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

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ABSTRACT:
The present report is on the synthesis of two new 3-imine-3,5-dimethylpyrazole ligands, N-[3-(3,5-dimethyl-1H-pyrazol-1-yl)propylidene]ethylamine (L1) and N-[3-(3,5-dimethyl-1H-pyrazol-1-yl)propylidene]propylamine (L2). These ligands form molecular complexes with the formula [ZnCl2(L)] (L¼L1 (1) and L2 (2)) when reacting with ZnCl2 in a metal (M)/ligand (L) ratio of 1 : 1. These new ZnII complexes have been characterised by elemental analyses, conductivity measurements, mass spectrometry, and infrared, 1H and 13C{1H} NMR spectroscopy techniques. The two crystalline structures of complexes 1 and 2 have been solved by X-ray diffraction methods. Finally, we have studied the self-assembly three-dimensional supramolecular structure through different intra- and intermolecular contacts. The application of these ZnII complexes in supramolecular crystal engineering is interesting due to (1) the easy preparation and the high efficiency of this system and (2) the different bonding properties of the heteroatoms (N-pyrazole vs N-imine) present in the structure of the ligands.
INTRODUCTION

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

In the recent past years, our research group has focussed its interest on the synthesis and characterisation of heterotopic ligands containing a N-pyrazole group with other donor group such as P-phosphine (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]

As an extension to these results, in the present paper, we report the synthesis of new pyrazole-derived ligands with an imine group: N-[3-(3,5-dimethyl-1H-pyrazol-1-yl)propyldiene] ethylamine (L1) and N-[3-(3,5-dimethyl-1H-pyrazol-1-yl) propyldiene]propylamine (L2). The L1 and L2 ligands contain one nitrogen pyrazole and one imine nitrogen as potential N-donor atoms (Scheme 1). We also describe the study of their reactivity with ZnII, isolating complexes [ZnCl2(L)] (L¼L1 (1) and L2 (2)). Complete characterisation of L1 and L2 and their ZnII complexes are reported, focusing on NMR studies discussion, crystallographic structures, and self-assembly three-dimensional (3D) arrangements.
RESULTS AND DISCUSSION

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

Elemental analyses, mass spectrometry, and all spectroscopic data for L1 and L2 are consistent with the proposed formulae. The positive ionisation spectra (ESIþ –MS; electrospray ionisation mass spectroscopy) of L1 and L2 ligands measured in acetonitrile display a peak attributable to [LþNa] þ (L¼L1, L2). In the IR spectra of the two ligands, the characteristic absorptions measured using NaCl pellets observed at 1667 cm–1 are attributed to n(C¼Nim) (L1, L2), 1553 cm–1 are attributed to the pyrazolyl group [n(C¼C), n(C¼N)]pz (L1, L2), and 773 cm–1 are attributed to d(C–H)oop (L1, L2), confirming the presence of the imine group in the structure of the ligand.

The NMR spectra were recorded in CDCl3 for the ligands. In the 1H NMR spectra, characteristic signals appear at 5.72 ppm (L1) and 5.74 ppm (L2), attributable to CHpz. Other signals are attributed to NpzCH2CH2CH¼Nim that appear at 7.65 ppm (L1, L2). In the 13C{1H} NMR, the most important signals appear at 105.1 ppm (L1) and 105.0 ppm (L2), which correspond to CHpz, and 160.7 ppm (L1) and 161.1 ppm (L2), attributable to NpzCH2CH2CH¼Nim.

Synthesis and Characterisation of the Complexes Complexes [ZnCl2(L)] (L¼L1 (1) and L2 (2)) were obtained by treatment of the corresponding ligand (Scheme 1c) with ZnCl2 in a 1 : 1 or 1 : 2 metal (M)/ligand (L) molar ratio in absolute ethanol for 24 h. Interestingly, stoichiometry of the complexes does not depend of the M/L molar ratio. Several techniques were used for the characterisation of all complexes: elemental analyses, mass spectrometry, conductivity measurements, and IR, and one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy techniques. In addition, a full 3D structure determination for compounds 1 and 2 was performed through single-crystal X-ray diffraction method.

The elemental analyses for compounds 1 and 2 are consistent with the formula [ZnCl2(L)]. The positive ionisation spectra (ESIþ –MS), in acetonitrile, of compounds 1 and 2 give a peak attributable to [ZnCl(L)] þ (L¼L1 (1), L2 (2)). The spectrum of complex 1 also shows another peak at m/z 218 (100 %), corresponding to [ZnCl2(L1)-3,5-Me2pz]. Molecular peaks of the cations are observed with the same isotope distribution as the theoretical ones. Moreover, conductivity values in methanol for
complexes 1 and 2 are in agreement with the presence of non-electrolyte compounds because reported values (59 O 1 cm\(^2\) mol\(^{-1}\) (1) and 61 O 1 cm\(^2\) mol\(^{-1}\) (2)) are lower than 80 O 1 cm\(^2\) mol\(^{-1}\).\(^{15}\)

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

The 1H, 13C\(^{1}\)H NMR, DEPT, COSY, HMQC, and NOESY spectra were recorded in CDCl\(_3\) for the two complexes are discussed. 1H and 13C\(^{1}\)H NMR spectra were consistent with the proposed formulation and showed the coordination of the ligands (L\(_1\) and L\(_2\)) to the Zn atom. NMR spectroscopic data are reported in the Experimental section. For compounds 1 and 2, the study of the Npz-CH2-CH2-CH\(_{4}\)Nim fragments as AA0XX0 systems gave a set of coupling constants for each compound. These constants were consistent with the simulated spectra for compounds 1 and 2, obtained with the aid of the gNMR program.\(^{16}\) All these results are reported in Table 1. Fig. 1 shows the experimentally determined and simulated spectra for 1.

In the 1H NMR spectra of 1 and 2 at room temperature, the methylene protons for Npz-CH2-CH2-CH\(_{4}\)Nim chain appear as two bands. One is a well-defined band (doublet of doublet of doublets) at d\(^{\text{H}}\) = 4.84 ppm (1) and 4.86 ppm (2) and other is a broad band at d\(^{\text{H}}\) = 2.94 ppm (1) and 2.93 ppm (2). This suggests that at 298 K, there is a fluxional process in which, with ringflipping, the two hydrogens of each CH2 are interconverted and only one signal can be observed. HMQC spectra were used to assign the signals of protons H-8 and H-9.

As observed from the NOESY spectra, the methyl linked to the pyrazole at d\(^{\text{H}}\) = 2.28 ppm (1) and (2) shows NOE interactions with d\(^{\text{H}}\) = 4.84 ppm (1) and 4.86 ppm (2), but not with the ones at d\(^{\text{H}}\) = 2.94 ppm (1) and 2.93 ppm (2). The other signal is attributable to Npz-CH2-CH2-C\(_{4}\)Nim, which appears at 7.95 ppm in both complexes.

Crystal Structures of the Complexes [ZnCl\(_2\)(L)] (L5L1 (1), L5L2 (2))

For complexes 1 and 2, it has been possible to obtain colourless monocrystals suitable for X-ray analyses through crystallisation from dichloromethane/diethyl ether (1 : 1) mixture. The structures consist of discrete ZnII molecules linked by diverse intermolecular interactions. It is important to mention that complex 2 contains two symmetrically independent molecules and two water solvent molecules in the unit cell. The environment around the ZnII centre in both complexes consists of two chlorine atoms and one ligand L (L\(_1\) (1) or L\(_2\) (2)) coordinated by (Npz, Nim), building a seven-membered metallocycle whose conformation can be described as deformed half chair (Figs 2 and 3, respectively). The ZnII centre adopts a pseudo tetrahedral coordination, where the tetrahedron is somewhat distorted by larger Cl–Zn–Cl, N–Zn–Cl, and N–Zn–N angles in comparison with the
tetrahedral value (Table 2). The values of the angles for complexes 1 and 2 are in agreement with the values reported in the literature for tetrahedral species Npz–Zn–Cl (101.38–122.98), Nim–Zn–Cl (102.98–120.08),[17] and Cl–Zn–Cl (112.08–116.18).[18] The Zn–Npz, Zn–Nim, and Zn–Cl distances in both complexes are in the known range for tetrahedral species: Zn–Npz (1.94–2.17 Å), Zn–Nim (1.98–2.09 Å), and Zn–Cl (2.18–2.37 Å).[17,18]

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

Extended Structures of the Complexes [ZnCl2(L)] (L5L1 (1), L5L2 (2)) In compound 1, the molecular units are further linked with 2 equivalent units (Fig. 4) through intermolecular hydrogen bond bridges (RC–HCl ≈ 2.91(2) Å; angle of C–HCl bond ≈ 166.96(3)°) to form undulating monodimensional chains (Fig. 4a) along the a-axis leading to intermolecular Zn· · · Zn distances of 7.80(2) Å (1 þ x, y, z). Furthermore, complex 1 shows the cooperative intermolecular interaction C–HCl between adjacent chains in the c-axis (RC–HCl ≈ 2.81(2) Å; angle of C–HCl bond ≈ 150.78(2)°) (Fig. 4b, c) and p intermolecular interaction between C9–H9B and the pyrazole ring (RC–HCl ≈ 2.79(2) Å; angle of C–HCl bond ≈ 156.66(2)°; –x, –y, –z). All the intermolecular interactions together stabilise the 3D supramolecular network (Fig. 5). Moreover, it is interesting to find that all the methyl groups are located on the external parts of the layer, generating important hydrophobic interactions (Fig. 5). Among the non-covalent interactions, hydrophobic interactions, usually existing among alkyl chains of biological macromolecules, are difficult to be observed from a crystallographic perspective.[20]

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

We have presented the reactivity of the new ligands 3-imino-3,5-dimethylpyrazole (L1 and L2) towards ZnCl2. The study of the coordination of these ligands to ZnII has revealed the formation of molecular complexes [ZnCl2(L)] (L¼L1 (1) and L2 (2)). NMR studies have shown to be very useful in the determination of the configuration of ligands in these complexes in solution; also, the single-crystal X-ray diffraction method has allowed confirmation of the structures in solid state. Finally, we have studied the 3D supramolecular structure through different intra- and intermolecular contacts leading to an easy approach to obtain supramolecular crystal structures with different bonding properties of the heteroatoms (N-pyrazole vs N-imine) present in the structure of the ligands.
EXPERIMENTAL

General Details

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

Elemental analyses (C, H, N) were carried out by the staff of Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Euro Vector 3100 instrument. Conductivity measurements were performed at room temperature (r.t.) in 10⁻³ M methanol solution, employing a Ciber-Scan CON 500 (Euthech Instruments) conductometer. IR spectra were run on a Perkin–Elmer FT spectrophotometer, series 2000 as NaCl disks in the range of 4000–1000 cm⁻¹, and also recorded at the Chemical Analysis Service of the Universitat Autònoma de Barcelona on a Tensor 27 (Bruker) spectrometer, equipped with an attenuated total reflectance (ATR) accessory model MKII Golden Gate with diamond window in the range of 4000–600 cm⁻¹. 1H NMR, 13C{¹H} NMR, COSY, HMQC, and NOESY spectra were recorded on a NMR-FT Bruker 250MHz spectrometer in CDCl₃ solution at room temperature. All chemical shifts values (δ) are given in ppm relative to TMS as internal standard.

Mass spectra were obtained on an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics. 3-(3,5-Dimethyl-1H-pyrazol-1-yl)propanal was synthesised according to published methods.[13]

Synthesis of 3-(3,5-Dimethyl-1H-pyrazol-1-yl)propanal Acrolein (C₃H₄O; 0.07 mol, 5 mL) was added to 3,5-dimethylpyrazole (0.05 mol, 4.85 g) dissolved in 40 mL of dry dioxane. This solution was placed in a water bath at 40°C for 24 h. After the reaction concluded, the solvent was removed under vacuum. The product was purified by flash chromatography (silica gel 60A°) with a mixture of ethyl acetate/dichloromethane (1:1) (RF¼0.3) as eluent, generating a yellow oil (5.78 g, 76%).

nmax (NaCl)/cm⁻¹ 3082 (n(C–H)ar), 2921 (n(C–H)al), 1720 (n(C=O)), 1553 (n(C=C), n(C=N))pz, 1461 (d(C=C), d(C=N))pz, 1423 (d(CH₃)as), 1387 (d(CH₃)s), 1021 (d(C–H)ip), 779 (d(C–H)oop). δH (CDCl₃, 250 MHz) 9.78 (1H, t, 3J 0.9, NpzCH₂CH₂CHO), 5.73 (1H, s, CHpz), 4.22 (2H, t, 3J 6.6, NpzCH₂CH₂CHO), 3.02 (td, 2H, 3J 6.6, 0.9, NpzCH₂CH₂CHO), 2.24, 2.16 (3H, s, CH₃(pz)). 13C{¹H} NMR (CDCl₃, 63 MHz) 199.9 (NpzCH₂CH₂CHO), 147.9, 139.2 (CCH₃), 105.1 (CH (pz)), 43.8 (NpzCH₂CH₂CHO), 41.4 (NpzCH₂CH₂CHO), 13.6, 11.1 (CCH₃). m/z (ESIþ) 175 (100 %, C₈H₁₂N₂O ṁ Na ṁ). Anal. Calc. for C₈H₁₂N₂O ṁ 0.5H₂O: C 59.61, H 8.12, N 17.38. Found: C 59.22, H 8.21, N 17.69 %.

Synthesis of N-[3-(3,5-Dimethyl-1H-pyrazol-1-yl)propylidene]ethylamine (L₁) and N-[3-(3,5-Dimethyl-1Hpyrazol-1-yl)propylidene]propylamine (L₂) The synthesis consists of the reaction between 3-(3,5-dimethyl-1H-pyrazol-1-yl)propanal (10 mmol, 1.52 g) in CH₂Cl₂ (7.5 mL) and 10 mmol of the appropriate amine (L₁: ethylamine 70 %, 0.80 mmol or L₂: propylamine 99 %, 0.83 mmol) in water (7.5 mL). The mixture was stirred at room temperature for 3 h and extracted three times with 5 mL of CH₂Cl₂. The organic phase was collected and dried overnight with anhydrous Na₂SO₄. The solution
was filtered off and the solvent was removed under vacuum. The L1 and L2 ligands were obtained as white solids.

L1: Yield: 1.11 g (62 %), mp 40–42°C. \( \text{n} \max \text{(NaCl)/cm} \ 13121 \text{(n(C—H)ar)}, 2967, 2928, 2869 \text{(n(C—H)al)}, 1667 \text{(n(C\%Nim))}, 1553 \text{(n(C\%C)}, \text{n(C\%N))pz, 1461 \text{(d(C\%C)}, \text{d(C\%N)}pz, 1423 \text{(d(CH3)}as), 1384 \text{(d(CH3)}s), 1022 \text{(d(C–H)ip)}, 773 \text{(d(C–H)oop)}. \text{dH (CDC13, 250 MHz)} 7.65 \text{(1H, t, 3J 4.1, NpzCH2CH2CH\%Nim)}, 5.72 \text{(1H, s, CHpz)}, 4.17 \text{(2H, t, 3J 7.3, NpzCH2CH2CH\%Nim)}, 3.30 \text{(2H, q, 3J 7.4, NimCH2CH3)}, 2.69 \text{(td, 2H, 3J 7.3, 3J 4.1, NpzCH2CH2CH\%Nim)}, 2.19, 2.17 \text{(3H, s, CH3(pz))}, 1.13 \text{(3H, t, 3J 7.4, NimCH2CH3)}, \text{dC (CDC13, 63 MHz)} 160.7 \text{(NpzCH2CH2CH\%Nim)}, 147.6, 138.9 \text{(CCH3)}, 105.1 \text{(CH (pz))}, 55.7 \text{(NimCH2CH3)}, 45.3 \text{(NpzCH2CH2CH\%Nim)}, 36.3 \text{(NpzCH2CH2CH\%Nim)}, 16.2 \text{(NimCH2CH3)}, 13.7, 11.2 \text{(CCH3)}. m/z \text{(ESI \%)} 202 (100 \%, L1 \% Na \%). \text{Anal. Calc. for C10H17N3 0.5H2O (188.3): C 63.80, H 9.64, N 22.32. Found: C 63.58, H 9.37, N 21.93 \%}.

L2: Yield: 1.83 g (95%), mp 45–47°C. \( \text{n} \max \text{(NaCl)/cm} \ 13121 \text{(n(C—H)ar)}, 2958, 2928, 2873 \text{(n(C—H)al)}, 1667 \text{(n(C\%Nim)}, 1553 \text{(n(C\%C)}, \text{n(C\%N))pz, 1461 \text{(d(C\%C)}, \text{d(C\%N)}pz, 1423 \text{(d(CH3)}as), 1384 \text{(d(CH3)}s), 1022 \text{(d(C–H)ip)}, 773 \text{(d(C–H)oop)}. \text{dH (CDC13, 250MHz)} 7.65 \text{(1H, t, 3J 4.1, NpzCH2CH2CH\%Nim)}, 5.74 \text{(s, 1H, CHpz)}, 4.18 \text{(t, 2H, 3J 7.1, NimCH2CH2CH3)}, 3.31 \text{(td, 2H, 3J 6.9, 4J 0.9, NpzCH2CH2CH\%Nim)}, 2.72 \text{(2H, td, 3J 6.9, 3J 4.1, NpzCH2CH2CH\%Nim)}, 2.21, 2.18 \text{(3H, s, CH3(pz))}, 1.57 \text{(2H, sx, 3J 7.1, NimCH2CH2CH3)}, 0.84 \text{(3H, t, 3J 7.1, NimCH2CH2CH3)}. \text{dC (CDC13, 63MHz)} 161.1 \text{(NpzCH2CH2CH\%Nim)}, 147.5, 138.9 \text{(CCH3)}, 105.0 \text{(CH(pz))}, 63.4 \text{(NpzCH2CH2CH\%Nim)}, 45.2 \text{(NimCH2CH2CH3)}, 36.3 \text{(NpzCH2CH2CH\%Nim)}, 23.9 \text{(NpzCH2CH2CH\%Nim)}, 13.6, 11.7 \text{(CCH3)}, 11.1 \text{(NimCH2CH2CH3)}. m/z \text{(ESI \%)} 225 (100 \%, L2 \% Na \%). \text{Anal. Calc. for C11H19N3 0.5H2O (202.3): C 65.29, H 9.98, N 20.77. Found: C 65.52, H 9.79, N 20.58 \%}.

Synthesis of the Complexes \([\text{ZnCl2(L)}] (L5L1 (1); L2 (2))\)

A solution of 2.0 mmol of the corresponding ligand (L1: 0.38 g; L2: 0.40 g) dissolved in 20 mL of absolute ethanol was added to a solution of 2.0 mmol (0.28 g) of \( \text{ZnCl2} \) and 4 mL of triethyl orthoformate (for dehydration purposes) in 10 mL of the same solvent. The mixture was stirred for 18 h. The solution was reduced to 5 mL and the precipitate appeared. The solid was filtered, washed with 5 mL of diethyl ether, and recrystallized with dichloromethane.

1: Yield: 0.25 g (39\%). Conductivity (2.4\% 10 3 Min methanol): 59 O 1 cm2 mol 1. \text{n} \max \text{(neat)/cm} 13020 \text{(n(C—H)ar)}, 2973, 2922 \text{(n(C—H)al)}, 1666 \text{(n(C\%Nim))}, 1554 \text{(n(C\%C)}, \text{n(C\%N))pz, (d(C\%C)}, 1469 \text{(d(C\%N)}pz, 1449 \text{(d(CH3)}as), 1392, 1381 \text{(d(CH3)}s), 1057 \text{(d(C–H)ip)}, 802 \text{(d(C–H)oop)}. \text{dH (CDC13, 250 MHz)} 7.95 \text{(1H, br, NpzCH2CH2CH\%Nim)}, 5.94 \text{(1H, s, CHpz)}, 4.84 \text{(2H, m, NpzCH2CH2CH\%Nim)}, 3.93 \text{(2H, q, 3J 7.4, NimCH2CH3)}, 2.94 \text{(2H, m, NpzCH2CH2CH\%Nim)}, 2.49, 2.28 \text{(3H, s, CH3(pz))}, 1.43 \text{(3H, t, 3J 7.4, NimCH2CH3)}. \text{dC (CDC13, 63 MHz)} 169.5 \text{(NpzCH2CH2CH\%Nim)}, 151.6, 141.6 \text{(CCH3)}, 107.6 \text{(CH(pz))}, 57.7 \text{(NimCH2CH3)}, 41.8 \text{(NpzCH2CH2CH\%Nim)}, 35.7 \text{(NpzCH2CH2CH\%Nim)}, 16.1 \text{(NimCH2CH3)}, 13.7, 11.3 \text{(CCH3)}. m/z \text{(ESI \%)}
278 (69%, ZnCl(L1)þ), 218 (100 %, ZnCl₂(L1)-3,5-Me₂pz). Anal. Calc. C₁₀H₁₇Cl₂N₃Zn (315.6): C 260 38.06, H 5.43, N 13.32. Found: C 38.13, H 5.45, N 13.30%.

2. Yield: 0.30 g (46 %). Conductivity (2.5×10⁻³ M in methanol): 61.0 cm² mol⁻¹ cm⁻¹. nmax (neat)/cm⁻¹ 3032 (n(C–H)ar), 2966, 2932 (n(C–H)al), 1664 (n(C¼Nim)), 1551 (n(C¼C), n (C¼N))pz, 1468 (d(C¼C), d(C¼N))pz, 1449 (d(CH₃)as), 1384 (d(CH₃)s), 1055 (d(C–H)ip), 794 (d(C–H)oop). dH (CDCl₃, 250 MHz) 7.95 (1H, br, NpzCH₂CH₂CH¼Nim), 5.94 (1H, s, CHpz), 4.86 (2H, m, NimCH₂CH₂CH3), 3.93 (2H, t, 3J 7.3, NpzCH₂CH₂CH¼Nim), 2.93 (2H, m, NpzCH₂CH₂CH¼Nim), 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, NimCH₂CH₂CH₃). dC (CDCl₃, 63 MHz) 169.7 (NpzCH₂CH₂CH¼Nim), 152.0, 141.7 (CCH₃), 107.8 (CH(pz)), 65.4 (NpzCH₂CH₂CH¼Nim), 42.1 (NimCH₂CH₂CH₃), 35.8 (NpzCH₂CH₂CH¼Nim), 23.8 (NimCH₂CH₂CH₃), 13.9, 11.9 (CCH₃), 11.6 (NimCH₂CH₂CH₃). m/z (ESI þ) 292 (100 %, ZnCl(L2) þ). Anal. Calc. for C₁₁H₁₉Cl₂N₃Zn (329.6): C 40.09, H 5.81, N 12.75. Found: C 40.11, H 5.92, N 12.82 %.

X-Ray Crystal Structures for Compounds 1 and 2

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

Data for 1 and 2 were collected on a MAR 345 diffractometer with an image plate detector. Unit cell parameters were determined from 890 reflections for compound 1 and 121 reflections for 2 (38,y,318), and refined by least-squares method. Intensities were collected with graphite monochromatised MoKa radiation using v/2y scan technique. For 1, 12674 reflections were measured in the range of 2.318°#y#32.358; 4152 of which were non-equivalent by symmetry (Rint (on I)¼0.082). Lorentz polarisation and absorption corrections were made; and 2598 reflections were assumed as observed by applying the condition I$2s(I). For 2, 26213 reflections were measured in the range of 1.768°#y#32.408; 9183 of which were non-equivalent by symmetry (Rint (on I)¼0.064); and 4616 reflections were assumed as observed by applying the condition I$2s(I).

Both structures were solved by direct methods using SHELXS computer program (SHELXS-97) and refined by full matrix least-squares method with SHELXL-97 computer program using 12674 reflections for 1 and 987 for 2. For 1, the minimised function was Sw||Fo|²|Fc|²/2, where w¼[s²(I)]/P 0.00449P)² 1 and P¼(|Fo|²|Fc|²/2)/3. For 2, the minimised function was Sw||Fo|²|Fc|²/2, where w¼[s²(I)]/P 0.00488P)² 1 and P¼(|Fo|²|Fc|²/2)/3. The H atoms were included in the calculated position and constrained for compound 1, and mixed for compound 2. The final R(F) factor and Rw(F2) values as well as the number of parameters refined and other details regarding the refinement of the crystal structures are gathered in Table 3.
ACKNOWLEDGEMENTS

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Legends to figures

**Figure 1.** 250MHz 1H NMR data obtained at 298K and the simulated g NMR spectra for the H8 and H9 protons of the Npz-CH2-CH2-CH¼Nim fragment of [ZnCl2(L1)] (1).

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

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

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

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

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

**Figure 7.** View of p–p intermolecular interaction between adjacent pyrazole rings of [ZnCl2(L2)] (2).
SCHEME 1.

(a) \[
\begin{align*}
&\text{3.5Pz} \\
\text{N} &\text{H}
\end{align*}
\]
\[+\]
\[
\begin{align*}
&\text{Acrolein} \\
\text{O} &\text{H}
\end{align*}
\]
dry dioxane
40°C, 24 h
\[
\begin{align*}
&\text{3.5PzO} \\
\text{N} &\text{H}
\end{align*}
\]

(b) \[
\begin{align*}
&\text{3.5PzO} \\
\text{N} &\text{H}
\end{align*}
\]
\[\xrightarrow{\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}}\]
\[
\begin{align*}
&\text{L1} \\
\text{N} &\text{H}
\end{align*}
\]
\[
\begin{align*}
&\text{L2} \\
\text{N} &\text{H}
\end{align*}
\]

(c) \[
\begin{align*}
&\text{L1-L2} \\
\text{ZnCl}_2 &\text{EtOH}
\end{align*}
\]
\[\xrightarrow{\text{ZnCl}_2/\text{EtOH}}\]
\[
\begin{align*}
&[\text{ZnCl}_2(\text{L})] \\
&\text{L} = \text{L1 (1); L2 (2)}
\end{align*}
\]
FIGURE 1.
FIGURE 2.
FIGURE 6
Table 1. 1H NMR results: Chemical shifts (δ) and 1H, 1H coupling constants (J) for 1 and 2 measured in CDCl₃ at 298K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ CH₂ (8) [ppm]</td>
<td>4.84</td>
<td>4.86</td>
</tr>
<tr>
<td>δ CH₂ (9) [ppm]</td>
<td>2.94</td>
<td>2.93</td>
</tr>
<tr>
<td>²J₇₈,9₂ [Hz]</td>
<td>-12.5</td>
<td>-12.3</td>
</tr>
<tr>
<td>²J₉₂,₉₂ [Hz]</td>
<td>-12.5</td>
<td>-12.3</td>
</tr>
<tr>
<td>³J₇₈,₉₂ [Hz]; ³J₉₂,₉₂ [Hz]</td>
<td>7.18; 3.02</td>
<td>7.20; 3.10</td>
</tr>
<tr>
<td>³J₈₀,₉₂ [Hz]; ³J₉₂,₉₂ [Hz]</td>
<td>7.18; 3.02</td>
<td>7.20; 3.10</td>
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Table 2. Selected bond lengths [Å] and bond angles [°] for 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths [Å]</th>
<th>Bond Angles [°]</th>
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<tbody>
<tr>
<td>1</td>
<td>Zn-N(1)</td>
<td>2.03 (2)</td>
</tr>
<tr>
<td></td>
<td>Zn-N3</td>
<td>2.099 (3)</td>
</tr>
<tr>
<td></td>
<td>Zn-C11</td>
<td>2.231 (2)</td>
</tr>
<tr>
<td></td>
<td>Zn-C12</td>
<td>2.2356 (14)</td>
</tr>
<tr>
<td></td>
<td>N1-Zn-N3</td>
<td>100.5 (10)</td>
</tr>
<tr>
<td></td>
<td>N1-Zn-C11</td>
<td>113.56 (8)</td>
</tr>
<tr>
<td></td>
<td>N3-Zn-C11</td>
<td>108.72 (8)</td>
</tr>
<tr>
<td></td>
<td>N1-Zn-C12</td>
<td>111.02 (8)</td>
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<tr>
<td></td>
<td>N3-Zn-C12</td>
<td>107.30 (9)</td>
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<td></td>
<td>C11-Zn-C12</td>
<td>114.54 (5)</td>
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<td>2</td>
<td>Zn1-N11</td>
<td>2.02 (4)</td>
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<td></td>
<td>Zn1-N13</td>
<td>2.07 (4)</td>
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<tr>
<td></td>
<td>Zn1-C111</td>
<td>2.243 (2)</td>
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<tr>
<td></td>
<td>Zn1-C112</td>
<td>2.279 (2)</td>
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<td>N11-Zn1-N13</td>
<td>100.96 (18)</td>
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<tr>
<td></td>
<td>N11-Zn1-C111</td>
<td>112.20 (14)</td>
</tr>
<tr>
<td></td>
<td>N11-Zn1-C112</td>
<td>110.44 (13)</td>
</tr>
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<td>N11-Zn1-C12</td>
<td>109.49 (13)</td>
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<tr>
<td></td>
<td>C111-Zn1-C112</td>
<td>114.46 (7)</td>
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<td></td>
<td>Zn2-N21</td>
<td>2.070 (4)</td>
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<td></td>
<td>Zn2-C21</td>
<td>2.227 (2)</td>
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<td></td>
<td>Zn2-C22</td>
<td>2.184 (2)</td>
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<td></td>
<td>N21-Zn2-N23</td>
<td>102.3 (2)</td>
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<td>N21-Zn2-C21</td>
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<td></td>
<td>N23-Zn2-C22</td>
<td>109.57 (14)</td>
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Table 3. Crystallographic data for compounds 1 and 2

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<tr>
<td>Formula</td>
<td>C$<em>{16}$H$</em>{11}$Cl$_2$N$_2$Zn</td>
<td>C$<em>{32}$H$</em>{34}$Cl$_6$N$<em>2$O$</em>{2}$Zn$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>616.53</td>
<td>677.14</td>
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<tr>
<td>Temperature [K]</td>
<td>293(2)</td>
<td>293(2)</td>
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<tr>
<td>Wavelength [Å]</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>System, space group</td>
<td>Monoclinic, $P2_1/c$</td>
<td>Orthorhombic, $Pna2_1$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
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</tr>
<tr>
<td>$a$ [Å]</td>
<td>8.596(6)</td>
<td>23.177(10)</td>
</tr>
<tr>
<td>$b$ [Å]</td>
<td>14.933(7)</td>
<td>8.48(5)</td>
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<tr>
<td>$c$ [Å]</td>
<td>12.869(7)</td>
<td>15.226(5)</td>
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<tr>
<td>$\beta$ [°]</td>
<td>121.95(4)</td>
<td>90</td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
<td>1.465.7(15)</td>
<td>299.3(2)</td>
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<tr>
<td>$Z$</td>
<td>4</td>
<td>4</td>
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<tr>
<td>$D_x$ [$g\cdot cm^{-3}$]</td>
<td>1.500</td>
<td>1.902</td>
</tr>
<tr>
<td>$\mu$ [mm$^{-1}$]</td>
<td>2.112</td>
<td>1.986</td>
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<tr>
<td>F(000)</td>
<td>652</td>
<td>1400</td>
</tr>
<tr>
<td>Crystal size [mm$^3$]</td>
<td>0.2 $\times$ 0.09 $\times$ 0.08</td>
<td>0.2 $\times$ 0.1 $\times$ 0.1</td>
</tr>
<tr>
<td>$h, k, l$ range</td>
<td>$-12 \leq h \leq 12, -22 \leq k \leq 20, -17 \leq l \leq 17$</td>
<td>$-34 \leq h \leq 34, -12 \leq k \leq 12, -22 \leq l \leq 20$</td>
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<tr>
<td>20 range [°]</td>
<td>2.311 to 33.251</td>
<td>1.751 to 32.401</td>
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<tr>
<td>Reflections collected/unique ($R_{int}$)</td>
<td>12674/4152 ($R_{int}=0.0227$)</td>
<td>2621391/835 ($R_{int}=0.0646$)</td>
</tr>
<tr>
<td>Completeness to $θ$ [%]</td>
<td>94.6</td>
<td>99.3</td>
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<tr>
<td>Absorption correction</td>
<td>Empirical</td>
<td>Empirical</td>
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<tr>
<td>Max. and Min. transmission</td>
<td>0.5 and 0.5</td>
<td>0.62 and 0.79</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>4152/2/145</td>
<td>918328/334</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.158</td>
<td>0.835</td>
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<tr>
<td>Final R indices ($I &gt; 2\sigma(I)$)</td>
<td>$R_I = 0.0555$, $wR_I = 0.1167$</td>
<td>$R_I = 0.0477$, $wR_I = 0.0862$</td>
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<tr>
<td>R indices (all data)</td>
<td>$R_I = 0.1014$, $wR_I = 0.1307$</td>
<td>$R_I = 0.1244$, $wR_I = 0.1022$</td>
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<tr>
<td>Largest difference peak and hole [e Å$^{-3}$]</td>
<td>+0.659, -0.362</td>
<td>+0.975, -0.997</td>
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</tbody>
</table>
Table 4. Supramolecular interactions C–H...X (X=Cl or C) parameters for complexes 1 and 2

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</thead>
<tbody>
<tr>
<td>1 (L1)</td>
<td>C4–H4B...C2C4... H4C–C11</td>
<td>2.819</td>
<td>3.688</td>
<td>150.78</td>
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<tr>
<td></td>
<td></td>
<td>2.913</td>
<td>3.755</td>
<td>166.96</td>
</tr>
<tr>
<td>2 (L2)</td>
<td>C9–H9B...pz sing</td>
<td>2.835</td>
<td>3.800</td>
<td>133.33</td>
</tr>
<tr>
<td></td>
<td>C12–H–O1–H... C12C11... H–O2–H–C12</td>
<td>2.633</td>
<td>3.071</td>
<td>122.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.323</td>
<td>3.372</td>
<td>121.64</td>
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