Non-covalent polymerisation in the solid state: halogen-halogen *vs*. methyl-methyl interactions in the complexes of 2,4-di(2-pyridyl)-1,3,5-triazine ligands[†]

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Fe(II), Co(II), Ni(II) and Cu(II) complexes based on the triazine ligand 2,4-di(2'-pyridyl)-6-(*p*-bromo-phenyl)-1,3,5-triazine have been synthesised and characterised. The electrochemical, magnetic and spectroscopic properties of the complexes have also been investigated, and the electron deficient triazine ligand has been shown to affect each of these properties. Further investigation of solid state structures of the ligand and its Fe(II), Co(II) and Cu(II) complexes has established that stabilising Br–Br interactions exist which link neighbouring molecules to form one-dimensional tapes. A slight modification of the ligand, *i.e.*, using 2,4-di(2'-pyridyl)-6-(*p*-methylphenyl)-1,3,5-triazine, in which the phenyl substituent has changed from a bromine to a methyl group, eliminates the one-dimensional tape and gives rise to significant π -stacking interactions in the solid state.

Introduction

Controlled aggregation of metallic supramolecular assemblies through covalent or non-covalent approaches is of interest for device applications depending on the magnetic,¹⁻³ redox⁴ or luminescent properties⁵⁻⁷ of the oligo- or poly-nuclear complexes under study. Facile and rapid syntheses of such assemblies is in itself important and as a consequence transition metal complexes of *N*-heterocyclic tridentate ligands based on 2,2':6':2"-terpyridine (tpy) have been the focus of much attention due to the wide variety of synthetic methods for their preparation.⁸ Whilst complexes of bidentate ligands such as 2,2'-bipyridine (bpy) possess interesting properties,⁶ rapid synthesis of polymetallic systems based on bpy can be problematic due to the difficulty in separation of *facial* and *meridonal* diastereomers.⁵ Three main approaches have been taken to obtain higher nuclearity complexes based on tridentate tpy-type ligands (Fig. 1). The first involves the synthesis of polytopic ligands that can be applied to the metal-directed assembly of higher nuclear complexes using covalent interactions (Fig. 1(a)).^{8–11} The second and third approaches involve the synthesis of monomeric complexes, which may be polymerised through the use of covalent or non-covalent interactions. Although 'chemistry-on-the-complex' synthetic methods may prove useful to build up polymetallic arrays through covalent interactions,^{12,13} this approach is limited by the solubility of the oligomeric complexes in solution (Fig. 1(b)). On the other hand, rapid and controlled aggregation of metal complexes in the solid state can be obtained using non-covalent interactions (Fig. 1(c)).¹⁴⁻¹⁶

Many synthetic strategies have been developed to improve the properties of complexes with tpy-type ligands.²⁴ Substitution on the terpyridine core has proved efficient in manipulating both magnetic and photophysical properties through electronic and steric interactions.²⁵⁻²⁷ Alternatively, the pyridyl rings can be replaced by different N-heterocyclic rings,^{28,29} as we previously reported for a Ru(II) family of complexes based on 2,4-di(2-pyridyl)-6-phenyl-1,3,5-triazine ligand family.^{30,31} The most widely studied triazine containing ligand, however, is the symmetric,



Fig. 1 Metal-containing polymers assembled by three approaches: (a) a classical coordination approach, $^{17-19}$ (b) a 'chemistry-on-the-complex' approach (including electrochemically), $^{20-23}$ and (c) a non-covalent assembling approach. 14,16

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commercially available 2,4,6-tris(2'-pyridyl)-1,3,5-triazine (tpt) ligand. Tpt has proved versatile in the synthesis of Fe(II),^{32–37} Co(II),³⁵ Ni(II)³⁸ and Cu(II)^{39–41} complexes with interesting properties and variable coordination modes. However, further direct substitution on the ligand is difficult, which in turn makes structural and electronic diversification of tpt and its complexes difficult. However, using the 2,4-di(2-pyridyl)-6-phenyl-1,3,5-triazine ligand family, a range of substituents can be introduced onto the ligand in order to tune and manipulate the photophysical and

electrochemical properties of their transition metal complexes.^{31,42} Herein, we report the synthesis and characterisation of a family of Fe(II), Co(II), Ni(II) and Cu(II) complexes of bromophenyland tolyl-substituted tridentate triazine-based ligands. The introduction of pendant Br-atoms enables us to gain directional control in the orientation of the metal complexes in the solid state through stabilising, non-covalent halogen-halogen interactions. These interactions have been exploited in both organic, inorganic and hybrid materials, and the influence of the $X \cdots X$ interaction is highly dependant on the polarity of a M-X and C-X bond.43-46 For example, Br · · · Br contacts as short as 3.55 Å are observed between molecules in the solid state structure of C6Br6.46c Halogen-halogen interactions in organic-based compounds may be classified into two types depending on the C-X \cdots X angle within the C-X \cdots X-C contact (Fig. 2).^{46b} In type I interactions, the angles θ_1 and θ_2 between the halogen atoms are essentially equal so that close contacts occur between identical portions of the halogen atom (Fig. 2). The interactions are allowed on consideration of the anisotropic behaviour of halogen atoms, allowing short Van der Waals interactions in the equatorial plane. These interactions may be shorter than the reported Van der Waals radii of the halogen in question but are permitted due to the elongation of the electronic distribution giving a non-spherical van der Waals radii.^{46c} Type II interactions are considered in terms of 'X atom-polarisation'. In such systems the halogen is polarised positively in the polar region and negatively in the equatorial region with a C-X bond lying perpendicular to the second C-X bond. The Br · · · Br interactions



Fig. 2 (a) Type I halogen–halogen interactions (left) and (b) Type II halogen–halogen interactions (right).

discussed in the complexes discussed herein may be classed as type I in nature.

Despite growing interest in the use of such interactions in crystal engineering, to the best of our knowledge, there are no examples in which this approach has been use to influence the aggregation of linear redox or magnetically active complexes based on tpy or alternative tridentate ligands.

Results and discussion

Synthesis

The ligands L1 and L2 were synthesised by modified triazine ring-forming reactions (Scheme 1).^{31,42} The original method could be improved by generating LiNMe₂ '*in-situ*', which proved more reliable than the use of LiNMe₂ in the solid state. Subsequent addition of *p*-bromobenzonitrile or tolunitrile afforded an amidinate intermediate which cyclised upon addition of 2 equivalents of 2-cyanopyridine to afford the triazine ligands L1 and L2.

The syntheses of complexes 1a-d and 2a-d were carried out in methanol or ethanol (Scheme 1). Anhydrous solvents were employed for the synthesis of Ni(II) and Cu(II) complexes in order to hinder hydrolysis of the triazine ligand which is promoted in aqueous solutions.⁴⁷⁻⁴⁹ A hot alcoholic solution of the appropriate



Scheme 1 Synthesis of ligands L1 and L2 and complexes 1a-d and 2a-d.

metal salts was added to an alcoholic solution of the ligand. Colour changes were observed immediately depending on the metal ions used and refluxing was continued for 15–30 minutes. Addition of alcoholic NH_4PF_6 or KPF_6 to the reaction mixture resulted in the precipitation of the complexes as their PF_6^- salts upon cooling which were collected, washed and dried to obtain complexes **1a–d** and **2a–d**.

The ¹H NMR spectra were obtained in CD₃CN for all complexes. Complexes **1b–d** and **2b–d** are paramagnetic and the ¹H signals are considerably shifted and broadened with respect to typical diamagnetic complexes. All of the ¹H signals are observed in the paramagnetic spectra of **1b–c** and **2b–c**, however, one peak is missing in complexes **1d** and **2d** due to the broadening of signals induced by the paramagnetic metal ions. The ¹H NMR spectra of **1a** and **2a** resemble that of a low spin diamagnetic Fe(II) complex although broadening of the resonance closest to the metal centre, H₆, is observed. This may indicate a small paramagnetic contribution in the complex for a largely diamagnetic ground state.

Solid-state structures

The solid-state structures (Table 1) of the ligand L1 and its complexes display interesting short-range $Br \cdots Br$ interactions (Fig. 3–6). The starting ligand, L1, crystallises in the monoclinic space group $P2_1/c$ with two water molecules associated with each triazine ligand in the asymmetric unit. The pyridyl and phenyl rings lie co-planar to the triazine rings with twists of 2.3(2) and 3.4(2)° for the pyridyl rings and 1.2(2)° for the bromophenyl ring due to favourable N-to-CH hydrogen bonding interactions between the N lone pairs and the H's *ortho* to the interannular bond. Relatively short $Br \cdots Br$ distances are observed between molecules, with each Br-atom being in close proximity to four others in a zigzag arrangement (Fig. 3).



Fig. 3 The Br \cdots Br interactions observed in L1: the *ac* plane (above) and the *ab* plane (below). The H₂O solvent molecules have been omitted for clarity.

Table 1 Summary of cry	ystal data and	l structure refinement	t for L1, 1a, 1c, 1d, 1d	and 2a-d					
Compound	L1	$1a \left(M = Fe \right)$	$\mathbf{1c} (\mathbf{M} = \mathbf{Ni})$	1d (M = Cu)	$1d' \ (M = Cu)$	2a (M = Fe)	2b (M = Co)	2c (M = Ni)	2d (M = Cu)
Colour	Colourless	Purple	Green-yellow	Green	Green	Purple	Orange	Green-yellow	Green
Formula	$C_{19}H_4BrN_5O$	$C_{38}H_{24}Br_2F_{12}FeN_{10}P_2$	$C_{40}H_{27}Br_2F_{12}N_{11}Ni_2P_2$	$C_{40}H_{27}Br_2CuF_{12}N_{11}P_2$	$C_{44}H_{36}Br_2CuF_{12}N_{10}O_2P_2$	$C_{40}H_{30}F_{12}FeN_{10}P_2$	$C_{40}H_{30}F_{12}N_{10}NiP_2$	$C_{40}H_{30}F_{12}N_{10}NiP_2$	$C_{40}H_{30}CuF_{12}N_{10}P_2$
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Tetragonal	Tetragonal	Tetragonal
T/K	150(2)	100(2)	100(2)	100(2)	150(2)	150(2)	125(2)	150(2)	150(2)
2/Å	1.54178	1.54178	1.54178	1.54178	1.54178 Å	1.54178	0.71070	1.54178	1.54178
Space group	$P2_1/c$	C2/c	$P\overline{1}$	$P\overline{1}$	C2/c	$P2_1/n$	$I4_1/acd$	$I4_1/acd$	$I4_1/acd$
a/Å	24.954(1)	14.4472(6)	8.5536(2)	8.5175(2)	14.8156(2)	8.9622(3)	22.200(2)	22.2925(3)	22.598(4)
$b/\text{\AA}$	3.9351(2)	21.045(1)	13.6850(2)	13.7974(3)	21.3172(4)	33.0144(8)	22.200(2)	22.2925(3)	22.598(4)
$c/\text{\AA}$	19.0793(8)	16.4940(9)	18.9796(3)	18.9148(4)	16.7458(3)	13.3712(4)	16.819(3)	16.6862(4)	17.155(7)
$a/^{\circ}$	90	06	91.086(1)	89.9110(1)	06	90	60	90	00
B/°	110.007(2)	99.350(4)	102.348(1)	78.4970(1)	95.3930(10)	92.053(2)	90	90	06
7,10	90	06	91.973(1)	87.8530(1)	00	60	90	90	90
$V/Å^3$	1760.4(1)	4948.2(4)	2168.21(7)	2176.64(8)	5265.37(15)	3953.8(2)	8289(2)	8292.3(3)	8761(4)
Z	4	4	2	2	4	4	8	8	8
$D_{\rm c}/{ m Mg}{ m m}^{-3}$	1.608	1.512	1.792	1.793	1.577	1.674	1.602	1.601	1.523
μ/mm^{-1}	3.406	5.699	4.392	4.44	3.732	4.763	0.591	2.300	2.242
Maximum $2\theta/^{\circ}$	68.24	72.72	73.11	67.94	68.64	68.97	28.37	68.83	57.24
No. refl. collected	23442	40326	26398	27217	60135	54135	44078	76131	37122
No. independent refl.	3232	4826	8310	7620	4823	7253	2517	1928	1494
Data/restraints/parameters	3232/0/256	4826/0/361	8310/2/663	7620/0/688	4823/0/425	7253/0/588	2517/0/152	1928/0/153	1494/0/153
R	4.4	9.61	5.28	3.18	6.17	3.80	3.54	4.16	2.96
wR2	12.15	28.9	13.38	8.69	18.89	9.88	9.43	11.40	7.97
Goodness-of-fit on F^2	1.048	1.008	0.910	1.027	1.046	1.002	1.073	1.094	1.022



Fig. 4 Br · · · Br interactions in the extended lattice in complex 1a.



Fig. 5 π -Stacking interactions in the extended lattice in complex 1d. The anions and solvent molecules of crystallisation have been omitted for clarity.

The molecules of L1 stack on top of each other with offset aromatic face-to-face interactions. Each Br atom is in close proximity to four other Br atoms and distances of 3.94 Å are observed vertically between layers of stacking ligands and 4.14 Å for the diagonal contacts.

The H-atoms on the water molecules are disordered and could not be found using electron-density maps but an ideal model was found using Calc-OH.[‡] In this model, a water molecule is Hbonded to the N-atoms of the distal pyridyl rings on the ligand. The H-atoms of the second water molecule are H-bonded to the oxygen of the first water molecule and in the extended lattice they form spiraling columns. Ligand L1 occupies gaps between pairs of columns.

Complexes 1a–d. The Fe(II) complex **1a** crystallises in the monoclinic space group, C2/c, and is isostructural to the previously published Co(II) complex **1b** (Table 1).⁴² Purple blocks of **1a** were obtained by slow diffusion of diisopropyl ether into an acetonitrile solution. The Fe(II) metal centre is in a distorted octahedral geometry coordinated to two tridentate ligands, as anticipated. Shorter Fe–N bond distances are observed to the central triazine

ring compared to the peripheral pyridyl rings due to the constraints imposed by the tridentate ligand (Table 2). The Fe–N distances at 100 K are in agreement with the low-spin Fe(tpy)₂²⁺ cation. The Fe–N(tpy) bond lengths were previously reported at 1.977–2.002 Å for the terminal pyridyl rings and 1.890–1.892 Å for central pyridyl rings.⁵⁰ The pendant phenyl rings are twisted by 18.6° in **1a** and 13.3° in **1b** relative to the central triazine ring. The twist in the interannular bond is a result of edge-to-face packing between the phenyl rings in different molecules, which are separated by 3.57 Å and 3.51 Å (Fig. 4), however, no favourable face-to-face packing interactions are observed.

Short $Br \cdots Br$ contacts are observed for **1a** and **1b** with distances of 3.45 and 3.40 Å, respectively, between adjacent molecules (Table 2), indicative of favourable van der Waals interactions which give rise to a linear one-dimensional tape in the solid state (Fig. 4).⁴² No solvent molecules of crystallisation are observed in the structure of complex **1b** and resolution of solvent in **1a** was not possible.

The Ni(II) and Cu(II) complexes, 1c and 1d, were initially recrystallised by slow diffusion of isopropyl ether into acetonitrile solutions. The crystals of 1c and 1d are isostructural and crystallise in the triclinic space group $P\bar{1}$ with a full cation, two PF₆ counteranions disordered over three sites, and variable amounts of solvent for either complex in the asymmetric unit. One PF₆⁻ anion is found

[‡] From the WinGX software suite, version 1.64.04: *J. Appl. Crystallogr.*, 1999, **32**, 563.

	1a	1c		1d		1ď	2a	2b	2c	2d
M–N(trz)	1.872(5)	1.977(4)	1.992(4)	1.942(2)	1.9995(19)	1.951(3)	1.875(2)	1.879(2)	1.962(2)	1.988(3)
M-N(py)	2.006(6)	2.146(4)	2.163(4)	2.152(2)	2.320(2)	2.205(3)	2.006(2)	2.009(2)	2.215(2)	2.155(2)
M-N(py')	2.004(6)	2.153(4)	2.157(4)	2.149(2)	2.283(2)	2.230(3)	2.008(2)	2.006(2)		
N(py)–M–N(py')	159.0(2)	152.83(14)	152.84(14)	153.88(8)	150.14(7)	153.0(1)	159.09(8)	159.04(7)	152.92(9)	153.07(11)
N(py)–M–N(trz)	79.3(2)	76.89(14)	76.75(14)	77.21(8)	75.79(7)	76.6(1)	79.70(8)	79.76(8)	76.46(5)	76.53(6)
N(trz)-M-N(py')	79.8(2)	76.07(14)	76.09(14)	77.10(8)	74.36(7)	76.6(1)	79.45(8)	79.29(8)		

 Table 2
 Selected bond distances (Å) and angles (°) for complexes 1a, 1c, 1d, 1d' and 2a-d (trz = triazine, py = pyridine)



Fig. 6 Arrangement of cations in the extended lattice of complex 2c. Counter-ions have been omitted for clarity.

on a general position with full occupancy. A second PF_6^- anion is found on an inversion centre with half occupancy per cation. The third PF_6^- anion, also with half occupancy per cation, is disordered about an inversion centre. In both complexes, the M– N bond distances differ from one ligand to the other, although the M–N elongation can be observed more clearly in the Cu(II) complex **1d** (Table 2). Cu(II) ions are Jahn–Teller unstable in a purely octahedral field and despite the distorted octahedral arrangement of the [Cu(L1)₂]²⁺ cation this effect is observed with the elongation of the Cu–N bond distances in complex **1d**, an effect previously reported for tpy-based systems.³⁹ The coordinated ligands are no longer related by symmetry which accounts for the change in the crystal structure system for complexes **1c–d** as compared to **1a–b** in which both ligands are equivalent.

Unlike complexes **1a–b**, significant face-to-face, π -stacking interactions are observed in **1c–d**, with the shortest contact between the pendant phenyl rings and the distal pyridyl rings being 3.37 Å (Fig. 5). The closest Br \cdots Br contacts in complexes **1c** and **1d** are 5.99 and 6.00 Å. The absence of the such interactions is possibly due to greater stabilisation gained from the π -stacking interactions, which inhibit short Br \cdots Br contacts.

The dihedral angle between the triazine ring and phenyl ring on both ligands are 21.00 and 7.31° in 1c and 19.45 and 7.62° in 1d. In each case the slightly higher dihedral angle accommodates the face-to-face π -stacking interaction which may preclude the formation of stable Br \cdots Br interactions. Both complexes have two PF₆⁻ counter ions disordered over three sites.§ Crystallisation of 1d by slow diffusion of diisopropyl ether into an acetone solution yields crystals isostructural to 1a and 1b. The shortest Br \cdots Br contacts are observed in 1d' with a distance of 3.33 Å. There is one molecule of acetone per asymmetric unit which is disordered over two independent sites. It appears that the acetone molecules of crystallisation inhibits the face-to-face π -stacking interactions, thereby allowing halogen–halogen interactions to play the determining role in the arrangement of cations in the extended lattice.

Complexes 2a–d. Crystals were obtained for complexes **2a–d** by slow diffusion of diethyl ether into an acetonitrile solution yielding thin needle-like blocks for all of the crystals. Complex **2a** crystallises in the monoclinic space group $P2_1/n$ with one molecule and two PF₆-counter-ions in the asymmetric unit (Table 1). Intermolecular face-to-edge π -stacking interactions between neighbouring tolyl groups link the cations. Additional offset face-to-face interactions can be found between tolyl and pyridyl groups, but no short contacts exist between the pendant methyl group and methyl groups of neighbouring molecules in the absence of a halogen group.

Complexes **2b–d** are isostructural and crystallise in the tetragonal space group $I4_1/acd$ with quarter of the cation, which lies on two C_2 axes, and half of a PF_6^- counter anion in the asymmetric unit. The M–N bond distances are in agreement with complexes **1a–d**, although the asymmetric Jahn–Teller distortion observed in **1a** is not observed in **2d** due to the higher symmetry in the cation resulting in both ligands being equivalent (Table 2). Zigzagging molecules are linked by face-to-face interactions between tolyl groups of neighbouring molecules which comprise the corners of a square. The cations form layers with each adjacent layer lying perpendicular to the previous (Fig. 6). The shortest $H \cdots H$ distance between diagonally bisecting tolyl groups is 4.51 Å.

Electronic spectroscopy and electrochemistry

The electronic absorption spectra of L1 and metal complexes 1a–d were measured in acetonitrile and the data are collected in Table 3.

[§] One anion is found on a general position with full occupancy. The remaining anion divided between two sites, one of which is situated on an inversion centre; the other is disordered around an inversion centre.

Table 3 Electronic absorption data $[\lambda_{max}/nm (10^{-3}\varepsilon/M^{-1} \text{ cm}^{-1})]$ in acetonitrile for L1, 1a–d and 2a–d

All of the complexes have ligand-centred $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the UV regions which are red-shifted as compared to their starting ligands. Complexes **1b–d** and **2b–d** are lightly coloured due to weak, forbidden d–d transitions in the visible and near IR region of their spectra. Complexes **1a** and **2a**, however, are intensely purple due to an allowed metal-to-ligand charge-transfer (¹MLCT) band in the low energy visible region. This absorption band is characteristic for low-spin, predominantly diamagnetic complexes of d⁶ metal ions. The ¹MLCT band can be resolved into two bands, which may be explained by the presence of ligandbased LUMO and LUMO+1 resulting in MLCT transitions to two ligand-based molecular orbitals.

The electrochemistry of complexes 1a-d were measured in acetonitrile *vs*. TBAPF₆ using a Pt electrode and ferrocene as the internal standard. The cyclic voltammogram of 1a is shown in Fig. 7. The anodic region has a reversible Fe(III)/(II) couple at +1.40 V. The cathodic region is rich with reversible ligand-based reductions involving two one-electron reductions observed on each triazine ligand which can be compared to the previously reported electrochemistry of 1b, in which only two ligand-based reductions were observed after the Co(II)/(I) couple in the anodic region.⁴²

The same Fe(III)/(II) couple and ligand-based reductive processes are observed for **2a**, although a shift to more negative potential is observed due to the electron-donating effect of the methyl substituent as compared to Br in **1a**. The ligand-based reductions of **2a** occur at similar potentials to $[Ru(L2)_2](PF_6)_2$ (Table 4), suggesting that the nature of the coordinating d⁶ metal has little effect on the relative energies of the ligand-based orbitals. However, the Fe(III)/(II) couple is 100 mV less positive when compared to the Ru(III)/(II) couple. This result supports those



Fig. 7 Cyclic voltammogram (200 mV $s^{-1})$ in acetonitrile with 0.1 M TBAPF_6 of complex 1a.

found in the UV-visible spectrum of **2a**, which indicates a red shift in the MLCT band relative to $[Ru(L2)_2](PF_6)_2$.³¹

For the Ni(II) complex 1c, no metal-based oxidative processes are observed due to the effect of the electron-deficient triazine rings on the Ni(II) centre. The first two reversible reductions are ligand based followed by an irreversible metal-centred reduction. As in the Fe(II) complexes, a second reduction is observed on each triazine ligand. For the Ni(II) complexes the difference between the tolyl- and bromo-phenyl-substituted triazine ligands is more significant. The first ligand-based reduction for 1c is 110 mV less negative as compared to 2c due to the electron-withdrawing nature of the bromo-substituent.

Highly irreversible, extremely broad reductive signals were observed for Cu(II) complexes **1d** and **2d** at -0.11 and -0.50 V, respectively, followed by adsorption spikes at -1.28 and -1.12 V, respectively. These are consistent with a reduction of Cu(II) followed by adsorption of Cu⁰ to the electrode.¹⁴ Despite the large difference reported for the initial reductive process between complexes **1d** and **2d**, the broadness of both signals makes the difference less significant. An additional triazine-based reduction is then observed for both complexes **1d** and **2d**.

Table 4 Electrochemical redox potentials vs. SCE for complexes in argon-purged acetonitrile solutions^a

	$E_{1/2}/\mathrm{V}\left(\Delta E_{\mathrm{p}}/\mathrm{mV}\right)$								
Complex	M(II/III)	Reductions							
$1a [Fe(L1)_2](PF_6)_2$	+1.40 (77)	-0.69 (65)	-0.85 (62)	-1.53 (79)	-1.76 (irr)				
$2a [Fe(L2)_2](PF_6)_2$	+1.36(97)	-0.75(62)	-0.91(75)	-1.56(99)	-1.82 (irr)				
$[Ru(L2)_2](PF_6)_2^{b}$	+1.50(101)	-0.74(64)	-0.90(70)	-1.53(84)	-1.78(87)				
1b $[Co(L1)_2](PF_6)_2$ ^c	+0.77 (irr)	-0.40(52)	-1.04(56)	-1.46(66)					
2b $[Co(L2)_2](PF_6)_2^{c}$	+0.74 (irr)	-0.47(64)	-1.11(66)	-1.52(64)					
$1c [Ni(L1)_2](PF_6)_2$		-0.76(72)	-0.88(76)	-1.46 (irr)	-1.64 (irr)	-1.76(90)			
$2c [Ni(L2)_2](PF_6)_2$		-0.87(42)	-1.00(46)	-1.70(71)					
$1d [Cu(L1)_2](PF_6)_2$		-0.11 (irr)	-1.28 (irr)	-1.56 (irr)					
2d $[Cu(L2)_2](PF_6)_2$		-0.50 (irr)	-1.12 (irr)	-1.53(100)					

^a Using ferrocene as an internal standard, ^b From ref. 31, ^c From ref. 42.

Conclusion

A bromo-functionalised triazine ligand has been synthesised and significant two-dimensional Br ... Br interactions are present in the solid state. When complexed to Fe(II), Co(II) and Cu(II) cations, halogen-halogen interactions are observed in the solid state structure to give linear one-dimensional tapes in the extended lattice depending on the solvent of crystallisation. The presence of solvent can modify the formation of the one-dimensional tape as exemplified by the Cu(II) complex 1d. The electrochemical, spectroscopic and magnetic properties of the complexes are significantly affected by the electron-deficient triazine ring and its weaker ligand field strength. The electrochemical properties of the complexes may be applied to the development of new redox mediators.42 Initial 1H NMR studies of the Fe(II) complex demonstrate that these complexes have a paramagnetic contribution to the diamagnetic ground state, which may indicate a spin transition from low spin to high spin. Further magnetic measurements will be carried out to elucidate the nature of their spin cross-over properties.

Experimental

Materials and instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded in CD₃CN at room temperature (r.t.) on a Bruker AV400 spectrometer at 400 MHz for ¹H NMR and at 100 MHz for ¹³C NMR. Chemical shifts are reported in part per million (ppm) relative to residual solvent protons (1.93 ppm for acetonitrile-d₃) and the carbon resonance of the solvent. Absorption spectra were measured in air equilibrated acetonitrile at r.t. on a Cary 500i UV-Vis-NIR spectrophotometer.

Electrochemical measurements were carried out in argonpurged acetonitrile at room temperature with a BAS CV50W multipurpose equipment interfaced to a PC. The working electrode was a Pt electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocinium sample at 395 mV vs. SCE in acetonitrile and 432 mV in DMF. The concentration of the compounds was 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as supporting electrolyte and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates of 50, 100, 200 and 500 mV s⁻¹. For irreversible oxidation processes, the cathodic peak was used as E, and the anodic peak was used for irreversible reduction processes. The criteria for reversibility were the separation of 60 mV between cathodic and anodic peaks, the close to unity ratio of the intensities of the cathodic and anodic currents, and the constancy of the peak potential on changing scan rate. The number of exchanged electrons was measured with OSWV, and by taking advantage of the presence of ferrocene used as the internal reference.

Experimental uncertainties are as follows: absorption maxima, ± 2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV.

Crystal structure determination

X-Ray crystallographic data for **1a-d** were collected from a single crystal sample, which was mounted on a loop fiber. Data were

collected using a Bruker Platform diffractometer, equipped with a Bruker SMART 2 K Charged-Coupled Device (CCD) Area Detector using the program SMART and normal focus sealed tube source graphite monochromated Cu-K α radiation.

X-Ray crystallographic data for L1, 2a, 2c and 2d were collected from a single crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker SMART 4 K Charged-Coupled Device (CCD) Area Detector using the program SMART and a rotating anode source Cu-Ka radiation. X-Ray crystallographic data for 2b was collected with Mo-Ka radiation ($\lambda = 0.71073$ Å, $2\theta_{max} =$ 57.5°, ω scan mode) on a Bruker SMART CCD diffractometer, at 125 K. Empirical adsorption corrections were applied using the SADABS program.

The structures were solved by direct method and refined using full-matrix least squares on F^2 using the SHELXTL suite of programs.⁵¹ The H atoms were generated geometrically and were included in the refinement in the riding model approximation.

CCDC reference numbers 611625–611633.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613883g

Syntheses

Metal salts and other chemicals (Aldrich) were used as supplied. L1 and L2 were synthesised by a modified literature method.⁴² Complexes 1b and 2b were prepared according to literature methods.⁴²

L1. *n*-BuLi (1.6 M in hexanes, 5.10 mL, 8.13 mmol) was added dropwise to a stirred solution of HNMe₂ (2 M in THF, 4.10 mL, 8.13 mmol) in anhydrous Et_2O (150 mL) under an inert atmosphere. The mixture was stirred for 20 min until a white suspension formed and *p*-bromobenzonitrile (1.35 g, 7.39 mmol) was added. The triazine precipitated immediately and stirring was continued for 1 h. The reaction was diluted with a 5 : 1 mixture of water–EtOH (200 mL) and the solution was heated to remove the Et_2O . The white precipitate thus formed was collected by filtration and washed with EtOH (10 mL) and Et_2O (50 mL) and dried to afford L1 as a white powder (1.96 g, 68% yield).

¹H NMR (CDCl₃, 400 MHz): δ 8.99 (d, J = 4 Hz, 2H, H_{6,6}"), 8.87 (d, J = 8 Hz, 2H, H_{3,3}"), 8.74 (d, J = 8 Hz, 2H, H₂"",6"), 8.0 (t, J = 7 Hz, 2H, H_{4,4}"), 7.73 (d, J = 8 Hz, 2H, H₃"",5"), 7.60 (t, J = 5 Hz, 2H, H_{5,5}"). Consistent with a previously published spectrum.⁴² Anal. Calc. for C₁₉H₁₂N₅Br·0.5H₂O: C, 57.16; H, 3.28; N, 17.54. Found: C, 57.38; H, 3.02; N, 17.27%. EIMS: [M⁺] 389.0.

[Fe(L)₂](PF₆)₂ (1a and 2a). FeCl₂·H₂O (0.046 g, 0.23 mmol) dissolved in ethanol (5 mL) was added to a stirred solution of the ligand (0.46 mmol) in ethanol (15 mL). The solution immediately turned intense purple and was heated to reflux for 20 min. On cooling, saturated KPF₆ (aq, 5 mL) was added and the product precipitated. The solid was collected and washed with water, ethanol and diethyl ether to yield complexes 1a (0.24 g, 91%) and 2a (0.15 g, 67%).

Ia. ¹H NMR (CD₃CN, 400 MHz): δ 9.16 (d, J = 8 Hz, 2H, H_{3,3"}), 9.12 (d, J = 8 Hz, 2H, H_{2",6"}), 8.11 (d, J = 8 Hz, 2H, H_{3",5"}), 8.11 (t, J = 8 Hz, 2H, H_{4,4"}), 7.74 (s (br), 2H, H_{6,6"}), 7.37 (t, J = 6 Hz, 2H, H_{5,5"}). Anal. Calc. for C₃₈H₂₄N₁₀Br₂FeP₂F₁₂·2H₂O:

C, 39.27; H, 2.43; N, 12.05. Found: C, 39.34; H, 2.22; N, 11.49%. ESMS: M²⁺ = 418.3.

2a. ¹H NMR (CD₃CN, 400 MHz): δ 9.21 (d, J = 8 Hz, 2H, H_{3,3"}), 9.12 (d, J = 8 Hz, 2H, H_{2",6"}), 8.12 (t, J = 8 Hz, 2H, H_{4,4"}), 7.88 (s (br), 2H, H_{6,6"}), 7.74 (d, J = 8 Hz, 2H, H_{3",5"}), 7.41 (t, J = 6 Hz, 2H, H_{5,5"}), 2.64 (s, 3H, H_{Me}). Anal. Calc. for C₄₀H₃₀N₁₀FeP₂F₁₂: C, 48.21; H, 3.03; N, 14.06. Found: C, 48.23; H, 3.32; N, 14.21%. ESMS: M²⁺ = 353.5.

[Ni(L)₂](PF₆)₂ (1c and 2c). Ni(OAc)₂ (0.038 g, 0.15 mmol) dissolved in ethanol (15 mL) was added to a stirred solution of the ligand (0.30 mmol) in ethanol (30 mL). The mixture turned green–yellow immediately and was heated to reflux for 15 min. On cooling, ethanolic KPF₆ was added and the green precipitate was collected and washed with water, ethanol and diethyl ether to yield complexes 1c (0.12 g, 68%) and 2c (0.085 g, 56%).

Ic. ¹H NMR (CD₃CN, 400 MHz): *δ* 7.8, 12.4, 13.9, 43.2, 72.0, ~124 (br).

Anal. Calc. for $C_{38}H_{24}N_{10}NiP_2F_{12}$: C, 40.42; H, 2.14; N, 12.41. Found: C, 40.66; H, 2.43; N, 12.48%.

2c. ¹H NMR (CD₃CN, 400 MHz): δ 0.1, 7.5, 12.5, 13.8, 43.1, 71.7, 123 (br).

Anal. Calc. for $C_{40}H_{30}N_{10}NiP_2F_{12}$: C, 48.07; H, 3.03; N, 14.02. Found: C, 48.42; H, 3.02; N, 13.83%.

[Cu(L)₂](PF₆)₂ (1d and 2d). Cu(NO₃)₂·H₂O (0.14 g, 0.62 mmol) dissolved in ethanol (15 mL) was added to a stirred solution of the ligand (1.23 mmol) in ethanol (30 mL). The mixture turned green immediately and was heated to reflux for 15 min. On cooling, ethanolic KPF₆ was added and the green precipitate collected and washed with water, ethanol and diethyl ether to yield complexes 1d (0.55 g, 79%) and 2d (0.42 g, 68%).

1d. ¹H NMR (CD₃CN, 400 MHz): δ 7.4, 9.3, 10.2, ~25 (br), ~37 (v br), 1 peak missing.

Anal. Calc. for $C_{38}H_{24}N_{10}Br_2CuP_2F_{12}$ ·H₂O: C, 39.62; H, 2.27; N, 12.16. Found: C, 39.46; H, 1.58; N, 12.03%.

2*d*. ¹H NMR (CD₃CN, 400 MHz): δ 1.0, 7.0, 9.4, 10.2, ~25 (br), ~38 (v br), 1 peak missing. Anal. Calc. for C₄₀H₃₀N₁₀CuP₂F₁₂: C, 47.84; H, 3.01; N, 13.95. Found: C, 48.01; H, 2.64; N, 13.88%.

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