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## Tautomerisation and hydrogen-bonding interactions in four-coordinate metal halide and azide complexes of N-donor-extended dipyrromethanes\*\*

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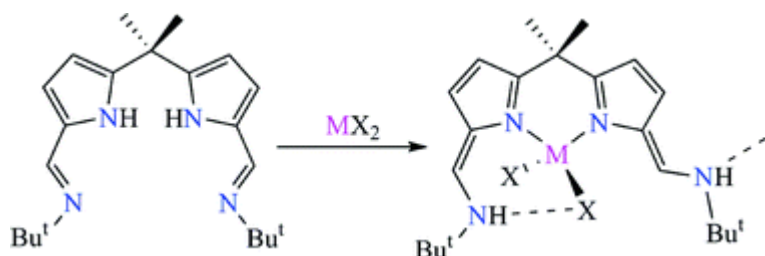
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### Graphical abstract:



## Abstract

The synthesis and structures of Fe, Co, and Zn halide complexes  $[MX_2(H_2L)]$  ( $M = Fe, X = Br; M = Co, Zn, X = Cl$ ) of the N-donor extended dipyrromethane ligand  $H_2L$  are described, from which it is clear that bond rearrangements from imine-pyrrole to amine-azafulvene tautomers occur on metal co-ordination, both in the solid state and in solution. In the structure of  $[FeBr_2(H_2L)]$ , this H-migration results in a pendant amine that is involved in both inter- and intramolecular hydrogen bonds to the bromide ligands, so forming a dimer. As the tautomerisation renders the N-H protons less acidic, metal-based ligand substitution reactions can occur in favour of deprotonation. As such, the reaction between  $[MCl_2(H_2L)]$  ( $M = Co, Zn$ ) and  $NaN_3$  results in the formation of the bis(azide) complexes  $[M(N_3)_2(H_2L)]$  which for Co displays both inter- and intramolecular N-H...N<sub>3</sub>-Co hydrogen bonds in the solid state. In contrast, reactions of the dihalides with the lithium bases  $LiNMe_2$  or  $LiMe$  ( $M = Fe$ ), or reduction reactions with  $C_8K$  ( $M = Fe, Co$ ) result in the formation of the known dinuclear helicates  $[M_2(L)_2]$ .

## Introduction

The use of hydrogen-bonding interactions to stabilise reactive metal-based ligands or to direct selectivity in metal-based chemical reactions is a burgeoning area of research, and takes much inspiration from the active sites of metalloenzymes in which these interactions are exploited in the regulation of biological activity.<sup>1</sup> In order to understand and potentially mimic these interactions, strategies to small molecule analogues have been developed in which suitable ligands are designed to incorporate hydrogen-bonding groups that are directed towards the secondary coordination sphere of the metal. Notably, Borovik and co-workers have exploited tetrapodal urea and amide tren-based ligands that result in a rigid trigonal pyramidal primary co-ordination sphere at the metal and a trigonal, hydrogen-bonding pocket around the (vacant) axial coordination site, and have shown that it is possible to stabilise a variety of reactive metal-functional groups such as high oxidation state Fe and Mn terminal oxo and hydroxyls.<sup>2,3</sup> Furthermore, Mareque-Rivas, Williams, and co-workers have shown that the rates of hydrolysis of phosphate esters are enhanced considerably by zinc complexes that incorporate hydrogen-bonding manifolds, and that this rate enhancement is similar to, or exceeds that seen when a second metal is introduced.<sup>4</sup> Alternatively, Nocera and co-workers have developed 'Hangman' ligands in which the primary metal coordination site, a porphyrin or a salen donor set, is linked to a carboxylic acid hydrogen-bonding site *via* a rigid single-pillared scaffold, and results in complexes that combine a metalloporphyrin redox site with a well-defined, orthogonal proton network; these features that are intrinsic to metalloenzymes that carry out proton-coupled-electron-transfer chemistry.<sup>5</sup> Significantly, Crabtree, Brudvig, and co-workers have shown that ligand design strategies that combine a known oxo-atom-transfer complex, in this case a  $Mn(\mu-O)_2Mn$  dimer with a carboxylic acid molecular recognition group, allows the regiospecific

oxygenation of distal C-H groups of ibuprofen as hydrogen-bonding between the carboxylate groups on the complex and the ibuprofen molecule induces selectivity.<sup>6</sup>

We developed recently a series of new acyclic<sup>7</sup> and macrocyclic ligands<sup>8</sup> derived from the dipyrromethanes  $R_2C(C_4H_4NH)_2$  ( $R = Me, Et, Ph$ ;  $R_2 = Me_4Cy^h, fluorenyl$ ) and found that the  $sp^3$ -hybridised *meso*-carbon in the  $N_4$ -donor Schiff-base ligands  $H_2L$  promoted a helical twist that resulted in the formation of a series of neutral dinuclear helicates  $[M_2(L)_2]$  for the first row transition metals Mn, Fe, Co, and Zn.<sup>9, 10</sup> Furthermore, we found that the use of chiral imine-nitrogen substituents derived from chiral amines promoted the sole formation of diastereomeric dinuclear mesocates instead of the expected helicates.<sup>11</sup> While investigating the mechanism of formation of these dinuclear complexes, we isolated the octahedral mononuclear complex  $[Mn(HL)_2]$  in which one half of the ligand had undergone an imine-pyrrole to amine-azafulvene tautomerisation and in which the pendant amine groups appeared accessible to the second metal reagent.<sup>9</sup> Here we describe the synthesis, structures, and reactions of the 1:1 complexes  $[MX_2(H_2L)]$  formed between the tetradentate ligand  $H_2L$  and the transition metal halides  $MX_2$  ( $M = Fe, X = Br$ ;  $M = Co, Zn, X = Cl$ ) in which tautomerisation has resulted in the presence of pendant amine groups that can be exploited as hydrogen bond donors to the ancillary ligands. Even though the dipyrromethane ligand provides an NN chelate, simple mononuclear transition metal complexes of this class of ligands remain relatively rare due to a tendency of the pyrrolide to take part in  $\pi$ -interactions that aggregate adjacent metal centres.<sup>12, 13</sup>

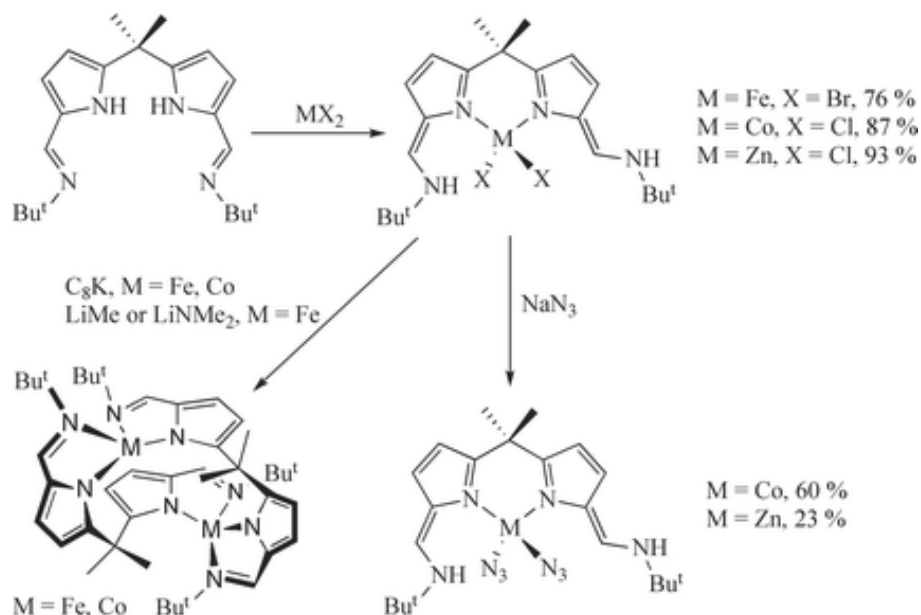
## Results and Discussion

### Synthesis and structures of $[MX_2(H_2L)]$ complexes

The transition metal adducts  $[MX_2(H_2L)]$ , ( $M = Fe, X = Br$ ;  $M = Co, Zn, X = Cl$ ) were prepared in high yields by combining the appropriate transition metal halide with  $H_2L$  in THF (Scheme 1), and their formulations are supported by elemental analyses.

The EIMS of the iron complex  $[FeBr_2(H_2L)]$  displayed a molecular ion at  $m/z$  556 (76 %) with the correct isotopic pattern, and further fragmentation due to loss of  $Br^-$  and Fe. While the  $^1H$  NMR spectrum of  $[FeBr_2(H_2L)]$  in  $CDCl_3$  displayed a series of paramagnetically-shifted resonances between 34.0 and -4.0 ppm, these proved difficult to assign due to line broadening and overlap; similar paramagnetically-shifted resonances were also observed for  $[CoCl_2(H_2L)]$  between 63.0 and -4.0 ppm and these were assigned by integration to CH,  $CH_3$  and  $CMe_3$  protons. Duplicate magnetic susceptibility measurements by Evans' method averaged to  $\mu_{eff} = 5.23 \mu_B$ , a value that is consistent with a high spin,  $g = 2$ , Fe(II) ion ( $\mu_{calc} = 4.90 \mu_B$ ). The IR spectrum of  $[FeBr_2(H_2L)]$  showed a weak band at  $3219 \text{ cm}^{-1}$  and a strong absorption at  $1641 \text{ cm}^{-1}$  that are attributable to ligand N-H and C=N/C=C stretches, respectively. In order to determine the binding mode of  $FeBr_2$  to  $H_2L$ , an X-ray diffraction study was undertaken on crystals of  $[FeBr_2(H_2L)]$  grown from a saturated

toluene solution. The solid state structure of  $[\text{FeBr}_2(\text{H}_2\text{L})]$  is shown in Figure 1, with selected bond lengths and angles and crystal data displayed in Tables 1 and 2, respectively.



**Scheme 1.** Synthesis and reactions of Fe, Co, and Zn complexes of the diiminodipyrromethane,  $\text{H}_2\text{L}$

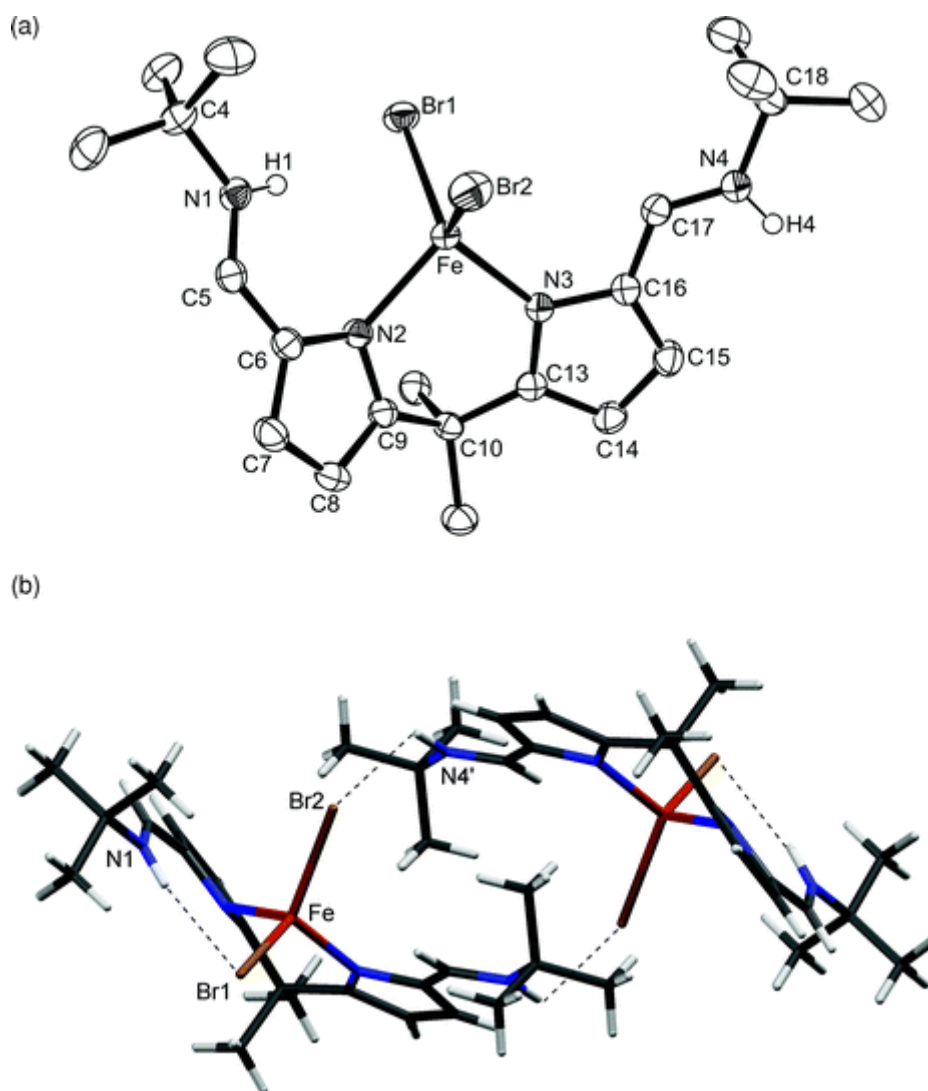
	$[\text{FeBr}_2(\text{H}_2\text{L})]$	$[\text{CoCl}_{0.25}(\text{N}_3)_{1.75}(\text{H}_2\text{L})]$
M-N2	2.0591(18)	1.985(3)
M-N3	2.0392(17)	1.977(3)
Fe-Br1	2.4213(4)	-----
Fe-Br2	2.4327(4)	-----
Co1-Cl1	-----	2.339(9)
N1-C5	1.310(3)	1.301(5)
N4-C17	1.300(3)	1.283(6)
N5-N6	-----	1.165(5)
N6-N7	-----	1.156(5)
N8-N9	-----	1.138(8)
N9-N10	-----	1.139(7)
N2-M-N3	93.20(7)	94.39(12)
Br1-Fe-Br2	100.596(14)	-----
N5-Co1-N8	-----	100.7(3)
N5-Co1-Cl1	-----	109.33(18)
Co1-N5-N6	-----	134.8(3)
Co1-N8-N9	-----	143.1(7)
N5-N6-N7	-----	177.3(4)
N8-N9-N10	-----	168.8(8)

**Table 1.** Selected bond lengths (Å) and angles (°) for  $[\text{FeBr}_2(\text{H}_2\text{L})]$  and  $[\text{CoCl}_{0.25}(\text{N}_3)_{1.75}(\text{H}_2\text{L})]$ .

	[FeBr <sub>2</sub> (H <sub>2</sub> L)]	[CoCl <sub>0.25</sub> (N <sub>3</sub> ) <sub>1.75</sub> (H <sub>2</sub> L)]
crystal size [mm]	0.31 × 0.30 × 0.18	0.20 × 0.16 × 0.03
crystal system	triclinic	Triclinic
space group	<i>P</i> -1	<i>P</i> -1
temperature [K]	150(2)	150(2)
<i>a</i> , <i>b</i> , <i>c</i> [Å]	8.9170 (8), 9.4120 (9), 14.4922 (14)	8.980 (2), 9.841 (2), 14.576 (3)
$\alpha$ , $\beta$ , $\gamma$ [°]	99.138 (2), 96.256 (2), 92.283 (2)	104.675 (3), 95.490 (3), 98.661 (3)
<i>V</i> [Å <sup>3</sup> ]	1191.7 (3)	1219.7 (7)
<i>Z</i> , $\rho$ [mg m <sup>-3</sup> ]	2, 1.550	2, 1.312
radiation type, $\lambda$ [Å]	Mo <i>K</i> $\alpha$ , 0.71073	Mo <i>K</i> $\alpha$ , 0.71073
$\mu$ [mm <sup>-1</sup> ]	4.00	0.76
$2\theta_{\max}$ [°]	55.0	50.0
diffractometer	Bruker SMART APEX CCD area detector	Bruker SMART APEX CCD area detector
scan mode	$\omega$	$\omega$
absorption correction	multi-scan	multi-scan
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.061, 0.122	0.766, 1.000
measured, independent reflns	7254, 5172	10550, 4309
reflns used in refinement	5169	4282
<i>R</i> (int)	0.024	0.024
structure solution	Patterson using <i>SHELXS97</i>	direct methods using <i>SHELXS97</i>
structure refinement	full-matrix least squares using <i>SHELXL</i>	full-matrix least squares using <i>SHELXL</i>
refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
$\theta_{\max}$ [°]	27.5	22.68
No. of parameters	253	279
H-atom treatment	Riding model	Riding model
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.027, 0.063	0.057, 0.133
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ [e Å <sup>-3</sup> ]	0.58, -0.26	0.56, -0.41
CSD numbers <sup>[a]</sup>	731449	731450

<sup>[a]</sup> CCDC 731449 – 731450 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

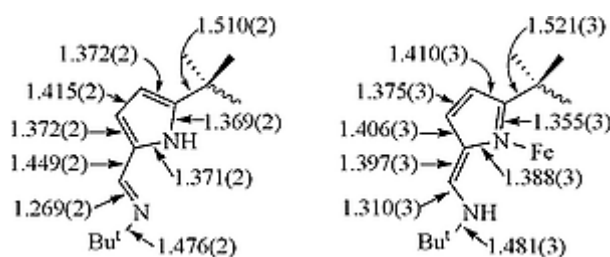
**Table 2.** Crystallographic data.<sup>[a]</sup>



**Figure 1.** Solid state structure of  $[\text{FeBr}_2(\text{H}_2\text{L})]$  (Top, asymmetric unit; bottom, dinuclear hydrogen-bonded structural unit). For clarity, all hydrogen atoms except those on N1 and N4 are omitted (50 % probability displacement ellipsoids).

In the solid state, the Fe(II) centre in  $[\text{FeBr}_2(\text{H}_2\text{L})]$  is in a distorted tetrahedral environment and is coordinated to the two pyrrolic nitrogens and two bromides. The Fe-N2 [2.0591(18) Å] and Fe-N3 [2.0392(17) Å] bond distances are similar to those in the tetranuclear Fe(II) dipyrrolide complex  $[\text{Fe}_4\{\eta:\kappa\text{-}(\text{C}_4\text{H}_4\text{N})_2\text{CMe}_2\}_4]$  (ave. 2.048 Å) and in the binuclear Fe(II) double-stranded helicate  $[\text{Fe}_2(\text{L})_2]$  (ave. 2.019 Å).<sup>9, 10, 13</sup> The NN chelate ring is not planar due to the flexibility at the  $sp^3$ -hybridised *meso*-carbon (C10), and the dihedral angle between the two pyrrole rings is 34.5°. Structurally-characterised, four-coordinate  $\text{FeBr}_2$  compounds of nitrogen donor ligands are very rare and limited to Fe(III)-nitride clusters and Fe(III) siloxyamido-chelates.<sup>14</sup> In these cases, the Fe-Br bond distances range between 2.393(6) and 2.471(2) Å, and are similar to the Fe-Br1 [2.4213(4) Å] and Fe-Br2 [2.4327(4) Å] bond distances in  $[\text{FeBr}_2(\text{H}_2\text{L})]$ .

Significantly, the complexation of  $\text{FeBr}_2$  by the pyrrolic nitrogens of  $\text{H}_2\text{L}$  has resulted in ligand tautomerisation with concomitant migration of the pyrrole hydrogen to the imine nitrogen, so forming an amine-azafulvene tautomer. This feature is best viewed by comparing the ligand bond distances in  $[\text{FeBr}_2(\text{H}_2\text{L})]$  with those in the crystallographically-characterised ligand  $\text{H}_2\text{L}$  (Figure 2),<sup>9</sup> and shows that the alternating short-long-short bond distances in  $\text{H}_2\text{L}$  are reversed in  $[\text{FeBr}_2(\text{H}_2\text{L})]$ . As mentioned above, we observed previously a similar phenomenon in the octahedral  $\text{Mn}(\text{II})$  complex  $[\text{Mn}(\text{HL})_2]$  in which one half of each ligand adopted an imine-pyrrolide tautomer, while the other half was best viewed as an amine-azafulvene.<sup>9</sup> A similar tautomerisation process was observed by Sessler and co-workers in the formation of a vanadyl complex of a Schiff-base expanded porphyrin in which an ene-amine bond rearrangement maximised the number of covalent and non-covalent bonds to the  $\text{VO}_2^+$  centre.<sup>15</sup> Also, Tasker and co-workers have shown recently that amine-functionalised, salicylaldoximine ligands undergo H-migration from the phenol oxygen to the amine nitrogen upon metal cation co-ordination, and that this event creates an anion-binding receptor that facilitates the solvent extraction of neutral  $\text{MX}_2$  metal salts from aqueous streams.<sup>16</sup>



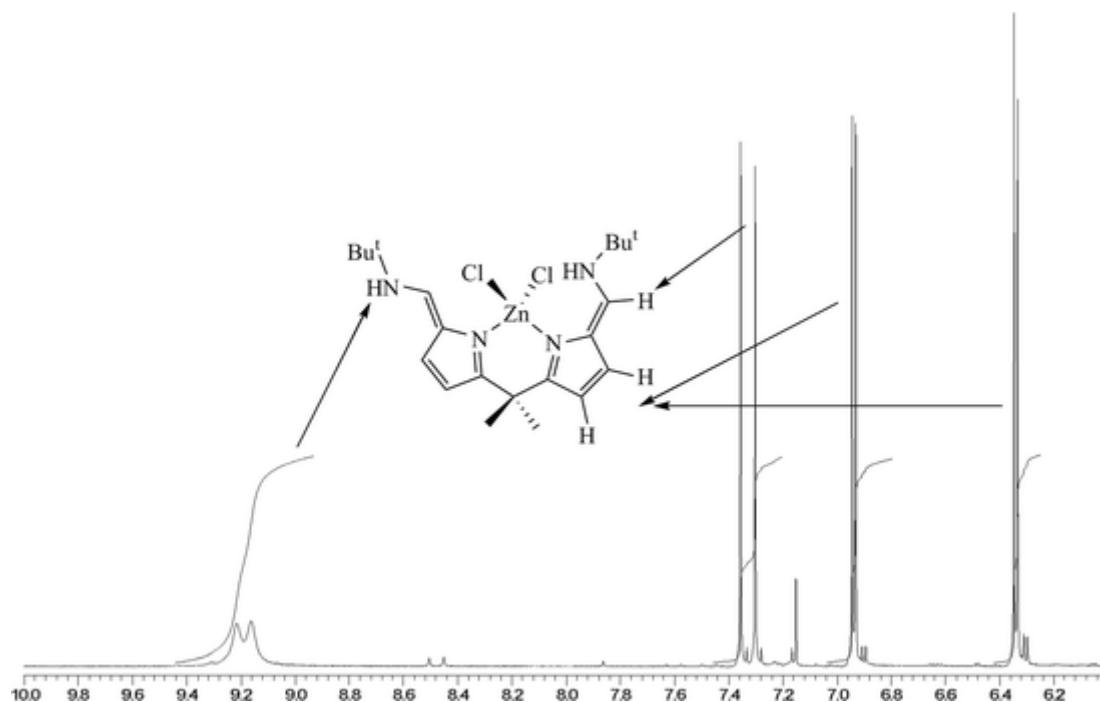
**Figure 2.** Bond length (Å) comparison between imino-pyrrole (from  $\text{H}_2\text{L}$ , left) and amino-azafulvene (from  $[\text{FeBr}_2(\text{H}_2\text{L})]$ , right) tautomers.

A consequence of this bond rearrangement is that the amine-hydrogen can become involved in hydrogen-bonding interactions. In the case of  $[\text{FeBr}_2(\text{H}_2\text{L})]$ , both inter- and intramolecular hydrogen-bonding interactions are seen, with one amine arm of the ligand in close, intramolecular  $\text{N}-\text{H}\cdots\text{Br}$  contact ( $\text{N1}\cdots\text{Br1}$  3.494 Å,  $\text{N1}-\text{H1}\cdots\text{Br1}$  162°) and the other, which adopts a transoid arrangement with the pyrrole group, interacting intermolecularly; this results in an overall dinuclear supramolecular structure (Figure 1). Similarly, Brooker and co-workers have found that  $\text{CuBr}_2$  complexes of a tridentate pyrrole-amine-pyridine ligand form dimers through intermolecular pyrrole  $\text{N}-\text{H}\cdots\text{Cl}/\text{Br}$  hydrogen bonds.<sup>17</sup>

In order to determine if this tautomerised structure is retained in solution, the diamagnetic  $\text{Zn}(\text{II})$  analogue  $[\text{ZnCl}_2(\text{H}_2\text{L})]$  was prepared. As with  $[\text{FeBr}_2(\text{H}_2\text{L})]$ , a molecular ion was observed at  $m/z$  476 (11 %) by EIMS and the IR spectrum indicated the presence of an N-H stretch ( $3192\text{ cm}^{-1}$ ). The  $^1\text{H}$  NMR spectrum of



[ZnCl<sub>2</sub>(H<sub>2</sub>L)] in CDCl<sub>3</sub> (Figure 3) provides the most structural insight as the number of resonances supports a symmetrical ligand arrangement, and importantly, the N-H protons at 9.2 ppm are found to couple to those of the azafulvene C=C(H); the magnitude of this coupling constant at 16.2 Hz suggests that the anti-conformation between this C=C(H) proton and the N-H proton observed in the solid state is retained in solution. It is therefore clear that the amine-azafulvene tautomer is dominant in this class of complexes, both in the solid state and in solution.



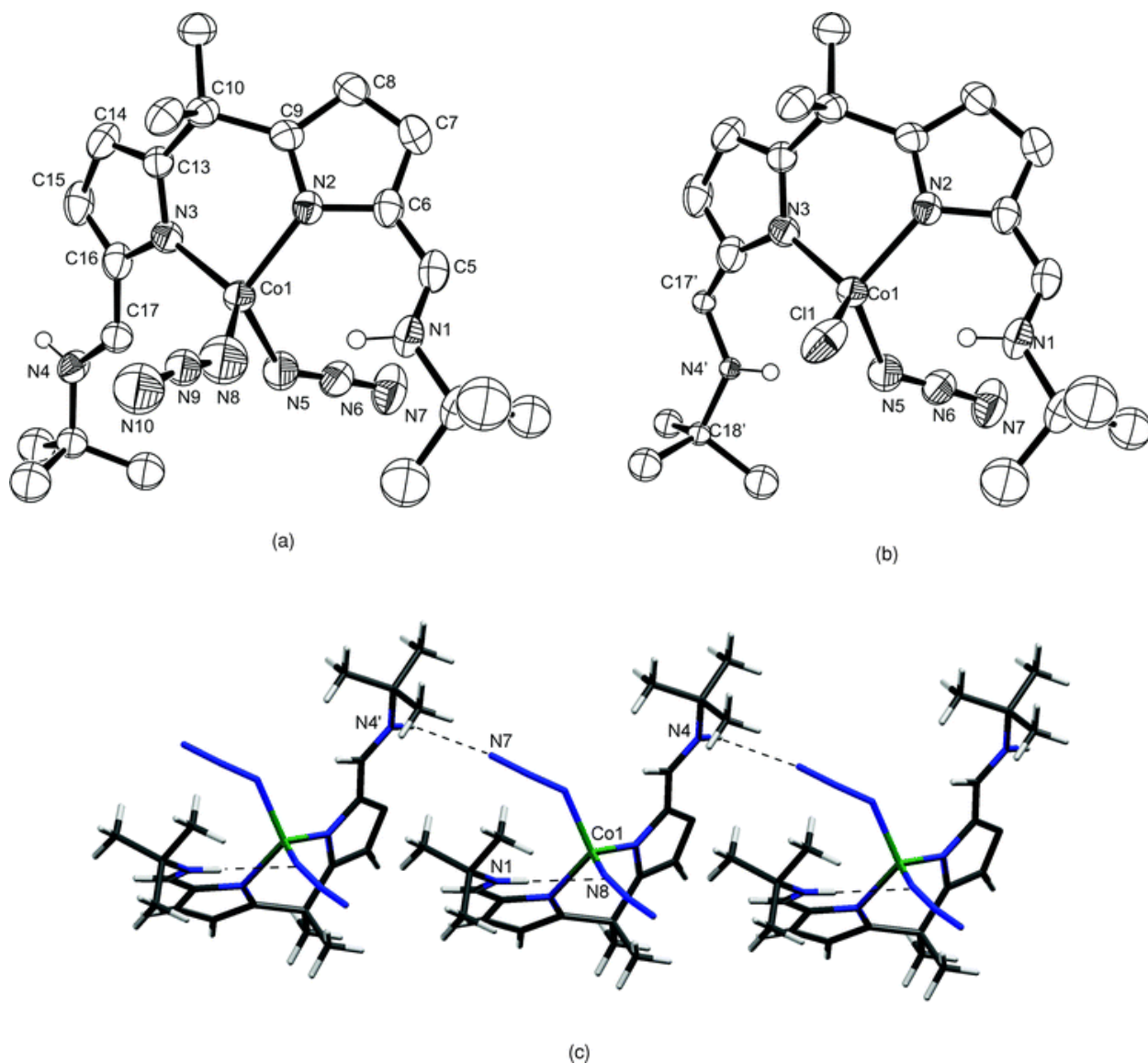
**Figure 3.** <sup>1</sup>H NMR spectrum of [ZnCl<sub>2</sub>(H<sub>2</sub>L)] (10.0 to 6.0 ppm region)

### Reactions of [MX<sub>2</sub>(H<sub>2</sub>L)] complexes

The ready formation of Fe, Co, and Zn [MX<sub>2</sub>(H<sub>2</sub>L)] complexes in which the imine-pyrrole to amine-azafulvene tautomerisation results in N-H hydrogen bond donor groups that can interact with the remaining ligands on the metals allows us to probe both the acidity of the new N-H bonds (*pK<sub>a</sub>* of amine versus pyrrole) and any ‘stabilisation’ of the attendant ligands through hydrogen-bonding interactions. In the first instance, reactions between [MX<sub>2</sub>(H<sub>2</sub>L)] and KC<sub>8</sub> were carried out (Scheme 1) to attempt to access low oxidation state chemistry of Fe and Co using this ligand set, particularly as five-coordinate dinitrogen pincer complexes of Fe display a rich and diverse chemistry,<sup>18</sup> and that few examples of hydrogen-bond-stabilised complexes with reactive, nitrogen-based ligands are known.<sup>3</sup>

Reactions between  $\text{KC}_8$  and  $[\text{MX}_2(\text{H}_2\text{L})]$  ( $\text{M} = \text{Fe}, \text{Co}$ ) led to the rapid formation of the known double-stranded binuclear helicates  $[\text{M}_2(\text{L})_2]$  (Scheme 1). For Fe, the helicate  $[\text{Fe}_2(\text{L})_2]$  was identified as a product by EIMS which displayed a characteristic molecular ion peak at  $m/z$  788, and by  $^1\text{H}$  NMR spectroscopy which showed paramagnetically-shifted resonances at 53.7, 10.3, and -6.8 ppm, while the Co analogue  $[\text{Co}_2(\text{L})_2]$  was identified by the broad resonances at 43.3 and -32.6 ppm in the  $^1\text{H}$  NMR spectrum.<sup>10</sup> It is therefore likely that while reduction of the metal centres occurs to eliminate  $\text{KX}$ , the low oxidation state metal inserts readily into the pyrrole N-H bond with subsequent elimination of  $\text{H}_2$  resulting in the formation of the stable [2+2] helicate; we have found previously that the [2+2] helicates form spontaneously from the reaction between  $\text{MX}_2$  and  $\text{K}_2\text{L}$ . Furthermore, salt elimination reactions between  $[\text{FeBr}_2(\text{H}_2\text{L})]$  and  $\text{LiMe}$  or  $\text{LiNMe}_2$  also resulted in the formation of the helicate  $[\text{Fe}_2(\text{L})_2]$ . It is therefore apparent that nucleophiles with a high basicity such as  $\text{LiMe}$  can either deprotonate the amine N-H bond directly, or can form reactive Fe-alkyl complexes that can rapidly undergo intramolecular protonolysis reactions or homolytic cleavage reactions.

In an attempt to hinder the formation of [2+2] helicates and yet still effect halide substitution, reactions between  $[\text{MX}_2(\text{H}_2\text{L})]$  complexes and the less basic nucleophile,  $\text{NaN}_3$  were undertaken. While the reaction between  $[\text{FeBr}_2(\text{H}_2\text{L})]$  led to an unidentifiable, paramagnetic product, the reactions between  $\text{NaN}_3$  and the Co and Zn halide complexes in THF resulted in the formation of the bis(azide) complexes  $[\text{M}(\text{N}_3)_2(\text{H}_2\text{L})]$  in moderate to good yields ( $\text{M} = \text{Co}$ , blue;  $\text{M} = \text{Zn}$ , yellow). The formulation of the blue Co complex  $[\text{Co}(\text{N}_3)_2(\text{H}_2\text{L})]$  was supported by elemental analysis, and the  $^1\text{H}$  NMR spectrum showed that no starting material was present, with new paramagnetically-shifted resonances between 61.0 and -5.0 ppm that were assignable to CH,  $\text{CH}_3$ , and  $\text{CMe}_3$  protons by integration. The magnetic susceptibility was measured in solution by Evans' method as  $3.56 \mu_{\text{B}}$  and is consistent with high spin Co(II) ( $\mu_{\text{calc}} 3.87 \mu_{\text{B}}$ ). As with  $[\text{CoCl}_2(\text{H}_2\text{L})]$ , weak N-H absorptions were seen in the IR spectrum at  $3275$  and  $3242 \text{ cm}^{-1}$ , and a new, strong absorption was observed at  $2062 \text{ cm}^{-1}$  that is attributable the azide group stretches. Similarly, the Zn analogue,  $[\text{Zn}(\text{N}_3)_2(\text{H}_2\text{L})]$  displays two, overlapped absorptions in the IR spectrum at  $2080$  and  $2060 \text{ cm}^{-1}$  and a broad N-H stretch at  $3185 \text{ cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum of  $[\text{Zn}(\text{N}_3)_2(\text{H}_2\text{L})]$ , a relatively large coupling constant between the N-H proton at 9.61 ppm and the azafulvene  $\text{C}=\text{C}(\text{H})$  proton at 7.57 ppm of 15.9 Hz is observed, and suggests that, in a similar manner to the halide analogue, these protons adopt a rigid *anti*-configuration, presumably enforced by some conjugation and hydrogen-bonding interactions. To confirm whether the azide ligand acts as a hydrogen-bond acceptor to the N-H groups of the ligand, an X-ray crystallographic study was carried out on dark blue crystals of  $[\text{Co}(\text{N}_3)_2(\text{H}_2\text{L})]$  grown from a  $\text{CH}_2\text{Cl}_2$ /pentane mixture. The solid state structure is shown in Figure 4 with selected bond lengths and angles and crystal data displayed in Tables 1 and 2, respectively.



**Figure 4.** Separated representations of  $[\text{Co}(\text{N}_3)_2(\text{H}_2\text{L})]$  and  $[\text{CoCl}(\text{N}_3)(\text{H}_2\text{L})]$  derived from the X-ray crystals structure of the mixed chloride-azide  $[\text{CoCl}_{0.25}(\text{N}_3)_{1.75}(\text{H}_2\text{L})]$  (Top, asymmetric unit; bottom, extended structure of  $[\text{Co}(\text{N}_3)_2(\text{H}_2\text{L})]$ ). For clarity, all hydrogen atoms except those on N1 and N4 are omitted (50% probability displacement ellipsoids except for disordered atoms).

Even though  $[\text{Co}(\text{N}_3)_2(\text{H}_2\text{L})]$  was determined to be pure analytically, the solid state structure was found to be a superimposed 75:25 mixture of di- and monosubstituted azide compounds  $[\text{Co}(\text{N}_3)_2(\text{H}_2\text{L})]$  and  $[\text{CoCl}(\text{N}_3)(\text{H}_2\text{L})]$ ; presumably, some concentration of trace monochloride complex has occurred during the crystal growing process. As with  $[\text{FeBr}_2(\text{H}_2\text{L})]$ , the Co adopts a distorted tetrahedral geometry bound to both pyrrole nitrogens and two azide nitrogens, and the ligand has retained its amine-azafulvene configuration. The cobalt to pyrrole nitrogen bond distances at 1.985(3) and 1.977(3) Å are similar to those seen in the binuclear helicate  $[\text{Co}_2(\text{L})_2]$  (1.989(3) and 1.980(3) Å) and support a Co(II) oxidation state.<sup>10</sup> Structurally-characterised,

four-coordinate Co azides are rare,<sup>19, 20</sup> with only one bis(azide)  $[\text{Co}(\text{N}_3)_2(\text{L}')_2]$ , where  $\text{L}'$  is a naphthylhydrazone-2-substituted imidazole ligand.<sup>19</sup> The cobalt to azido nitrogen bond distances in these compounds (average 1.947 Å) are similar to those in  $[\text{Co}(\text{N}_3)_2(\text{H}_2\text{L})]$  [1.973(4) and 1.914(8) Å], although the chloride co-occupancy with N8 meant that these azido N atoms were refined isotropically and therefore the latter bond distance is less reliable. The azido nitrogen bond distances N5-N6 and N6-N7 of 1.165(5) and 1.156(5) Å, respectively, are similar to those found in the other four-coordinate azides (average 1.161 and 1.151 Å) and suggest a double-bond resonance form for the azide. As a consequence, the azide ligands are linear [N5-N6-N7 177.3(4), N8-N9-N10 168.8(8)°] and the co-ordinated nitrogens subtend obtuse angles at the metal centre [Co1-N5-N6 134.8(3)° and Co1-N8-N9 143.1(7)°]. As with  $[\text{FeBr}_2(\text{H}_2\text{L})]$ , inter- and intramolecular hydrogen-bonding interactions are seen, with one amine arm of the ligand in close, intramolecular contact with a metal-bound azide nitrogen (N1...N8 3.135 Å) and the other, which adopts a transoid arrangement with the pyrrole group, interacting intermolecularly with a terminal azide nitrogen of a second molecule (N4'-N7 3.099 Å), and results in an extended zigzag chain structure. The 25% occupied compound  $[\text{CoCl}(\text{N}_3)(\text{H}_2\text{L})]$  is similar, although in this case both azafulvene arms of the ligand are directed towards the  $\text{Cl}^-$  and  $\text{N}_3^-$  ligands, which results in only intramolecular hydrogen bonding (N1...Cl1 3.369 Å and N4'...N5 3.188 Å) and no extended supramolecular structure.

## Conclusions

We have shown that the co-ordination of  $\text{MX}_2$  salts of Fe, Co, and Zn to the pyrrole nitrogens of the N-donor extended dipyrromethane  $\text{H}_2\text{L}$  results in the formation of four-coordinate metal complexes in which the pyrrolic hydrogen has migrated to the imine nitrogen with a concomitant bond rearrangement, so forming amine-azafulvene tautomers. The resulting N-H groups are able to act as both intra- and intermolecular hydrogen bond donors to the ancillary halide ligands. The decrease in the acidity of the N-H group (pyrrole vs. amine) associated with this tautomerisation process is reflected in reactions of  $[\text{MX}_2(\text{H}_2\text{L})]$  complexes with reagents of varying basicity. Here, reaction with the weakly basic azide nucleophile results in substitution at the metal and the formation of the bis(azide) complexes  $[\text{M}(\text{N}_3)_3(\text{H}_2\text{L})]$  ( $\text{M} = \text{Co}, \text{Zn}$ ), whereas in contrast more basic nucleophiles such as  $\text{LiMe}$  or  $\text{LiNMe}_2$  result ultimately in the formation of the known dinuclear helicates  $[\text{M}_2(\text{L})_2]$  ( $\text{M} = \text{Fe}, \text{Co}$ ), either through direct deprotonation of the ligand or a metal-based substitution/protonolysis mechanism.

## Experimental details

Unless otherwise stated, all reactions were carried out using standard Schlenk techniques under an atmosphere of nitrogen or argon or in a nitrogen-filled Vacuum Atmospheres OmniLab glovebox. Solvents were dried (hexanes, toluene, pentane,  $\text{Et}_2\text{O}$  and THF were passed through activated alumina towers,<sup>21</sup> dichloromethane was distilled from  $\text{CaH}_2$ ) and stored over 4 Å molecular sieves; all other solvents were used as purchased.

Deuteriated benzene was boiled over potassium, vacuum-distilled, and freeze-pump-thaw degassed three times.  $\text{CDCl}_3$  and  $\text{CD}_2\text{Cl}_2$  were dried over activated alumina, vacuum distilled, and freeze-pump-thaw degassed three times. The ligand  $\text{H}_2\text{L}$  was prepared according to literature procedures,  $\text{CoCl}_2(\text{H}_2\text{O})_6$  was dried under vacuum, and all other compounds were used as purchased. The  $^1\text{H}$  NMR and  $^{13}\text{C}\{\text{H}\}$  NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300.13 and 75.47 MHz respectively; residual protiosolvent served as an internal reference for the former. Magnetic susceptibilities were determined using Evans' method and corrected for diamagnetic contributions using Pascal constants. IR spectra were recorded using a Nicolet Avatar 360 spectrometer. Elemental analyses were carried out by Mr. Stephen Boyer at the London Metropolitan University and EIMS by Dr. Ali Abdul-Sada of the University of Sussex.

**Synthesis of  $[\text{FeBr}_2(\text{H}_2\text{L})]$**  - To a stirred slurry of  $\text{FeBr}_2$  (2.00 g, 9.23 mmol) in THF (20 mL), was added a solution of  $\text{H}_2\text{L}$  (3.17 g, 9.23 mmol) in THF (30 mL). The resulting red solution was heated at  $80^\circ\text{C}$  for 24 h, after which the mixture was filtered and the volatiles evaporated at reduced pressure. The resulting orange solids were washed with hot hexanes (10 mL) to yield 4.42 g, 76% of  $[\text{FeBr}_2(\text{H}_2\text{L})]$  as an orange powder.

Analysis: Found: C, 45.73; H, 5.51; N, 9.94.  $\text{C}_{21}\text{H}_{32}\text{N}_4\text{FeBr}_2$  requires: C, 45.51; H, 5.47; N, 10.11 %  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  33.3 (s, 1 H), 5.5 (s, 2 H), 4.7 (br.s, 6 H), 3.8 (s, 2 H), -0.1 (s, 1 H), -0.4 (s, 18 H), -3.4 (s, 1 H); EIMS:  $m/z$  556 ( $\text{M}^+$ , 74%), 475 ( $\text{M}^+ - \text{Br}$ , 28), 459 ( $\text{M}^+ - \text{Br} - \text{Me}$ , 9), 379 ( $\text{FeL}^+ - \text{Me}$ , 81), 340 ( $\text{H}_2\text{L}^+$ , 68), 325 ( $\text{H}_2\text{L}^+ - \text{Me}$ , 100);  $\mu_{\text{eff}}(\text{CDCl}_3) = 5.23 \mu_{\text{B}}$ ; IR (nujol):  $\nu$  3219 (bw), 1641 (s), 1503 (w), 1261 (s), 1197 (m), 1094 (s), 1066 (s), 1017 (s), 800 (s)  $\text{cm}^{-1}$ .

**Synthesis of  $[\text{CoCl}_2(\text{H}_2\text{L})]$**  - To a stirred slurry of  $\text{CoCl}_2$  (1.00 g, 7.82 mmol) in THF (20 mL) was added a solution of  $\text{H}_2\text{L}$  (2.66 g, 7.82 mmol) in THF (30 mL). The solids dissolved immediately to give a green-blue solution. The mixture was stirred at room temperature for 24 h, after which it was filtered, the volatiles removed under vacuum, and the residues washed with hexanes (10 mL), to yield 3.2 g, 87% of  $[\text{CoCl}_2(\text{H}_2\text{L})]$  as a turquoise powder.

Analysis: Found: C, 53.79; H, 6.71; N, 11.74.  $\text{C}_{21}\text{H}_{32}\text{N}_4\text{CoCl}_2$  requires: C, 53.52; H, 6.87; N, 11.91%  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K):  $\delta_{\text{H}}$  62.6 (s, 2 H), 29.3 (s, 2 H), 13.7 (s, 6 H), 1.3 (s, 18 H), -3.6 (s, 2 H); EIMS:  $m/z$  469 ( $\text{M}^+$ , 23 %), 433 ( $\text{M}^+ - \text{Cl}$ , 22), 418 ( $\text{M}^+ - \text{Cl} - \text{Me}$ , 6), 382 ( $\text{CoL}^+ - \text{Me}$ , 67), 42 ( $\text{Bu}^+ - \text{Me}$ , 100);  $\mu_{\text{eff}}(\text{CD}_2\text{Cl}_2) = 4.08 \mu_{\text{B}}$ ; IR (nujol):  $\nu$  3196 (bw), 1642 (s), 1503 (m), 1306 (s), 1236 (m), 1195 (s), 1110 (m), 1066 (s), 1017 (m), 913 (w), 812 (m), 776 (m), 729 (m)  $\text{cm}^{-1}$ .

**Synthesis of  $[\text{ZnCl}_2(\text{H}_2\text{L})]$**  - A solution of  $\text{ZnCl}_2$  (1.0 M) in  $\text{Et}_2\text{O}$  (9 mL) was added dropwise to a stirred solution of  $\text{H}_2\text{L}$  (3.00 g, 8.81 mmol) in THF (30 mL). The solution turned yellow and was stirred for 24 h, during which yellow  $[\text{ZnCl}_2(\text{H}_2\text{L})]$  precipitated and was isolated by filtration and dried under vacuum, yield 3.9 g, 93%.

Analysis: Found: C, 53.00; H, 6.95; N, 11.52.  $C_{21}H_{32}N_4ZnCl_2$  requires: C, 52.89; H, 6.78; N, 11.75%  $^1H$  NMR ( $CDCl_3$ , 298 K):  $\delta_H$  9.22 (d,  $J = 15.9$  Hz, 2 H, NH), 7.36 (d,  $J = 16.2$  Hz, 2 H, CH=N), 6.94 (d,  $J = 4.2$  Hz, 2 H, pyrrole H), 6.35 (d,  $J = 4.2$  Hz, 2 H, pyrrole H), 1.61 (s, 6 H, *meso*  $CH_3$ ), 1.42 (s, 18 H,  $CMe_3$ );  $^{13}C$   $\{^1H\}$  NMR ( $CDCl_3$ , 298 K):  $\delta_C$  166.9 (s,  $C_q$ ), 145.5 (s, CH=N), 132.9 (s, CH), 130.7 (s,  $C_q$ ), 113.6 (s, CH), 56.8 (s,  $C_q$ ), 39.9 (s,  $C_q$ ), 31.7 (s, *meso*  $CH_3$ ), 29.8 (s,  $CMe_3$ ); EIMS:  $m/z$  476 ( $M^+$ , 10 %), 438 ( $M^+ - Cl$ , 72), 423 ( $M^+ - Cl - Me$ , 37%), 387 ( $ZnL^+ - Me$ , 48), 57 ( $Bu^t$ , 100); IR (nujol):  $\nu$  3192 (m), 1648 (s), 1502 (w), 1377 (s), 1309 (m), 1295 (m), 1261 (s), 1197 (s), 1094 (s), 1067 (s), 1024 (s), 800 (s)  $cm^{-1}$ .

**Reaction between  $[FeBr_2(H_2L)]$  and  $KC_8$**  – A solution of  $[FeBr_2(H_2L)]$  (730 mg, 4.00 mmol) in THF (30 mL) was added dropwise to a stirred slurry of  $KC_8$  (1.00 g, 1.80 mmol) in THF (10 mL) at  $-78$  °C. The mixture was allowed to warm to room temperature and stirred for a further 72 h, after which the slurry was filtered and the solvents evaporated under vacuum. The red solid residues were extracted into toluene (5 mL) and 140 mg of a red product was precipitated by the addition of pentane (10 mL), isolated, and dried under vacuum.

$^1H$  NMR (THF/ $C_6D_6$ , 298 K):  $\delta_H$  53.7 (s, 2 H), 10.3 (s, 24 H), -6.8 (s, 2 H); EIMS:  $m/z$  788 (21 %), 58 ( $Bu^t$ , 100 %)

**Reaction between  $[CoCl_2(H_2L)]$  and  $KC_8$**  - A solution of  $[CoCl_2(H_2L)]$  (250 mg, 0.53 mmol) in THF (10 mL) was added dropwise to a stirred slurry of  $KC_8$  (158 mg, 1.17 mmol) in THF (5 mL) at  $-78$  °C. The reaction was allowed to warm to room temperature and was stirred for 24 h, after which the mixture was filtered and the volatiles evaporated under vacuum. The resulting maroon residues were extracted into hot toluene (5 mL), filtered through Celite, and evaporated to dryness. Dissolution of these solids in a minimum amount of  $Et_2O$  and cooling to  $-35$  °C resulted in the precipitation of 59 mg of  $[Co_2(L)_2]$ .

$^1H$  NMR ( $CDCl_3$ , 298 K):  $\delta_H$  43.3 (br.s, 2 H), -32.6 (br.s, 18 H).

**NMR Tube Reaction between  $[FeBr_2(H_2L)]$  and  $LiNMe_2$**  - To a suspension of  $Li(NMe_2) \cdot 0.5(THF)$  (4.7 mg, 54  $\mu$ mol) in THF (ca. 0.2 mL) was added a solution of  $[FeBr_2(H_2L)]$  (15 mg, 27  $\mu$ mol) in THF (ca. 0.3 mL). The resulting red solution was transferred to a Teflon-tapped NMR tube containing  $C_6D_6$  (ca. 0.05 mL) and analysed by  $^1H$  NMR spectroscopy.

$^1H$  NMR (THF/ $C_6D_6$ , 298 K):  $\delta_H$  53.7 (s, 2 H), 10.3 (s, 24 H), -6.8 (s, 2 H).

**Reaction between  $[FeBr_2(H_2L)]$  and  $LiMe$**  - To a stirred solution of  $MeLi$  (1 mL, 1.6 M in  $Et_2O$ ) in THF (10 mL) was added a solution of  $[FeBr_2(H_2L)]$  (450 mg, 0.8 mmol) in THF (10 mL). The resulting orange solution was stirred for 96 h, after which the volatiles were removed, the solids extracted into toluene (10 mL), filtered and cooled resulting in an orange precipitate that was analysed by  $^1H$  NMR spectroscopy.

$^1H$  NMR ( $CDCl_3$ , 298 K):  $\delta_H$  53.5 (s, 2 H), 10.3 (s, 24 H), -6.8 (s, 2 H).

**Synthesis of the Co Azide Complex, [Co(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>L)]** - A solution of [CoCl<sub>2</sub>(H<sub>2</sub>L)] (300 mg, 0.64 mmol) in THF (10 mL) was added dropwise to a stirred slurry of NaN<sub>3</sub> (124 mg, 1.91 mmol) in THF (5 mL) at room temperature. The resulting blue slurry was allowed to stir for 48 h, after which the solvents were evaporated under vacuum, the blue residues extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and filtered. Pentane (15 mL) was added until cloud point, and upon cooling, 184 mg, 60%, of [Co(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>L)] was isolated as a blue, crystalline material.

Analysis: Found: C, 52.25; H, 6.65; N, 28.88. C<sub>21</sub>H<sub>32</sub>N<sub>10</sub>Co requires: C, 52.16; H, 6.69; N, 28.97% <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ<sub>H</sub> 60.1 (s, 2 H), 28.2 (s, 2 H), 11.9 (s, 6 H), 1.3 (s, 18 H), -4.3 (s, 2 H); μ<sub>eff</sub> (CD<sub>2</sub>Cl<sub>2</sub>) = 3.56 μ<sub>B</sub>; IR (nujol): ν 3275 (w), 3242 (bm), 2062 (s), 1637 (s), 1505 (m), 1307 (m), 1282 (m), 1196 (m), 1111 (m), 1063 (m), 1022 (m), 997 (w), 977 (w), 813 (m), 771 (m), 725 (m) cm<sup>-1</sup>.

**Synthesis of the Zn Azide Complex, [Zn(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>L)]** - A solution of [ZnCl<sub>2</sub>(H<sub>2</sub>L)] (600 mg, 1.26 mmol) in THF (20 mL) was added dropwise to a stirred slurry of NaN<sub>3</sub> (246 mg, 3.78 mmol) in THF (10 mL) at room temperature. The resulting slurry was stirred for 120 h, after which the volatiles were removed under vacuum, the resulting yellow solids extracted with hot toluene, filtered and cooled to yield 144 mg, 23% of [Zn(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>L)] as yellow solids.

No satisfactory elemental analysis was obtained after repeated attempts.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 298 K): δ<sub>H</sub> 9.61 (d, *J* = 14.9 Hz, 2 H, NH), 7.57 (d, *J* = 15.9 Hz, 2 H, CH=N), 7.10 (d, *J* = 4.0 Hz, 2 H, pyrrole H), 6.50 (d, *J* = 4.0 Hz, 2 H, pyrrole H), 1.72 (s, 6 H, *meso* CH<sub>3</sub>), 1.59 (s, 18 H, CMe<sub>3</sub>); <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 298 K): δ<sub>C</sub> 166.2 (s, C<sub>q</sub>), 145.8 (s, CH=N), 132.4 (s, CH), 130.2 (s, C<sub>q</sub>), 133.5 (s, CH), 55.9 (s, C<sub>q</sub>), 39.2 (s, C<sub>q</sub>), 30.9 (s, *meso* CH<sub>3</sub>), 29.2 (s, CMe<sub>3</sub>); IR (nujol): ν 3185 (bw), 2726 (w), 2080 (s), 2060 (s), 1650 (s), 1584 (w), 1503 (w), 1309 (w), 1261 (w), 1227 (w), 1196 (w), 1097 (m), 1067 (m), 1023 (m), 912 (w), 801 (s), 778 (m), 723 (m) cm<sup>-1</sup>.

### Crystallography: General Methods and solution and refinement details

Single crystal diffraction data were collected using graphite monochromated Mo *K*α *X*-radiation on a SMART APEX CCD area detector diffractometer equipped with an Oxford Cryosystems open-flow cryostat operating at 150 K. Details of the individual data collections and refinements are given in Table 2. Structures were solved using *SHELXS97*<sup>22</sup> using heavy atom methods for [FeBr<sub>2</sub>(H<sub>2</sub>L)] and direct methods for [Co(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>L)]. Both structures were refined by least-squares full matrix refinement against *F*<sup>2</sup> using *SHELXL97*, and all fully occupied non-H atoms refined with anisotropic displacement parameters. The complex [Co(N<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>L)] showed an azide/chloride disorder (N8/Cl1) which was modelled with respective occupancies of 0.75 and 0.25. The *tert*-butyl group C4 showed disorder and was modelled over two sites with occupancies 0.70 and 0.30. The C=N<sup>t</sup>Bu group C14, N4, C18-C21 was disordered and modelled over two sites with occupancies 0.85 and 0.15. Geometric and rigid bond restraints were applied in all cases, and partially occupied atom sites were refined with isotropic displacement parameters.

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