

1 **ZnII Complexes Based on Hybrid N-Pyrazole, N9-imine Ligands: Synthesis, X-Ray Crystal**
2 **Structure, NMR Characterisation, and 3D Supramolecular Properties**

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28 **ABSTRACT:**

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30 The present report is on the synthesis of two new 3-imine-3,5-dimethylpyrazole ligands, N-[3-(3,5-
31 dimethyl-1H-pyrazol-1-yl)propylidene]ethylamine (L1) and N-[3-(3,5-dimethyl-1H-pyrazol-1-
32 l)propylidene]propylamine (L2). These ligands form molecular complexes with the formula $[ZnCl_2(L)]$
33 ($L/4L1$ (1) and $L2$ (2)) when the reacting with $ZnCl_2$ in a metal (M)/ligand (L) ratio of 1 : 1. These new
34 ZnII complexes have been characterised by elemental analyses, conductivity measurements, mass
35 spectrometry, and infrared, 1H and $^{13}C\{^1H\}$ NMR spectroscopy techniques. The two crystalline
36 structures of complexes 1 and 2 have been solved by X-ray diffraction methods. Finally, we have
37 studied the self-assembly three-dimensional supramolecular structure through different intra- and
38 intermolecular contacts. The application of these ZnII complexes in supramolecular crystal engineering
39 is interesting due to (1) the easy preparation and the high efficiency of this system and (2) the different
40 bonding properties of the heteroatoms (N-pyrazole vs N-imine) present in the structure of the ligands.

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47 INTRODUCTION

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49 The construction of molecular architectures[1] depends mostly on the combination of several factors
50 such as the coordination geometry of the metal ions, nature of the organic ligands and counterions, and
51 ratio between the metal salts and ligands, among others. One of the most interesting aspects of
52 coordination chemistry is the design of hybrid ligands, which are able to distinguish between different
53 metals depending on the reaction conditions.[2] The complexes, including pyrazolic ligands, are present
54 in many pharmacologically important compounds,[3] macromolecular chemistry,[4] and homogeneous
55 catalysis.[5] Particularly, group 12 metals (Zn, Cd, and Hg) are promising due to their wide variety of
56 coordination numbers and geometries provided by the d10 configuration of the metal centre.[6]

57 In the recent past years, our research group has focussed its interest on the synthesis and characterisation
58 of heterotopic ligands containing a N-pyrazole group with other donor group such as P-phosphine
59 (N,P),[7] P 0-phosphinite (N,P0),[8] O-alcohol (N,O),[9] S-thioether (N,S),[10] or N-amine (N,N0).[11]
60 As an extension to these results, in the present paper, we report the synthesis of new pyrazole-derived
61 ligands with an imine group: N-[3-(3,5-dimethyl-1H-pyrazol-1-yl)propylidene] ethylamine (L1) and N-
62 [3-(3,5-dimethyl-1H-pyrazol-1-yl) propylidene]propylamine (L2). The L1 and L2 ligands contain one
63 nitrogen pyrazole and one imine nitrogen as potential N-donor atoms (Scheme 1). We also describe the
64 study of their reactivity with ZnII, isolating complexes [ZnCl2(L)] (L¼L1 (1) and L2 (2)). Complete
65 characterisation of L1 and L2 and their ZnII complexes are reported, focusing on NMR studies
66 discussion, crystallographic structures, and self-assembly threedimensional (3D) arrangements.

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68 RESULTS AND DISCUSSION

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70 Synthesis and Characterisation of the Ligands New 3-imino-3,5-dimethylpyrazole ligands (L1 and L2)
71 were prepared following similar procedures as described in the literature.[12] The synthetic procedure
72 for the preparation of the L1 and L2 ligands consists of two steps (Scheme 1). First, 3,5-
73 dimethylpyrazole was reacted with acrolein in dry dioxane to give the 3-(3,5-dimethyl-1H-pyrazol-1-
74 yl)propanal (Scheme 1a).[13] In the second step, the corresponding amine (ethylamine (L1) or
75 propylamine (L2)) dissolved in water was added to generate the L1 and L2 ligands (Scheme 1b). The
76 ligands were obtained as pure products (62%(L1) and 95%(L2) yields). The ligands have been fully
77 characterised by melting points, elemental analyses mass spectrometry, and infrared (IR), ¹H, ¹³C{¹H}
78 NMR spectroscopy techniques. The NMR signals were assigned by reference to the literature[14] and
79 from the analysis of DEPT, COSY, and HMQC spectra.

80 Elemental analyses, mass spectrometry, and all spectroscopic data for L1 and L2 are consistent with the
81 proposed formulae. The positive ionisation spectra (ESI⁺-MS; electrospray ionisation mass
82 spectroscopy) of L1 and L2 ligands measured in acetonitrile display a peak attributable to [L_pNa]⁺
83 (L_p=L1, L2). In the IR spectra of the two ligands, the characteristic absorptions measured using NaCl
84 pellets observed at 1667 cm⁻¹ are attributed to ν(C=N_{im}) (L1, L2), 1553 cm⁻¹ are attributed to the
85 pyrazolyl group [ν(C=C), ν(C=N)]pz (L1, L2), and 773 cm⁻¹ are attributed to δ(C-H)_{oop} (L1, L2),
86 confirming the presence of the imine group in the structure of the ligand.

87 The NMR spectra were recorded in CDCl₃ for the ligands. In the ¹H NMR spectra, characteristic
88 signals appear at 5.72 ppm (L1) and 5.74 ppm (L2), attributable to CH_{pz}. Other signals are attributed to
89 NpzCH₂CH₂CH₂N_{im} that appear at 7.65 ppm (L1, L2). In the ¹³C{¹H} NMR, the most important
90 signals appear at 105.1 ppm (L1) and 105.0 ppm (L2), which correspond to CH_{pz}, and 160.7 ppm (L1)
91 and 161.1 ppm (L2), attributable to NpzCH₂CH₂CH₂N_{im}.

92 Synthesis and Characterisation of the Complexes Complexes [ZnCl₂(L)] (L_p=L1 (1) and L2 (2)) were
93 obtained by treatment of the corresponding ligand (Scheme 1c) with ZnCl₂ in a 1 : 1 or 1 : 2 metal
94 (M)/ligand (L) molar ratio in absolute ethanol for 24 h. Interestingly, stoichiometry of the complexes
95 does not depend of the M/L molar ratio. Several techniques were used for the characterisation of all
96 complexes: elemental analyses, mass spectrometry, conductivity measurements, and IR, and one-
97 dimensional (1D) and two-dimensional (2D) NMR spectroscopy techniques. In addition, a full 3D
98 structure determination for compounds 1 and 2 was performed through singlecrystal X-ray diffraction
99 method.

100 The elemental analyses for compounds 1 and 2 are consistent with the formula [ZnCl₂(L)]. The positive
101 ionisation spectra (ESI⁺-MS), in acetonitrile, of compounds 1 and 2 give a peak attributable to
102 [ZnCl(L)]⁺ (L_p=L1 (1), L2 (2)). The spectrum of complex 1 also shows another peak at m/z 218 (100
103 %), corresponding to [ZnCl₂(L1)-3,5-Me₂pz]. Molecular peaks of the cations are observed with the
104 same isotope distribution as the theoretical ones. Moreover, conductivity values in methanol for

105 complexes 1 and 2 are in agreement with the presence of non-electrolyte compounds because reported
106 values ($59 \text{ O}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (1) and $61 \text{ O}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (2)) are lower than $80 \text{ O}^{-1} \text{ cm}^2 \text{ mol}^{-1}$
107 1.[15]

108 The IR spectra of the two complexes in KBr pellets display absorptions of the 3-imine-3,5-
109 dimethylpyrazole ligands. For all complexes, the most characteristic bands are those attributable to the
110 pyrazolyl group: $[\text{n}(\text{C}^{1/4}\text{C}), \text{n}(\text{C}^{1/4}\text{N})]\text{pz}$ at 1554 cm^{-1} (1) and 1551 cm^{-1} (2), and $\text{d}(\text{C-H})_{\text{oop}}$ at 802
111 cm^{-1} (1) and 794 cm^{-1} (2), and other characteristic bands are those attributable to $\text{n}(\text{C}^{1/4}\text{Nim})$ at 1666
112 cm^{-1} (1) and 1664 cm^{-1} (2).[14] This band is shifted to the lower frequencies relative to that of the
113 free ligand upon coordination of the nitrogen atoms.

114 The ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR, DEPT, COSY, HMQC, and NOESY spectra were recorded in CDCl_3 for the
115 two complexes are discussed. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were consistent with the proposed
116 formulation and showed the coordination of the ligands (L1 and L2) to the Zn atom. NMR spectroscopic
117 data are reported in the Experimental section. For compounds 1 and 2, the study of the $\text{Npz-CH}_2\text{-CH}_2\text{-}$
118 $\text{CH}^{1/4}\text{Nim}$ fragments as AA0XX0 systems gave a set of coupling constants for each compound. These
119 constants were consistent with the simulated spectra for compounds 1 and 2, obtained with the aid of the
120 gNMR program.[16] All these results are reported in Table 1. Fig. 1 shows the experimentally
121 determined and simulated spectra for 1.

122 In the ^1H NMR spectra of 1 and 2 at room temperature, the methylene protons for $\text{Npz-CH}_2\text{-CH}_2\text{-}$
123 $\text{CH}^{1/4}\text{Nim}$ chain appear as two bands. One is a well-defined band (doublet of doublet of doublets) at
124 δ 4.84 ppm (1) and 4.86 ppm (2) and other is a broad band at δ 2.94 ppm (1) and 2.93 ppm (2). This
125 suggests that at 298 K, there is a fluxional process in which, with ringflipping, the two hydrogens of
126 each CH_2 are interconverted and only one signal can be observed. HMQC spectra were used to assign
127 the signals of protons H-8 and H-9.

128 As observed from the NOESY spectra, the methyl linked to the pyrazole at δ 2.28 ppm (1) and (2)
129 shows NOE interactions with δ 4.84 ppm (1) and 4.86 ppm (2), but not with the ones at δ 2.94 ppm (1)
130 and 2.93 ppm (2). The other signal is attributable to $\text{Npz-CH}_2\text{-CH}_2\text{-C}^{1/4}\text{Nim}$, which appears at 7.95 ppm
131 in both complexes.

132 Crystal Structures of the Complexes $[\text{ZnCl}_2(\text{L})]$ (L5L1 (1), L5L2 (2))

133 For complexes 1 and 2, it has been possible to obtain colourless monocrystals suitable for X-ray
134 analyses through crystallisation from dichloromethane/diethyl ether (1 : 1) mixture.

135 The structures consist of discrete Zn^{II} molecules linked by diverse intermolecular interactions. It is
136 important to mention that complex 2 contains two symmetrically independent molecules and two water
137 solvent molecules in the unit cell. The environment around the Zn^{II} centre in both complexes consists of
138 two chlorine atoms and one ligand L (L1 (1) or L2 (2)) coordinated by (Npz, Nim), building a seven-
139 membered metallocycle whose conformation can be described as deformed half chair (Figs 2 and 3,
140 respectively). The Zn^{II} centre adopts a pseudo tetrahedral coordination, where the tetrahedron is
141 somewhat distorted by larger Cl-Zn-Cl , N-Zn-Cl , and N-Zn-N angles in comparison with the

142 tetrahedral value (Table 2). The values of the angles for complexes 1 and 2 are in agreement with the
143 values reported in the literature for tetrahedral species Npz–Zn–Cl (101.38–122.98), Nim–Zn–Cl
144 (102.98–120.08), [17] and Cl–Zn–Cl (112.08–116.18). [18] The Zn–Npz, Zn–Nim, and Zn–Cl
145 distances in both complexes are in the known range for tetrahedral species: Zn–Npz (1.94–2.17 Å),
146 Zn–Nim (1.98–2.09 Å), and Zn–Cl (2.18–2.37 Å). [17,18]

147 The ligands adopt an E-, Z-configuration in these complexes. The angle between the planes Zn–N1–N2–
148 C6 and Zn–N3–C8–C7–C6 is 58.938 for 1, and those between planes Zn1–N11–N12–C16 and Zn1–
149 N13–C18–C17–C16, and planes Zn2–N21–N22–C26 and Zn2–N23–C28–C27–C26 are 56.098 and
150 54.358, respectively, for 2. All these values indicate the V-shaped form of the complexes studied here.
151 The [ZnCl₂(Npz) (Nim)] core is present in two complexes in the literature. [19] As seen in Table 2, the
152 Zn–Nim distances are significantly longer than the Zn–Npz distances. The numbers of parameters
153 refined and other details regarding the refinement of the crystal structures of complexes 1 and 2 are
154 gathered in Table 3.

155 Extended Structures of the Complexes [ZnCl₂(L)] (L5L1 (1), L5L2 (2)) In compound 1, the molecular
156 units are further linked with 2 equivalent units (Fig. 4) through intermolecular hydrogen bond bridges
157 (RC–H...Cl^{1/2}; 2.913(2) Å; angle of C–H...Cl bond^{1/4} 166.96(3)°) to form undulating mono-
158 dimensional chains (Fig. 4a) along the a-axis leading to intermolecular Zn...Zn distances of
159 7.809(2) Å (1/2 x, y, z). Furthermore, complex 1 shows the cooperative intermolecular interaction C–
160 H...Cl between adjacent chains in the c-axis (RC–H...Cl^{1/2}; 2.819(2) Å; angle of C–H...Cl
161 bond^{1/4} 150.78(2)°; x, 1/2 y, 1/2 z) (Fig. 4b, c) and p intermolecular interaction between C9–H9B
162 and the pyrazole ring (RC–H...Cl^{1/2}; 2.790(2) Å; angle of C–H...Cl bond^{1/4} 156.66(2)°; –x, –y,
163 –z). All the intermolecular interactions together stabilise the 3D supramolecular network (Fig. 5).
164 Moreover, it is interesting to find that all the methyl groups are located on the external parts of the layer,
165 generating important hydrophobic interactions (Fig. 5). Among the non-covalent interactions,
166 hydrophobic interactions, usually existing among alkyl chains of biological macromolecules, are
167 difficult to be observed from a crystallographic perspective. [20]

168 The two independent (not symmetrically related) molecules of 2 are alternately packed forming chains
169 along the direction [010]. Inside these chains, the molecules are linked by hydrogen bonding between
170 the oxygen atoms of two water molecules and the four chloride atoms of the complexes (Fig. 6, Table
171 4). Furthermore, these chains are connected by weak interactions C–H...Cl between molecules
172 related by symmetry of the neighbouring chains. Additionally, p–p interactions can be observed between
173 pyrazole rings of the two alternated molecules along the [100] direction (Fig. 7).
174

175 **CONCLUSIONS**

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177 We have presented the reactivity of the new ligands 3-imino-3,5-dimethylpyrazole (L1 and L2) towards
178 ZnCl₂. The study of the coordination of these ligands to ZnII has revealed the formation of molecular
179 complexes [ZnCl₂(L)] (L^{1/4}L1 (1) and L2 (2)). NMR studies have shown to be very useful in the
180 determination of the configuration of ligands in these complexes in solution; also, the single-crystal X-
181 ray diffraction method has allowed confirmation of the structures in solid state. Finally, we have studied
182 the 3D supramolecular structure through different intra- and intermolecular contacts leading to an easy
183 approach to obtain supramolecular crystal structures with different bonding properties of the
184 heteroatoms (N-pyrazole vs N-imine) present in the structure of the ligands.

185

186 **EXPERIMENTAL**

187

188 General Details

189 The reactions were carried out under nitrogen atmosphere using vacuum line and Schlenk techniques.
190 All reagents were of commercial grade and used without further purification. All solvents were dried
191 and distilled by standard methods.

192 Elemental analyses (C, H, N) were carried out by the staff of Chemical Analyses Service of the
193 Universitat Autònoma de Barcelona on a Euro Vector 3100 instrument. Conductivity measurements
194 were performed at room temperature (r.t.) in 10⁻³M methanol solution, employing a Ciber-Scan CON
195 500 (Euthech Instruments) conductometre. IR spectra were run on a Perkin–Elmer FT
196 spectrophotometer, series 2000 as NaCl disks in the range of 4000–100 cm⁻¹, and also recorded at the
197 Chemical Analysis Service of the Universitat Autònoma de Barcelona on a Tensor 27 (Bruker)
198 spectrometer, equipped with an attenuated total reflectance (ATR) accessory model MKII Golden Gate
199 with diamond window in the range of 4000–600 cm⁻¹. ¹H NMR, ¹³C{¹H} NMR, COSY, HMQC,
200 and NOESY spectra were recorded on a NMR-FT Bruker 250MHz spectrometer in CDCl₃ solution at
201 room temperature. All chemical shifts values (δ) are given in ppm relative to TMS as internal standard.

202 Mass spectra were obtained on an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics. 3-
203 (3,5-Dimethyl-1H-pyrazol-1-yl)propanal was synthesised according to published methods.[13]
204 Synthesis of 3-(3,5-Dimethyl-1H-pyrazol-1-yl)propanal Acrolein (C₃H₄O; 0.07 mol, 5 mL) was added
205 to 3,5-dimethylpyrazole (0.05 mol, 4.85 g) dissolved in 40mL of dry dioxane
206 This solution was placed in a water bath at 40°C for 24 h. After the reaction concluded, the solvent was
207 removed under vacuum. The product was purified by flash chromatography (silica gel 60A^o) with a
208 mixture of ethyl acetate/dichloromethane (1 : 1) (RF_{0.3}) as eluent, generating a yellow oil (5.78 g, 76
209 %). ν_{max} (NaCl)/cm⁻¹ 3082 (n(C–H)_{ar}), 2921 (n(C–H)_{al}), 1720 (n(C=O)), 1553 (n(C=C)),
210 n(C=N))_{pz}, 1461 (δ(C=C), δ(C=N))_{pz}, 1423 (δ(CH₃)_{as}), 1387 (δ(CH₃)_s), 1021 (δ(C–H)_{ip}), 779
211 (δ(C–H)_{oop}). δ_{H} (CDCl₃, 250 Mz) 9.78 (1H, t, 3J 0.9, NpzCH₂CH₂CHO), 5.73 (1H, s, CH_{pz}), 4.22
212 (2H, t, 3J 6.6, NpzCH₂CH₂CHO), 3.02 (td, 2H, 3J 6.6, 0.9, NpzCH₂CH₂CHO), 2.24, 2.16 (3H, s,
213 CH₃(pz)). ¹³C{¹H} NMR (CDCl₃, 63 MHz) 199.9 (NpzCH₂CH₂CHO), 147.9, 139.2 (CCH₃), 105.1
214 (CH (pz)), 43.8 (NpzCH₂CH₂CHO), 41.4 (NpzCH₂CH₂CHO), 13.6, 11.1 (CCH₃). *m/z* (ESI⁺) 175
215 (100 %, C₈H₁₂N₂O + Na⁺). Anal. Calc. for C₈H₁₂N₂O · 0.5H₂O (161.2): C 59.61, H 8.12, N 17.38.
216 Found: C 59.22, H 8.21, N 17.69 %.

217 Synthesis of N-[3-(3,5-Dimethyl-1H-pyrazol-1-yl)propylidene]ethylamine (L1) and N-[3-(3,5-
218 Dimethyl-1Hpyrazol- 1-yl)propylidene]propylamine (L2) The synthesis consists of the reaction between
219 3-(3,5-dimethyl- 1H-pyrazol-1-yl)propanal (10 mmol, 1.52 g) in CH₂Cl₂ (7.5 mL) and 10 mmol of the
220 appropriate amine (L1: ethylamine 70 %, 0.80 mmol or L2: propylamine 99 %, 0.83 mmol) in water (7.5
221 mL). The mixture was stirred at room temperature for 3 h and extracted three times with 5mL of
222 CH₂Cl₂. The organic phase was collected and dried overnight with anhydrous Na₂SO₄. The solution

223 was filtered off and the solvent was removed under vacuum. The L1 and L2 ligands were obtained as
224 white solids.

225 L1: Yield: 1.11 g (62 %), mp 40–428C. $n_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3121 ($n(\text{C-H})_{\text{ar}}$), 2967, 2928, 2869 ($n(\text{C-}$
226 $\text{H})_{\text{al}}$), 1667 ($n(\text{C}^{1/4}\text{Nim})$), 1553 ($n(\text{C}^{1/4}\text{C})$, $n(\text{C}^{1/4}\text{N})$)pz, 1461 ($d(\text{C}^{1/4}\text{C})$, $d(\text{C}^{1/4}\text{N})$)pz, 1423 ($d(\text{CH}_3)_{\text{as}}$),
227 1384 ($d(\text{CH}_3)_{\text{s}}$), 1022 ($d(\text{C-H})_{\text{ip}}$), 773 ($d(\text{C-H})_{\text{oop}}$). d_{H} (CDCl_3 , 250 MHz) 7.65 (1H, t, 3J 4.1,
228 $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 5.72 (1H, s, CHpz), 4.17 (2H, t, 3J 7.3, $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 3.30 (2H, q,
229 3J 7.4, $\text{NimCH}_2\text{CH}_3$), 2.69 (td, 2H, 3J 7.3, 3J 4.1, $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 2.19, 2.17 (3H, s, $\text{CH}_3(\text{pz})$),
230 1.13 (3H, t, 3J 7.4, $\text{NimCH}_2\text{CH}_3$). d_{C} (CDCl_3 , 63 MHz) 160.7 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 147.6, 138.9
231 (CCH₃), 105.1 (CH (pz)), 55.7 ($\text{NimCH}_2\text{CH}_3$), 45.3 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 36.3
232 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 16.2 ($\text{NimCH}_2\text{CH}_3$), 13.7, 11.2 (CCH₃). m/z (ESI $^+$) 202 (100 %, L1 $^+$ Na
233 $^+$). Anal. Calc. for $\text{C}_{10}\text{H}_{17}\text{N}_3 \cdot 0.5\text{H}_2\text{O}$ (188.3): C 63.80, H 9.64, N 22.32. Found: C 63.58, H 9.37, N
234 21.93 %.

235 L2: Yield: 1.83 g (95%), mp 45–478C. $n_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3121 ($n(\text{C-H})_{\text{ar}}$), 2958, 2928, 2873 ($n(\text{C-})_{\text{al}}$),
236 1667 ($n(\text{C}^{1/4}\text{Nim})$), 1553 ($n(\text{C}^{1/4}\text{C})$, $n(\text{C}^{1/4}\text{N})$)pz, 1461 ($d(\text{C}^{1/4}\text{C})$, $d(\text{C}^{1/4}\text{N})$)pz, 1423 ($d(\text{CH}_3)_{\text{as}}$), 1384
237 ($d(\text{CH}_3)_{\text{s}}$), 1022 ($d(\text{C-H})_{\text{ip}}$), 773 ($d(\text{C-H})_{\text{oop}}$). d_{H} (CDCl_3 , 250MHz) 7.65 (1H, t, 3J 4.1,
238 $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 5.74 (s, 1H, CHpz), 4.18 (t, 2H, 3J 7.1, $\text{NimCH}_2\text{CH}_2\text{CH}_3$), 3.31 (td, 2H, 3J
239 6.9, 4J 0.9, $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 2.72 (2H, td, 3J 6.9, 3J 4.1, $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 2.21, 2.18
240 (3H, s, $\text{CH}_3(\text{pz})$), 1.57 (2H, sx, 3J 7.1, $\text{NimCH}_2\text{CH}_2\text{CH}_3$), 0.84 (3H, t, 3J 7.1, $\text{NimCH}_2\text{CH}_2\text{CH}_3$). d_{C}
241 (CDCl_3 , 63MHz) 161.1 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 147.5, 138.9 (CCH₃), 105.0 (CH(pz)), 63.4
242 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 45.2 ($\text{NimCH}_2\text{CH}_2\text{CH}_3$), 36.3 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 23.9
243 ($\text{NimCH}_2\text{CH}_2\text{CH}_3$), 13.6, 11.7 (CCH₃), 11.1 ($\text{NimCH}_2\text{CH}_2\text{CH}_3$). m/z (ESI $^+$) 225 (100%, L2 $^+$ Nap).
244 Anal. Calc. for $\text{C}_{11}\text{H}_{19}\text{N}_3 \cdot 0.5\text{H}_2\text{O}$ (202.3): C 65.29, H 9.98, N 20.77. Found: C 65.52, H 9.79, N
245 20.58%.

246 Synthesis of the Complexes $[\text{ZnCl}_2(\text{L})]$ (L5L1 (1); L2 (2))

247 A solution of 2.0 mmol of the corresponding ligand (L1: 0.38 g; L2: 0.40 g) dissolved in 20mL of
248 absolute ethanol was added to a solution of 2.0 mmol (0.28 g) of ZnCl_2 and 4mL of triethyl
249 orthoformate (for dehydration purposes) in 10mL of the same solvent. The mixture was stirred for 18 h.
250 The solution was reduced to 5mL and the precipitate appeared. The solid was filtered, washed with 5mL
251 of diethyl ether, and recrystallized with dichloromethane.

252 1: Yield: 0.25 g (39 %). Conductivity (2.4×10^{-3} Min methanol): $59 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. $n_{\text{max}}(\text{neat})/\text{cm}^{-1}$
253 3020 ($n(\text{C-H})_{\text{ar}}$), 2973, 2922 ($n(\text{C-H})_{\text{al}}$), 1666 ($n(\text{C}^{1/4}\text{Nim})$), 1554 ($n(\text{C}^{1/4}\text{C})$, $n(\text{C}^{1/4}\text{N})$)pz, ($d(\text{C}^{1/4}\text{C})$),
254 1469 ($d(\text{C}^{1/4}\text{N})$)pz, 1449 ($d(\text{CH}_3)_{\text{as}}$), 1392, 1381 ($d(\text{CH}_3)_{\text{s}}$), 1057 ($d(\text{C-H})_{\text{ip}}$), 802 ($d(\text{C-H})_{\text{oop}}$). d_{H}
255 (CDCl_3 , 250 MHz) 7.95 (1H, br, $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 5.94 (1H, s, CHpz), 4.84 (2H, m,
256 $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 3.93 (2H, q, 3J 7.4, $\text{NimCH}_2\text{CH}_3$), 2.94 (2H, m, $\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$),
257 2.49, 2.28 (3H, s, $\text{CH}_3(\text{pz})$), 1.43 (3H, t, 3J 7.4, $\text{NimCH}_2\text{CH}_3$). d_{C} (CDCl_3 , 63 MHz) 169.5
258 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 151.6, 141.6 (CCH₃), 107.6 (CH(pz)), 57.7 ($\text{NimCH}_2\text{CH}_3$), 41.8 (NpzCH_2
259 $\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 35.7 ($\text{NpzCH}_2\text{CH}_2\text{CH}^{1/4}\text{Nim}$), 16.1 ($\text{NimCH}_2\text{CH}_3$), 13.7, 11.3 (CCH₃). m/z (ESI $^+$)

260 278 (69%, ZnCl(L1)β), 218 (100 %, ZnCl2(L1)-3,5-Me2pz). Anal. Calc. C10H17Cl2N3Zn (315.6): C
261 38.06, H 5.43, N 13.32. Found: C 38.13, H 5.45, N 13.30%.

262 2. Yield: 0.30 g (46 %). Conductivity (2.5 × 10⁻³ M in methanol): 61 Ω⁻¹ cm² mol⁻¹. n_{max} (neat)/cm
263 1 3032 (n(C–H)ar), 2966, 2932 (n(C–H)al), 1664 (n(C¹/₄Nim)), 1551 (n(C¹/₄C), n(C¹/₄N))pz, 1468
264 (d(C¹/₄C), d(C¹/₄N))pz, 1449 (d(CH₃)as), 1384 (d(CH₃)s), 1055 (d(C–H)ip), 794 (d(C–H)oop). dH
265 (CDCl₃, 250 MHz) 7.95 (1H, br, NpzCH₂CH₂CH¹/₄Nim), 5.94 (1H, s, CHpz), 4.86 (2H, m,
266 NimCH₂CH₂CH₃), 3.93 (2H, t, 3J 7.3, NpzCH₂CH₂CH¹/₄Nim), 2.93 (2H, m, NpzCH₂CH₂CH¹/₄Nim),
267 2.50, 2.28 (3H, s, CH₃(pz)), 1.92 (2H, td, 3J 7.4, 3J 5.3, NimCH₂CH₂CH₃), 0.94 (3H, t, 3J 7.4,
268 NimCH₂CH₂CH₃). dC (CDCl₃, 63 MHz) 169.7 (NpzCH₂CH₂CH¹/₄Nim), 152.0, 141.7 (CCH₃), 107.8
269 (CH(pz)), 65.4 (NpzCH₂CH₂CH¹/₄Nim), 42.1 (NimCH₂CH₂CH₃), 35.8 (NpzCH₂CH₂CH¹/₄Nim), 23.8
270 (NimCH₂CH₂CH₃), 13.9, 11.9 (CCH₃), 11.6 (NimCH₂CH₂CH₃). m/z (ESI β) 292 (100 %, ZnCl(L2)
271 β). Anal. Calc. for C11H19Cl2N3Zn (329.6): C 40.09, H 5.81, N 12.75. Found: C 40.11, H 5.92, N
272 12.82 %.

273 X-Ray Crystal Structures for Compounds 1 and 2

274 Tests with several solvents were conducted, but it was not possible to obtain single crystals of suitable
275 quality. Although with some indications of being slightly twinned in the case of compound 2,
276 eventually, crystals of compounds 1 and 2 were selected through recrystallisation from CH₂Cl₂ and
277 diethyl ether mixture.

278 Data for 1 and 2 were collected on a MAR 345 diffractometer with an image plate detector. Unit cell
279 parameters were determined from 890 reflections for compound 1 and 121 reflections for 2 (38,y,318),
280 and refined by least-squares method. Intensities were collected with graphite monochromatised MoKα
281 radiation using ω/2θ scan technique. For 1, 12674 reflections were measured in the range of
282 2.318°–32.358°; 4152 of which were non-equivalent by symmetry (R_{int} (on I)¹/₄0.082). Lorentz
283 polarisation and absorption corrections were made; and 2598 reflections were assumed as observed by
284 applying the condition I ≥ 2σ(I). For 2, 26213 reflections were measured in the range of 1.768°–32.408°;
285 9183 of which were non-equivalent by symmetry (R_{int} (on I)¹/₄0.064); and 4616 reflections were
286 assumed as observed by applying the condition I ≥ 2σ(I).

287 Both structures were solved by direct methods using SHELXS computer program (SHELXS-97) and
288 refined by full matrix least-squares method with SHELXL-97 computer program using 12674
289 reflections for 1 and 987 for 2. For 1, the minimised function was $\sum w ||F_o|^2 - |F_c|^2|^2$, where $w = 1/[s^2(I) +$
290 $(0.00449P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. For 2, the minimised
291 function was $\sum w ||F_o|^2 - |F_c|^2|^2$, where $w = 1/[s^2(I) + (0.00488P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. The H atoms
292 were included in the calculated position and constrained for compound 1, and mixed for compound
293 2.[21] The final R(F) factor and Rw(F₂) values as well as the number of parameters refined and other
294 details regarding the refinement of the crystal structures are gathered in Table 3.

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299 **ACKNOWLEDGEMENTS**

300

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303

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- 417 .

418 **Legends to figures**

419

420 **Figure 1.** 250MHz ¹H NMR data obtained at 298K and the simulated g NMR spectra for the H8 and H9
421 protons of the Npz-CH₂-CH₂-CH_{1/4}Nim fragment of [ZnCl₂(L1)] (1).

422

423 **Figure 2.** ORTEP drawing of [ZnCl₂(L1)] (1), showing all non-hydrogen atoms and the atom
424 numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

425

426 **Figure 3.** ORTEP drawing of [ZnCl₂(L2)] (2), showing all non-hydrogen atoms and the atom
427 numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

428

429 **Figure 4.** (Views of 1- and 2D layered supramolecular architectures of [ZnCl₂(L1)] (1) along the a-
430 direction, generated by C–H⋯Cl intermolecular interactions..

431

432 **Figure 5.** View of 3D supramolecular architecture of [ZnCl₂(L1)] (1).

433

434 **Figure 6.** Views of 1D supramolecular chain of [ZnCl₂(L2)] (2) along the [010] direction, generated by
435 O–H⋯Cl intermolecular interactions.

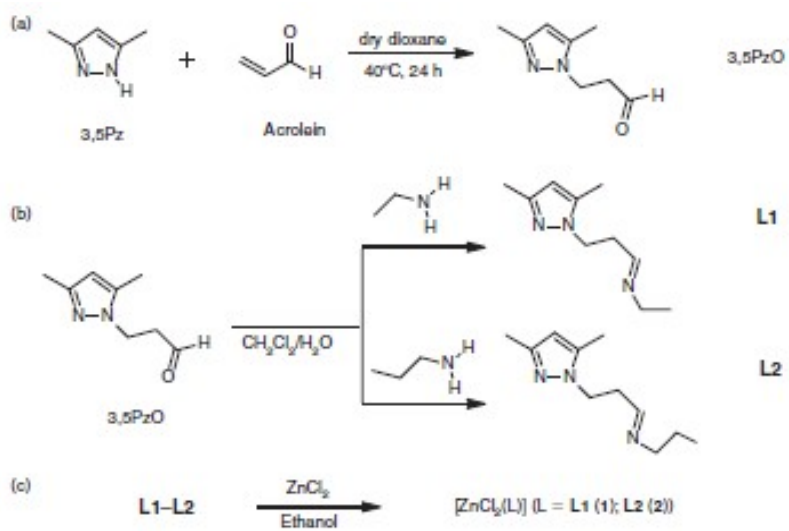
436

437 **Figure 7.** View of p–p intermolecular interaction between adjacent pyrazole rings of [ZnCl₂(L2)] (2).

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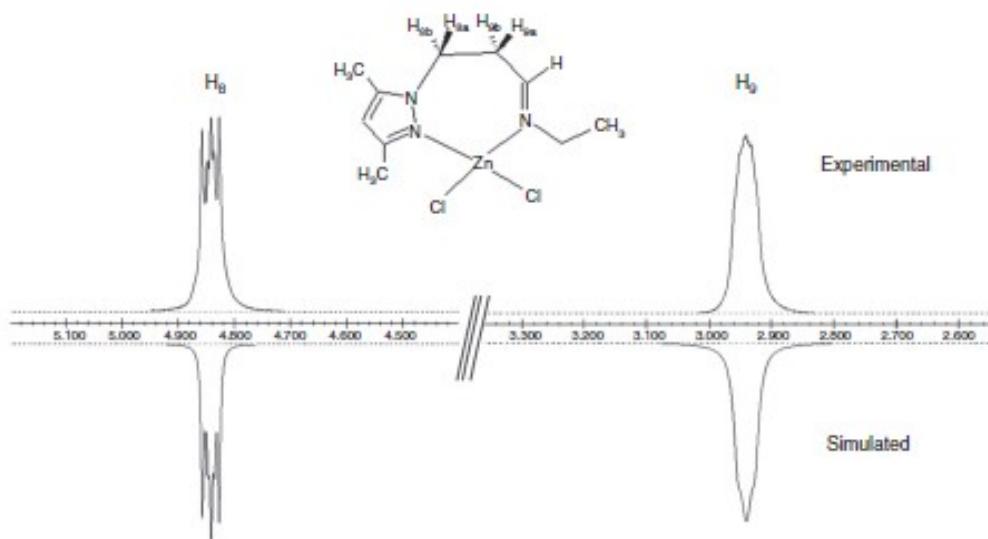
SCHEME 1.



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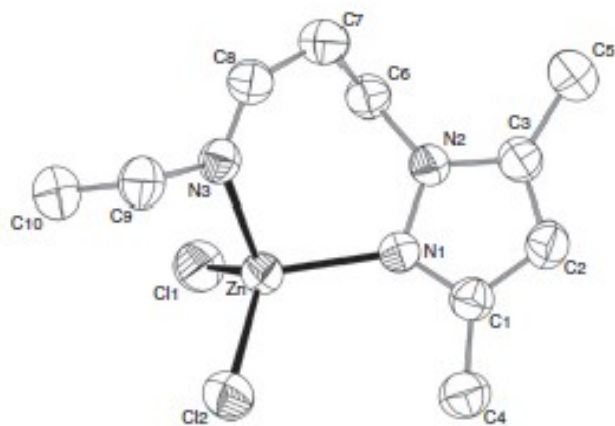
FIGURE 1.



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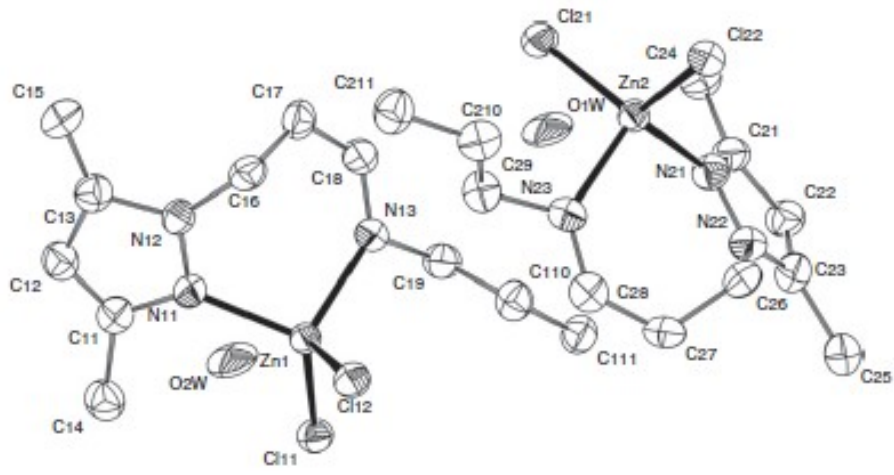
FIGURE 2.



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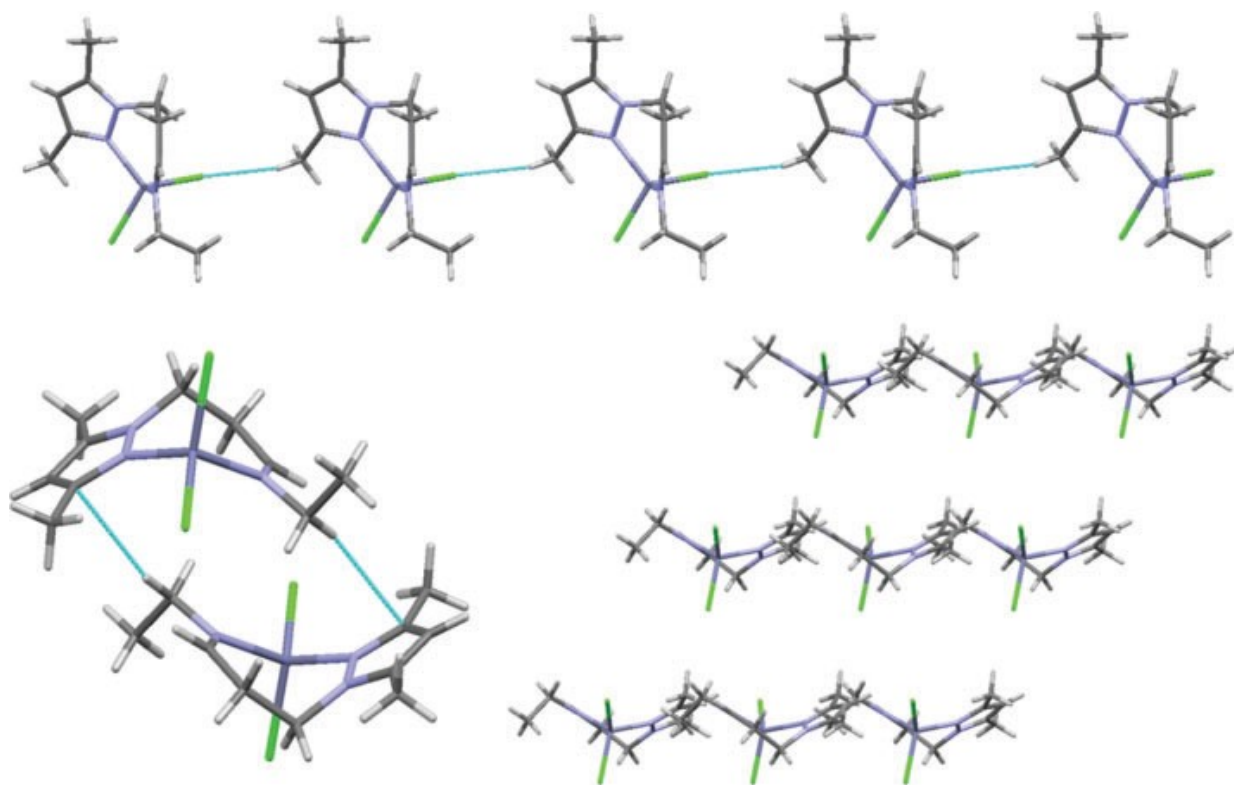
FIGURE 3.



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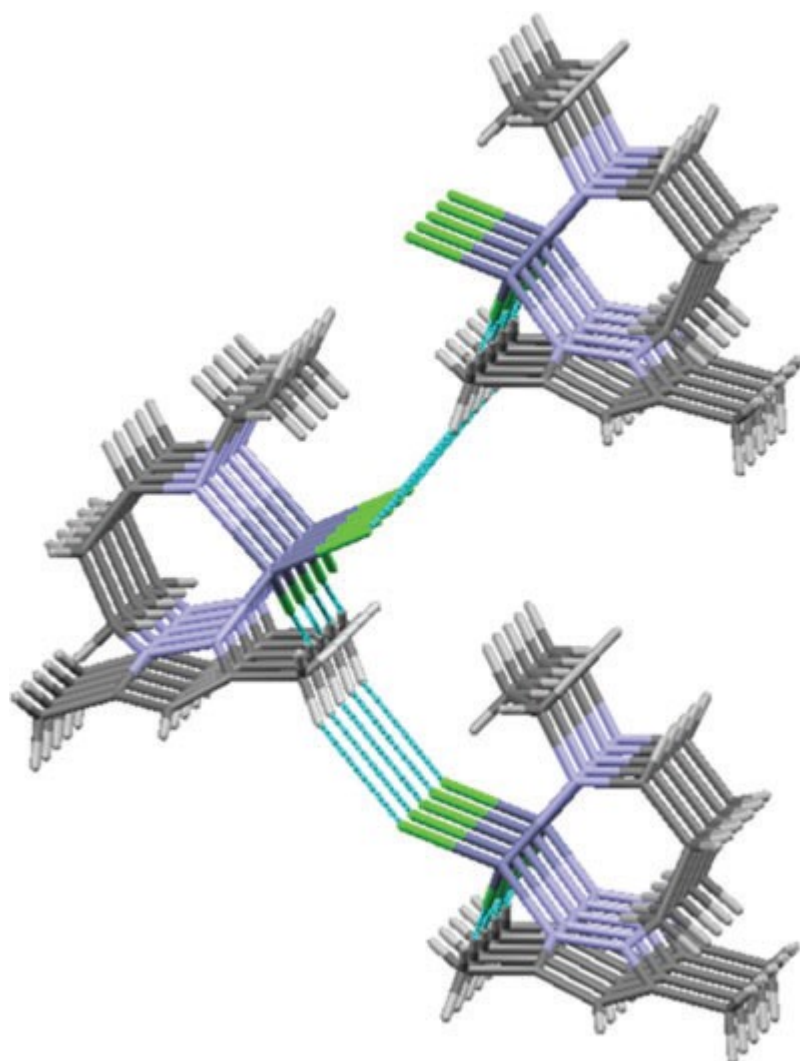
FIGURE 4.



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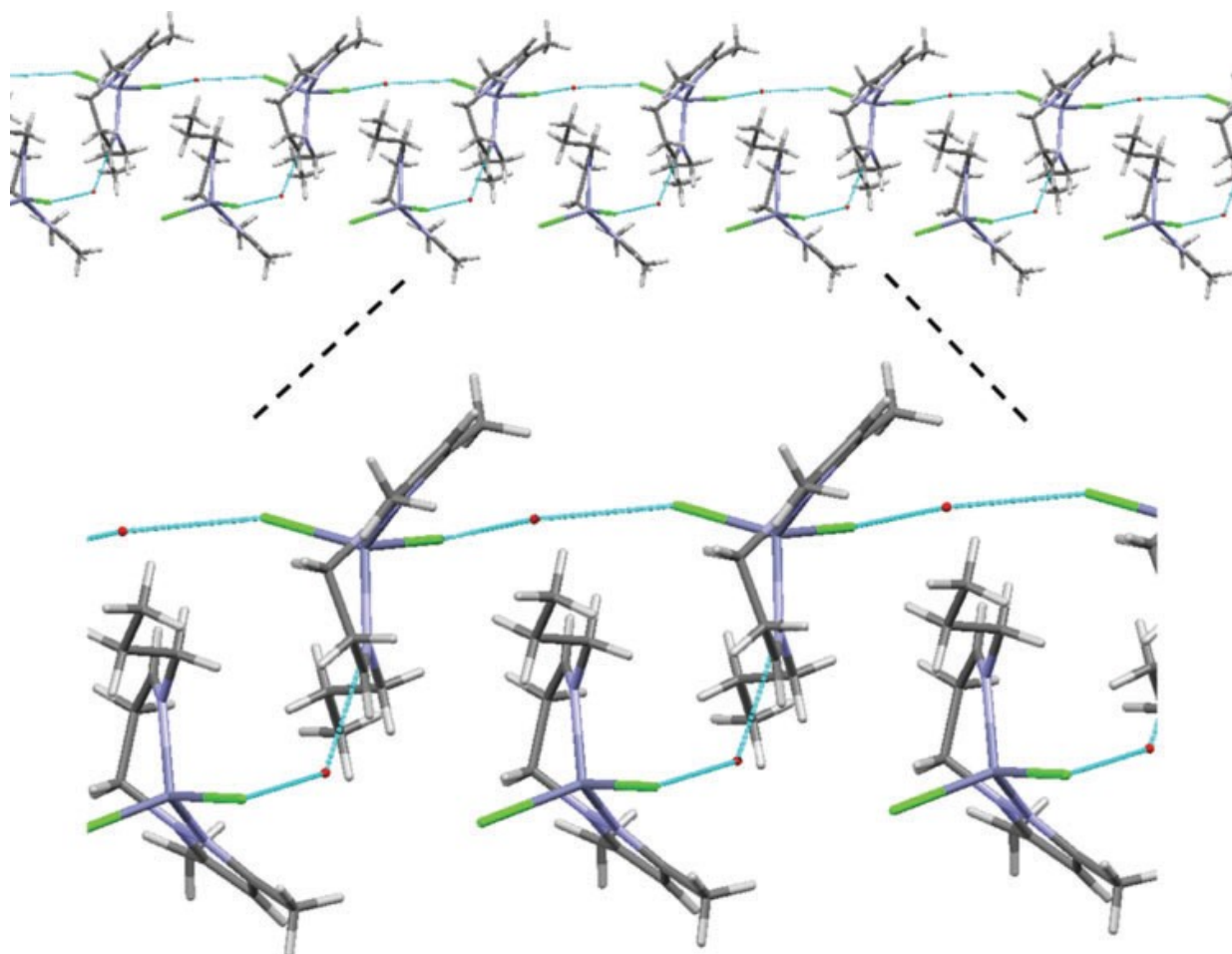
FIGURE 5.



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FIGURE 6

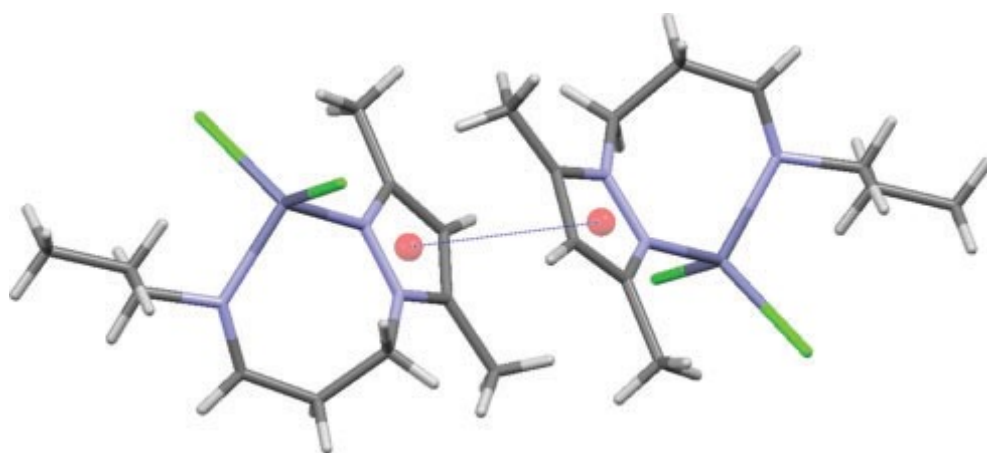


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FIGURE 7

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480 **Table 1.** ¹H NMR results: Chemical shifts (δ) and 1H, 1H coupling constants (J) for 1 and 2 measured
481 in CDCl₃ at 298K
482

Compound	1	2
δ CH ₂ (8) [ppm]	4.84	4.86
δ CH ₂ (9) [ppm]	2.94	2.93
² J _{8a,9a} [Hz]	-12.5	-12.3
² J _{9a,9b} [Hz]	-12.5	-12.3
³ J _{8a,9a} [Hz]; ³ J _{9a,9b} [Hz]	7.18; 3.02	7.20; 3.10
³ J _{8a,9b} [Hz]; ³ J _{9b,9a} [Hz]	7.18; 3.02	7.20; 3.10

483

484

485 **Table 2.** Selected bond lengths [\AA] and bond angles [8] for 1 and 2

486

1			
Zn-N(1)	2.031(2)		
Zn-N3	2.099(3)		
Zn-Cl1	2.231(2)		
Zn-Cl2	2.2356(14)		
N1-Zn-N3	100.53(10)		
N1-Zn-Cl1	113.56(8)		
N3-Zn-Cl1	108.72(8)		
N1-Zn-Cl2	111.02(8)		
N3-Zn-Cl2	107.30(9)		
Cl1-Zn-Cl2	114.54(5)		

2			
Zn1-N11	2.028(4)	Zn2-N21	2.070(4)
Zn1-N13	2.074(4)	Zn2-N23	2.067(5)
Zn1-Cl11	2.243(2)	Zn2-Cl21	2.227(2)
Zn1-Cl12	2.275(2)	Zn2-Cl22	2.184(2)
N11-Zn1-N13	100.96(18)	N21-Zn2-N23	102.3(2)
N11-Zn1-Cl11	112.20(14)	N21-Zn2-Cl21	108.74(14)
N13-Zn1-Cl11	108.38(13)	N23-Zn2-Cl21	103.83(15)
N11-Zn1-Cl12	110.44(13)	N21-Zn2-Cl22	111.63(14)
N13-Zn1-Cl12	109.49(13)	N23-Zn2-Cl22	109.57(14)
Cl11-Zn1-Cl12	114.46(7)	Cl21-Zn2-Cl22	119.19(7)

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489 **Table 3.** Crystallographic data for compounds 1 and 2

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	1	2
Formula	C ₁₀ H ₁₇ Cl ₂ N ₃ Zn	C ₂₂ H ₄₀ Cl ₄ N ₆ OZn ₂
Formula weight	315.53	677.14
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
System, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Orthorhombic, <i>Pna</i> 2 ₁
Unit cell dimensions		
<i>a</i> [Å]	8.596(6)	23.177(10)
<i>b</i> [Å]	14.933(7)	8.481(5)
<i>c</i> [Å]	12.869(7)	15.229(5)
β [°]	121.95(4)	90
<i>V</i> [Å ³]	1495.7(15)	2993(2)
<i>Z</i>	4	4
<i>D</i> _c [g cm ⁻³]	1.500	1.502
μ [mm ⁻¹]	2.112	1.986
<i>F</i> (000)	652	1400
Crystal size [mm ³]	0.2 × 0.09 × 0.08	0.2 × 0.1 × 0.1
<i>h</i> , <i>k</i> , <i>l</i> ranges	-12 ≤ <i>h</i> ≤ 12, -22 ≤ <i>k</i> ≤ 20, -17 ≤ <i>l</i> ≤ 17	-34 ≤ <i>h</i> ≤ 34, -12 ≤ <i>k</i> ≤ 12, -22 ≤ <i>l</i> ≤ 20
2 θ range [°]	2.311 to 32.351	1.757 to 32.401
Reflections collected/unique/ (<i>R</i> _{int})	12674/4152 (<i>R</i> _{int} = 0.0827)	26213/9183 (<i>R</i> _{int} = 0.0646)
Completeness to θ [%]	94.6	99.3
Absorption correction	Empirical	Empirical
Max. and Min. transmission	0.5 and 0.5	0.82 and 0.79
Data/restraints/parameters	4152/2/145	9183/28/334
Goodness-of-fit on <i>F</i> ²	1.158	0.835
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0555, <i>wR</i> ₂ = 0.1167	<i>R</i> ₁ = 0.0477, <i>wR</i> ₂ = 0.0862
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1014, <i>wR</i> ₂ = 0.1307	<i>R</i> ₁ = 0.1244, <i>wR</i> ₂ = 0.1022
Largest difference peak and hole [e Å ⁻³]	+0.459, -0.362	+0.975, -0.597

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493 **Table 4.** Supramolecular interactions C–H...X (X=Cl or C) parameters for complexes 1 and 2
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Complex	D–H...A	H...A [Å]	D...A [Å]	D–H...A [°]
1 (L1)	C4–H4B...Cl2C4–	2.819,	3.688,	150.78,
	H4C...Cl1	2.913	3.755	166.96
2 (L2)	C9–H9B...pz ring	2.835	3.800	133.33
	Cl2...H–O1–H...	2.633,	3.071,	122.11,
	Cl2Cl11...	2.323	3.372	121.64
	H–O2–H...Cl12			

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