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A new series of open chain diazine ligands that have a central bipyridne unit with two side-arms offering a range of ketone/alkoxide oxygen donors, diazine and pyridine terminal groups show a strong preference for binding three metals forming a trimetallic sub-unit but sufficient ligand flexibility to modify the coordination pockets for metal binding.



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## ARTICLE

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### A New Nitrogen Rich Open Chain Diazine Ligand System: Synthesis Coordination Chemistry and Magneto-Structural Studies

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The synthesis and coordination chemistry of a new series of open chain diazine base ligands ( $L_{3a}H_2$ ,  $L_{3b}H_2$ , and  $L_{3c}H_2$ ) is reported. The ligands comprise a central disubstituted bipyridine moiety with two bridging alkoxide oxygen donors, together with diazine and pyridine terminal groups strategically located to coordinate three metal centres. Reactions of  $L_{3a}H_2$  and  $L_{3b}H_2$  with  $CuX_2$  ( $X^- = CIO_4$ , CI,  $NO_3$ ) yield a trinuclear complex (**1**) and 1-D copper chains (**2**, **3**). In these complexes the ligands bind copper ions *via* N<sub>bipyridne</sub>, *trans* N<sub>diazine</sub>, O<sub>hydrazone</sub>, and N<sub>pyridne</sub> donors while vacant sites are occupied by counter ions or solvent molecules (methanol, water, acetonitrile). Reaction of  $L_{3c}H_2$  with MnCl<sub>2</sub> affords a linear trinuclear Mn complex (**4**), where the Mn(II) ions are connected *via*  $\mu_2$ -O<sub>hydrazone</sub> linkers with no N-N bridging. Reaction of  $L_{3a}H_2$  with Fe(SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub> yields a tetranuclear mixed valence Fe complex (**5**), in which both *trans* N-N and O<sub>hydrazone</sub> bridging is observed. Magnetic studies reveal the presence of moderate to strong antiferromagnetic interactions in complexes **1-4** while a mix of ferromagnetic and antiferromagnetic interactions is observed in complex **5**.

#### Introduction

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The controlled self-assembly of non-covalent architectures from programmed components involves the design of suitable ligands with well-defined binding sites coupled with the selection of metal ions with complimentary coordination geometries.<sup>1</sup> The metal ions then recognize the binding sites of the ligands according to the coordination algorithm defined by both the metal and the ligand.<sup>2</sup> This has led to the design of polydentate ligands with linear arrangements of coordination pockets which have been used to prepare square grid like architectures<sup>3</sup>, tetrahedra<sup>4</sup> as well as 3-D metal organic frameworks.<sup>5</sup> Alternatively, coordination chemists can follow a serendipitous approach in which ligands typically offer multiple binding modes, while the metals often exhibit flexibility in their coordination geometries.<sup>6</sup> The choice of a semi-rigid polydentate ligand which offers some degree of pre-determined coordination preference provides an interesting compromise between the two aforementioned strategies. In this respect, aspects of structural control are embodied within the ligand design, but the final outcome of the reaction still draws upon a certain

# design of ligand systems which are not only capable of binding metal sites in well-defined arrays but which also place them in close proximity to facilitate effective magnetic communication has led to fundamental studies in the field of magnetochemistry which includes the effect of the bridge angle on exchange coupling.<sup>7,8</sup> In addition, design strategies towards polynuclear high spin molecules have been developed which have led to the discovery of single molecule magnets, individual molecules capable of storing magnetic information below their blocking temperatures.<sup>9</sup> In these systems efficient magnetic exchange coupling is usually propagated *via* superexchange interactions through the one or two atom diamagnetic bridges of their bridging ligands.

degree of inherent conformational variation within the ligand geometry, as well as the metal ion's coordination preference. The

 $\mathbf{R} \xrightarrow{\beta'}_{\alpha} \xrightarrow{\beta}_{\mathbf{N}} \mathbf{R'}$ 

Figure 1: Conformational flexibility around the open chain N-N bond of a diazine based ligand



Figure 2: Conformational variation in diazine ligands and their coordination modes<sup>10</sup>

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Figure 4: Different coordination modes  $C_1$ ,  $C_2$ , and  $C_3$  found in ligands  $L_{3a}^{2-}$  (R = CH<sub>3</sub>),  $L_{3b}^{2-}$  (R = NH<sub>2</sub>), and  $L_{3c}^{2-}$  (R = H)

Figure 3: Molecular structures of ligands L1H2 to L3H2.

In recent years, diazine-based ligand systems (Fig. 1 & 2) have attracted attention due to their versatility and strong coordinating ability to a broad range of 3d- and 4f-metal ions.<sup>11</sup> Among diazines, the open chain ligands have shown a variety of geometrical conformations that together with appropriate metal (II/III) salts have afforded a number of interesting structural topologies comprising mononuclear through to polynuclear coordination complexes.<sup>12</sup> Interestingly, magnetic studies on binuclear Cu(II) systems have identified a linear relationship between the rotational angle around the N-N bond and the magnetic exchange integral.<sup>7</sup> In this respect, the torsional angle ( $\alpha$ ) about the N-N single bond, the bond angles at the two nitrogen atoms ( $\beta$ ,  $\beta$ ), and the nature of functional groups attached to the diazine moiety typically dictate the sign and magnitude of the exchange interaction (Fig. 1).6,7 Previously reported diazine bridged metal complexes have shown predominantly antiferromagnetic interactions.<sup>7</sup> In earlier studies, we reported the reactivity of  $L_1H$  (Fig. 3) with 3d-metal salts, where M = Cu(II), Ni(II), Co(II), Mn(II), Fe(II), which afforded a nonhomoleptic  $[2 \times 2]$  squares, together with a series of tetranuclear alkoxo-bridged  $M_4(\mu$ -O)<sub>4</sub> grids. Extension of the L<sub>1</sub>H series to include a second family of larger  $L_2$  based ligand systems (Fig. 1)<sup>3</sup> afforded several  $[3 \times 3]$  M<sub>9</sub>( $\mu$ -O)<sub>12</sub>) (M = Mn(II), Fe(II/III), Co(II), Cu(II)), square grids. Like the original series of  $[\textbf{L}_1M_4(\mu\text{-}O)_4]$  complexes, antiferromagnetic coupling was observed in the  $[L_2M_9(\mu-O)_{12}]$ compounds with the exception of the Cu(II) complex, where ferromagnetic coupling was dominant.<sup>7</sup> Such grids are generally formed by employing weakly coordinating anions such as  $\text{ClO}_4^-$  and  $BF_4$ , where the polydentate  $L_2H_2$  ligands complete the metal coordination environments. In contrast, more strongly coordinating anionic ligands tend to inhibit grid formation. For example, linear trinuclear Cu(II) complexes were isolated from reactions of  $L_2H_2$ together with copper salts containing relatively strong coordinating counter ions such as Cu(CH<sub>3</sub>COO)<sub>2</sub>.<sup>13</sup> Although both L<sub>1</sub>H and L<sub>2</sub>H<sub>2</sub> possess extended conjugation, structural studies reveal that a variety of geometrical conformations can be accommodated

depending on the nature of the co-ligands and the reaction conditions employed.<sup>13,14</sup>

In this paper, we present an extension to the  $L_1H$  and  $L_2H_2$ family of diazine-based ligands and report herein a new series of ligands  $L_{3a}H_2$ ,  $L_{3b}H_2$  and  $L_{3c}H_2$  in which the central 2',6'pyridine of  $L_2H_2$  is replaced by a 6,6'-bipyridine (bipy) unit and the functional groups attached to the diazine moiety are CH<sub>3</sub>,  $NH_2$  and H for  $L_{3a}H_2$  to  $L_{3c}H_2$  respectively (Fig 3). In its deprotonated form this  $L_{3}{}^{2\mathchar`-}$  family of ligands offers two potential bridging alkoxide oxygen donors, alongside diazine and pyridine terminal groups designed specifically to coordinate three metal centres. Bipyridine based ligands are very commonly employed in 3d-metal chemistry due to their predictable and rich coordination chemistry.<sup>15</sup> They are often referred to as non-innocent due to their potential to participate in redox reactions.<sup>16</sup> We report preliminary results from the reactions of these ligands with  $MX_2$  salts (where M = Cu(II), Mn(II), Fe(II);  $X^- = CI$ , NO<sub>3</sub>, ClO<sub>4</sub>, SO<sub>2</sub>CF<sub>3</sub>) which offer a range of both coordinating and non-coordinating anions. The different binding modes of  $L_{3a}H_2,\,L_{3b}H_2,\,and\,L_{3c}H_2$  identified in these studies are highlighted in Fig. 4. Despite the conjugated nature of the general backbone of the ligands, on coordination to 3d-metals some variation in the ligand geometry is observed based on the orientation of the amide side-arms in relation to the central 2,2'-bipyridine core. For example, in coordination mode  $C_1$  (Fig. 4), the carbonyl groups are both located exo to the central cavity, whereas in  $C_2$  they are both endo and in  $C_3$ they adopt an intermediate coordination geometry with one exo and one endo carbonyl group. Detailed structural and magnetic studies on the resulting trinuclear Cu<sup>II</sup> complexes (1 – 3), a trinuclear Mn<sup>II</sup> compound (4) and a tetranuclear mixed valence Fe<sup>II</sup><sub>2</sub>Fe<sup>II</sup><sub>2</sub> (5) system are also presented.

#### Experimental

Commercially available solvents and chemicals were purchased and used without further purification. 6,6'-dicyano-2,2'-bipyridine (a) was prepared according to the literature method.<sup>17</sup>

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#### **Physical Measurements**

NMR spectra were recorded on a Bruker 500 MHz spectrometer with a Broadband AX Probe using  $CDCl_3$  ( $\delta$  = 7.26 ppm, s) as an internal reference point relative to Me<sub>4</sub>Si ( $\delta$  = 0 ppm). IR spectra were obtained using a Bruker Alpha FT-IR spectrometer equipped with a Platinum single reflection diamond ATR module. Elemental compositions were determined on a PerkinElmer 2400 Series II Elemental Analyzer. Variable temperature magnetic data (2–300 K) were obtained using a Quantum Design MPMS SQUID magnetometer using a field strength of 0.1 T. Polycrystalline samples were optically screened and a random selection of crystals from each batch examined by unit cell determination to check phase purity. Background corrections for the sample holder assembly and sample diamagnetism were applied. No specific approaches were employed to avoid torqueing of the sample but data were recorded in warming and cooling modes for 4 and 5 which are likely to be most susceptible and there were no evident discontinuities in the data which might reflect sample movement.

#### **Ligands and Complex Synthesis**

**Preparation of 6,6'-bis(methoxycarbonyl)-2,2'-bipyridine:**<sup>18</sup> An excess of sodium methoxide (3.5 g, 64.79 mmol) was added to a suspension of 6,6'-dicyano-2,2'-bipyridine (2.0 g, 9.69 mmol) in MeOH (100 mL) and the mixture was refluxed for 5 hours. The off-white precipitate of the intermediate imine-diester was then dissolved in a MeOH/H<sub>2</sub>O mixture (50 mL, 50:50) and stirred for 10 min at rt. The resulting solution was adjusted to pH 1 by the addition of dilute H<sub>2</sub>SO<sub>4</sub> and stirred for 3 hours at rt. The solution was then neutralized with aq. NaOH solution. The resultant white precipitate was filtered, washed with water (100 mL) and dried in air. Yield 1.4 g (53 %). The <sup>1</sup>HNMR and melting point matched the literature data.<sup>18</sup>

**Preparation of 2,2'-bipyridine-6,6'-dicarbohydrazide:** Hydrazine hydrate (1.5 g, 30 mmol) was added dropwise to a suspension of 6,6'-bis(methoxycarbonyl)-2,2'-bipyridine (2.1 g, 7.7 mmol). The reaction mixture was refluxed overnight. The off-white precipitate was collected, washed with excess MeOH/ether and dried in air. Yield: 1.7 g, 81%, IR data (cm<sup>-1</sup>): 3550 (br), 3292 (m), 1674 (s), 1621 (m), 1582 (s), 1495 (s), 1431 (s), 1329 (br), 1260 (m), 1196 (w), 1117 (w), 1102 (m), 1071 (m), 996 (s), 962 (s), 832 (s), 765 (m), 737 (s), 705 (m), 671 (s), 632 (s), 586 (w), 545 (w), 476 (m). <sup>1</sup>H NMR (ppm, DMSO-d<sub>6</sub>) 10.31 (2H, s), 9.11 (2H, d), 8.13 (2H, t), 8.08 (2H, d), 4.71 (4H, s). Mass spectrum (m/z, EI<sup>+</sup>): 273 (M + 1), Anal. Calcd. for C<sub>12</sub>H<sub>12</sub>N<sub>6</sub>O<sub>2</sub>·0.5H<sub>2</sub>O: C, 51.24; H, 4.66; N, 29.88%. Found: C, 51.91; H, 4.41; N, 29.95%.

**Preparation of ligand L<sub>3a</sub>H<sub>2</sub>:** 2-Acetyl pyridine (0.5 mL, 0.45 mmol) was added to a suspension of 2,2'-bipyridine-6,6'-dicarbohydrazide (0.5 g, 1.81 mmol) in MeOH (50 mL) and the mixture was refluxed overnight. The resultant precipitate was filtered, washed with excess MeOH/ether and dried in air. Yield 0.45 g, ~43 % based on pure L<sub>3</sub>aH<sub>2</sub>. IR data (cm<sup>-1</sup>) 3327 (m), 3292 (w), 1699 (s), 1674 (m), 1621 (m), 1581 (s), 1519 (s), 1470 (s),1431 (s), 1364 (m), 1233 (w), 1260 (m), 1240 (m), 1163 (m), 1117 (m), 1102 (m), 1077 (m), 1044 (m), 945 (s), 963 (s), 912 (m), 833 (s), 819 (s), 793 (s), 752 (s), 703 (s), 650 (br), 620 (s), 601 (s), 558 (s), 477 (w). NMR (insoluble). Mass spectrum (m/z, El<sup>+</sup>): 272, 479 [M+H]<sup>+</sup>. Anal. Calcd. for

 $(C_{26}H_{22}N_8O_2)(C_{12}H_{12}N_6O_2).H_2O C, 59.37; H, 4.72; N, 25,51%, Cound: C, 59.56; H, 4.43; N, 25.73%. The analytical data and 7 the ana$ 

**Preparation of ligand L<sub>3b</sub>H<sub>2</sub>:** 2-pyridinecarboxaldehyde (2.0 g, 18.67 mmol) was added to a suspension of 2,2'-bipyridine-6,6'-dicarbohydrazide (1.7 g, 6.28 mmol) in MeOH (50 mL). The mixture was refluxed overnight and the resultant precipitate was filtered, washed with excess MeOH/ether and then dried in air. Yield 2.2 g, 78 %. IR data (cm<sup>-1</sup>): 3497 (br), 3287 (br), 1698 (s), 1661 (m), 1584 (m), 1511 (s), 1465 (s), 1435 (s), 1348 (m), 1295 (m), 1243 (s), 1138 (s), 1105 (w), 1077 (s), 1055 (m), 995 (s), 929 (s), 825 (s), 778 (s), 736 (m), 709 (m), 633 (m), 621 (m), 589 (s), 523 (w), 472 (w). NMR (insoluble). Mass spectrum (m/z, EI<sup>+</sup>): 451 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>24</sub>H<sub>18</sub>N<sub>8</sub>O<sub>2</sub>·2H<sub>2</sub>O: C, 59.25; H, 4.56%. N, 23.03. Found: C, 59.94; H, 4.26; N, 23.15%.

Preparation of ligand L<sub>3c</sub>H<sub>2</sub>: 2-Pyridinecarbonitrile (1.0 g, 9.60 mmol) was added to a dilute solution of sodium methoxide in MeOH (100 mL) and then refluxed overnight. The resultant solution was adjusted to neutral pH by the addition of glacial acetic acid. To this solution, 2,2'-bipyridine-6,6'-dicarbohydrazide (1.0 g, 3.62 mmol) was added in portions. The mixture was refluxed overnight and the resultant yellow precipitate obtained was then filtered, washed with excess MeOH/ether and dried in air. Yield 1.76 g, 100 %. IR data (cm<sup>-1</sup>): 3410 (m), 3313 (m), 3168 (br), 1688 (s), 1615 (s), 1582 (s), 1565 (s), 1519 (s), 1474 (s), 1438 (s), 1383 (s), 1310 (w), 1296 (w), 1253 (m), 1161 (s), 1102 (w), 1051 (w), 1080 (s), 1051 (m), 994 (s), 929 (s), 821 (s), 795 (s), 759 (s), 741 (w), 720 (w), 705 (m), 680 (w), 660 (w), 630 (m), 622 (m), 575 (w), 535 (w), 509 (w), 468 (w). <sup>1</sup>H NMR (ppm, DMSO-d<sub>6</sub>) = 10.79 (2H, s), 9.06 (2H, d), 8.66 (2H, d), 8.25 (4H, dd), 8.17 (2H, d), 7.97 (2H, dd), 7.55 (2H, t), 7.10 (4H, s). Mass spectrum (m/z, El<sup>+</sup>): 481 [M+H]<sup>+</sup>. Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>N<sub>10</sub>O<sub>2</sub>: C, 59.99; H, 4.20; N, 29.15%. Found: C, 59.35; H, 4.01; N, 28.65%.

Preparation of [Cu<sub>3</sub>L<sub>3a</sub>(ClO<sub>4</sub>)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] (1): L<sub>3a</sub>H<sub>2</sub> (0.025 g, 0.52 mmol) and Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.06 g, 0.16 mmol) were stirred together in MeCN (10 mL) until a clear green solution was obtained. This was then filtered and the solution was layered with diethyl ether. Dark green crystals suitable for single crystal X-ray diffraction formed over a few days. Yield = 0.01 g, 16%. IR data (cm<sup>-1</sup>): 3527 (br), 3437 (br), 1631 (br), 1601 (w), 1573 (w), 1548 (m), 1483 (m), 1472 (m), 1445 (w), 1431 (w), 1415 (w), 1366 (m, br), 1328 (m), 1271 (m), 1195 (m), 1172 (w), 1061 (s, br), 946 (w), 930 (w), 920 (w), 823 (m), 780 (m), 762 (m), 747 (w), 725 (m), 619 (s), 589 (m), 570 (w), 440 (m). Anal. Calcd. for (C<sub>26</sub>H<sub>20</sub>N<sub>8</sub>O<sub>2</sub>)Cu<sub>3</sub>(ClO<sub>4</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>: C, 30.00; H, 2.69; N, 11.66%. Found: C, 29.72; H, 2.57; N, 11.28%.

**Preparation of [Cu<sub>3</sub>L<sub>3a</sub>(Cl)<sub>4</sub>]**<sub>n</sub> (2): L<sub>3a</sub>H<sub>2</sub> (0.025 g, 0.52 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (0.03 g, 0.17 mmol) were stirred together in MeOH (10 mL) until a clear green solution obtained. It was then filtered and left undisturbed to generate a green microcrystalline solid whose IR and elemental analysis composition were consistent with a methanol solvate (Yield = 0.013 g, 28 %). IR data (cm<sup>-1</sup>): 3375 (br),

3074 (w), 1626 (w), 1569 (w), 1538 (s), 1532 (s), 1505 (m), 1480 (m), 1471 (m), 1443 (m), 1415 (m), 1377 (s), 1324 (m), 1298 (m), 1275 (s), 1183 (s), 1167 (m), 1145 (m)< 1124 (m), 1108 (m), 1071 (s), 1040 (m), 1025 (s), 945 (w), 933 (w), 903 (w), 825 (s), 782 (s), 765 (m), 764 (s), 743 (m), 719 (m), 710 (s), 688 (s), 648 (s), 605 (w), 590 (m), 568 (w), 513 (m), 489 (w), 466 (m), Anal. Calcd. for  $(C_{26}H_{20}N_8O_2)Cu_3Cl_4\cdot 2MeOH: C$ , 38.52; H, 3.23; N, 12.84. Found: C, 37.81; H, 2.91; N, 12.77%. A second crop of dark green solvent-free crystals suitable for single crystal X-ray diffraction formed over a few days.

**Preparation of**  $[Cu_3L_{3b}(NO_3)_4]_n$  (3):  $L_{3b}H_2$  (0.025 g, 0.55 mmol) was added to a solution of Cu(NO\_3)\_2·3H\_2O (0.06 g, 0.25mmol) in MeCN (10 mL). The mixture was gently heated for 5 min until a clear green solution obtained. It was then filtered and left undisturbed. Green crystals suitable for single crystal X-ray diffraction formed overnight. (Yield = 0.012 g, 22%) IR data (cm<sup>-1</sup>): 3381 (br), 3216 (br), 1659 (w), 1618 (w), 1560 (s), 1508 (s), 1471 (s), 1469 (br), 1449 (w), 1364 (br), 1344 (br), 1321 (br), 1302 (br), 1265 (s, br), 1213 (s), 1187 (s), 1161 (m), 1100 (br), 1081 (m), 1074 (m), 1041 (m), 1028 (m), 1015 (w), 991 (s, br), 868 (m), 830 (m), 816 (s), 802 (m), 784 (s), 757 (s), 733 (m), 711 (s), 700 (s), 645 (m), 520 (s). Anal. Calcd. for ( $C_{24}H_{16}N_8O_2$ )Cu<sub>3</sub>(NO<sub>3</sub>)<sub>4</sub>: C, 32.49; H, 1.82; N, 18.95%. Found: C, 32.19; H, 1.80; N, 18.61%.

Preparation of [Mn<sub>3</sub>L<sub>3c</sub>(Cl)<sub>4</sub>(CH<sub>3</sub>OH)<sub>2</sub>(H<sub>2</sub>O)] (4): L<sub>3c</sub>H<sub>2</sub> (0.025 g, 0.52 mmol) was added to a solution of MnCl<sub>2</sub> (0.06 g, 0.47 mmol) in MeOH (10 mL) followed by the addition of one drop of triethylamine. The mixture was stirred at rt for 10 min until a clear orange solution was obtained. It was then filtered and left undisturbed. Light yellow crystals suitable for single crystal X-ray diffraction appeared in a week. (Yield = 0.017 g, 42 %) IR data (cm<sup>-</sup> 1): 3140 (br), 3317 (br), 1651 (m), 1645 (s), 1615 (w), 1599 (m), 1563 (s), 1553 (s), 1538 (s), 1532 (s), 1506 (m), 1479 (m), 1464 (s), 1435 (m), 1407 (s), 1538 (s), 1296 (m), 1268 (s, br), 1183 (m, br) 1163 (m), 1091 (w), 1079 (w), 1047 (w), 1005 (m), 964 (w), 930 (w), 841 (w), 821 (s), 791 (s), 762 (s), 742 (s), 676 (s), 638 (s), 632 (s), 565 (w), 532 (w), 524 (w), 498 (w), 461 (s). Anal. Calcd. for (C<sub>26</sub>H<sub>28</sub>N<sub>10</sub>O<sub>5</sub>)Cl<sub>4</sub>Mn<sub>3</sub>· (H<sub>2</sub>O)<sub>2/3</sub>·(MeOH)<sub>2/3</sub> (estimated lattice solvent ratio from X-ray diffraction): C, 35.80; H, 3.53; N, 15.65%. Found: C, 35.65; H, 3.40; N, 15.79%.

Preparation of [Fe4(L3a)2(H2O)6][CF3SO3]6 (5): Ligand L3aH2 (0.025 g, 0.52 mmol) and Fe(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>·2MeCN (0.06 mg, 0.057 mmol) were stirred together in MeCN (10 mL) until a clear purple solution was obtained. This was then filtered and layered with diethyl ether. Dark purple crystals suitable for single crystal X-ray diffraction formed over a few days. (Yield = 0.011 g, 16%). IR data (cm<sup>-1</sup>): 3192 (br), 3078 (br), 1652 (m), 1645 (m), 1634 (m), 1600 (m, br), 1575 (m), 1558 (w), 1532 (m), 1565 (m), 1471 (w), 1435 (m, br), 1373 (m, br), 1274 (s), 1235 (s), 1221 (s), 1159 (s, br), 1083 (w), 1024 (s), 820 (m), 776 (m), 759 (m), 726 (w), 702 (w), 681 (w), 631 (s), 598 (w), 573 (m, br), 555 (w), 516 (s), 493 (m), 485 (m), 475 (m), 467 (m). Crystallographic studies indicated two MeCN molecules in the asymmetric unit (at least one part occupancy) and two Et<sub>2</sub>O molecules (again some part occupancy indicated) both of which were disordered and the crystals showed a strong tendency to desolvate when removed from the mother liquor. Anal. Calcd. for

#### X-ray Crystallography

Single crystals of 1 - 5 were mounted on a cryoloop with paratone oil and examined on a Bruker D8 Venture APEX diffractometer equipped with Photon 100 CCD area detector and Oxford Cryostream cooler at 173(2) K, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data were collected using the APEX-II software,<sup>19</sup> integrated using SAINT<sup>20</sup> and corrected for absorption using a multi-scan approach (SADABS).<sup>21</sup> Final cell constants were determined from full least squares refinement of all observed reflections. All non-H atoms were located in subsequent difference maps and refined anisotropically with SHELXL-97<sup>22</sup> using full least squares refinement against F<sup>2</sup>. H atoms were added at calculated positions and refined with a riding model. O-H atoms were located in the difference map and refined with U(iso) riding on the O with DFIX constraints applied. For compound 5 all triflate anions and some solvent molecules (two MeCN and one Et<sub>2</sub>O) were located in the difference map. Four of the six triflate anions and most solvent molecules exhibited disorder. One particularly problematic Et<sub>2</sub>O molecule was omitted in the latter stages of refinement and the residual electron density treated with SQUEEZE<sup>23</sup> within PLATON.<sup>24</sup> A summary of crystallographic data for complexes 1 – 5 is presented in Table S1 of the ESI and the structures have been deposited with the CCDC (CSD deposition numbers 1579185-1579189).

#### **Results and Discussion**

**Ligand Synthesis** 



Scheme 1: Reaction route to  $L_{3a}H_2$ ,  $L_{3b}H_2$ , and  $L_{3c}H_2$ 

Ligands  $L_{3a}H_2$ ,  $L_{3b}H_2$ , and  $L_{3c}H_2$  were prepared in 50 – 80 % yields by reacting 6,6'-dicarboxylicacid-2,2'-dihydrazide with their respective terminal pyridyl groups (Scheme 1). While ligands  $L_{3b}H_2$  and  $L_{3c}H_2$ were recovered in pure form,  $L_{3a}H_2$  proved more problematic precipitating as an insoluble 1:1 mixture of  $L_{3a}H_2$  with unreacted starting material, despite multiple adjustments to the synthetic protocol. In this case preliminary coordination chemistry studies were undertaken using this mixture. Fortuitously in the case of their reactivity with CuCl<sub>2</sub>·2H<sub>2</sub>O and Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, the complexes of  $L_{3a}^{2-}$  crystallized selectively (*vide infra*).

#### Syntheses of complexes 1 – 5

Reactions of ligands  $L_{3a}H_2$ ,  $L_{3b}H_2$ , and  $L_{3c}H_2$  with MX<sub>2</sub> (M = Cu(II), Mn(II), Fe(II); X = Cl, NO<sub>3</sub>, ClO<sub>4</sub>, SO<sub>2</sub>CF<sub>3</sub>) afforded the trinuclear complex Cu<sup>II</sup> (1) and 1-D Cu<sup>II</sup> chains (2, 3), a trinuclear Mn<sup>II</sup> complex (4) and a tetranuclear Fe<sup>II</sup>Fe<sub>2</sub><sup>III</sup> complex (5). All five complexes were



Figure 5: Crystal Structure of  $[Cu_3L_{3a}(ClO_4)_4(CH_3CN)_2(H_2O)_2]$  (1)

characterized by a variety of analytical techniques including single crystal X-ray diffraction, IR and elemental analysis. Single crystals were grown either directly from the mother liquor or layering with diethyl ether. The crystals of all five complexes proved slightly hygroscopic, absorbing small quantities of water upon standing, but otherwise appeared air stable.

#### **Description of Crystal Structures**

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 $[Cu_3L_{3a}(ClO_4)_4(CH_3CN)_2(H_2O)_2]$  (1): Dark green single crystals of 1were isolated from the reaction of  $L_{3a}H_2$  with  $Cu(ClO_4)_2 \cdot 6H_2O$  in a 1:1 mixture of acetonitrile/diethyl ether solution. The molecular structure of 1 is shown in Fig. 5 and selected interatomic distances and angles are listed in Table S2 of the ESI. The complex crystalizes in the monoclinic space group C2/c, with half a molecule of 1 in the asymmetric unit. The ligand binds three Cu(II) centres in a chain arrangement with Cu1 located on a two-fold rotation axis, flanked by two symmetry equivalent terminal divalent copper ions (Cu2 and Cu2A). These two peripheral copper ions exhibit distorted octahedral coordination geometry, with the dianionic ligand  $L_{3a}^{2-}$ acting as an N<sub>2</sub>O donor in the equatorial plane (Cu-N distances in the range 1.942(2) - 2.017(2) Å) and an acetonitrile solvent molecule adopting the fourth position in the equatorial plane. A perchlorate anion and a water molecule were found in the apical positions. The Cu-Owater distance is 2.215(2) Å while The Cu2-Operchlorate distances is 2.617(3) Å, reflecting the Jahn-Teller elongation axis. The central Cu1 ion, located on the two-fold rotation axis, exhibits a marked Jahn-Teller distortion. The equatorial plane comprises four N-donors derived from  $L_{3a}^{2-}$  with Cu1-N distances of 1.937(2) Å and 2.003(2) Å. Two symmetry equivalent perchlorates adopt the axially elongated positions with



Figure 6: Crystal Structure of  $[Cu_3L_{3a}Cl_4]_n$  (2) with additional symmetry clated choride anions included to emphasise the coordination geometry and the second state of the coordination geometry and the coordination geometry and the coordi



Figure 7: Polymeric structure of 2 highlighting the Cu-Cl-Cu bridges

Cu1–O8s distances of 2.748 (2) Å. Cu1 is connected to Cu2 and Cu2A by trans N–N diazine bridges with Cu1–N2–N–Cu2 torsional angle ( $\alpha$ ) of 157.7°, slightly less than that previously reported for similar structures.<sup>6</sup> The Cu···Cu separation is 4.769 Å which is consistent with other related diazine bridged complexes.<sup>6</sup> Given the +6 charge on the three Cu<sup>II</sup> ions and the presence of four perchlorate ligand being doubly-deprotonated L<sub>3a</sub><sup>2-</sup>. The diazine N2–N3 (1.380(3) Å) and C6–O4 (1.260(3) Å) bond distances imply single and double bond character respectively, consistent with deprotonation of the azine N-H. The torsional angle ( $\alpha$ ) around the diazine N–N bond is 157.7(1)° and the bond angles ( $\beta$ ,  $\beta$ ') are 108.9(2)° and 124.0(2)°.

 $[Cu_3L_{3a}(Cl)_4]_n$  (2): Reaction of  $L_{3a}H_2$  with CuCl<sub>2</sub>·2H<sub>2</sub>O afforded a 1-D coordination polymer with formula [Cu<sub>3</sub>L<sub>3a</sub>Cl<sub>4</sub>]<sub>n</sub>. Single crystals of 2 were grown via the slow evaporation of MeOH at rt. The complex crystalizes in the monoclinic space group I2/a with half of the molecule in the asymmetric unit. Selected bond lengths and angles are listed in Table S3 of the ESI. The fundamental repeat unit in 2 is a similar trinuclear  $[Cu_3L_{3a}]^{4+}$  motif to that observed in **1** (Fig. 6). The coordination geometry around Cu1 is octahedral with  $L_{3a}^{2-}$ coordinating via the bipyridine N (N1, N1A) and diazine N (N2,N2A) atoms with bridging  $\mu_2$ -chloride ions (Cl1 and Cl1A) in the axial positions forming a Cu1-Cl1-Cu2A link between trimers. The Cu-N distances are in the range 1.9753(3) – 2.0138(3) Å, normal for equatorial coordination to Cu<sup>II.3</sup> The symmetry equivalent Cu-Cl distances are 2.7314(16) Å. The peripheral pair of symmetry-related Cu<sup>2+</sup> ions (Cu2/Cu2A) exhibit square pyramidal coordination geometry with one chloride ion and an N<sub>2</sub>O donor set from  $L_{3a}^{2-}$ forming the basal plane and an apical chloride which offers a µ2bridge to Cu1 in a neighbouring molecule. The Cu2–N distances are 1.993(3) Å and 1.966(3), while the Cu2–Cl distances are 2.227(15) Å and 2.5488 (14) Å respectively for the basal and apical Cl atoms and the Cu2–O distance is 1.9992(3) Å. The diazine N2–N3 (1.387(4) Å) and C–O (1.251(5) Å) bond distances are similar to those found in 1 implying single and double bond character respectively. The torsional angle ( $\alpha$ ) around the diazine N–N bond is

165.4(2)° and the ( $\beta$ ,  $\beta'$ ) bond angles are 107.5 (3)° and 112.9(4)° similar to those found in **1**. Each trinuclear subunit of **2** is linked *via* apical

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Figure 8: Crystal Structure of  $[Cu_3L_{3b}(NO_3)_4]$  in 3. Selected H atoms have been removed for clarity



Figure 9: Nitrate bridged polymer chain in 3

connections between Cu1 and Cu2 via a  $\mu_2$ -chloride bridge affording a polymeric 1-D chain topology in which each trimer unit is connected to the next via two bridging chloride ions (Fig. 7). This arrangement resembles that of complex **3** described below, as well as a previously reported complex where hexanuclear subunits are linked to form chains *via* carboxylate bridges.<sup>11</sup>

 $[Cu_3L_{3b}(NO_3)_3]_n$  (3): Dark green single crystals of 3 were isolated from the reaction of  $L_{3b}H_2$  and  $Cu(NO_3)_2 \cdot 3H_2O$  via the evaporation of a hot solution of acetonitrile. The molecular structure of complex 3 is shown in Fig. 8 and selected interatomic distances and angles are listed in Table S4 of the ESI. The complex crystalizes in the monoclinic space group C2/c, with a half a crystallographically unique molecule of **3** in the asymmetric unit. The structure closely resembles complex 2 with respect to its coordination geometry and polymeric structural topology, the major difference being the replacement of the chlorides by nitrate ions (cf. Figs. 7 and 9). Once again the fundamental repeat unit in  $\mathbf{3}$  is a trinuclear  $[Cu_3L_{3b}]^{4+}$ moiety. The coordination geometry around Cu1 is octahedral with L<sub>3b</sub><sup>2-</sup> offering an N<sub>4</sub> donor set in the equatorial plane comprising the two bipyridine N atoms (N4, N4A) and the deprotonated diazine N (N2, N3) atoms. The Cu-N distances are 1.937(3) and 1.970(3) Å which are slightly less than the distance in complex 2 but can still be considered in the normal range for equatorial coordination to  ${\rm Cu}^{\rm II.11}$  The axial positions are occupied by two symmetry, equivalent in Q atoms (O7) of a bridging nitrate anion.  ${}^{\rm DFHe10CU20/CdiBTarRee45}{\rm fs}$ 2.572(16) Å. The peripheral Cu1 (Cu1A) ions exhibit a geometry intermediate between 5 and 6-coordinate. In the equatorial plane ligand  $L_{3b}^{2-}$  offers an N<sub>2</sub>O donor set from  $L_{3b}^{2-}$  which is completed by an O atom from a nitrate ligand (Cu1-O4). The Cu1-N distances are 1.935(3) and 2.056(3) Å, while the Cu1–O distances are in range 1.940(2) – 2.122(2) Å. The axial position is taken up by a nitrate O atom (O5) with a Cu-O distance of 2.204(3) Å. An additional O atom from the equatorially bound nitrate is also located in the vicinity of Cu(1) with a Cu-O distance of 2.626(3) Å but the O-Cu-O angle to O(5) (136.2(1)°) lies a long way from the idealised 180° expected from a Jahn-Teller distorted octahedron and Cu(1) is probably better considered as square pyramidal. Within these trimeric units Cu2 is connected to the symmetry equivalent Cu1/Cu1A atoms via trans N–N bridges (Cu–N–N–Cu torsional angle of 151.5°), leading to a Cu-Cu separation of 4.738 Å consistent with other related diazine bridging complexes.<sup>11</sup> The diazine N2-N3 (1.387(4) Å) and C–O (1.250(4) Å) bond distances are similar to those found in 1 and 2 implying single and double bond character respectively. The torsional angle ( $\alpha$ ) around the diazine C6–N3–N2–C7 bond is 165.3(3)° and the bond angles ( $\beta$ ,  $\beta'$ ) are 109.4(2)° and 122.5(3)°, again comparable with those found in 1 and 2. One of the two crystallographically independent nitrates adopts a 1,3-µ2-bridging mode between trimer units linking a terminal Cu(1) to the central Cu(2) of a neighbouring molecule such that each trimer exhibits two bridging nitrates to an adjoining trimer unit which propagates through the structure to form a polymeric chain arrangement. (Fig. 9).

[Mn<sub>3</sub>L<sub>3c</sub>H<sub>2</sub>(Cl)<sub>4</sub>(CH<sub>3</sub>O)<sub>2</sub>(H<sub>2</sub>O)] (4): A unique trinuclear manganese complex was isolated from the reaction of L<sub>3c</sub>H<sub>2</sub> with MnCl<sub>2</sub> in methanol. Suitable single crystals for X-ray diffraction were grown from slow evaporation of MeOH solution. The molecular structure of complex 4 is shown in Fig. 10 and selected interatomic distances and angles are listed in Table S5 of the ESI. The complex crystalizes in the triclinic space group *P*-1. The ligand L<sub>3c</sub><sup>2-</sup> adopts an alternative coordination environment to L<sub>3a</sub><sup>2-</sup> and L<sub>3b</sub><sup>2-</sup> previously described. In this case the carbonyl groups are located 'endo' (geometry C<sub>2</sub>, Fig. 4). The bond lengths within L<sub>3c</sub><sup>2-</sup> are significantly different from those in the closely related L<sub>3a</sub><sup>2-</sup> and L<sub>3b</sub><sup>2-</sup> ligands. The latter were consistent with C=O character and a C-N single bond whereas the



Figure 10: Crystal Structure of  $[Mn_3L_3cCl_4(CH_3OH)_2(H_2O)]$  (4) [Disordered methanol/water solvent omitted for clarity]

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geometric parameters for  $L_{3c}^{2-}$  show a marked lengthening of the C-O distances at 1.295(5) – 1.303(6) Å accompanied by a shortening of the C-N bond such that  $L_{3c}^{2-}$  has more alkoxide character. The light yellow colour of complex 4 and bond lengths around manganese atoms (vide infra) suggest all Mn ions carry a +2 charge and so the charge on the ligand is formally  $L_{3c}^{2-}$ . The central Mn1 ion adopts an unusual pentagonal bipyramidal coordination geometry comprising an  $N_2O_2$  donor set from  $L_{3c}{}^{2\text{-}}$  and an equatorially coordinated water molecule and two axially coordinated methanol solvent molecules.<sup>25</sup> The methanol solvent molecules form welldefined intermolecular O-H···Cl hydrogen bonds (O···Cl distances of 3.135(3) and 3.206(3) Å and C-O…Cl angles of 101.6(3) and 117.9(3)°) which clearly define each as a neutral coordinating methanol rather than a methoxide anion. The Mn1-N distances are 2.297(3) and 2.298(3) Å, while Mn1-O distances are in range 2.202(3) – 2.306(3) Å. The peripheral manganese atoms Mn2 and Mn3 both exhibit distorted square pyramidal geometries with Addison  $\tau$  values^{26} close to 0.203 for Mn2 and 0.375 for Mn3 with Mn-N bond lengths in the range 2.117(4) - 2.323(4) Å, Mn-Cl distances of 2.368(1) - 2.389(1) Å and Mn-O bond lengths of 2.203(3) – 2.227(3) Å. Unlike the copper complexes of  $L_{3a}^{2-}$  and  $L_{3b}^{2-}$ which link metal centers via a two-atom diazine bridge, the central and peripheral Mn ions in **4** are linked via  $\mu_2$ -O bridges leading to Mn1…Mn2 and Mn1…Mn3 separation of 4.176(1) and 4.0652(9) Å respectively, reflecting the harder oxophilic nature of the Mn centres. Unlike complexes 2 and 3, there are no covalent bonds between molecules.

 $[Fe_4(L_{3a})_2(H_2O)_6][CF_3SO_3]_6$  (5): In contrast to the trimetallic complexes derived from the copper and manganese reactions, the reaction of  $L_{3a}H_2$  with  $Fe(CF_3SO_3)_2 \cdot 2MeCN$  in acetonitrile under aerobic conditions unexpectedly afforded the tetranuclear complex  $[Fe_4(L_{3a})_2(H_2O)_6][CF_3SO_3]_6$ , 5. The molecular structure of 5 is shown in Fig. 11 and selected interatomic distances and angles are listed in Table S6 of the ESI. The compound crystallizes in the triclinic space group, P-1, with two ligands, four iron centres, six coordinated water molecules and six triflates in the asymmetric unit. In addition



Figure 11: Crystal Structure of  $[Fe_4(L_{3a})_2(H_2O)_6][CF_3SO_3]_6$  (5) with counter ions and solvent molecules removed for clarity.

poorly refined lattice solvent suggest a maximum of two MeCN and two  $Et_2O$  solvent molecules per formula unit but the crystals showed a strong propensity for desolvation when removed from the mother liquor. In **5**, there is a significant geometrical distortion

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of the ligand away from the nearly co-planar structures observed in complexes 1 – 4. In this context one of the side than the state 1-4remains planar with the central bipy plane (torsional angle ( $\alpha$ ) around C33–N11–N10–C32 is 178.5(5)° and bond angles ( $\beta$ ,  $\beta$ ') are 107.7(4)° and 120.3(4)°), while the other side chain twists around the diazine bond with the torsional angle ( $\alpha$ ) around C44–N14– N15–C45 = -87.5 (6)° and the bond angles ( $\beta$ ,  $\beta$ ') are 116.0(4)° and 117.7(4)° respectively. The loss of delocalization in the ligand framework occurs via rotation about the diazine N-N bond. Fe1 and Fe3, occupy the central bipy pocket of the two crystallographically independent units with pentagonal bipyramidal geometries. In the equatorial plane this comprises an N<sub>3</sub>O donor from one  $L_{3a}^{2-}$  ligand and a diazine N atom from a second  $L_{3a^{2-}}$  ligand. The axial positions in each case comprise a terminal pyridyl unit from the second  $L_{3a}^{2-}$ anion and coordinated water, providing each Fe centre with an  $N_5O_2$  coordinated geometry. The Fe1/Fe3–O and Fe1/Fe3–N distances are in the range 2.097(4) – 2.474(4) Å and 2.154(6) – 2.384(4) Å respectively. The remaining two Fe centres (Fe2 and Fe4) adopt a distorted  $N_2O_4$  octahedral geometry with one  $L_{3a}^{2-}$  ligand acting as an  $N_2O$  donor, the second  $L_{3a}^{2-}$  ligand acting as an O donor and two axially ligated water molecules completing the coordination sphere. The Fe2/Fe4-O and Fe2/Fe4-N distances fall in range 1.902(4) - 2.044(5) Å and 2.069(4) - 2.145(5) Å respectively. Fe1 and Fe2 are linked via a  $\mu_2$ -O atom as are Fe3 and Fe4, while the central Fe1 and Fe3 atoms are bridged via two cisdiazine bridges (Fe1-N14-N15-Fe3; torsional angle of 66.0 (4)° and Fe1–N6–N7–Fe3 torsional angle of 62.5(4)°) leading to an Fe1…Fe3 separation of 4.482(1) Å. (Fig. 9). Fe1 and Fe4 are linked via the 3atom NCO bridge of an  $L_{3a}^{2-}$  ligand as are Fe2 and Fe3. The six coordinated water molecules form a web of hydrogen bonded interactions to the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> counterions, but these tetranuclear units are otherwise well-separated in the crystal lattice with the closest hydrogen-bonded contact between complexes being 8.561 Å. Bond lengths around Fe1/Fe3 (BVS = 1.90) and Fe2/Fe4 (BVS = 3.036) suggest +2 and +3 oxidation states respectively for these four iron centres. The resulting +10 charge on these four ions is subsequently charge balanced by two  $L_{3a}^{2-}$  and six triflate anions.

#### Magnetic Properties

Variable temperature dc susceptibility data ( $\chi$ T vs T, 5 – 300 K) for **1** (Fig. 12), **2** (Fig. 1S) and **3** (Fig. 2S) indicate room temperature  $\chi$ T values of 1.16 emu·K·mol<sup>-1</sup>, 1.11 emu·K·mol<sup>-1</sup> and 1.02 emu·K·mol<sup>-1</sup> respectively. These are in reasonable agreement with the theoretical value expected for three magnetically isolated Cu<sup>2+</sup> ions ( $3 \times S = \frac{1}{2}$  with g ~ 2.1 gives an expected  $\chi$ T = 1.24 emu·K·mol<sup>-1</sup>). The  $\chi$ T value continuously decreases on cooling reaching a plateau at 0.42 emu·K·mol<sup>-1</sup>, 0.33 emu·K·mol<sup>-1</sup> and 0.40 emu·K·mol<sup>-1</sup> for complexes **1** and **2** and **3** respectively at the base temperature of 5 K. This behaviour is typical of antiferomagnetically coupled trinuclear Cu<sup>II</sup> complexes where an S<sub>T</sub> =  $\frac{1}{2}$  spin ground state is expected ( $\chi$ T = 0.41 emu·K·mol<sup>-1</sup> for S<sub>T</sub> =  $\frac{1}{2}$  and **g** ~ 2.1). The trinuclear cores of **1** – **3** are all similar but **2** and **3** differ from **1** in that they form coordination polymers via  $\mu_2$ -chloride or 1,3-bridging nitrate counterions respectively. Here the Jahn-Teller axes of the

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(emu.K/mol)

1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 0 50 100 150 200 250 300 Temperature (K)

**Figure 12:** Temperature dependence of  $\chi T$  for **1** with the solid line representing the fit to the linear trimer model (g = 2.096(3) and J/k = -35.5(3) K)

Cu<sup>2+</sup> ions clearly permit us to delineate the directionality of the  $d_{x^2-y^2}$  magnetic orbitals which help define the dominant exchange pathway(s). In all three complexes these magnetic orbitals are located in the basal plane providing efficient communication *via* the trans-N–N diazine bridges but the exchange coupling between trimeric units is therefore expected to be weak. It is therefore unsurprising that the three complexes exhibit similar magnetic responses and all three systems were modelled by the simple isotropic spin Hamiltonian described in Eq. (1).

$$\hat{H} = -2J[\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3]$$
 Eq.1

A fit to the linear trimer model (Eq. 1) within  $Phi^{27}$  afforded g = 2.096(3) and J/k = -35.5(3) K for 1 (Fig. 12). For 2 the behaviour was similarly modelled with a trimer model but a small downturn in  $\chi T$ was evident in the limiting low temperature region, suggesting the presence of weak through bond superexchange or through space dipolar coupling. The overall fitting parameters (g = 2.098(2), and J/k = -38.9(2) K,  $\theta = -1.0$  K) are similar to **1** and the mean field term for the inter-trimer exchange coupling an order of magnitude smaller than the intramolecular exchange. The presence of antiferromagnetic exchange between trimer units in 2 will generate a diamagnetic ground state and is reflected in the downturn in  $\chi T$ near the base temperature (see ESI). A somewhat larger exchange coupling was identified for **3** evidenced by a slightly lower  $\chi T$  value at room temperature and a more extended plateau in the low temperature region, reflecting a thermally well-isolated spin ground state. In this case the g-value was fixed at 2.03 (to replicate the low temperature value of  $\chi T$ ) and a single parameter fit provided J/k = -72(1) K). Data for 2 and 3 are available in the ESI. In all cases the presence of dominant antiferromagnetic exchange between Cu<sup>II</sup> centres leads to an  $S_T = \frac{1}{2}$  ground state, reflected in a plateau in the low temperature data. Previous studies on diazine systems suggest a linear relationship between the exchange coupling and the rotational angle of Cu magnetic planes relative to the single N-N bond.<sup>7</sup> Cu–N–N–Cu torsion angles ( $\alpha$ ,  $\alpha$ ') and bond angles ( $\beta$ ,  $\beta$ ') in **1**, **2**, and **3** are in range 151.4° – 165.3° and 107.5° - 125.5° respectively which are quite close to the related examples studies



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Figure 13: Temperature dependence of  $\chi T$  for 4 with the solid line representing the fit to the linear trimer model (g = 1.963(2) and J/k = -0.66(1)( K)

elsewhere.<sup>6,7</sup> The nature of the  $d_{\chi^2,\gamma^2}$  magnetic orbitals with diazine N atoms located in the basal plane appears to afford efficient exchange coupling through the  $\sigma$ -framework of the trans diazine unit.

Variable temperature dc susceptibility data for **4** indicates a room temperature (300 K)  $\chi$ T value of 12.33 emu·K·mol<sup>-1</sup>, slightly lower than the spin-only value (13.125 emu·K·mol<sup>-1</sup>) expected for three magnetically isolated high-spin Mn<sup>II</sup> ions. The value of  $\chi$ T for **4** appears almost temperature independent across the temperature range 300 – 75 K but begins to decrease rapidly below 50 K. An excellent fit to the linear trimer model (Eq. 1) within Phi<sup>27</sup> afforded g = 1.963(2) and J/k = -0.66(1) K consistent with antiferromagnetic coupling between Mn<sup>II</sup> centres, generating an S<sub>T</sub> = 5/2 ground state (Fig. 13).

The Fe<sub>4</sub> cluster (5) comprises two seven-coordinate Fe<sup>II</sup> centres (Fe1 and Fe3) and two six-coordinate FeIII centres (Fe2 and Fe4). The FeIII centres are expected to exhibit a simple spin-only  $^{6}A$  term (S = 5/2, g ~ 2.0,) but the pentagonal bipyramidal Fe<sup>II</sup> centres exhibit a  ${}^{5}E$ configuration in which the doubly degenerate ground state can contribute significant orbital angular momentum and has been shown to lead to very large zero field splitting  $(|D| < 15 \text{ cm}^{-1})$ .<sup>28</sup> In the high temperature region these ions approximate to S = 2 with g ~ 2.1 – 2.2. The temperature dependence of  $\chi T vs T$  for **5** is presented in Fig. 14 and reveals a complex evolution of  $\chi T$ . In the high temperature region (T > 250 K) a plot of  $1/\chi$  vs T follows Curie-Weiss behaviour with C = 15.17 emu·K·mol<sup>-1</sup> and  $\theta$  = -9.0 K (see Fig. 5S, ESI), comparable with that expected for two S = 5/2 and two S = 2 ions with g = 2.0 (14.75 emu·K·mol<sup>-1</sup>). On cooling the value of  $\chi T$ initially increases reaching a maximum of 20.34 emu·K·mol<sup>-1</sup> before decreasing monotonically to 1.92 emu·K·mol<sup>-1</sup> at 2.0 K. In the region 50 - 175 K the sample again obeys Curie-Weiss behaviour with C = 30.86 emu·K·mol<sup>-1</sup> and  $\theta$  = -88.6 K. This value of C is broadly consistent with ferromagnetic coupling between Fe<sup>3+</sup> and Fe<sup>2+</sup> ions via the  $\mu_2$ -oxo bridge giving rise to two independent S = 9/2 spin states (C = 24.74 emu·K·mol<sup>-1</sup> for g = 2.0) if other exchange

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pathways are neglected. The change of sign and large value of  $\theta$  in this low temperature regime is consistent with the emergence of additional weaker antiferromagnetic interactions plus residual orbital angular momentum arising from the Fe<sup>2+</sup> centers and/or significant zero field splitting. An examination of the crystal structure reveals **5** exhibits a non-crystallographic two-fold rotation axis such that a simple isotropic model of the exchange coupling approximates to:



Figure 14: Temperature dependence of  $\chi T$  for 5.

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where J reflects exchange coupling via the Fe-O-Fe one-atom bridge, J' describes exchange coupling via the diazine unit and J" describes exchange coupling via the three atom NCO linker. Attempts to fit the magnetic data to this isotropic model failed, presumably due to the presence of significant residual orbital angular momentum associated with the Fe<sup>2+ 5</sup>E term. Unfortunately taking into account the residual orbital contribution and all the exchange pathways defined in Eq. 2 is too large a computation to be processed within Phi.<sup>27</sup> Simplifying the system to include just the first exchange parameter and the presence of orbital angular momentum also failed to replicate the data. As a consequence we conclude that (i) the presence of residual orbital angular momentum and/or zero field splitting is significant and (ii) the magnitude of the exchange couplings J' and J" must also be considered non-negligible in relation to the effect of the spin-orbit coupling. The behaviour might be further complicated by the possibility for spin crossover which has been observed in related 7coordinate systems<sup>29</sup> and further magnetic and Mossbauer measurements will be necessary to gain a more detailed understanding of this system.

#### Conclusions

To summarize, we have successfully prepared a new series of open chain diazine ligands,  $L_{3a}H_2$ ,  $L_{3b}H_2$ , and  $L_{3c}H_2$  that have a central bipyridine unit with two side-arms offering a range of ketone/alkoxide oxygen donors, diazine and pyridine terminal groups. These ligands show a strong preference for binding three

metals forming a trimetallic sub-unit but sufficient ligand flexibility to modify the coordination pockets for metal binding/mithis tase the different coordination preferences of the metal play a role in determining the final outcome of the self-assembly process. For example Cu<sup>II</sup> has a preference for Jahn-Teller elongated or squarebased pyramidal geometry whereas they favour the formation of pentagonal bipyramidal geometries in the case of both Mn<sup>II</sup> and Fe<sup>II</sup> centres. These ligands support effective antiferromagnetic exchange coupling within the Cu<sup>II</sup> trimers  $\mathbf{1}$  –  $\mathbf{3}$  and also Mn<sup>II</sup> complex 4. While the pentagonal bipyramidal Mn<sup>II</sup> complex 4 exhibits an <sup>6</sup>A ground term, the Fe<sup>II</sup> center in **5** possesses a <sup>5</sup>E ground term with significant residual orbital angular momentum. The trimetallic copper species reveal the potential to create more complex architectures from these building units by exchanging noncoordinating anions in 1 for bridging ligands such as Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in 2 and 3 respectively. Further reactions of the series of L<sub>3</sub>H<sub>2</sub> ligands with other 3d- and 4f- metal ions are currently under investigation and will be reported in due course.

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