Structural characterization of a new polymeric Cu(II) complex with unexpected chlorinated pyrazole ligand

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ABSTRACT

A new coordination polymer based on copper(II) and pyrazole (pzH) ligand, [CuCl2(ClpzH)2]n, has been obtained by a very easy synthesis and green reaction conditions using water as solvent. The compound was characterized by single crystal X-ray diffraction elemental analyses, infrared and UV–Vis spectroscopies. For the first time the C(2)-chlorination of the pyrazolyl ring keeping the protonation of the N(2)–H is reported. The polymeric crystal structure consists of a one dimensional infinite neutral chain in which the copper(II) atoms are six-coordinated in a slightly distorted octahedral geometry with two nitrogen and four chlorine atoms. In this structure, intermolecular interactions have been identified and studied. Extended structure analyses revealed a novel two-dimensional network supported by intermolecular N\H\Cl and C\H\Cl hydrogen bonds, in addition to the π–π stacking interactions.

The synthesis and structural determination of copper complexes containing potential N-bridging or N-polydentate ligands are of wide interest [1,2]. Numerous complexes have been synthesized using pyrazole, imidazole, and bipyridine ligands. The different possible coordinations with these ligands can involve monodentate, bridging and polydentate structures. The reaction of copper with polydentate N-ligands used to yield polynuclear copper complexes such as polymers [3], dimmers [4,5], trimmers [2,6], and tetramers [7], with a large variety of attractive structures at the supramolecular framework [2,8]. Additionally, polynuclear Cu(II) complexes present important characteristics such as electric, magnetic [9,6], luminescent [2], catalytic [10] and antimicrobic properties, among others, that make them useful for several applications. Recently, copper complexes with N-ligands have been used for biomedical applications [11,12]. There are even some reports about of the anticancer activity of these complexes [13,14].

Pyrazole is a common ligand in the synthesis of interesting polynuclear metal complexes because it presents suitable chemical properties (the anion of pyrazole iswell suited for its coordination tometal ions via the N,N′-bridging mode) [8]. In the course of our studies on pyrazolederived ligands, some polynuclear complexes with Cd(II) and Hg(II) [15], Ag(I) [16], Rh(I) [17], Ni(II) [18], Pd(II) [19–21], Cu(II) [22], and Zn(II) [23] have been isolated and characterized. Recently, we have shown that the dinuclear complex, [CuCl2(L2)]2 (L2 = 1-[2- (ethylamino)methyl] pyrazole), is centrosymmetric, and the two copper ions are coordinated by two chlorine bridge atoms. This complex presented attractive structural designs at the supramolecular framework [24].

Herein, we present a new polymeric copper(II) complex with pyrazole obtained by a very simple reaction using water as solvent. For the first time an unexpected C(2)-chlorination in presence of the protonation of the N(2)–H in the pyrazole (pzH) ring is observed. Novel and interesting metal-organic framework designs are displayed at the supramolecular structure, which are supported by N\H\Cl and C\H\Cl hydrogen bonding interactions.

As part of a major study to evaluate the reactivity of pyrazolederived ligands with copper salts, we assayed the following reaction. A pzH solution (1.47 M) was mixed with ammoniacal water (2 M) overnight and after that a CuCl2 solution (0.88 M) was added under stirring and the reaction was allowed for 6 h at room temperature. The final molar ratio Hpz:NH3:CuCl2 was 1:2.3:1 and distilled water was used as solvent and reaction medium. The green solid obtained was filtered off, washed with cold diethyl ether, and dried at vacuum. Studies of crystallization of the product synthesized, in order to obtain suitable crystals for X-ray diffraction, were carried out. Green prisms like monocrystals were isolated during the evaporation by diffusion in ethanol/hexane at room temperature.

The structure of the new complex, [CuCl2(ClpzH)2]n, was unequivocally determined by single crystal X-ray diffraction [25]. The compound crystallizes in the triclinic space group P(−1) and it consists of a polymeric structure showing an one-dimensional (1D) infinite neutral chain [CuCl2(ClpzH)2]n parallel to [100] direction, wherein two bridging chlorine atoms link the adjacent octahedral metal centres. The local coordination environment around the Cu(II) atom is formed by two terminal protoned pyrazole ligands and four chlorine bridges. The coordination sphere of Cu(II) can be described as a slightly distorted octahedral geometry with angles between 88.86° and 179.82°, where the copper atom is coordinated to two trans pyrazolyc nitrogen. The molecular structure and its polymeric nature are illustrated in Fig. 1A and B, respectively.

Additional characterizations have corroborated the crystallographic results [26]. The green product gave satisfactory C, H, and N elemental analyses for this structure. A special feature in this complex is the deprotonation and chlorination of the pzH ring in the C(2) position with the N(2)–H remaining protonated. The mass spectra of the complex were a valuable tool in the determination of the chlorine atoms present in the ligand. The spectrum shows five peaks with m/z values between 347 and 340 and with intensity values between 100 and 8%, peaks attributable to [CuCl2(ClpzH)2 + H]+ ion, and other five peaks appear with m/z between 371 and 363, and abundance between 60 and 5%, corresponding to [CuCl2(ClpzH)2 + Na]+ ion. The observed molecular peaks of the cations exhibit the same isotope distribution as theoretical ones. The conductivity data for this compound in methanol is in agreement with the non-electrolyte nature of the complex [27]. According to the IR data, the copper(II) atoms are coordinated to nitrogen atoms (ν(C_C), ν(C_N) 1658 cm−1) and to chlorine atoms (ν(Cu–Cl) 321 cm−1). The pyrazole is protoned because the band ν(N–H) is observed at 3103 cm−1, also it observed the band ν(C–Cl) at 965 cm−1, confirming the chlorination of the pyrazole ligand [28,29]. The spectrum UV–Vis of the Cu(II) compound in methanol solution, shows one band in the visible region (702 nm, ε = 21 mol−1 cm−1 l), which is characteristic for octahedral Cu(II) complexes [30].

The chlorination of the C2-pyrazole ligand has been described in the literature [31–37], nevertheless, it is the first time that the C(2)-chlorination (pzH) occurs remaining protonated the N(2)-H. This chlorination generally takes place using hard conditions and oxidising media, for example, with tBuOCl [31,34] or Cl2 [32]. In our group, the chlorination of the ligand 3-phenyl-[5-(6-methyl)-2-pyridyl] pyrazole (HL1) was observed with very soft conditions [33] during the recrystallization of [CuCl2(HL1)2]EtOH in DMSO solvent, at room temperature. In all these complexes the pyrazole-derived ligands were deprotonated, while in the complex studied in this paper, the ClpzH ligand is protonated.

The [CuCl4N2] core (coordinated with two chloride terminal (Clt), two chloride bridging (Clbr) and two N atoms) [38,39] and the [Cu2Cl2N4] one [40,41] are present in some copper(II) complexes. However the [Cu2Cl4N4] and the [Cu2Cl6N4] cores are not found in the previous literature [42]. They are reported here for the first time.

Adams et al. [39] reported a similar structure with the [CuCl4N2] core based on the pzH ligand instead of the ClpzH one described here. This structure also consists of a chain of edge-sharing octahedral trans-CuCl4(Hpz)2 moieties. The Cu\Cl bond lengths of the compound described here are Jahn–Teller distorted, with two long Cu\Cl distances (2.9343(4) and 2.8124(4) Å) and two short distances (2.3400(4) and 2.3503(4) Å), similar to the previous reference. Also the Cu\Npz bond distances (1.9751 and 1.9804 Å) are in the same order that those for other complexes described in the literature.

The CuCl2 core lies on an equatorial plane in relation with the CuNpzNpzClbrClbr plane. The angles Cu(1)\Cl(2)\Cu(1)i and Cu(1)\Cl(1)\Cu(1)i (where i is equivalent by a translation along a axis) are 91.82° and 89.03°, respectively. It gives rise to a Cu\Cu distance of 3.7219 Å, which is too long to consider a metal–metal interaction. This value of the copper distance is also in agreement with the values reported in the literature for other complexes with [Cu2Cl2] core [3.1963–3.7543 Å] [43,44]. The angle between coordination plane formed by two Clbr and two Clt, and the plane N(1)\Cu\N(3) is 89.90°. Selected values of bond lengths and angles for this complex are shown in Table 1.

Interestingly, the [CuCl2(ClpzH)2]n complex presents novel and attractive structural designs at the supramolecular framework, so the intermolecular interactions have been identified and studied. Double hydrogen bond via bridged chlorines with the hydrogen atoms of the nitrogens in the pyrazole rings (N2\H2···Cl2 and N4\H4···Cl1) between molecules related by symmetry centers are the main interactions that support the supramolecular self-assembly of two neighbouring polymeric chains. Additionally, these polymeric chains are interconnected sharing multiple intermolecular interactions via chlorine atoms (Cl4 and Cl3) of the pyrazole ring with the hydrogen atoms of the neighbours' pyrazole rings' ending in a 2D framework structure [45]. Both hydrogen bond interactions, the N\H···Cl and the C\H···Cl, are represented in a view of the supramolecular structure along the a axis in Fig. 2B and 2C, respectively. These X–H···Cl (X_N or C) intermolecular contacts can be considered as weak on the basis of the contact distances and angles [46]. It is important to take into account that the X–H···Cl hydrogen bond interactions present in this structure are intermolecular, whereas in most of the corresponding pyrazole compounds they are intramolecular [47]. Furthermore the structure framework is additionally supported by weak π–π stacking interactions between the perfectly coplanar pyrazole rings along the crystallographic b and c axes (interplanar angle of 0° and distance of 3.722 Å). Fig. 3 shows two views of engaging arrays of the packing of the complex at the b (Fig. 3A) and c (Fig. 3B) directions, where the π–π stacking interactions are represented. A singular supramolecular array of the 2D chains along the [010] direction is illustrated in Fig. 3B, while other arrays of the 2D chains are displayed along the [001] direction (Fig. 3B).

CONCLUSIONS

A new polymeric copper(II) complex, [CuCl2(ClpzH)2]n, has been obtained using very simple reaction conditions in water as solvent. The new compound has been characterized by elemental analyses, conductivity measurements, infrared and UV–vis spectroscopies, and single crystal X-ray diffraction. The crystal structure consists of 1D infinite neutral chain in which the copper(II) atoms are sixcoordinated in a slightly distorted octahedral geometry with two nitrogen and four chlorine atoms. This structure has the particularity that the hydrogen atom of the C2 is substituted by a chlorine atom in the pyrazolyl ring with the N(2)–H remaining protonated. In addition, intermolecular interactions have been identified and studied. Extended structure analyses revealed a novel two-dimensional network formed by intermolecular N\H···Cl and C\H···Cl hydrogen bonds and weak π–π stacking interactions. This paper shows howa simple and environmental reaction with common and cheap reagents can lead to an interesting and new complex taking advantage of the catalytic properties of the coordination metal.

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[25] Experimental X-ray structure determination of the [CuCl2(ClpzH)2]n complex: A green prism-like crystal (0.060 × 0.110 × 0.790 mm) was measured on a D8 Venture system equipped with a Multilayer monochromate and a Mo microfocus (λ = 0.71073 Å). C6H6Cl4CuN4, M = 339.49, Triclinic space group P(−1) with Z = 2, and a = 3.7219(2), b = 10.6120(5), c = 13.4678(7) Å, α = 87.742(2)°, β = 87.9060(10)°, γ = 80.3350(10)°, and V = 523.74(5) Å3. The integration of the data using a triclinic unit cell yielded a total of 21,226 reflections to a maximum θ angle of 28.30° (0.75 Å resolution), of which 2571 were independent (average redundancy 8256, completeness = 99.5%, Rint = 2.53%, Rsig = 1.23%) and 2469 (96.03%) were greater than 2σ(F2). The refinement of the XYZ-centroids of reflections above 20 σ(I). The final cell constants are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using themulti-scanmethod (SADABS). The calculatedminimum and maximum transmission coefficients are 0.6319 and 0.7457. The structure was solvent using the Bruker SHELXTL, and refined using SHELXL program. The final anisotropic full-matrix least squares refinement on F2 with 137 variables converged at R1=2.28% for the observed data and wR2=7.04% for all data. The goodness-of-fit was 1.172. The largest peak in the final difference electron density synthesis was 0.663 eÅ−3 and the largest hole was −0.587 eÅ−3 with a RMS deviation of 0.120 eÅ−3. On the basis of the final model, the calculated density was 2.153 g cm−3 and F(000) was 334.

[26] Analyses for C6H6Cl4CuN4 calc/found (%): C, 21.23/21.20; H, 1.78/1.72;N16.50/16.43 giving a satisfactory C, H and N elemental analyses. ESI-MS (+) (H2O/MeOH) (higher peaks, relative abundance, %). m/z 347, 345, 343, 341, 340 (25, 84, 100, 49, 8) and 371, 369, 367, 365, 363 (15, 51, 60, 30, 5) peaks attributable to [CuCl2(ClpzH)2+H]+ and [CuCl2(ClpzH)2+Na]+ ions, respectively. Conductivity (1.04 × 10−3 M in methanol): 21 Ω−1cm2mol−1, is in agreement with a nonelectrolyte complex. IR (KBr, cm−1): 3175, 3142 ν(C\H)ar, 3103 ν(N\H)ar, 1658 [ν(C_C), ν(C_N)]ar, 1408 [δ(C_C), δ((C_N)]ar, 965 ν(C\Cl), 776 δ(C\H)oop. Moreover the bands at 436 ν(Cu\N) and 321 ν(Cu\Cl), corroborate the copper coordination too. UV–vis (1.2 × 10−3Minmethanol) exhibits a single band at 702 nm (ε=21mol−1 cm−1 l).

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[45] The Npz\H bonds are intermolecularly hydrogen bridged to a chlorine atom from another molecule. The value of N\H bond lengths is 0.88 Å, and the contact parameters between N(2)\H(2 N)\Cl(2) are H(2 N)\Cl(2) 2.60 Å, N(2)\Cl(2) 3.2739 Å, N(2)\H(2 N)\Cl(2) 134°, symmetry code: 1-x,-y,1-z; and N(4)\H(4 N)\Cl(1) are H(4 N)\Cl(1) 2.68 Å, N(4)\Cl(1) 3.3334 Å, N(2)H(2 N)\Cl(2) 132°, symmetry code: 2-x,-y,-z. Other intermolecular interactions are C(6)\H(6)\Cl(3), the C\H bond is 0.95 Å, and the contact parameters are H(6)\Cl(3) 2.80 Å, C(6)\ Cl(3) 3.6131 Å, C(6)\H(6)\Cl(3) 145°, symmetry code: x,−1 + y,z.

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Legends to figures

Figure 1 A) ORTEP diagram of the [CuCl2(ClpzH)2]n complex showing an atom labelling scheme. 50% probability of the amplitude displacement ellipsoids is shown. The hydrogen atoms are omitted for clarity. Scheme colour: copper, orange; chlorine, green; nitrogen, blue and carbon, grey. B) One-dimensional polymeric chain of the [CuCl2(ClpzH)2] units view along [001] direction.

Figure 2. View of the two dimensional (2D) layers of the supramolecular structure of the [CuCl2(ClpzH)2]n complex along the a axis. (B) Illustration of the N\H\Cl intermolecular hydrogen bond between two different polymeric chains and a view of the pyrazole ring packing. (C) Representation of the C–H · · · Cl intermolecular hydrogen bond interactions through of the framework array.

Figure 3 Representation of the π–π stacking interactions through interesting 2D arrays of the network packing in the complex. (A) Supramolecular self-assembly of the two chains in the framework along the b axis with beach chair-like shape. (B) Supramolecular self-assembly of the two chains in the framework along the c axis.

FIGURE 1.

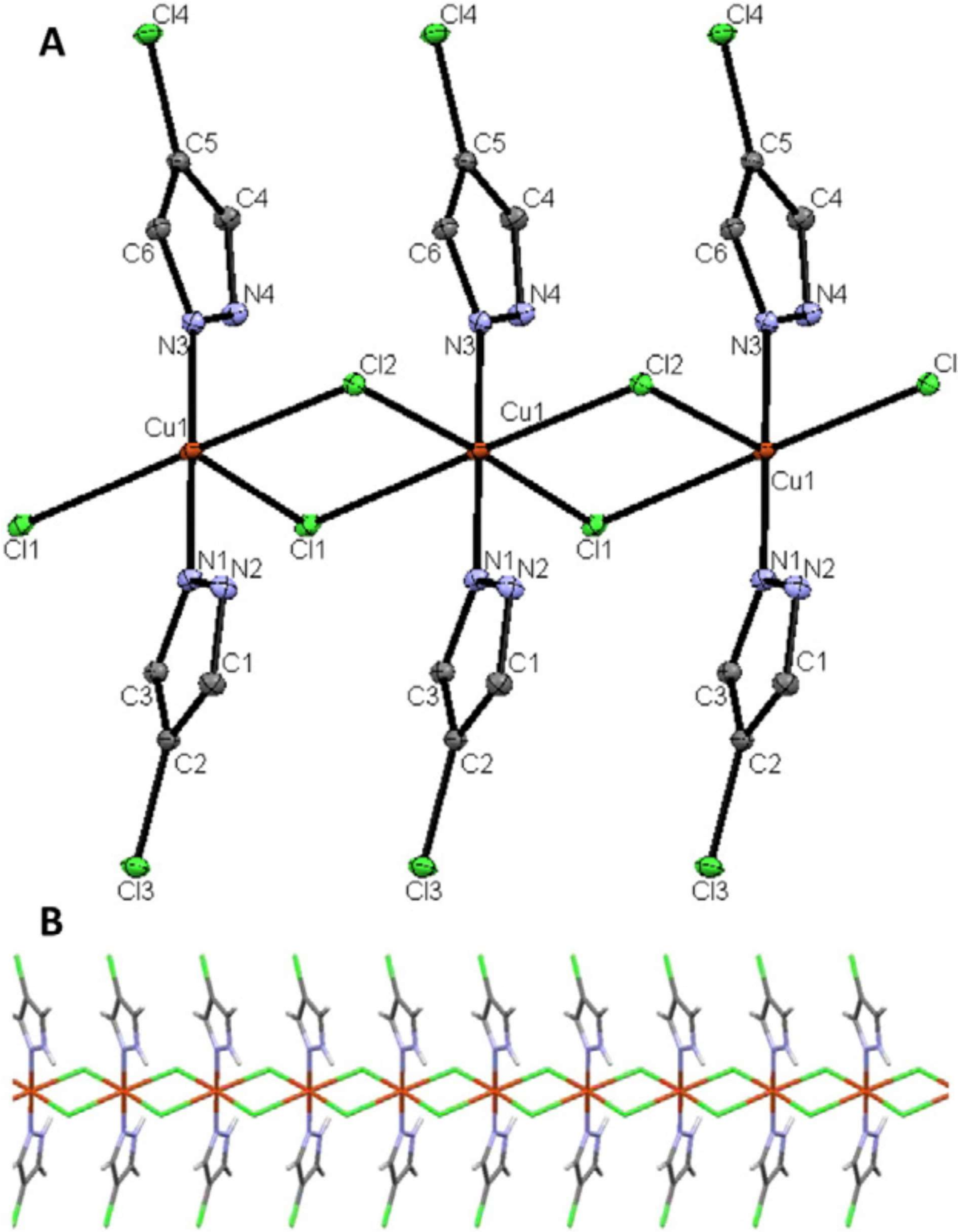

FIGURE 2.

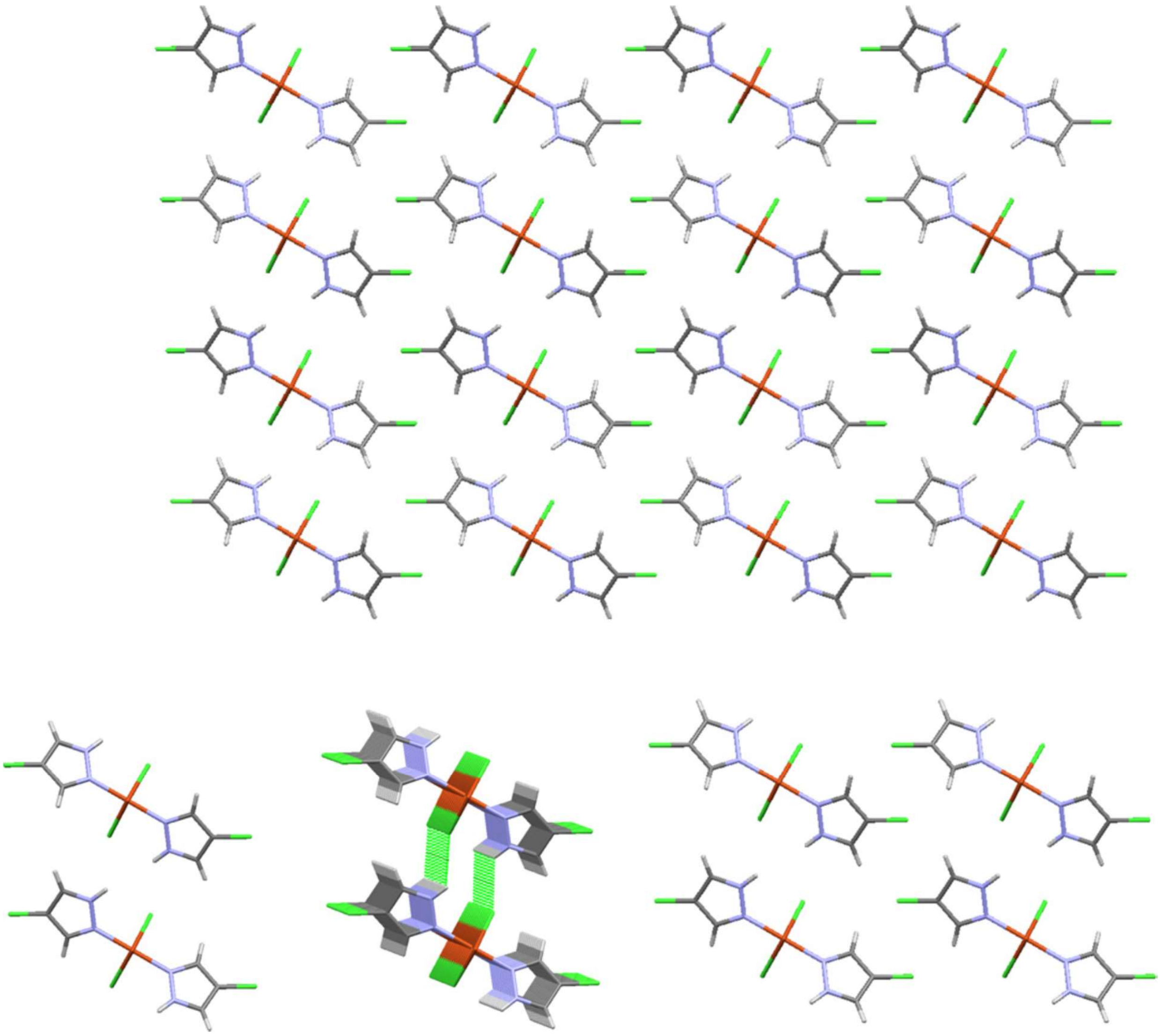

FIGURE 3.

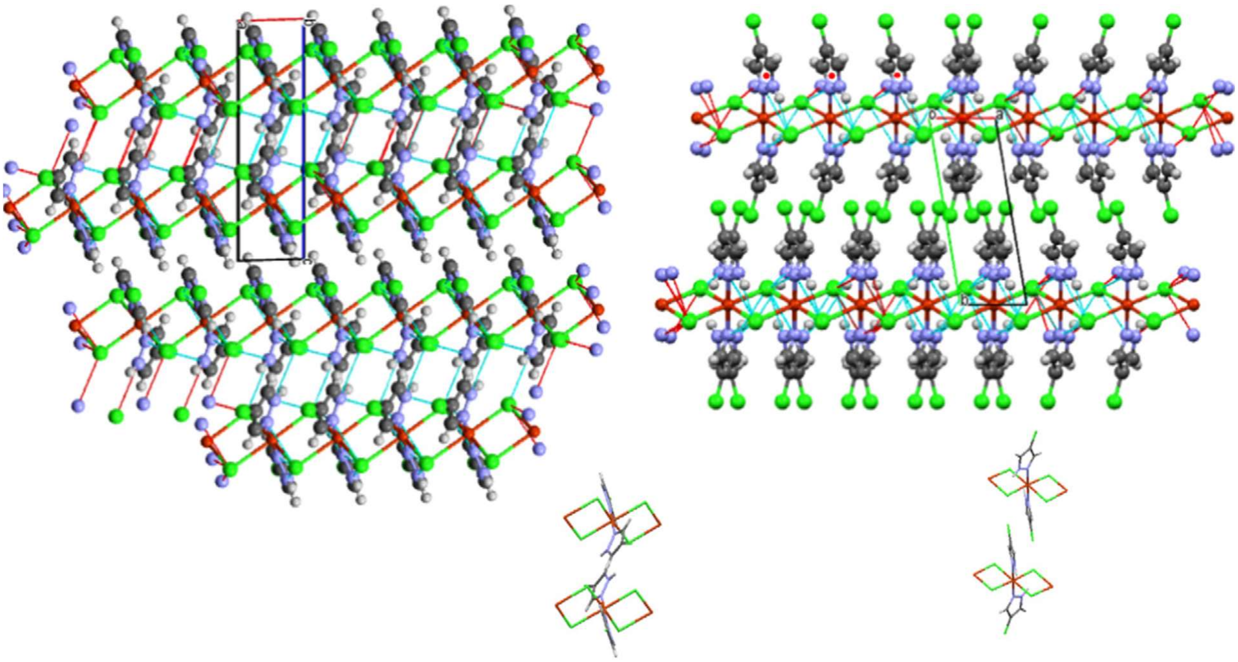

Table 1. Selected bond length (Å) and bond angle (°) values for the [CuCl2(ClpzH)2]n complex. The estimated standard deviations (e.s.d.s) are shown in parentheses.

Bond lengths (Å)		Bond angles (°)	
Cu(1)–N(1)	1.9751(13)	N(1)–Cu(1)–N(3)	179.82(5)
Cu(1)–N(3)	1.9804(13)	N(1)–Cu(1)–Cl(1)	89.33(4)
Cu(1)–Cl(1)	2.3400(4)	N(3)–Cu(1)–Cl(1)	90.61(4)
Cu(1)–Cl(2)	2.3503(4)	N(1)–Cu(1)–Cl(2)	88.86(4)
		N(3)–Cu(1)–Cl(2)	91.19(4)
		Cl(1)–Cu(1)–Cl(2)	176.49(13)