27] and is indicative of a stereoelectronic effect between an oxygen lone pair and the N–C(O) bond. The bond length from the amino group to the pyridine ring is 1.382(3) Å, indicating that this lone pair is conjugated with the aromatic ring. The molecules pack in alternating layers of slipped stacks along the *b*-axis of the unit cell, giving rise to a herringbone motif, Fig. 4. The distances between the centroids of the two offset bipyridine rings within neighbouring

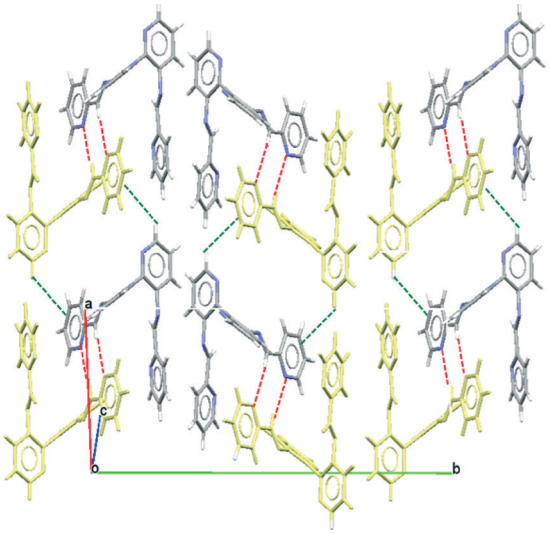


Fig. 2 Crystal packing of **3**. View down the *c*-axis showing herringbone arrangement of dimers. H-bond between dimers are shown as red dashed lines; CH–π interactions between sets of dimers are shown as green dashed lines.

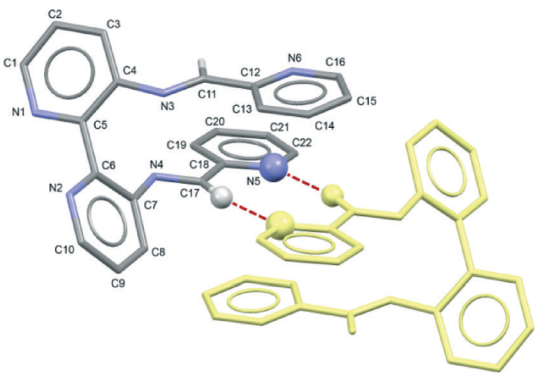


Fig. 1 Molecular structure of the 2,2′-bipyridyl bis-imine ligand **3** showing hydrogen bonding interactions as dashed lines. Aryl H-atoms are excluded for clarity.

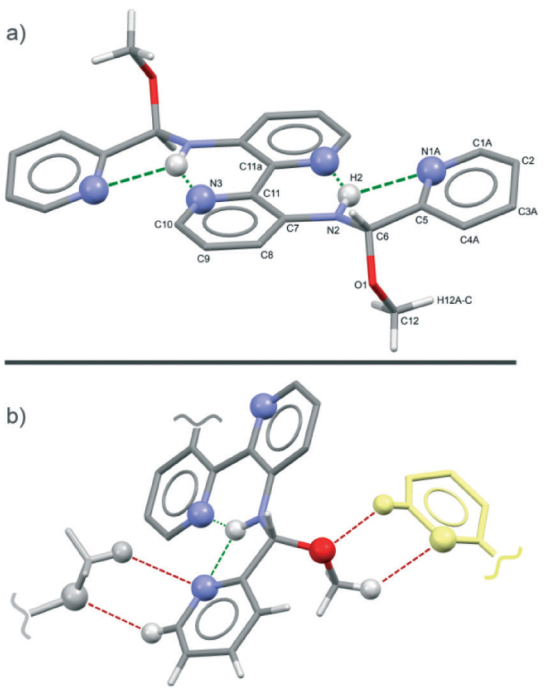


Fig. 3 a) Molecular structure of the bis-methanol adduct **4** showing a) bifurcated NH···N intramolecular H-bonding interactions as green dashed lines); b) extended hydrogen bonding interactions between pyridine and methoxy groups as red dashed lines. Only one conformation of the pyridine rings is shown.

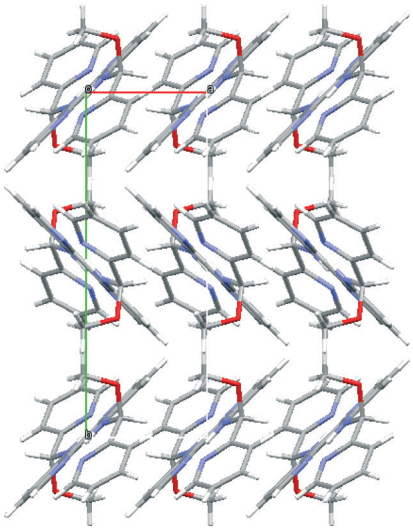


Fig. 4 Crystal packing of 4. View down the *c*-axis showing the herringbone arrangement of molecules.

stacks are 5.01 Å and the distance between two pyridine rings is a little shorter at 4.90 Å. This spacing serves to accommodate both the pyridyl and methoxy substituents.

A second example highlighting the susceptibility of the imine groups towards nucleophilic attack is shown in Fig. 5.

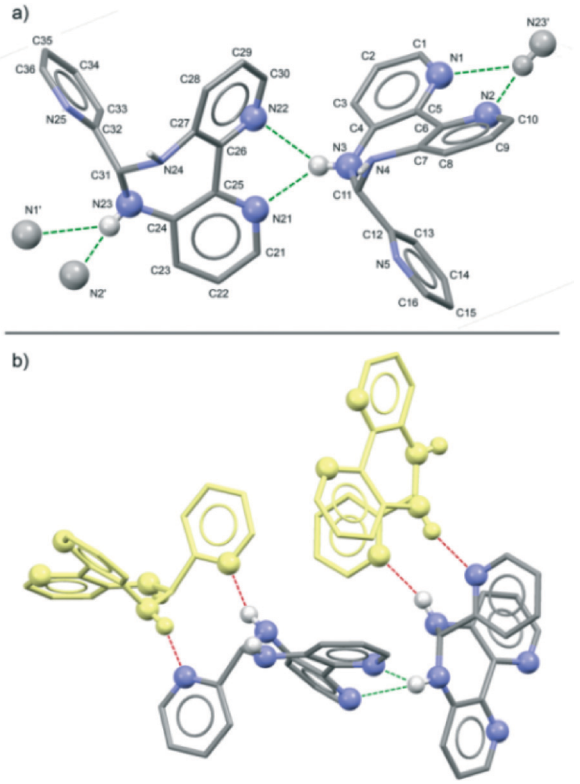


Fig. 5 Molecular structure of the two crystallographically independent molecules of 5. a) Bifurcated hydrogen bonding interactions between an NH group and the 2,2′-bipyridine are shown as green dashed lines; b) hydrogen bonding interactions between the other NH group and the pendant pyridine are shown as red dashed lines.

Single crystals of the dihydrodipyrido[1,3]diazepine adduct 5 were obtained *via* the slow evaporation of an acetonitrile solution of ligand 3. In fact it should be noted that the bis-imine ligand 3 is very reactive in solution and unless stored in dry conditions it readily undergoes hydrolysis and cyclization to the diaepine compound 5.

Compound 5 crystallizes in the triclinic space group $P\bar{1}$ with two crystallographically independent molecules in the asymmetric unit which adopt reasonably similar conformations in their 1,3-diazepine rings. The nitrogen atoms are displaced to opposite sides of the ring's best plane with one nitrogen, N(4) or N(24), displaced much more than the second N atom of the ring (Fig. 5). The formation of the diazepine ring forces the two rings of the bipyridine out of co-planarity, so that the distance between the two bipyridine N atoms increases to 2.613(3) and 2.684(3) Å in the two molecules. The best planes of the pyridine rings of the 2,2′-bipyridine lie at 26.18(10) and 32.83(10)° to each other. Crystallographically independent pairs of molecules are linked along the *c*-axis *via* a bifurcated hydrogen bond from a diazepine NH (N(3) or N(23)) to the two nitrogen atoms of a neighbouring 2,2′-bipyridine residue (N(3)–H(3A): 0.92 (3) Å, H(3A)···N(21): 2.19(3) Å and H(3A)···N(22): 2.41(3) Å) and (N(23)···H(23A) 0.86(3) Å, H(23A)···N(1): 2.40(3) Å and H(23A)···N(2): 2.42(3) Å) (Fig. 5 and 6). There are also short contacts involving the aromatic protons on one ring and the π-system of a neighbor, such that Ar–H(10)···π = 2.89 Å (Fig. 6, green dashed line).

Formation of this ligand can be explained by the initial hydrolysis of one of the imine groups in 3 releasing an amino group which then adds to the remaining imine group to form the fused dihydro-1,3-diazepine ring system in 5 (Scheme 1). DFT calculations[26] carried out on the unoptimised solid state structure of 3 reveal a large coefficient on one of the imine carbons in the LUMO, while the HOMOs of the

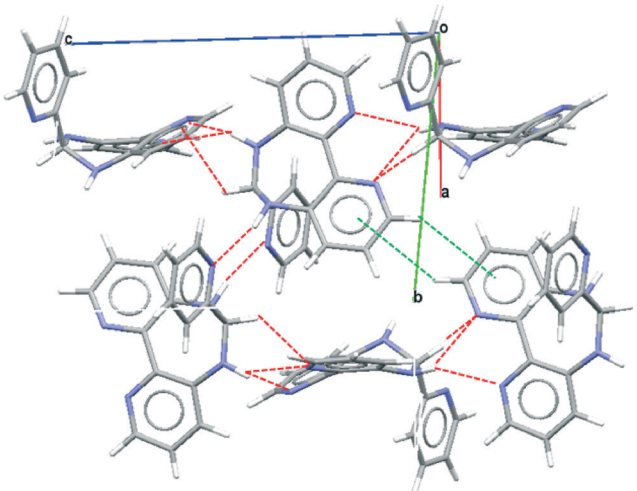
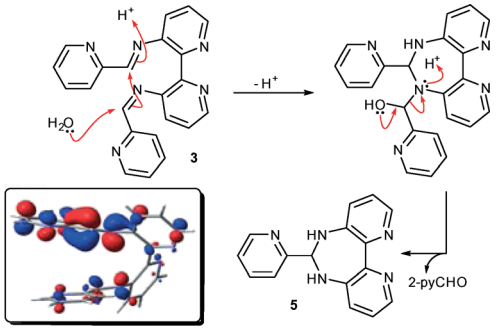


Fig. 6 Crystal packing of 5. H-bonded interactions are shown as red dashed lines and C–H···π interactions as green dashed lines.



Scheme 1 Proposed mechanism for the intramolecular cyclisation of **3** to form **5**; LUMO‡ (B3LYP/6311G*) of **3** shows largest coefficient on carbon of imine.

system are highly associated with the bipyridyl backbone of the molecule.‡

Since the HOMO is of bipyridine character, protonation by H^+ is unlikely to be imine-based, thus favouring a mechanism initiated by nucleophilic attack by water. It should be noted that diazepine analogues belong to a class of 7-membered heterocycles that display a range of diverse pharmacological activities that include anxiolytic,[28] hypnotic,[28] HIV protease inhibitors[29] and cardiovascular.[30] This particular 5*H*-dipyrido[*d*,*f*][1,3] diazepine ring system has not been explored with respect to its biological activity, however the facile rearrangement of **3** into this ring system offers a synthetic procedure for the construction of 7-membered heterocycles which could be useful for making and screening the medicinal properties of new functionalized systems in the future.

Coordination chemistry

With six sp^2 N atoms, ligand **3** has two potential binding modes, symmetric (a) and asymmetric (b) as demonstrated in Fig. 7. In the symmetric binding mode, **3** could coordinate metal ions with the bipyridine backbone and/or the tetradentate binding site formed by both imine bonds and their corresponding pyridine ring, closely resembling the coordination preferences of the biphenyl bis-imine ligands reported in the literature.[31] On the other hand, in the asymmetric mode, the ligand adopts a *trans*-coplanar conformation chelating as a bis-tridentate ligand in a similar manner to the previously reported dicarboxamide ligand **2**.[17]

The susceptibility of **3** towards nucleophilic attack at its imine functionality assisted *via* chelation to Lewis acidic metal ions adds an interesting dimension to its coordination chemistry.[18] In order to probe this reactivity further, coordination complexes with transition metal ions were prepared, but single crystals of only two complexes were obtained for X-ray diffraction studies.

‡ The LUMO+1 is very similar in energy and shape, with the major coefficient based upon the carbon of the second imine group; this difference can be explained by the fact that, while the molecule is symmetric, it adopts an unsymmetrical conformation in the solid state.

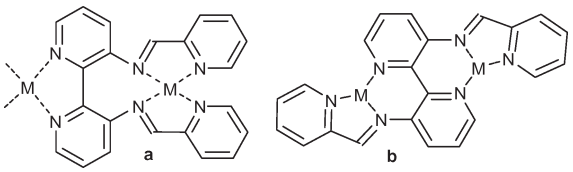


Fig. 7 Potential symmetric (a) and asymmetric (b) binding modes of **3**.

Reaction of the bis-imine ligand **3** with $Cu(hfac)_2$ in acetonitrile afforded a green solid that was recrystallized from acetonitrile to afford single crystals of **8**, [Cu(**5**)(hfac)(tfa)]. The complex crystallizes in the triclinic space group $P\bar{1}$, with a pentacoordinate Cu^{II} centre coordinated to a diazapine ligand **5**, one hfac anion and surprisingly, one trifluoroacetate (tfa) anion derived from the hydrolysis of a second hfac anion (Fig. 8). The bipyridine ligand, tfa and one oxygen atom of the hfac anion form a distorted square planar arrangement confirmed by determining the Addison distortion parameter[32] which has a value of 0.318 in contrast to 0 for square planar geometry around the Cu^{II} ion. The second hfac O atom coordinates copper in the axial position with an axial Cu–O bond of 2.210(2) Å that is significantly longer than the other two equatorial Cu–O distances.

The fluorine positions around C23 on the trifluoroacetate group are disordered. The diazepine ligand system is almost planar with the exception of the carbon atom carrying the isolated pyridine ring which lies 0.732(4) Å out of the plane defined by the other fourteen ring atoms giving rise to an envelope type conformation for the central seven-membered ring. The isolated pyridine ring lies at 66.0(17)° to the bipyridine's best plane. The binding of the bipyridine fragment to the Cu^{II} ion promotes the planarity of the bipyridine rings, and removes the repulsion between nitrogen lone pairs which is partly responsible for the non-planar configuration of the bipyridine rings in the free ligand.

The complex packs in a head-to-tail arrangement of two sets of dimers, (Fig. 9, silver and gold). The distances from the centroids of two pyridyl rings within the silver dimer are 4.503 Å. Each end of this dimer unit is stabilized hydrogen bonding interactions from the tfa oxygen atom to both the

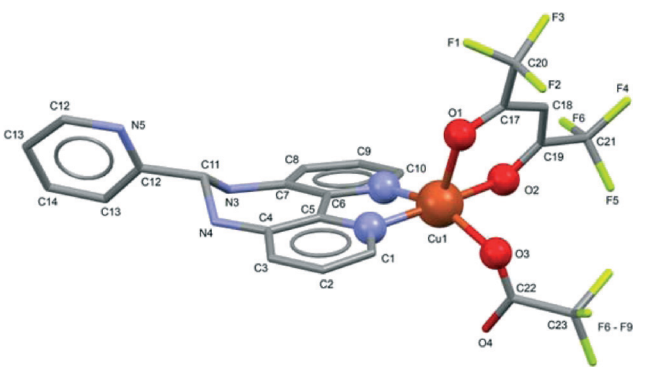


Fig. 8 Molecular structure of **8**, [Cu(**5**)(hfac)(tfa)]. H-atoms are omitted for clarity. The CF_3 group of the TFA is disordered; only one orientation is shown.

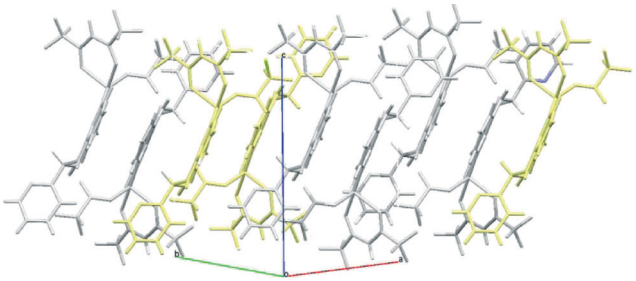


Fig. 9 a) Crystal packing of **8**, the two pairs of dimer units are shown in silver and gold respectively.

amine and an aromatic proton of a pyridyl ring such that N–H(4)···O(4) = 2.14(1) Å and C–H(8)···O(4) = 2.49(2) Å. The Cu···Cu distances within the silver dimer are 7.489(2) Å. In contrast, the two molecules of the gold dimer are further apart, displaying no close contacts and longer Cu···Cu distances of 8.201(1) Å. Magnetic susceptibility studies of **8** are presented in the ESI† and reveal that comprises of isolated Cu^{II} centers, obeying Curie Weiss law with C = 0.490 emu K mol^{-1} and θ = +1.15 K.

Clearly during the formation of this complex the bis-imine ligand **3** has undergone hydrolysis and cyclization resulting in the chelation of a diazepine ligand **5** as previously presented in Scheme 1. In this case, coordination of the bipyridine to the Cu^{II} ions would organize the imine functionality into the optimal *cis* geometry for the cyclization reaction. The presence of tfa can be explained based on the literature precedent for the decomposition of hfac ligands.[33] As shown in Scheme 2, water present in the reaction mixture could act as a nucleophile and carry out a *retro*-Claisen condensation, assisted by coordination of the Lewis acidic Cu^{II} ion to the hfac ligand.

Following the same strategy, reaction of ligand **3** with $Zn(hfac)_2$ in acetonitrile afforded single crystals of $[Zn(\mathbf{6})(hfac)_2]$ **5**, containing the oxidized diazepine ligand **6**. The crystal structure of this complex shows a Zn^{II} ion coordinated by two hfac ions and **6** which has a fully unsaturated 5*H*-dipyridinodiazepine ring system with a 2-pyridyl group on the ring C(11) carbon atom and a 2-pyridinoyl group at a diazepine nitrogen atom (Fig. 10). The Zn^{II} cation adopts a distorted octahedral coordination environment with small N–Zn–N angles of 78.2(1)° for the bipyridine and O–Zn–O angles of 86.6(1) and 87.2(1)° for the hfac ligands. The Zn–N bond distances are 2.127(3) and 2.155(3) Å, and the Zn–O distances are 2.074(3)–2.118(3) Å.

In contrast to **8** in the Cu^{II} complex, the bipyridine rings in complex **9** lie at 26.29(18)° to each other, due to the reduced flexibility of the diazepine ring which now contains an endocyclic amidine group and an exocyclic amide group. The diazepine ring system adopts a twisted conformation. The pyridine attached to the C(11) atom of the amidine is almost coplanar with this group, and lies at 85.8(2)° to the other pyridyl substituent. The N–C bond lengths in the N(3)═C(11)–N(4)–C(17)═O(5) fragment are 1.257(5), 1.438(5) and 1.374(5) Å respectively, indicating that the amide nitrogen atom makes a stronger conjugation with the carbonyl than with the imine group. This ligand is derived from the bis-imine by addition of water across the imine bond followed by oxidation to generate the carbonyl group and a double bond in the ring, Scheme 3.

It is interesting to note that the two coordination complexes comprise of two different diazapene heterocycles. In

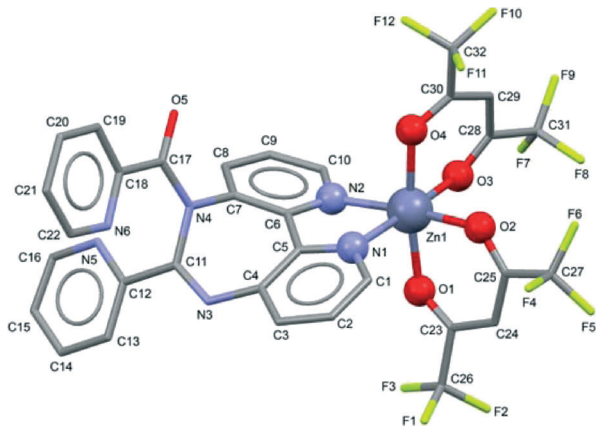
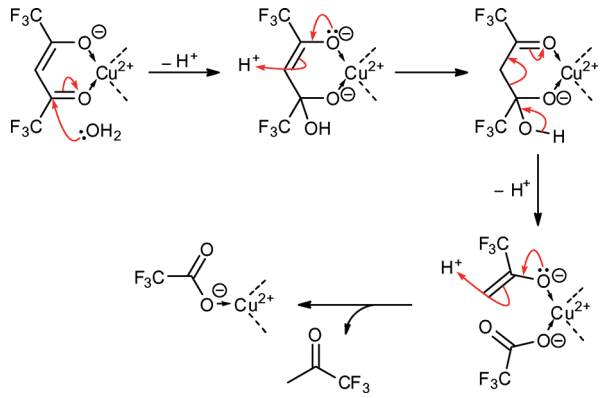
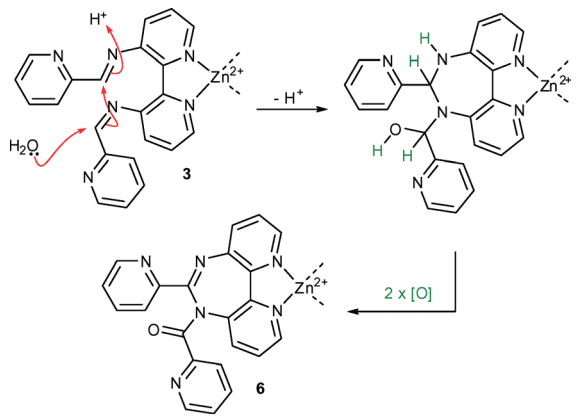


Fig. 10 Crystal structure of $[Zn(\mathbf{6})(hfac)_2]$, **9**, showing the atomic labelling scheme. H-atoms are omitted for clarity.



Scheme 2 Proposed mechanism for the metal-assisted hydrolysis of the hfac anion to give tfa in complex **8**.



Scheme 3 Proposed mechanism for the rearrangement of **3** into **6**.

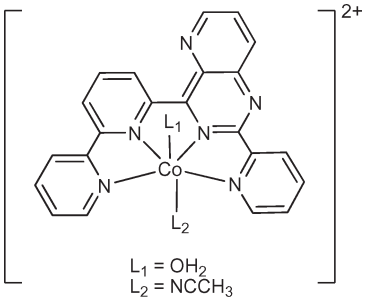


Fig. 11 Molecular structure of $[Co(\mathbf{7})(OH_2)(NCCH_3)](ClO_4)_2$.

the case of the Cu^{II} complex, the hfac ligand undergoes hydrolysis, but for the Zn^{II} derivative, the hfac ligand remains intact, but the ligand after intramolecular cyclization, undergoes further oxidation to afford the ketone derivative **4**, instead of eliminating PhCHO to give **3**. The higher Lewis acidity of Zn^{II} compared with Cu^{II} may in part account for the different reactivity of the ligand in the two reactions however, given that the yields of the complexes are not quantitative, it is more likely that single crystals of the thermodynamically most favourable complex were obtained that contains the hydrolysed ligand in **8** and the hydrolysed and oxidized ligand in **9**. In the case of **9**, the crystals took longer to grow (2 weeks *vs.* a few days) so this additional time may have helped facilitate the oxidation process. Attempts were made to investigate the ^1H NMR spectrum of the Zn^{II} complex, but overlapping peaks corresponding to more than one product made interpretation of the spectrum impossible. The diverse reactivity of this ligand in the presence of Lewis acidic metal ions is not too surprising given that we previously isolated a complex of stoichiometry $[Co(7)(OH_2)(NCCH_3)](ClO_4)_2$, from reaction of **3** with an excess of cobalt(II) perchlorate.[18] In this case, instead of obtaining a diazapene heterocycle, a quaterpyridine type ligand was obtained comprising four contiguous heterocycles (three pyridines and one pyrido[2,3-*d*]pyrimidine) coordinated to the Co(II) ion (Fig. 11).[18] The full mechanism by which the bis-imine ligand rearranges into **7** in the presence of the Co(II) ion has been reported elsewhere,[18] but the first step in the reaction involves the metal assisted nucleophilic attack of one of bipyridyl N lone pairs on an imine bond, in contrast to hydrolysis followed by the nucleophilic addition of the resultant amine to the second imine bond that we have observed for both the free ligand and the Cu^{II} and Zn^{II} complexes in this study.

Conclusions

We have demonstrated by carrying out X-ray crystallographic studies on the Schiff-base ligand **3** together with its rearrangement products both in the presence and absence of Lewis acidic transition metal ions that the imine bonds are sensitive towards hydrolysis, oxidation and nucleophilic addition reactions. Addition of methanol to **3** affords the adduct **4** where methanol molecules have added across both of the bis-imine bonds. The susceptibility of **3** towards intramolecular nucleophilic addition reactions is demonstrated by the formation of two new cyclized diazapene ligands **5** and **6** as well the previously reported quaterpyridine ligand **7** and adds a unique and interesting dimension to its coordination chemistry. Further work is in progress to prepare and investigate the coordination chemistry of new families of Schiff-base bis-imine ligands, working towards the preparation of magnetic clusters and metal organic frameworks.

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