Coordination Studies of Copper(II), Nickel(II), Cobalt(II) and Zinc(II) Salts with Pyridyl–Tetrazole Ligands Containing Alkyl or Alkyl Halide Pendant Arms

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Kelleher, F., Sheridan, U. McGinley, J. Gallagher, J. and Fleming, A. Coordination studies of copper(II), nickel(II), cobalt(II) and zinc(II) salts with pyridyl–tetrazole ligands containing alkyl or alkyl halide pendant arms. *Polyhedron* Volume 59, 1 August 2013, Pages 8–16. doi.org/10.1016/j.poly.2013.04.025,
Coordination studies of copper(II), nickel(II), cobalt(II) and zinc(II) salts with pyridyl–tetrazole ligands containing alkyl or alkyl halide pendant arms.

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Abstract

The reaction of 2-(2H-tetrazol-5-yl)pyridine (L1) with 1,n-dibromoalkane (n = 3, 4, 6 or 8) results in the formation of the isomers 2-(n''-bromoalkyl-(1-tetrazol-5-yl)pyridine (L2A-D) and 2-(n''-bromoalkyl-(2-tetrazol-5-yl)pyridine (L3A-D). The reaction of L1 with 1-bromoalkanes also resulted in the formation of isomeric materials, namely 2-(n''-alkyl-(1-tetrazol-5-yl)pyridine (L4A-C) and 2-(n''-alkyl-(2-tetrazol-5-yl)pyridine (L5A-C). Complexation reactions of these ligands with the transition metal salts CuCl₂.2H₂O, Co(NCS)₂, NiCl₂.2H₂O and ZnCl₂ were carried out in methanol and resulted in complexes containing a 1:1 metal:ligand stoichiometry except in the cases of the cobalt complexes where a 1:2 metal:ligand stoichiometry was obtained. The ¹H NMR spectra of the zinc complexes showed that the ligands containing the pendant arm in the 2-N position of the tetrazole ring bind the zinc ion more strongly than those containing the pendant arm in the 1-N position. The X-ray structures of two cobalt salts, Co(L5A)₂(NCS)₂ and Co(L5C)₂(NCS)₂, are also discussed.

Keywords

Tetrazole, pyridyl, transition metal complexes, synthesis, NMR, X-ray structures.
Introduction

The development of “click” chemistry, as described by Sharpless and co-workers [1-2], has resulted in a recent increase in the synthesis of functional compounds containing polyazole rings, particularly triazoles, tetrazoles and their derivatives [3-7]. Tetrazoles have been recognised as bioisosteres for carboxylic acids and as a result have found widespread applications in medicinal chemistry [3]. Tetrazoles and its derivatives have also been studied as ligands in coordination chemistry, exhibiting several coordination modes [8]. Our interest in tetrazoles concerns their use in molecular recognition. We have previously reported the synthesis of various bis- and tetra-tetrazole molecules [9]. To expand this area, we are currently investigating the use of tetrazole-containing compounds as potential metal-based therapeutic agents, especially as anti-cancer or anti-fungicidal agents. Recently, we have described the synthesis of some pyridyl-tetrazole compounds containing bromohexyl pendant arms and examined their coordination chemistry with Fe(II), Co(II) and Cu(II) salts, a range of metal cations which the human body can tolerate [10]. As part of our current investigations into the coordination chemistry of pyridyl-tetrazole derivatives, we have altered the pendant arm extending from the tetrazole ring to include other alkyl bromide chains as well as alkyl chain on their own (see Scheme 1). In this paper, we describe the synthesis of pyridyl-tetrazole compounds containing other bromoalkyl and alkyl pendant arms and examine the coordination chemistry of these tetrazole derivatives with the transition-metal salts CuCl2.2H2O, Co(NCS)2, NiCl2.2H2O and ZnCl2 and also the crystal structures of two cobalt(II) complexes.

Results and Discussion

Ligand synthesis

The reaction of 2-(2H-tetrazol-5-yl)pyridine (L1) with either the appropriate 1,n-dibromoalkanes (n = 3, 4, 6 or 8) or bromoalkane in acetonitrile with potassium carbonate as base resulted in the formation of either 2-(n’)-bromoalkyl-(1-tetrazol-5-yl)pyridine (L2A-D) and 2-(n’)-bromoalkyl-(2-tetrazol-5-yl)pyridine (L3A-D) or 2-(alkyl-(1-tetrazol-5-yl)pyridine (L4A-C) and 2-(alkyl-(2-tetrazol-5-yl)pyridine (L5A-C), arising from alkylation at either the 1-N or 2-N positions, in a manner similar to that described in the literature [10], as shown in Scheme 1. Column chromatography was used to separate the isomeric products. In all cases,
the loss of the CH$_2$Br signal in the $^1$H NMR spectra of the products and the appearance of a triplet at $\sim$5.00 ppm for the 1-N compounds or $\sim$4.80 ppm for the 2-N compounds was taken as evidence for the formation of the products. The isomers are readily distinguishable by their $^{13}$C NMR spectra with the $^{13}$C NMR chemical shift of the tetrazole carbon atom appearing at $ca$. 154.0 or 164.0 ppm in the 1,5- and 2,5-disubstituted tetrazoles, respectively [9,11]. In these reactions, the 1-N isomers (L2A-D and L4A-C) gave a signal at $\sim$151 ppm, while the 2-N isomers (L3A-D and L5A-C) gave a signal at $\sim$164 ppm.

Scheme 1

Reaction conditions: i) 1,n-dibromoalkane ($n$ = 3, 4, 6 or 8) or 1-RBr ($R$ = C$_4$H$_9$, C$_6$H$_{13}$ or C$_8$H$_{17}$), K$_2$CO$_3$, MeCN, $\Delta$, 24 hr; L2/L3 A: $R$ = C$_3$H$_6$Br, B: $R$ = C$_4$H$_8$Br, C: $R$ = C$_6$H$_{12}$Br, D: $R$ = C$_8$H$_{16}$Br; L4/L5 A: $R$ = C$_4$H$_9$, B: $R$ = C$_6$H$_{13}$, C: $R$ = C$_8$H$_{17}$.

Coordination Reactions

The transition-metal salts CuCl$_2$.2H$_2$O, Co(NCS)$_2$, NiCl$_2$.6H$_2$O and ZnCl$_2$ were reacted with L2A-D, L3A-D, L4A-C and L5A-C, respectively, in methanol at reflux temperature under an inert atmosphere for two hours. The reactions with the cobalt salt were only carried out with the L4 and L5 derivatives. The chloride salts of copper, nickel and zinc were used since the structures of the L2C and L3C ligands with copper chloride has previously shown the formation of halide bridging [14] and it was felt that similar structures would be observed with these metal chloride salts. All reactions were carried out using a 1:1 metal to ligand stoichiometry. The resulting solutions were allowed to stand for several days, after which time the solid products were filtered. All the copper and nickel complexes of the L2 and L3 ligands were green in colour, while the zinc complexes were either pale orange or cream, which was the colour of the starting ligand. The copper and nickel reactions with the L4 and L5 derivatives also resulted in green solids being formed, while the cobalt complexes yielded
green solids in the cases of the 1-N derivatives and rust coloured solids in the cases of the 2-N derivatives. The zinc complexes were either yellow or brown in colour, which was the colour of the starting tetrazole derivative. Elemental analyses on all of the copper, nickel and zinc products obtained showed that all the complexes have a 1:1 metal:ligand composition. Based on the X-ray structures of [Cu(L2C)Cl]2 and [Cu(L3C)Cl]2 previously reported [10] which contained a 1:1 metal:ligand composition and also a dichloro-bridged dimeric {Cu(II)(μ-Cl)Cl}2 unit, it is proposed that all the metal chloride complexes synthesised herein will have a similar structure, as shown in Figure 1.

![Proposed structures for all metal complexes](image)

**Figure 1** Proposed structures for all metal complexes (M = Cu, Ni or Zn; R = C3H6Br, C4H9Br, C6H12Br, C8H16Br, C8H9, C6H13 or C8H17).

The cobalt complexes of the L4 and L5 derivatives were shown to have a 1:2 metal to ligand composition. We have previously reported the X-ray structures of the cobalt(II) isothiocyanate complexes of 2-(6''-bromohexyl-(1-tetrazol-5-yl)pyridine (L2C) and 2-(6''-bromohexyl-(2-tetrazol-5-yl)pyridine (L3C) [10], both of which contained a 1:2 metal to ligand composition. We were able to grow crystals of both Co(5A)2(NCS)2 and Co(5C)2(NCS)2 from methanol, which were suitable for X-ray structural studies, and so can compare these structures.

*Magnetic measurements*
All of the copper complexes have a magnetic moment in the range of 2.1-2.4 B.M., which is indicative of the presence of copper(II) in the complexes. The magnetic moments for the nickel complexes are between 2.9 and 4.1 B.M. These values are high for either four coordinate tetrahedral geometry or five coordinate trigonal bipyramidal geometry at the nickel centre. The magnetic measurements of the cobalt(II) complexes indicated the presence of high-spin cobalt(II) ions. Previously reported magnetic moments for complexes containing pyridyl-tetrazole ligands have been high in value and high-spin in nature [10,12].

$^1$H NMR spectra

The $^1$H NMR spectra of the zinc chloride complexes of the ligands $\text{L2A-D}$ and $\text{L3A-D}$ were all obtained in CDCl$_3$. Table 1 shows the $^1$H NMR spectral data for the four pyridyl-tetrazole ligands with the alkyl bromides attached at the 1-$N$ position ($\text{L2A-D}$) and the four corresponding zinc chloride complexes while Table 2 contains the $^1$H NMR spectral data for the four pyridyl-tetrazole ligands with the alkyl bromides attached at the 2-$N$ position ($\text{L3A-D}$) and the four corresponding zinc chloride complexes.

Table 1.
Selected $^1$H NMR data for the ligands $\text{L2A-D}$ and their ZnCl$_2$ complexes.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>pyr-H</th>
<th>pyr-H</th>
<th>pyr-H</th>
<th>pyr-H</th>
<th>CH$_2$N</th>
</tr>
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<tbody>
<tr>
<td>L2A</td>
<td>8.75</td>
<td>8.37</td>
<td>7.93</td>
<td>7.47</td>
<td>5.15</td>
</tr>
<tr>
<td>$\text{[Zn(L2A)Cl}_2\text{]}_2$</td>
<td>8.78</td>
<td>8.35</td>
<td>7.95</td>
<td>7.45</td>
<td>5.18</td>
</tr>
<tr>
<td>L2B</td>
<td>8.74</td>
<td>8.37</td>
<td>7.93</td>
<td>7.47</td>
<td>5.04</td>
</tr>
<tr>
<td>$\text{[Zn(L2B)Cl}_2\text{]}_2$</td>
<td>8.78</td>
<td>8.36</td>
<td>7.96</td>
<td>7.50</td>
<td>5.02</td>
</tr>
<tr>
<td>L2C$^b$</td>
<td>8.77</td>
<td>8.37</td>
<td>7.96</td>
<td>7.52</td>
<td>5.00</td>
</tr>
<tr>
<td>$\text{[Zn(L2C)Cl}_2\text{]}_2$</td>
<td>8.92</td>
<td>8.29</td>
<td>8.06</td>
<td>7.61</td>
<td>4.92</td>
</tr>
<tr>
<td>L2D</td>
<td>8.73</td>
<td>8.37</td>
<td>7.90</td>
<td>7.45</td>
<td>4.98</td>
</tr>
<tr>
<td>$\text{[Zn(L2D)Cl}_2\text{]}_2$</td>
<td>8.76</td>
<td>8.32</td>
<td>7.97</td>
<td>7.49</td>
<td>4.96</td>
</tr>
</tbody>
</table>

$^a$: obtained in CDCl$_3$

$^b$: data from reference 14

Table 2.
Selected $^1$H NMR data for the ligands L3A-D and their ZnCl$_2$ complexes.$^a$

<table>
<thead>
<tr>
<th>Compound</th>
<th>pyr-H</th>
<th>pyr-H</th>
<th>pyr-H</th>
<th>pyr-H</th>
<th>CH$_2$N</th>
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<tbody>
<tr>
<td>L3A</td>
<td>8.78</td>
<td>8.26</td>
<td>7.87</td>
<td>7.41</td>
<td>4.91</td>
</tr>
<tr>
<td>[Zn(L3A)Cl$_2$]$_2$</td>
<td>8.88</td>
<td>8.31</td>
<td>8.16</td>
<td>7.60</td>
<td>5.01</td>
</tr>
<tr>
<td>L3B</td>
<td>8.78</td>
<td>8.25</td>
<td>7.87</td>
<td>7.40</td>
<td>4.77</td>
</tr>
<tr>
<td>[Zn(L3B)Cl$_2$]$_2$</td>
<td>8.96</td>
<td>8.29</td>
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<td>7.84</td>
<td>4.88</td>
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<tr>
<td>L3C$^b$</td>
<td>8.80</td>
<td>8.27</td>
<td>7.90</td>
<td>7.43</td>
<td>4.73</td>
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<tr>
<td>[Zn(L3C)Cl$_2$]$_2$</td>
<td>8.86</td>
<td>8.28</td>
<td>8.19</td>
<td>7.76</td>
<td>4.81</td>
</tr>
<tr>
<td>L3D</td>
<td>8.79</td>
<td>8.25</td>
<td>7.87</td>
<td>7.40</td>
<td>4.70</td>
</tr>
<tr>
<td>[Zn(L3D)Cl$_2$]$_2$</td>
<td>8.89</td>
<td>8.31</td>
<td>8.22</td>
<td>7.81</td>
<td>4.81</td>
</tr>
</tbody>
</table>

$^a$: obtained in CDCl$_3$

$^b$: data from reference 14

From the data in Tables 1 and 2, it is evident that stronger binding of the zinc chloride occurs with the series of ligands L3A-D, which contain the alkyl bromide at the 2-N position, as seen from the larger differences in chemical shift for both the pyridyl proton signals and the signal for the methylene group attached to the tetrazole ring. The spectra of the zinc complexes from the L2A-D series of ligands shows only slight variation in signal position compared to the starting ligands. It is not obvious why the position of the pendant arm on the tetrazole ring (1-N or 2-N) should have such a bearing on the signals in the $^1$H NMR spectra of the zinc chloride complexes, especially since the metal ion is believed to coordinate to the pyridine nitrogen atom and one tetrazole nitrogen atom to form a five-membered ring, as depicted in Figure 1. In the crystal structure of [Cu(L2C)Cl$_2$]$_2$, the two bromohexyl arms are above and below the central Cu$_2$Cl$_2$ core and are also pointing away from the core, while in the crystal structure of [Cu(L3C)Cl$_2$]$_2$ both arms point in the same direction but again away from the central core [14]. Furthermore, if the pendant arm was in some way blocking the binding site, then it would be expected that the longer length arms would be more influential in this regard than the shorter length chains, but this does not appear to be the case. Further studies, including computational studies, are currently being undertaken in order to try to elucidate the reason for the regiochemical differences in binding strengths. The $^1$H NMR spectra of the zinc chloride complexes of the ligands L4A-C and L5A-C were also obtained in CDCl$_3$. The spectral data was in agreement with the proposed binding of the zinc ion to the
pyridyl nitrogen atom and one of the tetrazole nitrogen atoms, as can be seen from the shift in the signals associated with the pyridine ring and also the methylene group bonded to the tetrazole ring.

**X-ray structures of Co(L5A)₂(NCS)₂ and Co(L5C)₂(NCS)₂**

The molecular structures for Co(L5A)₂(NCS)₂ and Co(L5C)₂(NCS)₂ (with the cobalt atom residing on inversion centres) are depicted in Figures 2 and 3, respectively. Crystallographic information is detailed in Table 3. In both structures, the cobalt(II) atom has an octahedral coordination geometry with the pyridyl-tetrazole L5A and L5C ligands chelating in the equatorial plane and with the two isothiocyanate anions coordinating along the axial direction. Each pyridyl-tetrazole ligand binds to the cobalt(II) ion through one tetrazole nitrogen atom at the 1-N site and through the pyridyl nitrogen atom. As previously observed [10], the pyridine rings are not coplanar with the tetrazole rings and so both complexes display a slightly puckered conformation. The planes between the pyridine and tetrazole rings form interplanar angles of 3.8(5)° and 1.6(5)° in Co(L5A)₂(NCS)₂ and 4.5(4)° in Co(L5C)₂(NCS)₂. The Co-NCS distances are in the range from 2.037(6) to 2.060(6) Å, whereas the remaining Co-N distances are 0.10 Å longer and in the range 2.140(4) to 2.170(3) Å. These bond lengths are typical of Co²⁺-N distances involving isothiocyanate and heteroaromatic ring donor groups from an analysis of the Cambridge Structural Database.

The isothiocyanate moieties in both complexes are regular with NCS angles of 178.5(6)°, 176.9(5)° and 178.5(4)°. The coordination geometry is close to ideal octahedral in Co(L5A)₂(NCS)₂ with all three trans angles within 1° of 180° [range from 179.3(2) to 179.9(3)°], whereas, Co(L5C)₂(NCS)₂ resides with the cobalt atom on inversion centres and trans N-Co-N angles of 180°. There are no classical hydrogen bonds in either structures and aggregation is by weak interactions and contacts.
Figure 2. A view of Co(L5A)$_2$(NCS)$_2$ with atoms depicted with displacement ellipsoids at their 20% probability level.

Figure 3. A view of Co(L5C)$_2$(NCS)$_2$ with atoms depicted with displacement ellipsoids at the 20% probability level; only one component of the disordered n-octyl chain is shown.

Table 3.
Crystalllographic Data for Co(L5A)$_2$(NCS)$_2$ and Co(L5C)$_2$(NCS)$_2$

<table>
<thead>
<tr>
<th></th>
<th>Co(L5A)$_2$(NCS)$_2$</th>
<th>Co(L5C)$_2$(NCS)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{22}$H$</em>{26}$CoN$_{12}$S$_2$</td>
<td>C$<em>{30}$H$</em>{42}$CoN$_{12}$S$_2$</td>
</tr>
<tr>
<td>M/g mol$^{-1}$</td>
<td>581.60</td>
<td>693.81</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Space group</td>
<td>$Pca2_1$</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$T$/K</td>
<td>294(1)</td>
<td>294(1)</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>15.9466(4)</td>
<td>13.5506(10)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>8.4530(2)</td>
<td>8.4428(5)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>20.6129(5)</td>
<td>15.9122(10)</td>
</tr>
<tr>
<td>$\alpha$/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>90</td>
<td>99.063(7)</td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$V$/Å$^3$</td>
<td>2778.55(12)</td>
<td>1797.7(2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>$D_c$/g cm$^{-3}$</td>
<td>1.39</td>
<td>1.282</td>
</tr>
</tbody>
</table>

Reflections collected

|                      | 14564       | 17401     |
|                      | 5529        | 4759      |

$R_{int}$

|                      | 0.026       | 0.046     |

Obs. reflections \([I > 2\sigma(I)]\)

|                      | 4007        | 3108      |

No. of parameters

|                      | 337         | 224       |

No. of restraints

|                      | 37          | 5         |

$R1$ \([I > 2\sigma(I)]\)

|                      | 0.052       | 0.080     |

$wR2$ (all data)

|                      | 0.132       | 0.199     |

$GoF$

|                      | 1.036       | 1.116     |

### Experimental

$^1$H and $^{13}$C NMR (δ ppm; $J$ Hz) spectra were recorded on a Bruker Avance 300 MHz NMR spectrometer using saturated CDCl$_3$ solutions with Me$_4$Si reference, unless indicated otherwise, with resolutions of 0.18 Hz and 0.01 ppm, respectively. Infrared spectra (cm$^{-1}$) were recorded as KBr discs using a Perkin Elmer System 2000 FT-IR spectrometer. UV-vis spectra were recorded using a Unicam UV 540 spectrometer. Melting point analyses were carried out using a Stewart Scientific SMP 1 melting point apparatus and are uncorrected. Electrospray (ESI) mass spectra were collected on an Agilent Technologies 6410 Time of Flight LC/MS. Compounds were dissolved in acetonitrile-water (1:1) solutions containing 0.1% formic acid, unless otherwise stated. The interpretation of mass spectra was made with the help of the program “Agilent Masshunter Workstation Software”. Magnetic susceptibility measurements were carried out at room temperature using a Johnson Matthey Magnetic Susceptibility Balance with [HgCo(SCN)$_4$] as reference. Microanalyses were carried out at the Microanalytical Laboratory of the National University of Ireland Maynooth. Standard Schlenk techniques were used throughout. Starting materials were commercially obtained and used without further purification. The compound 2-(2$H$-tetrazol-5-yl)pyridine (L1), the bromohexyl derivatives 2-(6''-bromoalkyl-(1-tetrazol-5-yl)pyridine (L2C) and 2-(6''-
bromoalkyl-(2-tetrazol-5-yl)pyridine (L3C) as well as the copper complexes \([\text{Cu(L2C)}\text{Cl}_2]_2\) and \([\text{Cu(L3C)}\text{Cl}_2]_2\) have been reported previously \[10\].

**Caution!** Nitrogen-rich compounds such as tetrazole derivatives are used as components for explosive mixtures \[13\]. In our laboratory, the reactions described were run on a few gram scale, and no problems were encountered. However, great caution should be exercised when heating or handling compounds of this type.

General synthesis of 2-(n’’-bromoalkyl-(1-tetrazol-5-yl)pyridine (L2) and 2-(n’’-bromoalkyl-(2-tetrazol-5-yl)pyridine (L3)

To L1 (2.00 g, 13.6 mmol) dissolved in acetonitrile (60 mL) was added potassium carbonate (18.8 g, 136 mmol). The resulting solution was heated at reflux temperature for 30 minutes and to the hot solution was added 1, n-dibromoalkane (48.0 mmol, n = 3, 4, 6 or 8). The reaction mixture was then stirred at reflux temperature for a further 24 h. After cooling, the inorganic solids were removed by filtration and the solvent was removed under reduced pressure to afford an oil, which was purified by column chromatography on silica gel (initially at a ratio of petroleum ether:ethyl acetate 80:20, followed by the ratio of 60:40). This gave the products L2A-D and L3A-D.

**L2A:** Dark brown solid (0.46 g, 13 %). m.p. 190-192 °C. \(\text{C}_9\text{H}_{10}\text{N}_5\text{Br}\): calcd. C 40.32, H 3.76, N 26.12; found C 39.99, H 3.88, N 25.89. IR (KBr): \(\nu = 2980, 2909, 1624, 1586, 1502, 1447, 1374, 1301, 1166, 1140, 971, 799, 720 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 8.75 \text{ (m, 1H, pyr-H)}, 8.37 \text{ (m, 1H, pyr-H)}, 7.93 \text{ (m, 1H, pyr-H)}, 7.47 \text{ (m, 1H, pyr-H)}, 5.15 \text{ (t, 2H, } J = 6.8 \text{ Hz, CH}_2\text{N)}, 3.47 \text{ (t, 2H, } J = 6.4 \text{ Hz, CH}_2\text{Br)}, 2.57 \text{ (m, 2H, CH}_2\text{)} \text{ ppm. } ^{13}\text{C NMR (CDCl}_3\): \(\delta = 151.8 \text{ (CN}_4\), 149.5, 144.7, 137.5, 125.4, 124.5, 48.2 \text{ (CH}_2\text{N)}, 34.8 \text{ (CH}_2\text{Br)}, 31.1 \text{ ppm. ESI-HRMS: calcd for C}_9\text{H}_{11}\text{N}_5\text{Br [M+1]}^+ 268.0192, \text{ found 268.0188.}

**L3A:** Waxy orange solid (1.38 g, 38 %). m.p. 158-160 °C. \(\text{C}_9\text{H}_{11}\text{N}_5\text{Br}\): calcd. C 40.32, H 3.76, N 26.12; found C 39.98, H 3.71, N 25.88. IR (KBr): \(\nu = 2980, 2931, 1623, 1589, 1533, 1469, 1432, 1357, 1283, 1119, 1042, 993, 799, 740 \text{ cm}^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 8.78 \text{ (m, 1H, pyr-H)}, 8.26 \text{ (m, 1H, pyr-H)}, 7.87 \text{ (m, 1H, pyr-H)}, 7.41 \text{ (m, 1H, pyr-H)}, 4.91 \text{ (t, 2H, } J = 6.7 \text{ Hz, CH}_2\text{N)}, 3.46 \text{ (t, 2H, } J = 6.2 \text{ Hz, CH}_2\text{Br)}, 2.65 \text{ (m, 2H, CH}_2\text{)} \text{ ppm. } ^{13}\text{C NMR (CDCl}_3\): \(\delta = 164.9 \text{ (CN}_4\), 150.3, 146.6, 137.4, 124.9, 122.4, 51.5 \text{ (CH}_2\text{N)}, 31.8 \text{ (CH}_2\text{Br)}, 28.7 \text{ ppm. ESI-HRMS: calcd for C}_9\text{H}_{11}\text{N}_5\text{Br [M+1]}^+ 268.0192, \text{ found 268.0196.}
**L2B:** Waxy brown solid (0.86 g, 23 %). m.p. 41-45 °C. C_{10}H_{12}N_{5}Br: calcd. C 42.57, H 4.29, N 24.82; found C 42.51, H 4.30, N 24.77. IR (KBr): ν = 2958, 2865, 1590, 1530, 1471, 1432, 1403, 1330, 1277, 1122, 1092, 993, 796, 742 cm\(^{-1}\).\(^{1}\)H NMR (CDCl\(_3\)): δ = 8.74 (m, 1H, pyr-H), 8.37 (m, 1H, pyr-H), 7.93 (m, 1H, pyr-H), 7.47 (m, 1H, pyr-H), 5.04 (t, 2H, J = 7.0 Hz, CH\(_2\)N), 3.44 (t, 2H, J = 6.2 Hz, CH\(_2\)Br), 2.15 (m, 2H, CH\(_2\)), 1.94 (m, 2H, CH\(_2\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): δ = 151.7 (CN\(_4\)), 149.5, 144.9, 137.5, 125.3, 124.6, 48.6 (CH\(_2\)N), 32.5 (CH\(_2\)Br), 30.9, 29.2 ppm. ESI-HRMS: calcd for C\(_{10}\)H\(_{13}\)N\(_5\)Br [M+1]\(^{+}\) 282.0349, found 282.0352.

**L3B:** Waxy brown solid (0.62 g, 16 %). m.p. 34-36 °C. C_{10}H_{12}N_{5}Br: calcd. C 42.57, H 4.29, N 24.82; found C 42.51, H 4.42, N 25.01. IR (KBr): υ = 2942, 2866, 1624, 1586, 1456, 1434, 1350, 1292, 1164, 1050, 1010, 792, 750 cm\(^{-1}\).\(^{1}\)H NMR (CDCl\(_3\)): δ = 8.78 (m, 1H, pyr-H), 8.25 (m, 1H, pyr-H), 7.87 (m, 1H, pyr-H), 7.40 (m, 1H, pyr-H), 4.77 (t, 2H, J = 6.8 Hz, CH\(_2\)N), 3.44 (t, 2H, J = 6.4 Hz, CH\(_2\)Br), 2.29 (m, 2H, CH\(_2\)), 1.95 (m, 2H, CH\(_2\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): δ = 164.9 (CN\(_4\)), 150.3, 146.8, 137.1, 124.8, 122.4, 52.4 (CH\(_2\)N), 32.1 (CH\(_2\)Br), 29.2, 27.8 ppm. ESI-HRMS: calcd for C\(_{10}\)H\(_{13}\)N\(_5\)Br [M+1]\(^{+}\) 282.0349, found 282.0350.

**L2D:** Waxy orange solid (0.77 g, 17 %). m.p. 41-44 °C. C\(_{14}\)H\(_{20}\)N\(_5\)Br: calcd. C 49.71, H 5.96, N 20.70; found C 49.72, H 5.85, N 20.37. IR (KBr): ν = 2937, 2860, 1613, 1593, 1467, 1433, 1417, 1354, 1150, 1091, 1043, 991, 803, 747 cm\(^{-1}\).\(^{1}\)H NMR (CDCl\(_3\)): δ = 8.73 (m, 1H, pyr-H), 8.25 (m, 1H, pyr-H), 7.90 (m, 1H, pyr-H), 7.45 (m, 1H, pyr-H), 4.98 (t, 2H, J = 7.2 Hz, CH\(_2\)N), 3.39 (t, 2H, J = 6.9 Hz, CH\(_2\)Br), 1.96 (m, 2H, CH\(_2\)), 1.80 (m, 2H, CH\(_2\)), 1.30 (m, 8H, CH\(_2\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): δ = 151.5 (CN\(_4\)), 149.4, 145.1 137.4, 125.2, 124.6, 49.5 (CH\(_2\)N), 33.9 (CH\(_2\)Br), 32.9, 29.8, 28.7, 28.4, 27.9, 26.1 ppm. ESI-HRMS: calcd for C\(_{14}\)H\(_{21}\)N\(_5\)Br [M+1]\(^{+}\) 338.0975, found 338.0990.

**L3D:** Waxy orange solid (0.86 g, 19 %). m.p. 41-50 °C. C\(_{14}\)H\(_{20}\)N\(_5\)Br: calcd. C 49.71, H 5.96, N 20.70; found C 49.60, H 5.48, N 19.67. IR (KBr): ν = 2931, 2852, 1620, 1593, 1466, 1435, 1416, 1351, 1149, 1092, 1042, 989, 803, 746 cm\(^{-1}\).\(^{1}\)H NMR (CDCl\(_3\)): δ = 8.79 (m, 1H, pyr-H), 8.25 (m, 1H, pyr-H), 7.87 (m, 1H, pyr-H), 7.40 (m, 1H, pyr-H), 4.70 (t, 2H, J = 7.1 Hz, CH\(_2\)N), 3.39 (t, 2H, J = 6.8 Hz, CH\(_2\)Br), 2.08 (m, 2H, CH\(_2\)), 1.83 (m, 2H, CH\(_2\)), 1.36 (m, 8H, CH\(_2\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): δ = 164.7 (CN\(_4\)), 150.3, 146.9, 137.1, 124.7, 122.3, 53.4
(CH₂N), 33.8 (CH₂Br), 32.6, 29.2, 28.6, 28.4, 27.9, 26.2 ppm. ESI-HRMS: calcd for C₁₄H₂₁N₅BrK [M+K]⁺ 376.0534, found 376.0545.

**General synthesis of 2-(alkyl-(1-tetrazol-5-yl)pyridine (L4) and 2-(alkyl-(2-tetrazol-5-yl)pyridine (L5)**

To L1 (2.00 g, 13.6 mmol) dissolved in acetonitrile (60 mL) was added potassium carbonate (18.8 g, 136 mmol). The resulting solution was refluxed for 30 minutes and to the hot solution was added Br(CH₂)nCH₃ (48.0 mmol, n = 3, 5 or 7). The reaction mixture was then stirred at reflux temperature for a further 24 h. After cooling, the inorganic solids were removed by filtration and the solvent was removed under reduced pressure to afford an oil, which was purified by column chromatography on silica gel (initially at a ratio of petroleum ether : ethyl acetate 80:20, followed by the ratio of 60:40). This gave the products L4A-C and L5A-C.

2-(1-butyl-1H-tetrazol-5-yl)pyridine (L4A):

Brown oil (0.85 g, 31 %). IR (neat): ν = 2961, 2934, 2874, 1591, 1571, 1532, 1471, 1433, 1409, 1380, 1287, 1121, 1085, 1037, 994, 798, 744 cm⁻¹. ¹H NMR (CDCl₃): δ = 8.73 (m, 1 H, pyr-H), 8.36 (m, 1 H, pyr-H), 7.91 (m, 1 H, pyr-H), 7.45 (m, 1 H, pyr-H), 4.99 (t, 2 H, J = 7.3 Hz, CH₂N), 1.94 (m, 2 H, CH₂), 1.39 (m, 2 H, CH₂), 0.95 (t, 3 H, J = 7.3 Hz, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 151.7 (CN₄), 149.4, 145.1, 137.4, 125.2, 124.6, 49.4 (CH₂N), 31.9, 19.5, 13.4 ppm. ESI-HRMS: calcd for C₁₀H₁₃N₅Na [M+Na]⁺ 226.1069, found 226.1063.

2-(2-butyl-2H-tetrazol-5-yl)pyridine (L5A):

Yellow oil (0.61 g, 22 %). IR (neat): ν = 2961, 2935, 2874, 1594, 1571, 1466, 1432, 1419, 1387, 1356, 1156, 1043, 804, 747 cm⁻¹. ¹H NMR (CDCl₃): δ = 8.79 (m, 1 H, pyr-H), 8.25 (m, 1 H, pyr-H), 7.86 (m, 1 H, pyr-H), 7.39 (m, 1 H, pyr-H), 4.71 (t, 2 H, J = 7.1 Hz, CH₂N), 2.07 (m, 2 H, CH₂), 1.41 (m, 2 H, CH₂), 0.97 (t, 3 H, J = 7.3 Hz, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 164.7 (CN₄), 150.3, 146.9, 137.0, 124.7, 122.3, 53.2 (CH₂N), 31.3, 19.6, 13.3 ppm. ESI-HRMS: calcd for C₁₀H₁₄N₅ [M+1]⁺ 204.1244, found 204.1248.

2-(1-hexyl-1H-tetrazol-5-yl)pyridine (L4B):
Brown oil (0.43 g, 14 %). IR (neat): \( \nu = 2987, 2929, 2858, 2305, 1592, 1434, 1421, 1256, 896, 744, 705 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): \( \delta = 8.72 (\text{m}, 1 \text{ H, pyr-H}), 8.36 (\text{m}, 1 \text{ H, pyr-H}), 7.90 (\text{m}, 1 \text{ H, pyr-H}), 7.44 (\text{m}, 1 \text{ H, pyr-H}), 4.97 (\text{t}, 2 \text{ H, } J = 7.3 \text{ Hz, CH}_2\text{N}), 1.95 (\text{m}, 2 \text{ H, CH}_2), 1.30 (\text{m}, 6 \text{ H, CH}_2), 0.87 (\text{t}, 3 \text{ H, } J = 7.1 \text{ Hz, CH}_3) \text{ ppm.} \) \(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 151.6 (\text{CN}_4), 149.4, 145.1, 137.4, 125.2, 124.5, 49.6 (\text{CH}_2\text{N}), 31.1, 29.8, 25.9, 22.3, 13.9 \text{ ppm.} \) ESI-HRMS: calcd for C\(_{12}\)H\(_{18}\)N\(_5\) [M+1]\(^+\) 232.1557, found 232.1557.

2-(2-hexyl-2\text{H}-tetrazol-5-yl)pyridine (L\text{SB}):

Yellow oil (0.54 g, 17 %). IR (neat): \( \nu = 2957, 2929, 2858, 2305, 1595, 1466, 1434, 1420, 1265, 802, 738, 704 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): \( \delta = 8.79 (\text{m}, 1 \text{ H, pyr-H}), 8.26 (\text{m}, 1 \text{ H, pyr-H}), 7.86 (\text{m}, 1 \text{ H, pyr-H}), 7.40 (\text{m}, 1 \text{ H, pyr-H}), 4.70 (\text{t}, 2 \text{ H, } J = 7.2 \text{ Hz, CH}_2\text{N}), 2.12 (\text{m}, 2 \text{ H, CH}_2), 1.29 (\text{m}, 6 \text{ H, CH}_2), 0.88 (\text{t}, 3 \text{ H, } J = 7.1 \text{ Hz, CH}_3) \text{ ppm.} \) \(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 164.7 (\text{CN}_4), 150.3, 146.9, 137.0, 124.7, 122.3, 53.5 (\text{CH}_2\text{N}), 31.0, 29.3, 26.0, 22.3, 13.9 \text{ ppm.} \) ESI-HRMS: calcd for C\(_{12}\)H\(_{18}\)N\(_5\) [M+1]\(^+\) 232.1557, found 232.1568.

2-(1-octyl-1\text{H}-tetrazol-5-yl)pyridine (L\text{4C}):

Brown oil (0.82 g, 23 %). IR (neat): \( \nu = 2956, 2927, 2856, 1591, 1467, 1433, 1377, 1120, 1036, 797, 743, 730 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): \( \delta = 8.73 (\text{m}, 1 \text{ H, pyr-H}), 8.36 (\text{m}, 1 \text{ H, pyr-H}), 7.90 (\text{m}, 1 \text{ H, pyr-H}), 7.45 (\text{m}, 1 \text{ H, pyr-H}), 4.97 (\text{t}, 2 \text{ H, } J = 7.3 \text{ Hz, CH}_2\text{N}), 1.92 (\text{m}, 2 \text{ H, CH}_2), 1.27 (\text{m}, 10 \text{ H, CH}_2), 0.86 (\text{t}, 3 \text{ H, } J = 6.9 \text{ Hz, CH}_3) \text{ ppm.} \) \(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 151.6 (\text{CN}_4), 149.4, 145.1, 137.3, 125.2, 124.5, 49.6 (\text{CH}_2\text{N}), 31.7, 29.8, 29.1, 28.9, 26.2, 22.5, 14.0 \text{ ppm.} \) ESI-HRMS: calcd for C\(_{14}\)H\(_{22}\)N\(_5\) [M+1]\(^+\) 260.1870, found 260.1881.

2-(2-octyl-2\text{H}-tetrazol-5-yl)pyridine (L\text{5C}):

Yellow oil (0.76 g, 22 %). IR (neat): \( \nu = 2985, 2927, 2856, 1593, 1571, 1522, 1466, 1432, 1419, 1386, 1356, 1158, 1043, 803, 746, 726 \text{ cm}^{-1} \). \(^1\)H NMR (CDCl\(_3\)): \( \delta = 8.78 (\text{m}, 1 \text{ H, pyr-H}), 8.25 (\text{m}, 1 \text{ H, pyr-H}), 7.86 (\text{m}, 1 \text{ H, pyr-H}), 7.39 (\text{m}, 1 \text{ H, pyr-H}), 4.70 (\text{t}, 2 \text{ H, } J = 7.1 \text{ Hz, CH}_2\text{N}), 2.10 (\text{m}, 2 \text{ H, CH}_2), 1.28 (\text{m}, 10 \text{ H, CH}_2), 0.86 (\text{t}, 3 \text{ H, } J = 6.9 \text{ Hz, CH}_3) \text{ ppm.} \) \(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 164.7 (\text{CN}_4), 150.3, 146.9, 137.0, 124.7, 122.3, 53.5 (\text{CH}_2\text{N}), 31.6, 29.3,
28.9, 28.8 26.2, 22.5, 14.0 ppm. ESI-HRMS: calcd for C_{14}H_{22}N_{5} [M+1]^+ 260.1870, found 260.1879.

General coordination reactions

The appropriate tetrazole ligand, **L2A-D, L3A-D, L4A-C** or **L5A-C** (0.20 g) was dissolved in methanol (30 mL) and was added to a solution of the appropriate metal chloride salt (one equivalent) in methanol (25 mL). The resulting strongly-coloured solution was then heated to reflux temperature for 2 h before being allowed to stand at room temperature for several days.

[Zn(L2A)Cl]_2

Waxy cream solid (0.17 g, 56 %). C_{18}H_{20}Br_{2}Cl_{4}Zn_{2}N_{10}: calcd. C 26.73, H 2.49, N 17.32; found C 26.72, H 2.53, N 16.96. IR (KBr): \( \nu = 2945, 2823, 1610, 1565, 1453, 1058, 1015, 770 \) cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \( \delta = 8.78 \) (m, 1H, pyr-H), 8.35 (m, 1H, pyr-H), 7.95 (m, 1H, pyr-H), 7.45 (m, 1H, pyr-H), 5.18 (t, 2H, \( J = 7.0 \) Hz, CH\(_2\)N), 3.49 (t, 2H, \( J = 6.2 \) Hz, CH\(_2\)Br), 2.18 (m, 2H, CH\(_2\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 157.1 \) (CN\(_4\)), 149.5, 148.2, 138.6, 125.7, 124.9, 49.1 (CH\(_2\)N), 33.2 (CH\(_2\)Br), 29.4 ppm.

[Cu(L2A)Cl]_2

Green solid (0.12 g, 40 %). C_{18}H_{20}Br_{2}Cl_{4}Cu_{2}N_{10}: calcd. C 26.85, H 2.50, N 17.40; found C 27.13, H 2.56, N 17.76. IR (KBr): \( \nu = 2855, 1616, 1484, 1455, 1261, 1167, 1109, 1012, 794, 745, 718 \) cm\(^{-1}\). \( \lambda_{\max} \) (MeOH) 856 nm, \( \varepsilon = 59 \) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 2.1 B.M.

[Ni(L2A)Cl]_2

Dark green solid (0.12 g, 41 %). C_{18}H_{20}Br_{2}Cl_{4}Ni_{2}N_{10}: calcd. C 27.18, H 2.53, N 17.61; found C 26.41, H 3.06, N 16.97. IR (KBr): \( \nu = 2923, 2850, 1614, 1481, 1455, 1297, 1251, 1165, 1112, 1013, 793, 725 \) cm\(^{-1}\). \( \lambda_{\max} \) (MeOH) 348 nm, \( \varepsilon = 86 \) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 3.2 B.M.

[Zn(L3A)Cl]_2
Waxy orange solid (0.12 g, 40 %). C_{18}H_{20}Br_{2}Cl_{4}Zn_{2}N_{10}: calcd. C 26.73, H 2.49, N 17.32; found C 26.32, H 2.67, N 16.60. IR (KBr): ν = 2958, 2848, 1614, 1573, 1546, 1451, 1288, 1063, 1027, 800, 730 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): δ = 8.88 (m, 1H, pyr-H), 8.31 (m, 1H, pyr-H), 8.16 (m, 1H, pyr-H), 7.60 (m, 1H, pyr-H), 5.01 (t, 2H, J = 6.8 Hz, CH\(_2\)N), 3.51 (t, 2H, J = 6.0 Hz, CH\(_2\)Br), 2.71 (m, 2H, CH\(_2\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): δ = 161.8 (CN\(_4\)), 149.8, 141.1, 128.2, 123.0, 52.3 (CH\(_2\)N), 40.7 (CH\(_2\)Br), 31.4 ppm.

[Cu(L3A)Cl\(_2\)]

Green solid (0.17 g, 57 %). C_{18}H_{20}Br_{2}Cl_{4}Cu_{2}N_{10}: calcd. C 26.85, H 2.50, N 17.40; found C 27.66, H 2.47, N 18.34. IR (KBr): ν = 2860, 1619, 1552, 1450, 1267, 1228, 1064, 1021, 804, 761, 724 cm\(^{-1}\). \(λ_{\text{max}}\) (MeOH) 800 nm, ε = 36 M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 2.2 B.M.

[Ni(L3A)Cl\(_2\)]

Pale green solid (0.14 g, 48 %). C_{18}H_{20}Br_{2}Cl_{4}Ni_{2}N_{10}: calcd. C 27.18, H 2.53, N 17.61; found C 27.64, H 3.06, N 17.69. IR (KBr): ν = 2955, 2853, 1614, 1549, 1452, 1288, 1104, 1026, 806, 762 cm\(^{-1}\). \(λ_{\text{max}}\) (MeOH) 384 nm, ε = 53 M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 3.2 B.M.

[Zn(L2B)Cl\(_2\)]

Waxy orange solid (0.17 g, 59 %). C_{20}H_{24}Br_{2}Cl_{4}Zn_{2}N_{10}: calcd. C 28.70, H 2.89, N 16.74; found C 28.34, H 2.25, N 16.68. IR (KBr): ν = 2949, 2870, 1610, 1481, 1458, 1441, 1252, 1168, 1010, 794, 748, 724 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): δ = 8.78 (m, 1H, pyr-H), 8.36 (m, 1H, pyr-H), 7.96 (m, 1H, pyr-H), 7.50 (m, 1H, pyr-H), 5.02 (t, 2H, J = 7.0 Hz, CH\(_2\)N), 3.57 (t, 2H, J = 6.4 Hz, CH\(_2\)Br), 2.18 (m, 2H, CH\(_2\)), 1.97 (m, 2H, CH\(_2\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): δ = 159.1 (CN\(_4\)), 149.5, 147.1, 137.6, 125.4, 124.6, 48.8 (CH\(_2\)N), 32.5 (CH\(_2\)Br), 29.2, 29.1 ppm.

[Cu(L2B)Cl\(_2\)]

Green solid (0.19 g, 65 %). C_{20}H_{24}Br_{2}Cl_{4}Cu_{2}N_{10}: calcd. C 28.83, H 2.90, N 16.81; found C 28.21, H 2.15, N 16.41. IR (KBr): ν = 2941, 2851, 1614, 1483, 1456, 1250, 1151, 1012, 791, 746, 718 cm\(^{-1}\). \(λ_{\text{max}}\) (MeOH) 848 nm, ε = 145 M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 2.3 B.M.
\[\text{[Ni(L2B)]Cl}_2\]

Pale green solid (0.15 g, 50 %). \(\text{C}_{20}\text{H}_{24}\text{Br}_2\text{Cl}_4\text{Ni}_2\text{N}_{10}\): calcd. C 29.17, H 2.94, N 17.01; found C 28.28, H 3.34, N 16.78. IR (KBr): \(\nu = 2961, 2866, 1613, 1481, 1457, 1252, 1108, 1015, 794, 725 \text{ cm}^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 376 nm, \(\varepsilon = 40 \text{ M}^{-1}\text{cm}^{-1}\). Magnetic moment: 2.8 B.M.

\[\text{[Zn(L3B)]Cl}_2\]

Cream solid (0.15 g, 51 %). \(\text{C}_{20}\text{H}_{24}\text{Br}_2\text{Cl}_4\text{Zn}_2\text{N}_{10}\): calcd. C 28.70, H 2.89, N 16.74; found C 28.37, H 2.92, N 16.20. IR (KBr): \(\nu = 2957, 2870, 1614, 1572, 1548, 1452, 1395, 1285, 1064, 1028, 800, 753, 729 \text{ cm}^{-1}\). \(^1\text{H NMR (CDCl}_3\): \(\delta = 8.96 \text{ (m, 1H, pyr-H)}, 8.29 \text{ (m, 1H, pyr-H)}, 7.82 \text{ (m, 1H, pyr-H)}, 4.88 \text{ (t, 2H, } J = 7.0 \text{ Hz, CH}_2\text{N)}, 3.47 \text{ (t, 2H, } J = 6.2 \text{ Hz, CH}_2\text{Br)}\), 2.33 (m, 2H, CH2), 2.00 (m, 2H, CH2) ppm. \(^{13}\text{C NMR (CDCl}_3\): \(\delta = 161.7 \text{ (CN}_4\), 149.7, 141.7, 141.3, 128.3, 122.9, 54.6 \text{ (CH}_2\text{N)}, 43.7 \text{ (CH}_2\text{Br)}, 32.1, 29.0 \text{ ppm.}\)

\[\text{[Cu(L3B)]Cl}_2\]

Green solid (0.16 g, 55 %). \(\text{C}_{20}\text{H}_{24}\text{Br}_2\text{Cl}_4\text{Cu}_2\text{N}_{10}\): calcd. C 28.83, H 2.90, N 16.81; found C 29.57, H 2.91, N 17.57. IR (KBr): \(\nu = 2951, 2849, 1617, 1552, 1451, 1259, 1156, 1101, 1062, 1023, 797, 757, 724 \text{ cm}^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 832 nm, \(\varepsilon = 145 \text{ M}^{-1}\text{cm}^{-1}\). Magnetic moment: 2.1 B.M.

\[\text{[Ni(L3B)]Cl}_2\]

Pale green solid (0.14 g, 47 %). \(\text{C}_{20}\text{H}_{24}\text{Br}_2\text{Cl}_4\text{Ni}_2\text{N}_{10}\): calcd. C 29.17, H 2.94, N 17.01; found C 28.49, H 3.51, N 16.24. IR (KBr): \(\nu = 2951, 2862, 1613, 1545, 1451, 1391, 1259, 1154, 1103, 1025, 805, 763 \text{ cm}^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 380 nm, \(\varepsilon = 37 \text{ M}^{-1}\text{cm}^{-1}\). Magnetic moment: 3.6 B.M.

\[\text{[Zn(L2C)]Cl}_2\]

Waxy cream solid (0.17 g, 60 %). \(\text{C}_{24}\text{H}_{32}\text{Br}_2\text{Cl}_4\text{Zn}_2\text{N}_{10}\): calcd. C 32.28, H 3.61, N 15.69; found C 33.01, H 4.00, N 15.12. IR (KBr): \(\nu = 2931, 2857, 1610, 1543, 1482, 1459, 1249, 1108, 1010, 793, 724 \text{ cm}^{-1}\). \(^1\text{H NMR (CDCl}_3\): \(\delta = 8.92 \text{ (m, 1H, pyr-H)}, 8.29 \text{ (m, 1H, pyr-H)},\)
8.06 (m, 1H, pyr-H), 7.61 (m, 1H, pyr-H), 4.92 (t, 2H, J = 7.2 Hz, CH₂N), 3.42 (t, 2H, J = 6.7 Hz, CH₂Br), 2.02 (m, 2H, CH₂), 1.90 (m, 2H, CH₂), 1.48 (m, 4H, CH₂) ppm. 

13C NMR (CDCl₃): δ = 151.5 (CN₄), 150.0, 143.3, 138.5, 126.3, 124.6, 62.8 (CH₂N), 49.7 (CH₂Br), 33.6, 32.3, 29.3, 27.9 ppm.

[Ni(L2C)Cl₂]₂

Pale green solid (0.12 g, 42 %). C₂₄H₃₂Br₂Cl₄Ni₂N₁₀: calcd. C 32.77, H 3.67, N 15.92; found C 32.65, H 3.74, N 15.88. IR (KBr): ν = 2934, 2853, 1608, 1478, 1457, 1252, 1051, 1012, 799, 726 cm⁻¹. λₘₐₓ (MeOH) 376 nm, ε = 48 M⁻¹cm⁻¹. Magnetic moment: 3.9 B.M.

[Zn(L3C)Cl₂]₂

Waxy cream solid (0.14 g, 49 %). C₂₄H₃₂Br₂Cl₄Zn₂N₁₀: calcd. C 32.28, H 3.61, N 15.69; found C 32.45, H 3.68, N 15.34. IR (KBr): ν = 2939, 2862, 1614, 1573, 1451, 1287, 1262, 1063, 1048, 801, 731 cm⁻¹. ¹H NMR (CDCl₃): δ = 8.86 (m, 1H, pyr-H), 8.28 (m, 1H, pyr-H), 8.19 (m, 1H, pyr-H), 7.76 (m, 1H, pyr-H), 4.81 (t, 2H, J = 7.1 Hz, CH₂N), 3.41 (t, 2H, J = 6.5 Hz, CH₂Br), 2.16 (m, 2H, CH₂), 1.89 (m, 2H, CH₂), 1.53 (m, 4H, CH₂) ppm. ¹³C NMR (CDCl₃): δ = 162.5 (CN₄), 149.9, 143.2, 140.1, 127.2, 122.7, 54.8 (CH₂N), 44.8 (CH₂Br), 32.1, 29.2, 25.5, 25.4 ppm.

[Ni(L3C)Cl₂]₂

Pale green solid (0.10 g, 35 %). C₂₄H₃₂Br₂Cl₄Ni₂N₁₀: calcd. C 32.77, H 3.67, N 15.92; found C 31.12, H 4.16, N 15.52. IR (KBr): ν = 2935, 2823, 1615, 1451, 1261, 1063, 1027, 801, 756, 731 cm⁻¹. λₘₐₓ (MeOH) 376 nm, ε = 92 M⁻¹cm⁻¹. Magnetic moment: 4.1 B.M.

[Zn(L2D)Cl₂]₂

Orange oil (0.14 g, 50 %). C₂₈H₄₀Br₂Cl₄Zn₂N₁₀•2H₂O: calcd. C 34.14, H 4.50, N 14.22; found C 34.11, H 5.08, N 13.53. IR (film): ν = 2932, 2856, 1654, 1589, 1465, 1390, 1253, 1119, 798, 744 cm⁻¹. ¹H NMR (CDCl₃): δ = 8.76 (m, 1H, pyr-H), 8.32 (m, 1H, pyr-H), 7.97 (m, 1H, pyr-H), 7.49 (m, 1H, pyr-H), 4.96 (t, 2H, J = 7.3 Hz, CH₂N), 3.38 (t, 2H, J = 6.2 Hz,
CH$_2$Br), 1.94 (m, 2H, CH$_2$), 1.80 (m, 2H, CH$_2$), 1.32 (m, 8H, CH$_2$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ = 151.7 (CN$_4$), 149.6, 144.1, 137.9, 125.7, 124.6, 49.7 (CH$_2$N), 37.5 (CH$_2$Br), 32.7, 29.6, 28.8, 28.5, 27.9, 26.6 ppm.

$[\text{Cu(L2D)}\text{Cl}_2]_2$

Green solid (0.21 g, 75%). C$_{28}$H$_{40}$Br$_2$Cl$_4$Cu$_2$N$_{10}$: calcd. C 35.57, H 4.26, N 14.82; found C 36.17, H 4.57, N 15.79. IR (KBr): $\nu$ = 2932, 2855, 1611, 1481, 1451, 1411, 1289, 1229, 1162, 1008, 788 cm$^{-1}$. $\lambda_{\text{max}}$ (MeOH) 840 nm, $\varepsilon$ = 126 M$^{-1}$cm$^{-1}$. Magnetic moment: 2.3 B.M.

$[\text{Ni(L2D)}\text{Cl}_2]_2$

Pale green solid (0.19 g, 70%). C$_{28}$H$_{40}$Br$_2$Cl$_4$Ni$_2$N$_{10}$: calcd. C 35.94, H 4.31, N 14.97; found C 35.82, H 4.39, N 14.81. IR (KBr): $\nu$ = 2929, 2856, 1606, 1478, 1459, 1436, 1255, 1105, 1014, 802, 725 cm$^{-1}$. $\lambda_{\text{max}}$ (MeOH) 376 nm, $\varepsilon$ = 46 M$^{-1}$cm$^{-1}$. Magnetic moment: 3.9 B.M.

$[\text{Zn(L3D)}\text{Cl}_2]_2$

Cream solid (0.15 g, 53 %). C$_{28}$H$_{40}$Br$_2$Cl$_4$Zn$_2$N$_{10}$: calcd. C 35.43, H 4.25, N 14.76; found C 34.91, H 4.22, N 14.21. IR (KBr): $\nu$ = 2926, 2855, 1613, 1572, 1546, 1453, 1395, 1260, 1063, 1027, 804, 756, 731 cm$^{-1}$. $^1$H NMR (CDCl$_3$): $\delta$ = 8.89 (m, 1H, pyr-H), 8.31 (m, 1H, pyr-H), 8.22 (m, 1H, pyr-H), 7.81 (m, 1H, pyr-H), 4.81 (t, 2H, $J$ = 7.1 Hz, CH$_2$N), 3.40 (t, 2H, $J$ = 6.7 Hz, CH$_2$Br), 2.14 (m, 2H, CH$_2$), 1.85 (m, 2H, CH$_2$), 1.41 (m, 8H, CH$_2$) ppm. $^{13}$C NMR (CDCl$_3$): $\delta$ = 161.7 (CN$_4$), 149.8, 142.0, 141.2, 128.1, 122.9, 55.2 (CH$_2$N), 45.1 (CH$_2$Br), 34.0, 32.4, 28.9, 27.9, 26.6, 26.1 ppm.

$[\text{Cu(L3D)}\text{Cl}_2]_2$

Green solid (0.20 g, 71 %). C$_{28}$H$_{40}$Br$_2$Cl$_4$Cu$_2$N$_{10}$: calcd. C 35.57, H 4.26, N 14.82; found C 36.17, H 4.42, N 15.19. IR (KBr): $\nu$ = 2927, 2851, 1621, 1548, 1449, 1283, 1267, 1227, 1010, 796, 757 cm$^{-1}$. $\lambda_{\text{max}}$ (MeOH) 808 nm, $\varepsilon$ = 105 M$^{-1}$cm$^{-1}$. Magnetic moment: 2.4 B.M.

$[\text{Ni(L3D)}\text{Cl}_2]_2$
Pale green solid (0.15 g, 55 %). \( \text{C}_{28}\text{H}_{40}\text{Br}_{2}\text{Cl}_{4}\text{Ni}_{2}\text{N}_{10} \): calcd. C 35.94, H 4.31, N 14.97; found C 36.26, H 4.90, N 14.28. IR (KBr): \( \nu = 2930, 2857, 1614, 1452, 1259, 1156, 1025, 807, 732 \) cm\(^{-1}\). \( \lambda_{\text{max}} \) (MeOH) 384 nm, \( \varepsilon = 194 \text{ M}^{-1}\text{cm}^{-1} \). Magnetic moment: 3.5 B.M.

\[\text{[Zn(L4A)Cl]_2} \]

Orange solid (0.21 g, 72%). \( \text{C}_{20}\text{H}_{26}\text{Cl}_{4}\text{Zn}_{2}\text{N}_{10} \cdot \text{H}_{2}\text{O}: \) calcd. C 34.44, H 4.05, N 20.09; found C 34.13, H 4.30, N 19.49. IR (KBr): \( \nu = 2961, 2873, 1609, 1535, 1482, 1459, 1445, 1379, 1301, 1252, 1168, 1110, 1049, 1012, 800, 753, 725 \) cm\(^{-1}\). \( ^1\text{H NMR (CDCl}_3): \delta = 9.00 \) (m, 1 H, pyr-H), 8.21 (m, 1 H, pyr-H), 8.12 (m, 1 H, pyr-H), 7.69 (m, 1 H, pyr-H), 4.86 (t, 2 H, \( J = 7.3 \) Hz, CH\(_2\)N), 1.98 (m, 2 H, CH\(_2\)), 1.45 (m, 2 H, CH\(_2\)), 0.99 (t, 3 H, \( J = 7.3 \) Hz, CH\(_3\)) ppm. \( ^{13}\text{C NMR (CDCl}_3): \delta = 150.0 \) (CN\(_4\)), 149.1, 145.1, 138.0, 125.8, 124.4, 49.5 (CH\(_2\)N), 31.7, 19.6, 13.4 ppm.

\[\text{[Cu(L4A)Cl]_2} \]

Green solid (0.17 g, 51 %). \( \text{C}_{20}\text{H}_{26}\text{Cl}_{4}\text{Cu}_{2}\text{N}_{10} \): calcd. C 35.57, H 3.88, N 20.74; found C 35.39, H 3.92, N 20.27. IR (KBr): \( \nu = 2961, 2873, 1609, 1546, 1482, 1457, 1437, 1378, 1251, 1166, 1049, 1003, 719 \) cm\(^{-1}\). \( \lambda_{\text{max}} \) (MeOH) 836 nm, \( \varepsilon = 110 \text{ M}^{-1}\text{cm}^{-1} \). Magnetic moment: 2.1 B.M.

\[\text{[Ni(L4A)Cl]_2} \]

Green solid (0.29 g, 80 %). \( \text{C}_{20}\text{H}_{26}\text{Cl}_{4}\text{Ni}_{2}\text{N}_{10} \cdot 4\text{H}_{2}\text{O}: \) calcd. C 32.54, H 4.65, N 18.99; found C 32.97, H 4.76, N 19.01. IR (KBr): \( \nu = 2960, 2934, 2873, 1615, 1451, 1393, 1287, 1224, 1100, 1063, 1027, 802, 758, 732 \) cm\(^{-1}\). \( \lambda_{\text{max}} \) (MeOH) 392 nm, \( \varepsilon = 25 \text{ M}^{-1}\text{cm}^{-1} \). Magnetic moment: 3.2 B.M.

\[\text{Co(L4A)}_2\text{(NCS)}_2 \]

Green crystalline solid (0.15 g, 53 %). \( \text{C}_{22}\text{H}_{26}\text{CoN}_{12}\text{S}_{2} \): calcd. C 45.43, H 4.51, N 28.90; found C 46.15, H 3.74, N 28.43. IR (KBr): \( \nu = 2960, 2876, 2068, 1609, 1478, 1456, 1291, \)
1251, 1160, 1045, 1007, 792, 746 cm\(^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 520 nm, \(\varepsilon = 40\) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 5.4 B.M.

\([\text{Zn(L5A)Cl}_2]\)  

White solid (0.19 g, 66 %). \(\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{Zn}_2\text{N}_{10}\): calcd. C 35.37, H 3.86, N 20.63; found C 34.88, H 3.97, N 20.15. IR (KBr): \(\nu = 2963, 2875, 1614, 1573, 1547, 1453, 1394, 1288, 1259, 1063, 1046, 1028, 804, 757\) cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 8.94 \text{ (m, 1 H, pyr-H), 8.28 \text{ (m, 1 H, pyr-H), 8.09 \text{ (m, 1 H, pyr-H), 7.67 \text{ (m, 1 H, pyr-H), 4.75 \text{ (t, 2 H, \(J = 7.2\) Hz, CH}_2\text{N), 2.08 \text{ (m, 2 H, CH}_2\), 1.42 \text{ (m, 2 H, CH}_2\), 0.98 \text{ (t, 3 H, \(J = 7.3\) Hz, CH}_3\) ppm.} \)

\([\text{Cu(L5A)Cl}_2]\)  

Green solid (0.12 g, 36 %). \(\text{C}_{20}\text{H}_{26}\text{Cl}_4\text{Cu}_2\text{N}_{10}\): calcd. C 35.57, H 3.88, N 20.74; found C 35.63, H 4.05, N 20.45. IR (KBr): \(\nu = 2961, 2880, 1619, 1609, 1552, 1461, 1449, 1352, 1269, 1100, 1026, 799, 758, 724\) cm\(^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 808 nm, \(\varepsilon = 115\) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 2.0 B.M.

\([\text{Ni(L5A)Cl}_2]\)  

Pale green solid (0.20 g, 56 %). \(\text{C}_{20}\text{H}_{26}\text{Cl}_4\text{Ni}_2\text{N}_8\text{H}_2\text{O}\): calcd. C 32.54, H 4.65, N 18.99; found C 32.71, H 4.69, N 18.87. IR (KBr): \(\nu = 2961, 2934, 2873, 1611, 1479, 1457, 1294, 1254, 1162, 1050, 1010, 795, 752, 727\) cm\(^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 392 nm, \(\varepsilon = 19\) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 2.9 B.M.

\([\text{Co(L5A)_2(NCS)_2}\)  

Rust coloured crystals (0.19 g, 67 %). \(\text{C}_{22}\text{H}_{26}\text{CoN}_2\text{S}_2\): calcd. C 45.43, H 4.51, N 28.90; found C 46.99, H 4.30, N 29.56. IR (KBr): \(\nu = 2959, 2873, 2077, 1610, 1458, 1447, 1375, 1285, 1256, 1153, 1059, 1046, 802, 754\) cm\(^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 508 nm, \(\varepsilon = 50\) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 5.3 B.M.
[Zn(L4B)Cl2]2

Orange solid (0.30 g, 83 %). C24H34Cl4Zn2N10•3H2O: calcd. C 36.50, H 5.11, N 17.75; found C 36.77, H 5.56, N 17.30. IR (KBr): υ = 2955, 2927, 2856, 1610, 1480, 1460, 1433, 1377, 1164, 1051, 1013, 796, 747, 724 cm⁻¹. ¹H NMR (CDCl3): δ = 9.04 (m, 1 H, pyr-H), 8.26 (m, 1 H, pyr-H), 7.75 (m, 1 H, pyr-H), 4.81 (t, 2 H, J = 7.3 Hz, CH2N), 2.00 (m, 2 H, CH2), 1.33 (m, 6 H, CH2), 0.86 (t, 3 H, J = 6.9 Hz, CH3) ppm. ¹³C NMR (CDCl3): δ = 151.4 (CN4), 150.7, 140.7, 140.2, 128.0, 125.0, 50.6 (CH2N), 31.6, 29.0, 26.3, 22.5, 14.0 ppm.

[Cu(L4B)Cl2]2

Green solid (0.11 g, 35 %). C24H34Cl4Cu2N10: calcd. C 39.41, H 4.68, N 19.15; found C 39.23, H 4.75, N 18.66. IR (KBr): υ = 2955, 2927, 2872, 1611, 1541, 1482, 1455, 1382, 1112, 1050, 1008, 792, 751, 719 cm⁻¹. λmax (MeOH) 840 nm, ε = 111 M⁻¹cm⁻¹. Magnetic moment: 2.0 B.M.

[Ni(L4B)Cl2]2

Green solid (0.22 g, 71 %). C24H34Cl4Ni2N10•4H2O: calcd. C 36.31, H 5.33, N 17.64; found C 36.45, H 5.87, N 17.27. IR (KBr): υ = 2955, 2926, 2856, 1642, 1613, 1479, 1456, 1415, 1378, 1294, 1253, 1163, 1108, 1012, 796, 752 cm⁻¹. λmax (MeOH) 404 nm, ε = 31 M⁻¹cm⁻¹. Magnetic moment: 3.2 B.M.

Co(L4B)2(NCS)2

Green crystalline solid (0.18 g, 66 %). C26H34CoN12S2: calcd. C 48.97, H 5.37, N 26.36; found C 49.48, H 6.21, N 25.88. IR (KBr): υ = 2925, 2854, 2067, 1609, 1476, 1456, 1293, 1106, 1008, 793, 745, 725 cm⁻¹. λmax (MeOH) 520 nm, ε = 56 M⁻¹cm⁻¹. Magnetic moment: 5.1 B.M.

[Zn(L5B)Cl2]2
White solid (0.26 g, 72 %). C_{24}H_{34}Cl_4Zn_2N_{10} \cdot 2CH_3OH: calcd. C 39.05, H 5.30, N 17.53; found C 38.18, H 5.30, N 16.81. IR (KBr): \nu = 2925, 2855, 1653, 1613, 1573, 1547, 1454, 1395, 1286, 1260, 1161, 1102, 1063, 1046, 1027, 804, 756, 731 \text{ cm}^{-1}. ^1H NMR (CDCl_3): \delta = 9.02 (m, 1 H, pyr-H), 8.34 (m, 1 H, pyr-H), 7.92 (m, 1 H, pyr-H), 4.82 (t, 2 H, J = 7.1 Hz, CH_2N), 2.12 (m, 2 H, CH_2), 1.32 (m, 6 H, CH_2), 0.87 (t, 3 H, J = 7.1 Hz, CH_3) ppm. ^13C NMR (CDCl_3): \delta = 161.1 (CN_4), 149.7, 142.0, 141.3, 128.7, 123.0, 55.5 (CH_2N), 31.6, 28.8, 26.2, 22.5, 14.0 ppm.

[Cu(L5B)Cl_2]_2

Green solid (0.12 g, 38 %). C_{24}H_{34}Cl_4Cu_2N_{10}: calcd. C 39.41, H 4.68, N 19.15; found C 39.20, H 4.76, N 18.87. IR (KBr): \nu = 2953, 2925, 2858, 1617, 1551, 1452, 1354, 1286, 1103, 1025, 801, 757, 726 \text{ cm}^{-1}. \lambda_{\text{max}} (\text{MeOH}) 812 \text{ nm}, \epsilon = 129 \text{ M}^{-1}\text{cm}^{-1}. Magnetic moment: 2.0 B.M.

[Ni(L5B)Cl_2]_2

Green solid (0.29 g, 93 %). C_{24}H_{34}Cl_4Ni_2N_{10} \cdot 4H_2O: calcd. C 36.31, H 5.33, N 17.64; found C 36.85, H 5.23, N 18.64. IR (KBr): \nu = 2954, 2926, 2856, 1614, 1452, 1392, 1354, 1286, 1261, 1225, 1157, 1100, 1047, 1063, 1026, 804, 759, 732 \text{ cm}^{-1}. \lambda_{\text{max}} (\text{MeOH}) 400 \text{ nm}, \epsilon = 17 \text{ M}^{-1}\text{cm}^{-1}. Magnetic moment: 4.3 B.M.

Co(L5B)\_2(NCS)_2

Rust coloured crystals (0.17 g, 63 %). C_{26}H_{34}CoN_12S_2\cdot CH_3OH: calcd. C 48.42, H 5.72, N 25.11; found C 48.80, H 6.02, N 24.28. IR (KBr): \nu = 2922, 2852, 2074, 1609, 1459, 1447, 1372, 1154, 1099, 1046, 1025, 802, 756 \text{ cm}^{-1}. \lambda_{\text{max}} (\text{MeOH}) 508 \text{ nm}, \epsilon = 49 \text{ M}^{-1}\text{cm}^{-1}. Magnetic moment: 4.0 B.M.

[Zn(L4C)Cl_2]_2

Orange solid (0.20 g, 86 %). C_{28}H_{42}Cl_4Zn_2N_{10} \cdot 4H_2O: calcd. C 38.93, H 5.84, N 16.23; found C 37.95, H 5.78, N 15.25. IR (KBr): \nu = 2955, 2927, 2856, 1610, 1481, 1460, 1377, 1297,
1051, 1012, 795, 747, 724 cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 9.11\) (m, 1 H, pyr-H), 8.18 (m, 2 H, pyr-H), 7.76 (m, 1 H, pyr-H), 4.78 (t, 2 H, \(J = 7.3\) Hz, CH\(_2\)N), 2.02 (m, 2 H, CH\(_2\)), 1.32 (m, 10 H, CH\(_2\)), 0.88 (t, 3 H, \(J = 6.9\) Hz, CH\(_3\)) ppm. \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 151.2\) (CN\(_4\)), 151.1, 141.7, 138.8, 128.7, 125.2, 50.8 (CH\(_2\)N), 31.6, 29.0, 28.9, 28.8, 26.4, 22.6, 14.0 ppm.

\([\text{Cu(L4C})\text{Cl}_2]\)\(_2\)

Green solid (0.13 g, 43%). C\(_{28}\)H\(_{42}\)Cl\(_2\)Cu\(_2\)N\(_{10}\): calcd. C 42.70, H 5.37, N 17.78; found C 41.66, H 5.39, N 17.53. IR (KBr): \(\nu = 2955, 2924, 2857, 1611, 1540, 1482, 1446, 1384, 1113, 1049, 1007, 792, 748, 719\) cm\(^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 832 nm, \(\varepsilon = 114\) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 1.8 B.M.

\([\text{Ni(L4C})\text{Cl}_2]\)\(_2\)

Green solid (0.18 g, 60%). C\(_{28}\)H\(_{42}\)Cl\(_2\)Ni\(_2\)N\(_{10}\)•4H\(_2\)O: calcd. C 39.55, H 5.93, N 16.48; found C 39.08, H 5.41, N 15.65. IR (KBr): \(\nu = 2955, 2925, 2855, 1611, 1479, 1456, 1377, 1254, 1162, 1049, 1012, 797, 752\) cm\(^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 396 nm, \(\varepsilon = 455\) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 4.2 B.M.

Co\((\text{L4C})_2\)(NCS)\(_2\)

Orange crystalline solid (0.15 g, 58%). C\(_{30}\)H\(_{42}\)CoN\(_{12}\)S\(_2\): calcd. C 51.93, H 6.10, N 24.23; found C 51.23, H 5.40, N 24.14. IR (KBr): \(\nu = 2925, 2854, 2068, 1610, 1476, 1457, 1412, 1161, 1010, 789, 725\) cm\(^{-1}\). \(\lambda_{\text{max}}\) (MeOH) 516 nm, \(\varepsilon = 55\) M\(^{-1}\)cm\(^{-1}\). Magnetic moment: 6.7 B.M.

\([\text{Zn(L5C})\text{Cl}_2]\)\(_2\)

White solid (0.16 g, 70%). C\(_{28}\)H\(_{42}\)Cl\(_2\)Zn\(_2\)N\(_{10}\): calcd. C 42.50, H 5.35, N 17.70; found C 42.86, H 6.23, N 18.35. IR (KBr): \(\nu = 2926, 2854, 1610, 1571, 1543, 1452, 1393, 1285, 1259, 1158, 1099, 1061, 1045, 1025, 805, 757, 732\) cm\(^{-1}\). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 8.87\) (m, 1 H, pyr-H), 8.28 (m, 1 H, pyr-H), 8.11 (m, 1 H, pyr-H), 7.69 (m, 1 H, pyr-H), 4.76 (t, 2 H, \(J = 7.2\) Hz, CH\(_2\)N), 2.10 (m, 2 H, CH\(_2\)), 1.30 (m, 10 H, CH\(_2\)), 0.88 (t, 3 H, \(J = 6.8\) Hz, CH\(_3\)) ppm. \(^{13}\)C
NMR (CDCl$_3$): $\delta = 162.3$ (CN$_4$), 149.9, 143.2, 140.1, 127.2, 122.6, 54.8 (CH$_2$N), 31.6, 29.1, 28.9, 28.7 26.2, 22.5, 14.0 ppm.

$[\text{Cu}(\text{L5C})\text{Cl}_2]_2$

Green solid (0.10 g, 33 %). C$_{28}$H$_{42}$Cl$_4$Cu$_2$N$_{10}$: calcd. C 42.70, H 5.37, N 17.78; found C 43.61, H 5.39, N 17.24. IR (KBr): $\nu =$ 2955, 2923, 2850, 1616, 1537, 1466, 1454, 1432, 1360, 1158, 1014, 801, 765, 726 cm$^{-1}$. $\lambda_{\text{max}}$ (MeOH) 812 nm, $\varepsilon = 86$ M$^{-1}$cm$^{-1}$. Magnetic moment: 2.2 B.M.

$[\text{Ni}(\text{L5C})\text{Cl}_2]_2$

Pale green solid (0.21 g, 70 %). C$_{28}$H$_{42}$Cl$_4$Ni$_2$N$_{10}$$\cdot$2H$_2$O: calcd. C 41.30, H 5.70, N 17.21; found C 41.05, H 6.11, N 17.25. IR (KBr): $\nu =$ 2955, 2925, 2855, 1615, 1452, 1392, 1286, 1262, 1226, 1101, 1047, 1063, 1027, 802, 758, 732 cm$^{-1}$. $\lambda_{\text{max}}$ (MeOH) 396 nm, $\varepsilon = 21$ M$^{-1}$cm$^{-1}$. Magnetic moment: 4.4 B.M.

Co(\text{L5C})$_2$(NCS)$_2$

Rust coloured crystals (0.13 g, 50 %). C$_{30}$H$_{42}$CoN$_{12}$S$_2$: calcd. C 51.93, H 6.10, N 24.23; found C 51.47, H 6.11, N 24.09. IR (KBr): $\nu =$ 2923, 2852, 2074, 1609, 1541, 1447, 1389, 1258, 1154, 1099, 1046, 1024, 801, 756 cm$^{-1}$. $\lambda_{\text{max}}$ (MeOH) 508 nm, $\varepsilon = 50$ M$^{-1}$cm$^{-1}$. Magnetic moment: 5.1 B.M.

$X$-ray structure determination

Single-crystal X-ray data for both Co(\text{L5A})$_2$(NCS)$_2$ and Co(\text{L5C})$_2$(NCS)$_2$ were collected on an Oxford Diffraction Gemini-S Ultra diffractometer at 294(1) K, with $\theta$ range 2-25º minimum and 100% data coverage to 25º (on $\theta$) [14]. Data reduction procedures and absorption corrections are standard [14]; comprehensive details have been published elsewhere [15]. All structures were solved using the SHELXS97 [16] direct methods program and refined by full matrix least squares calculations on $F^2$ with all non-hydrogen atoms having anisotropic displacement parameters. Hydrogen atoms were treated as riding atoms.
using the SHELXS97 defaults at 294(1) K using the OSCAIL software [17]. Selected crystallographic and structural information are detailed in Table 3 and the ESI. Molecular diagrams (Figures 2 and 3) were generated using PLATON [18]. All searches and analyses of the Cambridge Structural Database (CSD) were performed with the November 2011 release (version 5.33) [19,20].

The Co(L5A)2(NCS)2 structure refined without any problems although the six C atoms C22-C24 and C42-C44 were treated with moderate DFIX/DELU/SIMU restraints. The Co(L5C)2(NCS)2 structure exhibits considerable disorder and librational motion along the n-octyl chain (Figure 3) and primarily in the mid-part (this was treated using two separate sites for C31A/B and C32A/B and moderate DFIX restraints so as to give satisfactory results). Disorder in long chain n-alkyl groups is not uncommon in structural chemistry and with large displacement parameters associated with the carbon atoms. The refinements of Co(L5A)2(NCS)2 and Co(L5C)2(NCS)2 converged at 5.2% and 8.0% respectively.

CCDC reference codes 898052 and 898053. Copies available, e-mail: deposit@ccdc.cam.ac.uk.

Conclusions

In this follow-on paper from the X-ray crystallographic study of 2-(2H-tetrazol-5-yl)pyridine derivatives containing a 6-bromohexyl pendant arm [10], 2-(2H-tetrazol-5-yl)pyridine derivatives containing either an n-bromoalkyl pendant arm (n = 3, 4, 6, 8) or an n-alkyl chain (R = butyl, hexyl or octyl) at either the I-N or 2-N position of the tetrazole ring were synthesised. Their complexation reactions with several M(II) chloride complexes (M = Cu, Ni, Zn) and also Co(NCS)2 were studied. In all cases, the pyridyl-tetrazole ligand coordinates with the metal ion in a bidentate fashion through the pyridine N atom and the 1-N atom of the tetrazole ring. The notable difference between the various complexes is that, in the case of the cobalt complexes, the metal:ligand stoichiometry is 1:2 while in all the metal chloride complexes it is 1:1. The X-ray structure determination of two cobalt complexes Co(L5A)2(NCS)2 and Co(L5C)2(NCS)2 confirmed this. The 1H NMR spectra of the zinc complexes showed that the ligands containing the pendant arm in the 2-N position of the tetrazole ring (L3A-D) bind the zinc ion more strongly than those containing the pendant arm in the 1-N position (L2A-D).
Acknowledgements

We are thankful to NUIM for financial assistance through the provision of a John & Pat Hume Fellowship (US) and to Barbara Woods for carrying out the MS experiments. JFG thanks Dublin City University for grants in aid of research.

References