A new dinuclear copper(II) complex of unexpected formation with the 1-[2-(ethylamino)methyl]pyrazole ligand presents a curious Ferris wheel-like shape at supramolecular self-assembly

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Keywords: Binuclear copper(II) complex N-alkylaminopyrazole Supramolecular array

ABSTRACT

The crystallization of [CuCl2(L1)] (L1= bis-[(1-pyrazolyl)methyl]ethylamine) by ethanol/hexane solvent diffusion afforded the compound [CuCl2(L2)]2 (L2= 1-[2-(ethylamino)methyl]pyrazole), which has been characterized by single-crystal X-ray diffraction, elemental analysis, conductivity measurements, infrared and UV–vis spectroscopies. There are very fewpolynuclear complexeswith N-alkylaminopyrazole ligands reported so far. Especially L2 ligand, which is forming the binuclear copper(II) complex has been obtained for the first time here. The crystal structure consists of a dimeric unit in which the copper(II) atoms are five-coordinated in a distorted square pyramidal geometry with two nitrogen and two chlorine atoms in the base and one chlorine in the apical vertex. At the supramolecular level attractive structural designs are obtained, particularly, a peculiar Ferris wheel-like shape along the (110) direction. Hydrogen bonds constitute the main pillars of the supramolecular self-assembly observed.

The bi NN′- and tridentate NN′N-pyrazole derived ligands posses a remarkable capacity for coordination with transition metals. They present interesting chemical properties, which are well documented through the numerous metal complexes with various coordination geometries and nuclearity. Several metallocycles and cages composed of N-polydentate pyrazole derived ligands have facilitated the understanding of basic factors governing the supramolecular self-assembly of the coordination complexes [1–4]. The N-alkylaminopyrazole derived ligands are one type of bi- and tridentate pyrazole based ligands. The syntheses of these ligands and the studies of their reactivity with Ni(II), Co(II), Zn(II) and Cu(II) were carried out by Driessen et al. and Sheu et al. [5–10]. Other studies of the reactivity of theses ligands are reported by Calderazzo et al. using Fe(II) [11] and Carpentier et al. using Al(III) and Zn(II) [12] as coordination metals.More recently, the syntheses of new types of N-alkylaminopyrazole ligands and the evaluation of their reactivitywith Rh(I) [13–16], Pd(II) [17–20], Pt(II) [21], Zn(II) [22] and Cd(II) [23] have been continued by our group. Some of them have been used in the synthesis and stabilization of nanoparticles, even as metal recognizer molecules in metal sensing systems [24–26].

The formation of polynuclear copper(II) complexes with pyrazole derived ligands, in addition to their extensive coordination chemistry, has considerably attracted the interest of the scientific community due to their properties and potential applications in catalysis [27,28], or as (anti)ferromagnetic [28–30], opto-electric [31,32], and fluorescent and bactericide [33] devices, to mimic metalloproteins in order to understand the fundamental role played by these metal systems in several catalytic biological processes [34,35] and as gas selective adsorbent [36]. Alternatively, copper pyrazole based complexes have shown anticancer activity and cytotoxic effects, the copper being crucial to the angiogenic process that sustains the tumor and the metastasis development while the organic ligand guides the metal to the molecular targets [37–40].

In the frame of our studies focussed on the characterization of new copper complexes with N-alkylaminopyrazole derived ligands of variable coordination geometries an unexpected binuclear copper(II) complex is obtained here. Few polynuclear copper complexes with N-alkylaminopyrazole derived ligands have been reported so far [8, 10], and in addition the 1-[2-(ethylamino)methyl]pyrazole (L2) chelating ligand of this novel binuclear complex has been found for the first time. The crystal structure and spectroscopic properties of the [CuCl2(L2)]2 are described. In the structure the copper(II) atoms are five-coordinated each copper(II) atom being coordinated to Npz, Nam chelate bidentate ligand (L2) and three chlorine atoms, one terminal and two bridged. The new complex at supramolecular self-assembly presented an unprecedented Ferriswheel-like shape along the (110) direction supported by bi-hydrogen bonds.

To evaluate the reactivity of several N-alkylaminopyrazole ligands with CuCl2 under different metal:ligand molar ratios, the reaction of CuCl2·2H2O with bis-[(1-pyrazolyl)methyl]ethylamine (L1) [5] (at 1:1 molar ratio) was carried out in ethanol. The obtained product is a green powder and gives satisfactory C, H, and N elemental analysis that corresponds with the [CuCl2(L1)] complex [6]. During the recrystallization of the [CuCl2(L1)] complex via ethanol/hexane solvent diffusion a minority of green single crystals of about 0.1× 0.1× 0.2mmwere afforded. The structure of these crystalswas unequivocally determined by single crystal X-ray diffraction [41] and unexpectedly, a new dinuclear compound [CuCl2(L2)]2 was obtained (Fig. 1A). Moreover, other characterizations to these single crystals were carried out [42].

It looks like that the [CuCl2(L1)] complex cleavages during its crystallization. First, by rupture of one of the Cu\Npz bonds and second, the cleavage of theNam\CH2(Pz), which becomes the bis-[(1-pyrazolyl) methyl]ethylamine ligand into the mono-[(1-pyrazolyl)methyl] ethylamine one by losing a pyrazole arm. Subsequently, two copper moieties like [CuCl2L2] join and reorganize giving the new binuclear copper complex ([CuCl2L2]2). In the [CuCl2(L1)] complex, the Npz\Cu\Nam angles present certain strain, due to the short chains of the methylene bridges and the five-coordinated structure around the copper in a distorted square-pyramidal geometry [6,43], that promotes the cleavage of the Cu\Npz bond. The lability of the metal\Nbond in the NN′N-alkylaminopyrazole ligands has been already reported for similar complexes [44]. Additionally, the cleavage of the Nam\C bond in the fragment Nam\CH2\Npz (which has been reported before [45,46]) occurs, undergoing the rearrangement via Cu\Cl bonds of two mononuclear copper(II) moieties into a final thermodynamically favored binuclear complex (Fig. 1B).

The structure of this new compound consists of a centrosymmetric neutral dimeric unit of [CuCl2(L2)], where two units of L2 bind two copper(II) chloride molecules finding a stable structural conformation. The L2 ligand behaves as a bidentate ligand that coordinates with the copper center by means of the nitrogen atom of the pyrazole ring (Npz) and the nitrogen atom of the amine group (Nam) moieties. In this complex the copper atoms are five coordinated to Npz, Nam, Clt and two Clbr. The Npz and the Nam atom along with a terminal chlorine and two bridging chlorine atoms, form a slightly distorted square pyramid geometry around each of the two crystallographically equivalent Cu atoms with a τ value of 0.2 (the τ that ranges from 0 to 1 represents the geometric distortion from a perfect square pyramid to a trigonal bipyramid, respectively) [47]. The bridging chlorine [Cl(1A)] is in the apical position while the Npz and Nam atoms from the chelated ligand (L2) and bridging chlorine [Cl(1)] and the terminal chlorine [Cl(2)] atoms occupy the equatorial positions. The copper atoms arises 0,137 Å above the equatorial plane defined by the Clbr, Clt , Npz and Nam atoms. The two terminal chlorine atoms have trans orientation with respect to the plane of the Cu2Cl2 core forming an angle of 94.46° with this plane. The Cu–Clt bond distances (2.2651(9) Å) are intermediate with respect to the Cu–Clbr bond distances (2.2609(10) and 2.7527(10) Å), while the Cu–Npz (1.975(2) Å) bond distances are shorter than the Cu–Nam (2.073(2) Å) ones, indicating a stronger coordination of the Npz moieties than that of the Nam ones. These facts show that the dinuclear Cu2Cl4N4 core is asymmetric.

The square-planar angles of the Cu2Cl2 core, with the ideal values of 90°, vary between 97.06(4)° [Cl(1)\Cu(1)\Cl(1A)] and 82.94(4)° [Cu(1A)\Cl(1A)\Cu(1)], and those with ideal values of 180° vary between 163.28(7)° [Cl(1)\Cu(1)\N(1)] and 175.83(7)° [Cl(2)\Cu(1)\N(3)]. The angles formed by the chlorine apical atom and those in the square-plane of the Cu2Cl2 core, with ideal values of 90°, vary between 93.98 (7)° [Cl(2)\Cu(1)\Cl(1)] and 94.46 (4)° [Cl(2)\Cu(1)\Cl(1A)]. The Npz\Cu\Nam angle is 80.81(9)°.

The Cu2Cl2 core lies on an equatorial plane in relation with the CuNpzNamCltClbr plane. The Cu(1A)\Cl(1A)\Cu(1) angle is 82.94(4)° which gives rise to a Cu···Cu distance of 3.340 Å, which is too long to consider any metal···metal interaction. The value of Cu···Cu bond distance is in agreement with the values reported in the literature for other complexes with the Cu2Cl4N4 core [3.1963–3.7543 Å] [48–53]. Selected values of bond lengths and angles for this complex are shown in Table 1.

Although the same [Cu2Cl4] core coordinated with two Clt, two Clbr, and two Npz atoms is present in several copper binuclear complexes with pyrazole derived ligands [48–53], few times this kind of core is formed with N-alkylaminopyrazole ligand coordinating both the Npz and Nam atoms [8,10]. Similar to the closest structures reported before in the literature, Cu2Cl4(Npz)4 core in bidentated coordination to two Npz atoms, the distances of the common bond lengths and bond angles in this complex here described are in agreement with those values reported [48–53].

Nevertheless, the [CuCl2(L2)]2 complex presents attractive structural designs at the supramolecular framework. Especially, a curious selfassembly of the molecular packing gives an array of Ferris wheel-like shape through the plane (110) (Fig. 2).

In the supramolecular crystal arrange, each molecule is surrounded by other 14 neighboring molecules in the unit cell. They form a pair of adjacent chains that are in parallelwith the other pair of adjacent chains having incorporated one more chain in the hollow cage of the center formed by these two pairs of parallel adjacent chains (typical ABA structure). A view of this supramolecular distribution, that along the c axis simulates a Ferris wheel-like shape, is represented in Fig. 2.

Double hydrogen bond formations via the trans terminal chlorines with the hydrogen atoms of the C(1) and C(3) of the pyrazole rings of differentmolecules are themain interactions that support the supramolecular self-assembly of the whole network. The Cl(2) of each molecule (M1) forms bi-hydrogen bonds with the hydrogen atoms of the C(1) and C(3) of the two closest molecules (M2 and M3) at distances of 2.730 and 2.858 Å and angles of 144.26 and 134.19°, respectively (Fig. 3). Simultaneously the hydrogens of the C(1) and C(3) atoms in the same molecule (M1) are forming interactions with two terminal chlorines of the closest molecules (M2 and M5).

Other interesting views of the supramolecular network are displayed in the Fig. 4A and B.

By expanding one molecule by the C(1)\H(1)···Cl(2)\Cu(1) or the C(3)\H(3)···Cl(2)\Cu(1) interaction, one dimensional (1D) adjacent chains are generated. These 1D adjacent chains are interconnected by the bi-hydrogen bonds C(3)\H(3)···Cl(2)\Cu(1)···H(1)\C(1) that stabilize the supramolecular building (Fig. 4A). As consequence of these driving forces of the supramolecular network, intermolecular short contacts of 2.388 Å between the hydrogen of the methyl group [H(6A)] of the ethyl amino chain and the hydrogen of the C(2) of the pyrazole ring in the closest molecule are present. Nevertheless, the distance between the neighboring pyrazole rings is too large (4.750 Å) and the angle between them is very far from the ideal value of 0° (67.10°) to consider some kind of interaction. Fig. 4B represents a zig-zag design of the framework similar to Indian tapestry through the b axis in the (101) plane. In this view the pyrazole rings seem to be superimposed but the distances between themare 5.664 and 6.021 Å and, consequently, there is no interaction. Although this molecule presents aromatic rings the disposition of the supramolecular structure array does not favor the π–π stacking interactions. Here, the hydrogen bond bridges are the cooperative noncovalent interactions and the dominated forces to build these attractive supramolecular architectures.

In conclusion, we have obtained and successfully determined the crystal structure of the [CuCl2(L2)]2 complex, which presents an unprecedented Ferris wheel-like shape at supramolecular self-assembly along the c axis. In addition, analyses of the interactions that support the supramolecular self-assembly of the framework have been carried out.

Acknowledgements

The MEC CTQ2007-63913/BQU and the 2009SGR76 projects are acknowledged. A. Lopez-Marzo thanks Generalitat of Catalunya for the FI-2010 scholarship given.

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[41] Experimental X-ray structure determination of the [CuCl2(L2)]2 complex: A prismatic green crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a MAR345 diffractometer with an image plate detector. C12H22Cl4Cu2N6, M = 519. 24, Orthorhombic space group Pbcn and a = 9.538(4), b = 11.646(3), c = 18. 481(7) Å, and V = 2052.9(13) Å3 unit-cell parameters were determined from 3860 reflections (3 b θ b 31°) and refined by least-squares method. Intensities

were collected with graphite monochromatizedMoKα radiation. 19,114 reflections were measured in the range 2.20 ≤ θ ≤ 32.35. 3060 of which were non-equivalent by symmetry (Rint(on I)= 0.052). 2740 reflections were assumed as observed applying the condition I N 2σ(I). Lorentz-polarization and absorption corrections were made. The structure was solved by direct methods and refined by fullmatrix least-squares method using the SHELXS computer program (Sheldrick, G. M. [54], a program for automatic solution of crystal structure, University of Goettingen, Germany), using 19,114 reflections (very negative intensities were not assumed). The function minimized wasΣw||Fo|2 − |Fc|2|2, wherew=[σ2(I) + (0.0823P)2 + 0.1940P]−1, and P= (|Fo|2+ 2|Fc|2) / 3; f, f′ and f″ were taken from International Tables of X-Ray Crystallography (International Tables of X-Ray Crystallography (1974), Ed. Kynoch press, Vol. IV, pp 99–100 and 149).AllHatomswere computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atoms which are linked. The final R (on F) factor was 0.049, wR(on |F|2)= 0.138 and goodness of fit= 1.175 for all observed reflections. The number of refined parameters was 110. Max. shift/esd =0.00 and mean shift/esd = 0.00. Max. and min. peaks in final difference synthesis were 0. 934 and −0.589 eÅ−3, respectively.

[42] The [CuCl2(L2)]2 compound was obtained by slow solvent diffusion in ethanol/hexane of [CuCl2(L1)]. Analysis for C12H22Cl4Cu2N6 calcd/found (%): C, 27.76/27. 42; H, 4.27/4.13; N, 16.18/15.94 giving a satisfactory C, H, and N elemental analyses. ESI-MS(+) (H2O/MeOH) (higher peaks; relative abundance, %): m/z 282.6 (100) and 483.8(42) peaks attributable to [CuCl2(L2) +Na]+ and [Cu2Cl3(L2)2]+ ions, respectively. IR (KBr, cm−1): 3190, 3120 ν(C\H)ar; 2940, 2920 ν(C\H)al; 1650 [ν(C_C), ν(C_N)]ar; 1400 [δ(C_C), δ(C_N)]ar; and 773 γ(_C\H)oop present shifts (in relation with the free ligand) produced by the coordination with copper(II). Moreover the bands at 472, 428 ν(Cu\N) 356, and 322 ν(Cu\Cl) corroborate the copper coordination too. Conductivity (1.02 × 10−3 M in methanol): 32 Ω−1cm2mol−1 in agreement with a non-electrolyte complex. UV–vis (1.1 × 10−3 M in methanol) exhibits a single band at 620 nm.

[43] In the crystal structure of the [CuBr2(L1)], analogous to the [CuCl2(L1)] one, the Npz\Cu\Nam angles are about 80° which is too small for this kind of tridentate ligand with square-pyramidal geometry (usual angle of 90°) resulting in steric constraint that could promote the complex cleavage [6]. Similar Npz\Cu\Nam constrain angles (79.03° and 79.52°) have been observed in complex 5, ref. [10]. This behavior of the Npz\Cu\Nam angles with values near 80° is often observed in bidentate ligands, as the values obtained here for the [CuCl2(L2)]2 complex (Npz\Cu\Nam angles of 80.82°).

[44] Similar to [CuCl2(L1)], the complexes formed by bis[(3,5-dimethyl-1-pyrazolyl) methyl]ethylamine with Rh(I) [16] and Cd(II) [23] presented a strain in their Npz\metal\Nam angles induced by the short methylene bridges, undergoing the hemilability of the metal\Nam bonds and the coalescence in solution of two isomeric species of the complexes.

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Legends to figures

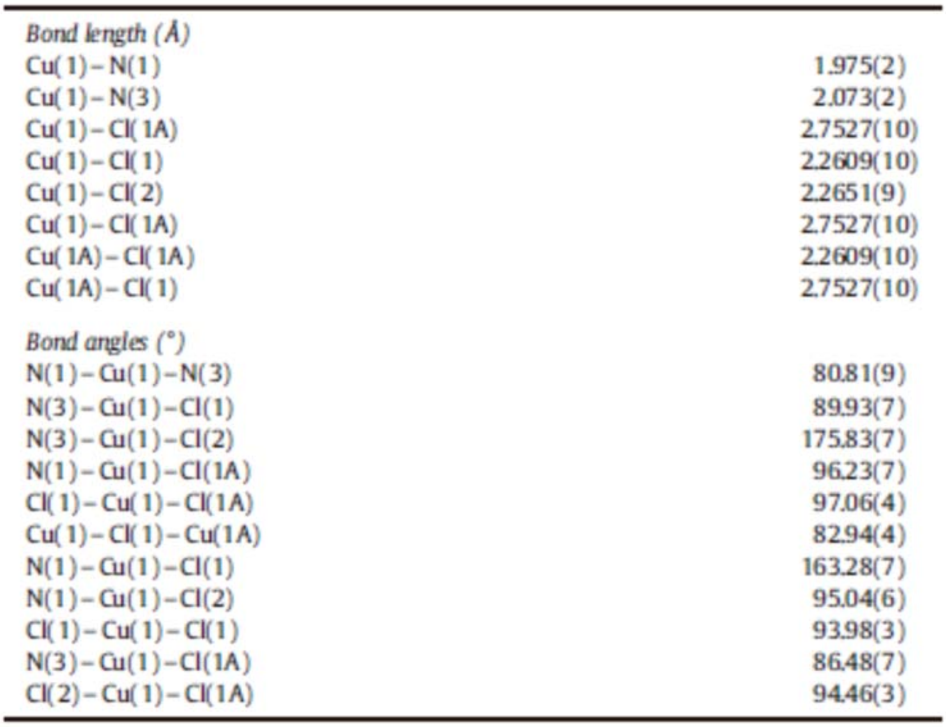
Figure 1. A) ORTEP diagramof the $[CuCl2(L2)]2$ binuclear complex showing an atomlabeling scheme. 50% probability of the amplitude displacement ellipsoids is shown. The hydrogen atoms are omitted for clarity. Scheme color: copper, orange; chlorine, green; nitrogen, blue and carbon, gray. B) Scheme of the possible formation of the $[CuCl2(L2)]2$ complex from the initial $[CuCl2(L1)]$ one in solution: step 1, rupture of the Cu\Npz bond, step 2, rupture of the Nam\CH2(Pz) bond and step 3, formation of the Cu\Cl bonds between two as formed mononuclear complexes.

Figure 2. Ferris wheel-like supramolecular self-assembly array along c direction of $[CuCl2(L2)]2$ complex.

Figure 3. Illustration of some of the intermolecular hydrogen bond interactions and the short contacts in the supramolecular structure. The blue dashed lines correspond to C(3)\H(3)···Cl(2)\Cu(1)···H(1)\C(1) double hydrogen bridges and the red dashed lines correspond to C(6)H2\H(6A)···H(2)\C(2) short distances.

Figure 4. Two dimensional (2D) layers of structural supramolecular arrays of the $[CuCl2(L2)]2$ complex through the a axis in the (011) plane (A) and along the b axis in the (101) plane (B). The red, blue and black dash lines indicate the hydrogen interactions, the short contacts and the distance between pyrazole rings, respectively.

Table 1 Selected bond lengths (Å) and bond angles (°) for the [CuCl2(L2)]2 complex. In parenthesis the estimated standard deviations (e.s.d.s.) are shown.



Bond length (Å)	
Cu(1)–N(1)	1.975(2)
Cu(1)–N(3)	2.073(2)
Cu(1)–Cl(1A)	2.7527(10)
Cu(1)–Cl(1)	2.2609(10)
Cu(1)–Cl(2)	2.2651(9)
Cu(1)–Cl(1A)	2.7527(10)
Cu(1A)–Cl(1A)	2.2609(10)
Cu(1A)–Cl(1)	2.7527(10)
Bond angles (°)	
N(1)–Cu(1)–N(3)	80.81(9)
N(3)–Cu(1)–Cl(1)	89.93(7)
N(3)–Cu(1)–Cl(2)	175.83(7)
N(1)–Cu(1)–Cl(1A)	96.23(7)
Cl(1)–Cu(1)–Cl(1A)	97.06(4)
Cu(1)–Cl(1)–Cu(1A)	82.94(4)
N(1)–Cu(1)–Cl(1)	163.28(7)
N(1)–Cu(1)–Cl(2)	95.04(6)
Cl(1)–Cu(1)–Cl(1)	93.98(3)
N(3)–Cu(1)–Cl(1A)	86.48(7)
Cl(2)–Cu(1)–Cl(1A)	94.46(3)

Figure 1

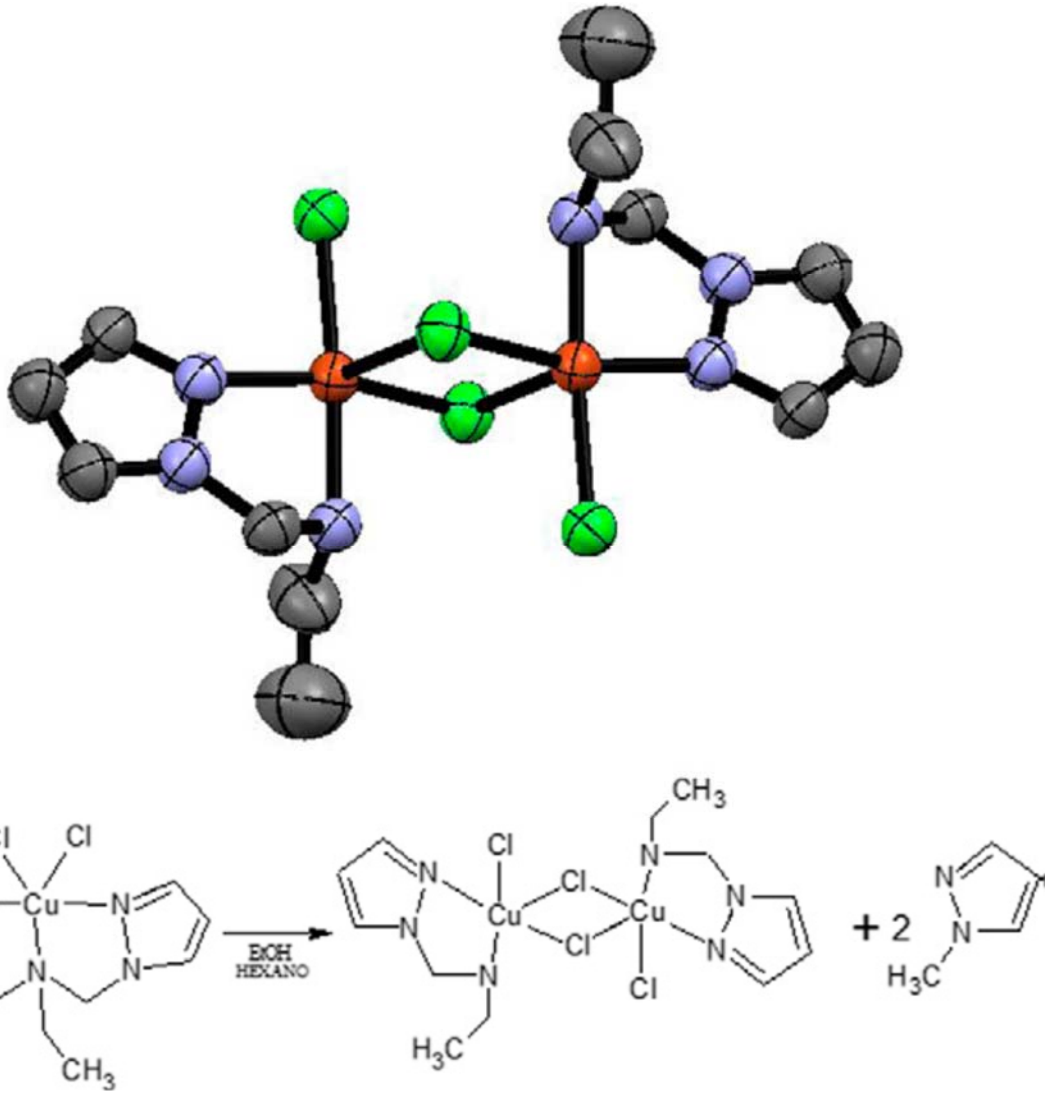


Figure 2

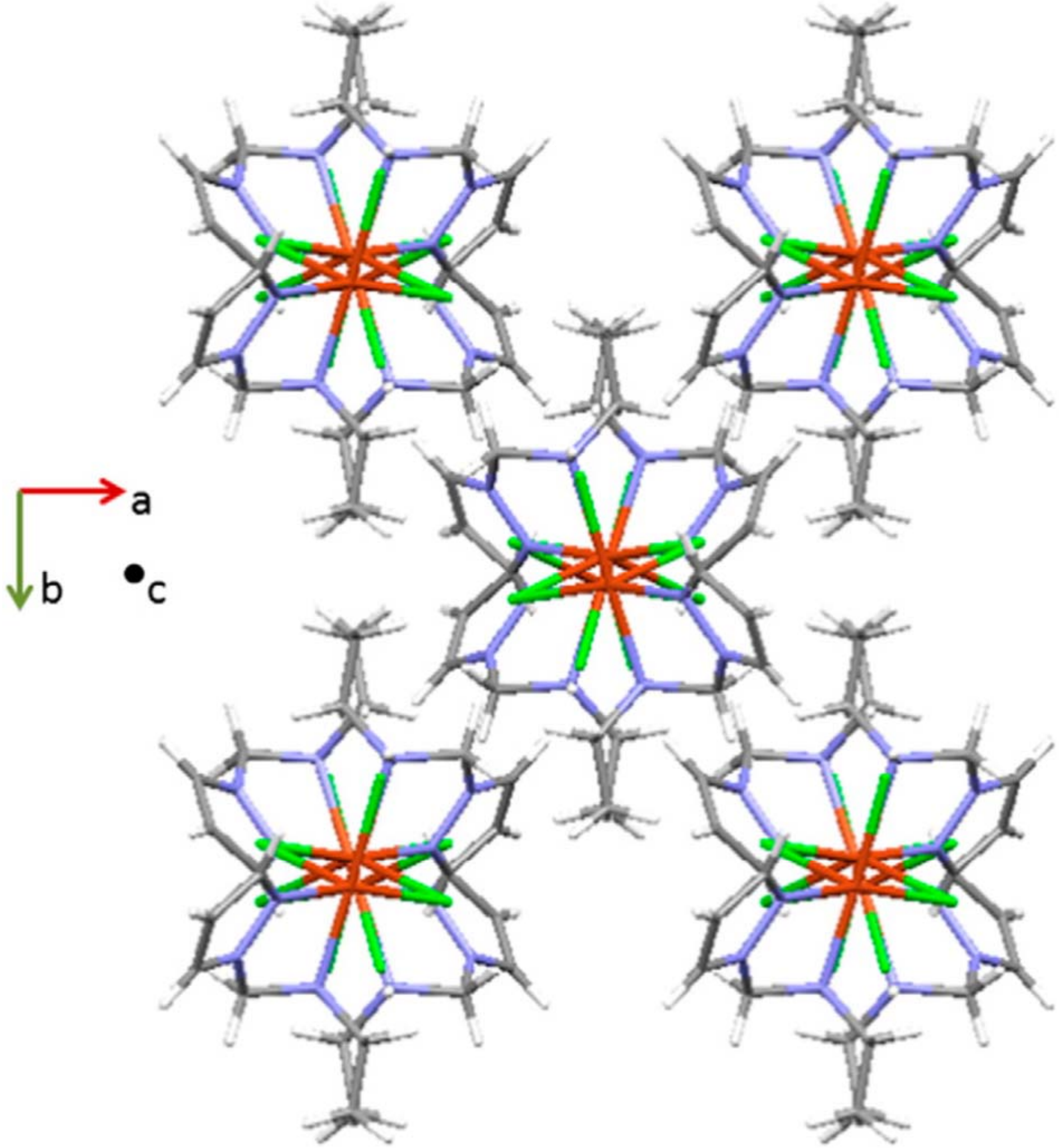


Figure 3

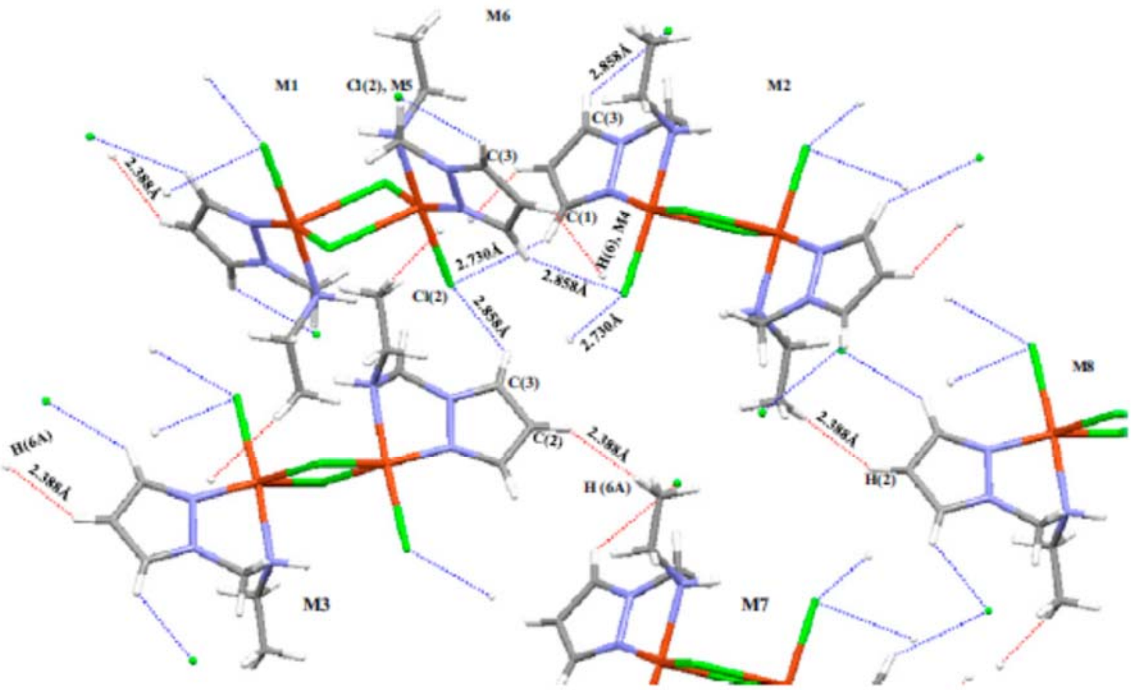

M6
M1
Cl(2), M5
2.858Å
C(3)
M2
2.388Å
C(3)
C(1)
H(6), M4
2.730Å
2.858Å
Cl(2)
2.858Å
2.730Å
C(3)
M8
H(6A)
2.388Å
C(2)
2.388Å
H (6A)
2.388Å
H(2)
M3
M7

Figure 4