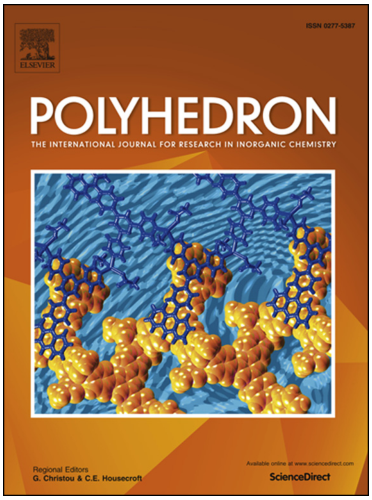

Anion modulated structural variations in copper(II) complexes with a semicarbazone Schiff base: Synthesis, characterization and self assembly

Mithun Das, Biswa Nath Ghosh, Kari Rissanen, Shouvik Chattopadhyay

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Anion modulated structural variations in copper(II) complexes with a semicarbazone Schiff base: Synthesis, characterization and self assembly

Mithun Das[a], **Biswa Nath Ghosh**[b], **Kari Rissanen**[b], **Shouvik Chattopadhyay** [a,*]

[a] *Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata 700032, India*

[b] *Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014 Jyväskylä, Finland*

e-mail: shouvik.chem@gmail.com Tel:+91-33-24572941

Abstract

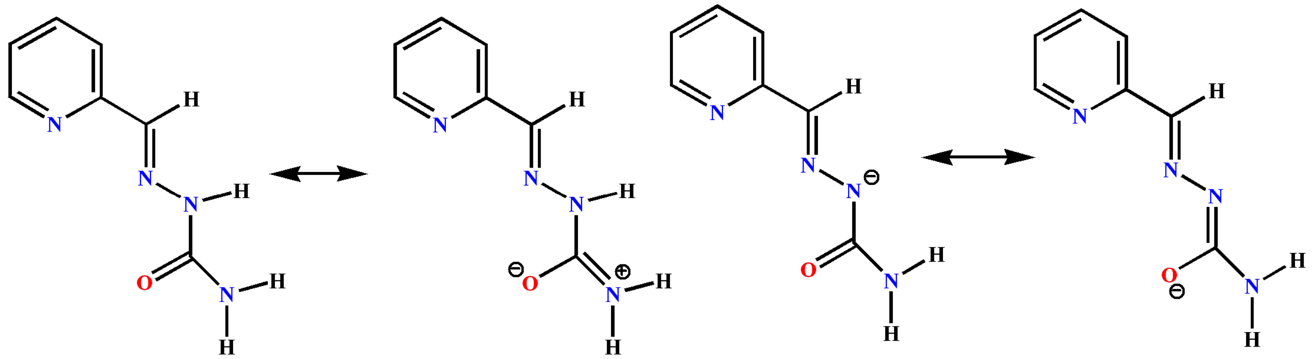
Two copper(II) complexes, $[Cu(L)N_3]_n$ (**1**) and $[Cu(HL)_2](I_3)(ClO_4)$ (**2**), where *HL= 2-pyridylaldehydesemicarbazone*, have been prepared and characterized by elemental analysis, IR and UV–Vis spectroscopy and single crystal X-ray diffraction studies. Complex **1** is a stair-like coordination polymer with square pyramidal geometry of copper(II), whereas, complex **2** is a mononuclear cationic bis-ligand complex of octahedral copper(II). Both the complexes show two-dimensional hydrogen bonded self assemblies.

Keywords: Schiff base; Copper(II); Square pyramidal; Stair-like polymer; Octahedral; Self assembly.

1. Introduction

Considerable research effort has been focused on the rational design and synthesis of functional coordination polymers with transition-metal cores owing to their potential applications in catalysis, porosity, chirality, luminescence, magnetism, electrical conductivity, spin-transition and non-linear optics [1-12]. In fact, they can behave as multifunctional materials [13-17]. Coordination polymers with diverse architectures such as 1D linear chain, zigzag chain, 2D square network, interwoven honeycomb, 3D square grid etc. have already been extensively developed [18-23]. Tunable bonding modes of the multi-dentate ligands have been exploited by several researchers to form several coordination polymers with structural diversities and tunable properties [24,25]. The ease of synthesis, stability under various conditions and structural versatility of the multi-dentate Schiff bases made them very popular in forming coordination polymers [26-28]. Amongst them, semicarbazone based Schiff bases constitute a special class as both their neutral and anionic forms (Scheme 1) may coordinate the metal ions to form a variety of complexes [29-32]. This family of ligands and their complexes is also known to be used as anticancer, antibacterial, antifungal and antivirus agents [33-38]. Reaction of semicarbazide hydrochloride with pyridine-2-carboxaldehyde to prepare the corresponding semicarbazone Schiff base has already been reported by several groups [39-41]. Even though the ligand has five potential donor atoms, it usually binds as a tridentate ligand using one oxygen and two nitrogen (pyridinic and azomethinic) atoms [42-44].

On the other hand, the chemistry of polynuclear copper(II) complexes is getting more importance now-a-days because of their relevance to various metallo-proteins and metallo-enzymes [45-49]. Their synthesis and characterization have also attracted the attention of the synthetic inorganic chemists due to their relevance in understanding the magneto-structural correlations arising from the electronic exchange coupling among copper(II) centers and in developing new molecular-based functional materials [50-53]. In the present work, we have used a semicarbazone based Schiff base to prepare two new copper(II) complexes. The structures of the complexes have been confirmed by single crystal X-ray diffraction studies. Presence of different counter anions with different coordination abilities favours the formation of complexes with different stereochemistry. Thus, a bis-ligand complex containing distorted octahedral copper(II) is formed, in absence of any coordinating counter anions and a polymeric complex with square-pyramidal copper(II) is produced in presence of strongly coordinating azide. Hydrogen bonding interactions in both the complexes form two-dimensional self assemblies. Herein, we report the synthesis, structural features, spectroscopic characterization, X-ray crystal structure analysis and hydrogen bonded self assemblies of the two new copper(II) complexes with a semicarbazone Schiff base.



HL

$(L)^{-}$

Scheme 1: Neutral (*HL*) and deprotonated $(L)^{-}$ forms of the *2-pyridylaldehyde semicarbazone* Schiff base.

2. Experimental

All chemicals were of reagent grade and purchased from Sigma-Aldrich. They were used without further purification.

2.1. Preparations

2.1.1 Preparation of the ligand [2-pyridylaldehydesemicarbazone (HL)]

The tridentate Schiff base ligand, *HL,* was synthesized by refluxing pyridine-2-carboxaldehyde (1 mmol, 0.10 mL) with semicarbazide hydrochloride (1 mmol, 120 mg) in methanol solution (20 mL) for ca. 1 h following the literature method [39-41]. Yellow solid was obtained from the reaction mixture on slow evaporation in open atmosphere. The ligand is stable in air and freely soluble in methanol. (Yield: 135 mg, 82%). Anal. Calc. for $C_7H_8N_4O$ (164.16): C, 51.21; H, 4.91; N, 34.13%. Found: C, 51.4; H, 4.7; N, 34.4%. IR (cm^{-1}): 3410, 3352 (NH_2); 1692 (C=O); 1589 (C=N). UV–Vis, λ_{max} (nm) [ε_{max} ($Lmol^{-1}cm^{-1}$)] (DMSO): 312 ($4.99x10^4$). ^1H NMR (DMSO-d_6) (ppm) δ: 10.49 (s, 1H), 8.51 (d, J = 4.59 Hz, 1H), 8.13 (d, J = 7.98 Hz, 1H), 7.78 (dd, J = 7.77, 7.56 Hz, 1H), 7.31 (dd, J = 7.31, 5.19 Hz, 1H), 7.87 (s, 1H), 6.60 (s, 2H).

*2.1.2. Preparation of complex $[Cu(L)N_3]_n$ (**1**)*

A methanol solution (20 mL) of copper(II) perchlorate hexahydrate (1 mmol, 370 mg) was added to the methanol solution (10 mL) of *HL* (1 mmol) and refluxed for 30 min. 10 mL methanol-water (2:1) solution of sodium azide (1 mmol, 65 mg) was added into it and refluxed for additional 2 h. The resulting dark green solution was set aside at room temperature. Single crystals, suitable for X-ray diffraction, were obtained from the reaction mixture on slow evaporation in open atmosphere. (Yield: 198 mg, 74%). Anal. Calc. for $C_7H_7CuN_7O$ (268.74): C, 31.29; H, 2.63; N, 36.49%. Found: C, 31.4; H, 2.3; N, 36.7%. IR (cm^{-1}): 3381, 3298 (NH_2); 2067 (N_3); 1642 (C=O); 1606 (C=N). UV–Vis, λ_{max} (nm) [ε_{max} ($Lmol^{-1}cm^{-1}$)] (DMSO): 301 ($3.97x10^4$), 393 ($6.57x10^4$), 671 ($3.94x10^2$).

*2.1.2. Preparation of complex $[Cu(HL)_2](I_3)ClO_4$ (**2**)*

A methanol solution (10 mL) of copper(II) perchlorate hexahydrate (1 mmol, 370 mg) was added to the methanol solution (10 mL) of *HL* (1 mmol) and refluxed for 30 min. 10 mL methanol-water (2:1) solution of potassium iodide (1 mmol, 166 mg) was added into it and refluxed for additional 2 h. The resulting dark green solution was kept at room temperature. Single crystals, suitable for X-ray diffraction, were obtained from the reaction mixture on slow evaporation in open atmosphere. (Yield: 542 mg, 62%). Anal. Calc. for $C_{14}H_{16}CuN_8O_6ClI_3$ (872.04): C, 19.28; H, 1.85; N, 12.85%. Found: C, 19.1; H, 1.7; N, 13.1%. IR (cm^{-1}): 3427, 3337 (NH_2); 1675 (C=O); 1599 (C=N): 1088 (Cl–O). UV–Vis, λ_{max} (nm) [ε_{max} (Lmol^{-1}cm^{-1})] (DMSO): 301 (3.52x10^4), 388 (2.88 x10^4), 844 (1.41 x10^2).

2.2. Physical measurements

Elemental analysis was performed using a PerkinElmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a PerkinElmer Spectrum Two FT-IR spectrophotometer. Electronic spectra in DMSO (1100–300 nm) were recorded in a JASCO V-630 spectrophotometer. Fluorescence spectra were obtained on SHIMADZU RF-5301PC spectrofluorophotometer at room temperature. ^{1}H NMR spectrum was recorded on Bruker DRX-300 NMR Spectrometer at 300 MHz using DMSO-d$_6$ as solvent.

2.3. Crystal data collection and refinement

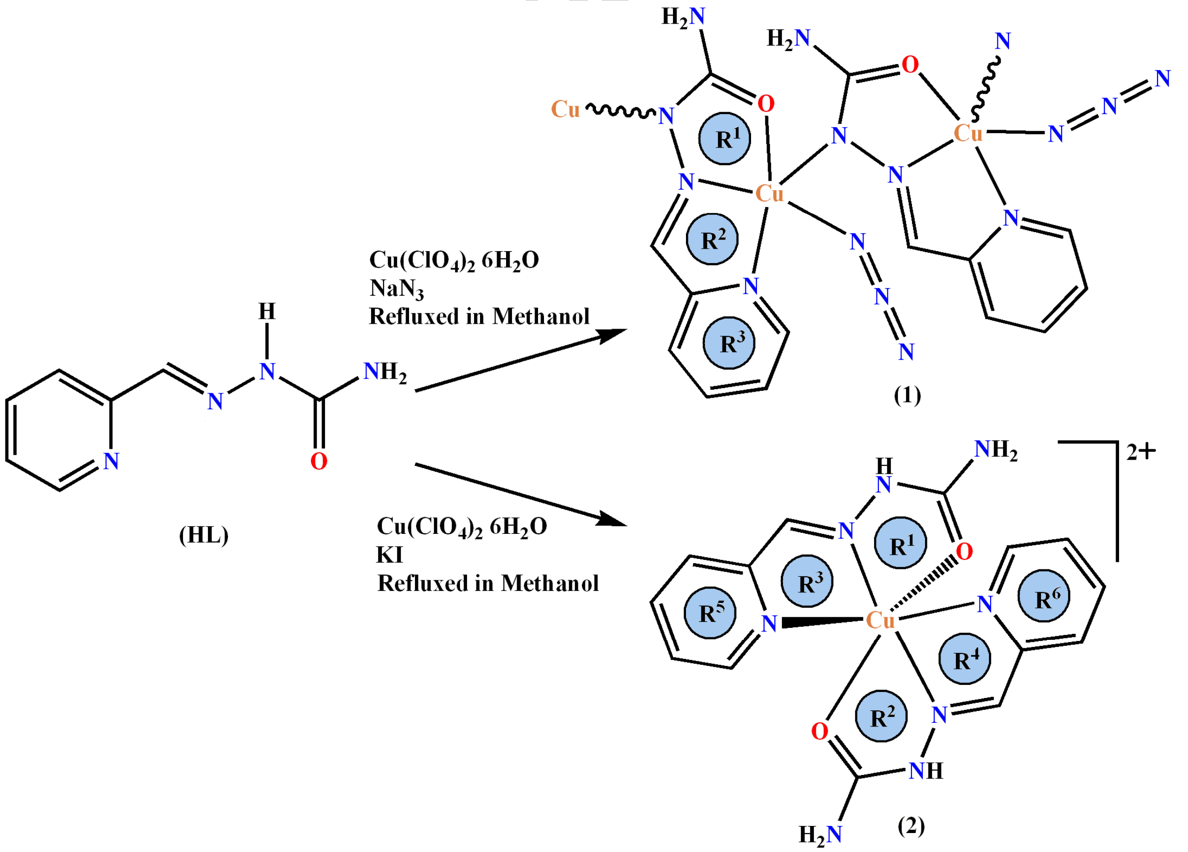
The structural analysis of **1** was performed using Bruker-Nonius Kappa CCD diffractometer equipped with APEX II detector with graphite-monochromatized Mo-*K*α (λ = 0.71073 Å) radiation at 123 K. Collect software was used for the data measurement [54] and DENZO-SMN for the processing [55]. Absorption correction was applied using the multi-scan

SADABS programme [56]. In **1**, two nitrogen atoms, N(6) and N(7) were disordered and two sets of atoms were refined with occupancies of x and 1-x with x = 0.60(1) in both the cases. Data for **2** were collected at 123 K on an Agilent Super Nova Dual diffractometer with Atlas detector using mirror-monochromatized Mo-*K*α (λ = 0.71073 Å) radiation. CrysAlis Program was used for the data collection and processing [57]. The intensities were corrected for absorption using the Analytical face index absorption correction method [58]. The structures were solved by charge flipping method with SUPERFLIP [59] and refined by full-matrix least-squares methods using the WinGX software [60], which utilizes the SHELXL-97 module [61]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached with carbon atoms were introduced in calculated positions with isotopic thermal parameters using the 'riding model'. The hydrogen atoms, attached with nitrogen atoms, were located by difference Fourier maps and were kept fixed. ORTEP figures were plotted using *Ortep-3 for Windows* [62] and structures were analysed with the *Mercury* v 2.3 [63].

3. Results and discussion

3.1. Synthesis

The ligand *HL* (*2-pyridylaldehydesemicarbazone*) was prepared by the 1:1 condensation of the pyridine-2-carboxaldehyde with semicarbazide hydrochloride in methanol following literature method [39-41]. The methanol solution of ligand was then made to react with copper(II) perchlorate hexahydrate. Addition of sodium azide into the solution produced stair-like polymeric complex **1**. On the other hand, addition of potassium iodide resulted the formation of mononuclear cationic bis-ligand complex **2**, with tri-iodide and perchlorate as counter anions. In-situ formation of tri-iodide (from iodide) was not unlikely in the acidic medium, used in the synthesis of the complex. The formation of both the complexes is shown in Scheme 2. Lower coordinating ability of tri-iodide or perchlorate compared to azide could be related with the variations of the structures of **1** and **2**. In absence of any coordinating anion, octahedral bis-ligand complex (**2**) was resulted as the sole product, even if the copper(II): ligand ratio is varied. On the other hand, strongly coordinating azide occupied one coordination site of copper(II) and the formation of the bis-ligand complex could be stopped. The potential tridentate semicarbazone Schiff base ligand behaved as a tetradentate ligand and coordinated to a neighbouring copper(II) moiety through a nitrogen donor to form a stair-like polymeric complex **1**. Use of sodium azide (a salt of strong base and weak acid) increases the pH of the medium and the deprotonation of the ligand is favoured. On the other hand, KI being a salt of strong acid and strong base, cannot impart a considerable increase in the pH of the medium. Thus use of KI cannot deprotonate the ligand.



Scheme 2: Synthetic route of the complexes **1** and **2**.

3.2. X-ray crystallographic studies

*3.2.1. Complex $[Cu(L)N_3]_n$ (**1**)*

Complex **1** crystallizes in monoclinic space group $P2_1/a$. The asymmetric unit consists of a copper(II) center with one deprotonated semicarbazone ligand $(L)^-$ and a coordinated azide (Figure 1). Copper(II) is penta-coordinated. The geometry of penta-coordinated metal center may conveniently be measured by the Addison parameter (τ), which is 0.044 in this case [$\tau = (\alpha - \beta)/60$, where, α and β are the two largest ligand-metal-ligand angles of the coordination sphere], suggesting square pyramidal geometry ($\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid) [64]. Copper(II) is coordinated by two nitrogen atoms, N(1) and N(2), and one oxygen atom, O(1), of the deprotonated ligand $(L)^-$ and one azide nitrogen, N(5), in the equatorial plane. Another nitrogen atom, $N(3)^*$of $(L)^-$ from a symmetry related molecule (*=1/2+x,1/2-y,z) coordinates copper(II) in its apical position to form a stair-like polymer (Figure 2). Selected bond lengths and angles are listed in Table 2. The C(7)–N(3) and C(7)–N(4) bond lengths {1.364(5) and 1.344(4) Å} are comparable and are close to the carbon-nitrogen single bond length for these type of systems [65]. On the other hand, C(7)–O(1) bond length {1.283(4) Å} indicates the partial cabon-oxygen double bond character [66]. These bond lengths indicate the presence of deprotonated form of semicarbazone Schiff base $(\boldsymbol{L})^-$ in complex **1**.

The copper(II)····copper(II) distance in the complex core is 5.2087(6) Å and the torsion angle $Cu(1)\text{-}N(2)^*\text{-}N(3)^*\text{-}Cu(1)^*$ is 175.9(1)º. The deviations of the coordinating atoms, N(1), N(2), N(5) and O(1), from the mean square basal plane through them are 0.054(2), -0.063(2), -0.045(2) and 0.055(2) respectively. As usual for a square pyramid structure, the copper(II) is slightly pulled out of the mean squares plane towards the apical donor atom $N(3)^*$ at a distance

0.2962(4) Å. The ligand creates two coordinating ring **R^1** and **R^2** with central copper(II) having slight deviations from their ideal planner orientation (Ring numbering refers to Scheme 2). The five atoms Cu(1), N(2), N(3), C(7) and O(1) of one coordinating ring **R^1** show r.m.s. deviation 0.025(1), -0.030(2), 0.017(3), 0.015(3) and -0.028(2) respectively, whereas five atoms Cu(1), N(1), C(5), C(6) and N(2) of another coordinating ring **R^2** show r.m.s. deviation 0.023(1), -0.035(2), 0.032(3), -0.003(3) and -0.017(2) respectively.

There are two hydrogen atoms, H(4A) and H(4B), available in the ligand part of **1** for hydrogen bonding. Of these, H(4A) is hydrogen bonded with an oxygen atom, O(1), of the symmetry related (* = -1/2+x,1/2-y,z) molecule and H(4B) is hydrogen bonded with the azide nitrogen atom, N(7) of another symmetry related ($^\Delta$ = 1-x,-y,-z) molecule (Figure 3). The combination of these two hydrogen bonding interactions produces two-dimensional hydrogen bonded self assembly as shown in Figure 4. The detail geometric features of hydrogen bonding interactions are given in Table 4.

The complex shows significant cation$\cdots\pi$, C–H$\cdots\pi$ interactions and $\pi\cdots\pi$ stacking. One copper centre, Cu(1), creates bi-furcated cation$\cdots\pi$ interactions with chelate ring **R^2** and pyridine ring **R^3** of a symmetry related (1-x,-y,1-z) molecule (Ring numbering refers to Scheme 2). Again, one aromatic hydrogen, H(6) of the pyridine ring creates bi-furcated C–H$\cdots\pi$ interactions with same chelate ring **R^2** and pyridine ring **R^3** of another symmetry related (-1/2+x,1/2-y,z) molecule. There are three significant $\pi\cdots\pi$ stacking of two chelate ring **R^1**, **R^2** and one pyridine ring **R^3** with **R^3**, **R^2** and **R^1** of symmetry related (1-x,-y,1-z) molecule respectively. These C–H$\cdots\pi$, cation$\cdots\pi$ interactions and $\pi\cdots\pi$ stacking are shown in Figure 5. Combinations of these supramolecular forces create same self-assembled plane (Figure 6) as hydrogen bonded self assembly produces. Geometric features of the cation···π, C–H···π interactions and π···π stacking are given in Tables 5-7 respectively.

*3.2.2. Complex $[Cu(HL)_2](I_3)ClO_4$ (**2**)*

Complex **2** crystallizes in triclinic space group $P\bar{1}$. The asymmetric unit consists of discrete cation $[Cu(HL)_2]^{2+}$ with one tri-iodide and one perchlorate as counter anions. Single-crystal X-ray diffraction studies revealed that the cationic unit features a distorted octahedron structure having CuN_4O_2 core. Copper(II) is coordinated meridionally by one oxygen atom, O(1), one pyridyl nitrogen atom, N(1) and one imine nitrogen atoms, N(2) of a non-deprotonated semicarbazone ligand (*HL*) and one oxygen atom, O(2), one pyridyl nitrogen atom, N(5) and one imine nitrogen atoms, N(6) of another a non-deprotonated semicarbazone ligand (*HL*) to form bis-ligand complex (Figure 7). The C(7)–N(4) and C(14)–N(8) bond lengths {1.330(5) and 1.324(6) Å} are shorter compared to the bond lengths of C(7)–N(3) and C(14)–N(7) {1.379(7) and 1.384(5) Å} respectively. On the other hand, C(7)–O(1) and C(14)–O(2) distances (1.250(5) and 1.243(5) Å) are in the range of carbon-oxygen double bond [40], which indicates the presence of non-deprrotonated (neutral) form of the semicarbazone Schiff base (***HL***) in complex **2**, contrary to complex **1**.

These two ligands create two sets of chelate ring $\mathbf{R^1}$, $\mathbf{R^3}$ and $\mathbf{R^2}$, $\mathbf{R^4}$ (two chelate ring by each ligand) with central copper(II), where, each of the chelate rings shows slight deviations from their ideal planner orientation (Ring numbering refers to Scheme 2). The five atoms Cu(1), N(2), N(3), C(7), O(1) of ring $\mathbf{R^1}$ and another five atoms of Cu(1), N(1), C(5), C(6), N(2) of ring $\mathbf{R^3}$ show r.m.s. deviations -0.021(1), 0.030(2), -0.023(3), -0.006(4), 0.019(3) and -0.010(1), 0.021(3), 0.002(3), -0.024(3), 0.012(4) respectively. On the other hand, five atoms Cu(1), N(6), N(7), C(14), O(2) of ring $\mathbf{R^2}$ and five atoms Cu(1), N(5), C(12), C(13), N(6) of ring $\mathbf{R^4}$ show r.m.s. deviation -0.056(1), 0.065(4), -0.024(4), -0.060(4), 0.075(3) and -0.007(1), 0.002(3), 0.005(4), -0.015(4), 0.014(3) respectively. The Cu–N [1.940(4), 1.993(4) and 2.077(4) Å] and Cu–O [2.154(3) Å] bond lengths in the equatorial plane are comparable with those in related copper(II) complexes [67–70]. However, the axial bond lengths [Cu(1)–O(2): 2.340(3) Å and Cu(1)–N(5): 2.237(3) Å] are longer than that in the equatorial plane, as a consequence of static Jahn-Teller effect.

There are six hydrogen atoms, H(3), H(4A), H(4B), H(7), H(8A) and H(8B), available for hydrogen bonding interactions. Of these, H(3) and H(4B) are hydrogen bonded with two oxygen atoms, O(6) and O(5) respectively, of a perchlorate and H(4A) is hydrogen bonded with the iodine atom, I(1), of the tri-iodide counter anion. There is another hydrogen bond between the hydrogen atom, H(8A) and a symmetry related ($^{\lozenge}$=-x,1-y,2-z) iodine atom, I(3)$^{\lozenge}$ of a tri-iodide. On the other hand, H(8B) and H(7) form bifurcated hydrogen bonds with a symmetry related ($^{☼}$=-1+x,-1+y,1+z) perchlorate oxygen atom, O(4)$^{☼}$. H(7) is hydrogen bonded with O(1)† of a symmetry related (†=-x,-y,2-z) molecule. All these hydrogen bonding interactions are shown in Figure 8. The combination of all these hydrogen bonded interactions creates a two-dimensional self assembly (Figure 9). The detail geometric features of hydrogen bonding interactions are given in Table 4.

The complex shows significant C–H···π interactions and π···π stacking. One aromatic hydrogen, H(1) of one $(L)^-$ creates intra-molecular C–H···π interactions with the chelate ring $\mathbf{R}^2$ of another $(L)^-$ present in the complex (Ring numbering refers to Scheme 2). Another aromatic hydrogen, H(10), attached with $\mathbf{R}^6$ shows inter-molecular C–H···π interactions with pyridine ring $\mathbf{R}^5$ of symmetry related (-x,-y,1-z) molecule. There are four significant π···π stacking present within the complex. Two chelate ring $\mathbf{R}^2$ and $\mathbf{R}^4$ of one $(L)^-$ create two π···π stacking with $\mathbf{R}^4$ and $\mathbf{R}^2$ of a symmetry related (-x,-y,2-z) molecule and pyridine ring $\mathbf{R}^6$ of same $(L)^-$ shows π···π stacking with $\mathbf{R}^6$ of another symmetry related (-x,-y,1-z) molecule. Again one chelate ring $\mathbf{R}^3$ of another $(L)^-$ present in the complex shows π···π stacking with $\mathbf{R}^3$ of symmetry related (-x,1-y,2-z) molecule. These C–H···π interactions and π···π stacking are shown in Figure 10. Combinations of these supramolecular forces create self-assembled plane as shown in Figure 11. Geometric features of C–H···π interactions and π···π stacking are given in Tables 6 and 7 respectively.

3.3. IR and electronic spectra and photo-physical study

The infrared spectra of both complexes are quite similar with the ligand (***HL***). In the IR spectra of **1**, **2** and ***HL***, distinct bands due to azomethine (C=N) group appear at 1606, 1599 and 1588 cm^{-1} whereas, bands for carbonyl (C=O) group are noticed at 1642, 1675 and 1692 cm^{-1} respectively [44,71]. The sharp bands (doublet) for the asymmetric and symmetric stretching vibrations, due to the amino NH_2 group appear at 3381, 3298 cm^{-1} (for **1**), 3427, 3337 cm^{-1} (for **2**) and 3410, 3352 cm^{-1} (for ***HL***) [72]. In the IR spectrum of **1**, the appearance of a strong band at 2067 cm^{-1} indicates the presence of monodentate azide [73]. The sharp, strong, single peak at 1088 cm^{-1} gives evidence for the presence of ionic perchlorate in the spectrum of **2** [74].

The electronic spectrum of complex **1** shows an absorption band at 671 nm which is assigned as d-d transition of square pyramidal copper(II) centre [75]. Complex **2** shows a single absorption band at 844 nm in the visible range, as also observed in other octahedral copper(II) complexes [76]. The electronic spectra of complexes **1** and **2** show absorption bands at 393 and 388 nm respectively, which are characteristics of transition metal complexes with Schiff base ligands [77]. Another high energy bands are observed at 301, 300 and 312 nm for **1**, **2** and ***HL*** respectively. No other bands are observed at higher wavelength in the electronic spectrum of the ligand.

Both the complexes exhibit emission in the visible region (427 nm for **1** and 423 nm for **2**) upon irradiation with UV-light (301 nm) in DMSO at room temperature. Ligand molecule (***HL***) also shows same type of emission band at 421 nm on irradiation at 312 nm in DMSO at room temperature. These emission bands can be attributed to intra-ligand fluorescent $^1(\pi \rightarrow \pi^*)$ emission of the coordinated ligand [78]. The emission spectra are depicted in Figure 12.

4. Conclusion

In the present work, we have used a semicarbazone Schiff base to prepare two copper(II) complexes. The ligand is acting as a tridentate ligand in complex **2**, but is acting as tetradentate ligand in complex **1**. The change in the denticity of the ligand is controlled by the presence of the counter anions in the medium. In absence of azide, the pH of the medium is relatively lower, and therefore, the deprotonation of the semicarbazone Schiff base is stopped and the ligand acts as a tridentate one to form an octahedral bis-ligand complex. On the other hand, when azide is added, the pH of the medium increases and the deprotonation of the ligand is favoured. The deprotonation makes the ligand tetradentate one and a polynuclear complex, **1**, is formed. The isolation and crystal structure determination of complex **1** unambiguously show that the semicarbazone Schiff base, which is generally used as tridentate ligand, can also act as tetradentate ligand to form coordination polymers. Such bonding mode is unprecedented for these types of ligands. Thus it opens up new possibilities for the synthesis of several multinuclear complexes with semicarbazone Schiff bases.

Acknowledgments

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Appendix A. Supplementary data

CCDC 974903 and 974904 contain the supplementary crystallographic data for **1** and **2** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] K. Hong, H. Chun, Chem. Commun. 49 (2013) 10953-10955.

[2] M. Karthikeyan , B. Bhagyaraju , C.R. Mariappan , S.M. Mobin , B. Manimaran, Inorg. Chem. Commun. 20 (2012) 269–272.

[3] A. Akou, C. Bartual-Murgui, K. Abdul-Kader, M. Lopes, G. Molnár, C. Thibault, C. Vieu, L. Salmon, A. Bousseksou, Dalton Trans. 42 (2013) 16021-16028.

[4] X.-Y. Chen, H.-Y. Shi, R.-B. Huang, L.-S. Zheng, J. Tao, Chem. Commun. 49 (2013) 10977-10979.

[5] V. Mahalakshmi, A. Lincy, J. Thomas, K.V. Saban, Optik 125 (2014) 191– 195.

[6] F. Du, M. Zhao, X. Long, S. Du, Inorg. Chem. Commun. 38 (2013) 39–42.

[7] R.L. Prasad, A. Kushwaha, J. Coord. Chem. 65 (2012) 4230–4244.

[8] V. Bon, I. Senkovska, M.S. Weiss, S. Kaskel, CrystEngComm 15 (2013) 9572–9577.

[9] R. Sen, D. Saha, D. Mal, P. Brandão, Z. Lin, Eur. J. Inorg. Chem. (2013) 5103–5109.

[10] Y.-H. Liao, W. Hsu, C.-C. Yang, C.-Y. Wu, J.-D. Chen, J.-C. Wang, CrystEngComm 15 (2013) 3974–3983.

[11] H.-Y. Cao, Q.-Y. Liu, C.-M. Liu, Y.-L. Wang, L.-L. Chen, L.-H. Xiong, Inorg. Chem. Commun. 34 (2013) 12–14.

[12] Y. Wang, X.-X. Li, H. Jiang, B.-W. Xia, N. Deng, Y.-W. Zhu, G.-P. Jin, X.-M. Ni, J.-B. He, Inorg. Chem. Commun. 35 (2013) 34–37.

[13] A. Gallego, O. Castillo, C.J. Gómez-García, F. Zamora, S. Delgado, Inorg. Chem. 51 (2012) 718–727.

[14] B. Gole, A.K. Bar, A. Mallick, R. Banerjee, P.S. Mukherjee, Chem. Commun. 49 (2013) 7439-7441.

[15] Q. Han, C. He, M. Zhao, B. Qi, J. Niu, C. Duan, J. Am. Chem. Soc. 135 (2013) 10186–10189.

[16] N. Xu, J. Yang, Y.-C. He, Y.-Y. Liu, J.-F. Ma, CrystEngComm 15 (2013) 7360–7371.

[17] H.-F. Chen, W.-B. Yang, L. Lin, X.-G. Guo, X.-J. Dui, X.-Y. Wu, C.-Z. Lu, C.-J. Zhang, J. Solid State Chem. 201 (2013) 215–221.

[18] W. Ju, H. Zhang, P. Wang, L. Chen, L. Huang, Y. Xu, Inorg. Chim. Acta 407 (2013) 160–166.

[19] Q. Zha, C. Ding, X. Rui, Y. Xie, Cryst. Growth Des. 13 (2013) 4583–4590.

[20] X. Zhao, J. Dou, D. Sun, P. Cui, D. Sun, Q. Wu, Dalton Trans. 41 (2012) 1928-1930.

[21] R. Sanz, F. Martínez, G. Orcajo, L. Wojtas, D. Briones, Dalton Trans. 42 (2013) 2392–2398.

[22] A. Mitra, C.T. Hubley, D.K. Panda, R.J. Clark, S. Saha, Chem. Commun. 49 (2013) 6629-6631.

[23] T. Borjigin, F. Sun, J. Zhang, K. Cai, H. Ren, G. Zhu, Chem. Commun. 48 (2012) 7613–7615.

[24] M. Wei, X. Wang, X. Duan, Chem. Eur. J. 19 (2013) 1607–1616.

[25] F. Luo, Y.-X. Che, J.-M. Zheng, Inorg. Chem. Commun. 9 (2006) 1045–1048.

[26] P.-P. Yang, X.-Y. Song, R.-N. Liu, L.-C. Li, D.-Z. Liao, Dalton Trans. 39 (2010) 6285-6294.

[27] L. Zhao, J. Wu, H. Ke, J. Tang, CrystEngComm15 (2013) 5301–5306.

[28] T. Lei, Q. Gao, W.-Q. Chen, Y.-M. Chen, W. Liu, S.-M. Yang, W.-W. Chen, W. Li, Y. Li, Inorg. Chem. Commun. 30 (2013) 92–96.

[29] T.A. Reena, E.B. Seena, M.R.P. Kurup, Polyhedron 27 (2008) 1825-1831.

[30] R. Vafazadeh, R. Esteghamat-Panah, A.C. Willis, A.F. Hill, Polyhedron 48 (2012) 51–57.

[31] B. Shaabani, A.A. Khandar, F. Mahmoudi, M.A. Maestro, S.S. Balula, L. Cunha-Silva, Polyhedron 57 (2013) 118–126.

[32] Z. Afrasiabi, R. Almudhafar, D. Xiao, E. Sinn, A. Choudhury, A. Ahmad, A. Vyas, F. Sarkar, S. Padhye, Transition Met. Chem. 38 (2013) 665–673.

[33] É.A. Enyedy, G.M. Bognár, N.V. Nagy, T. Jakusch, T. Kiss, D. Gambino, Polyhedron 67 (2014) 242–252.

[34] P. Anitha, N. Chitrapriya, Y.J. Jang, P. Viswanathamurthi, J. Photochem. Photobiol. B 129 (2013) 17–26.

[35] L. Jafri, F.L. Ansari, M. Jamil, S. Kalsoom, S. Qureishi, B. Mirza, Chem. Biol. Drug Des. 79 (2012) 950-959.

[36] M.C. Rodríguez-Argüelles, S. Mosquera-Vázquez, J. Sanmartín-Matalobos, A.M. García-Deibe, C. Pelizzi, F. Zani, Polyhedron 29 (2010) 864-870.

[37] K. Alomar, V. Gaumet, M. Allain, G. Bouet, A. Landreau, J. Inorg. Biochem. 115 (2012) 36–43.

[38] N.C. Kasuga, K. Onodera, S. Nakano, K. Hayashi, K. Nomiya, J. Inorg. Biochem. 100 (2006) 1176-1186.

[39] J. Zhou, Z.-F. Chen, Y.-S. Tan, X.-W. Wang, Y.-H. Tan, H. Liang, Y. Zhang, Acta Cryst. E60 (2004) m519-m521.

[40] E.R. Garbelini, M. Hörner, V.F. Giglio, A.H. da Silva, A. Barison, F.S. Nunes, Z. Anorg. Allg. Chem. 635 (2009) 1236-1241.

[41] Q. Yu, X. Bao, L. Zhu, H. Bian, H. Liang, Chem. J. Internet. 8 (2006) 49.

[42] L.-F. Deng, G.-Q. Guo, D.-C. Zhong, J.-H. Deng, M.-P. Guo, Acta Cryst. E63 (2007) m2434-m2435.

[43] J. Zhou, Z.-F. Chen, X.-W. Wang, Y.-S. Tan, H. Liang, Y. Zhang, Acta Cryst. E60 (2004) m568-m570.

[44] E.R. Garbelini, M. Hörner, M.B. Behm, D.J. Evans, F.S. Nunes, Z. Anorg. Allg. Chem. 634 (2008) 1801-1806.

[45] A. Matuz, M. Giorgi, G. Speier, J. Kaizer, Polyhedron 63 (2013) 41–49.

[46] K.D. Karlin, Z. Tyeklár, Bioinorganic Chemistry of Copper, Chapman & Hall, New York, 1993.

[47] K.D. Karlin, J.C. Hayes, Y. Gultneh, R.W. Cruse, J.W. McKown, J.P. Hutchinson, J. Zubieta, J. Am. Chem. Soc. 106 (1984) 2121-2128.

[48] R.C. Maji, S.K. Barman, S. Roy, S.K. Chatterjee, F.L. Bowles, M.M. Olmstead, A.K. Patra, Inorg. Chem. 52 (2013) 11084−11095.

[49] G. Csire, J. Demjén, S. Timári, K. Várnagy, Polyhedron 61 (2013) 202–212.

[50] M.A. Halcrow, Chem. Soc. Rev. 42 (2013) 1784-1795.

[51] Y.-Z. Zhang, H.-Y. Wei, F. Pan, Z.-M. Wang, Z.-D. Chen, S. Gao, Angew. Chem., Int. Ed. 44 (2005) 5841-5846.

[52] B. Chen, M. Eddaoudi, T.M. Reineke, J.W. Kampf, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 11559-11560.

[53] J.Y. Lu, Coord. Chem. Rev. 246 (2003) 327-347.

[54] R.W. Hooft, COLLECT, Nonius BV, Delft, The Netherlands, 1998.

[55] Z. Otwinowski, W. Minor, Methods in Enzymology, 1997, 276, Macromolecular Crystallography, Part A, 307.

[56] G.M. Sheldrick (2008). SADABS, Bruker Analytical X-ray system, Inc., Madison, Wisconsin.

[57] CrysAlisPro, Agilent Technologies. Version 1.171.36.21 (2012).

[58] R.C. Clark, J.S. Reid, Acta Cryst. A51 (1995) 887-897.

[59] L. Palatinus, G. Chapuis, J.Appl. Cryst. 40 (2007) 786-790.

[60] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837-838.

[61] G.M. Sheldrick, Acta Cryst. A64 (2008) 112-122.

[62] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565-566.

[63] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Cryst. 41 (2008) 466-470.

[64] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349-1356.

[65] E.R. Garbelini, R.R. Ribeiro, M. Horner, A. Locatelli, F.S. Nunes, Spectrochim. Acta, A 78 (2011) 1337-1341.

[66] E.R. Garbelini, M. da Graça, M.B. Martin, D.F. Back, D.J. Evans, M. Müller-Santos, R.R. Ribeiro, E.S. Lang, F.S. Nunes, J. Mol. Struct. 1008 (2012), 35-41.

[67] O.Z. Yeşilel, Y. Kılıç, O. Şahin, O. Büyükgüngör, Polyhedron 67 (2014) 122–128.

[68] J. Halaška, A. Pevec, P. Strauch, B. Kozlevčar, M. Koman, J. Moncol, Polyhedron 61 (2013) 20–26.

[69] D. Schweinfurth, M.M. Khusniyarov, D. Bubrin, S. Hohloch, C.-Y. Su, B. Sarkar, Inorg. Chem. 52 (2013) 10332‒10339.

[70] C.V. Esteves, P. Lamosa, R. Delgado, J. Costa, P. Désogère, Y. Rousselin, C. Goze, F. Denat, Inorg. Chem. 52 (2013) 5138‒5153.

[71] M. Das, S. Chattopadhyay, J. Mol. Struct. 1051 (2013) 250–258.

[72] M. Das, S. Chatterjee, S. Chattopadhyay, Polyhedron 68 (2014) 205–211.

[73] M. Das, S. Chattopadhyay, Polyhedron 50 (2013) 443–451.

[74] M. Das, S. Chatterjee, S. Chattopadhyay, Inorg. Chem. Commun. 14 (2011) 1337–1340.

[75] M. Das, B.N. Ghosh, A. Valkonen, K. Rissanen, S. Chattopadhyay, Polyhedron 60 (2013) 68–77.

[76] P.K. Bhaumik, S. Chattopadhyay, Inorg. Chem. Commun. 22 (2012) 14–17.

[77] M. Das, S. Chattopadhyay, Inorg. Chim. Acta 378 (2011) 303–306.

[78] M. Das, S. Chattopadhyay, Transition Met. Chem. 38 (2013) 191–197.

Table 1: Crystal data and structure refinement details in complexes **1** and **2**

Complex	**1**	**2**
Formula	$C_7H_7CuN_7O$	$C_{14}H_{16}CuN_8O_6ClI_3$
Formula Weight	268.74	872.04
Crystal Size (mm)	0.06 x 0.18 x 0.25	0.08 x 0.17 x 0.30
Temperature (K)	123	123
Crystal system	Monoclinic	Triclinic
Space group	*P2₁/a*	$P\bar{1}$
a(Å)	8.1285(3)	10.9546(5)
b(Å)	11.1068(4)	10.9709(5)
c(Å)	10.5660(4)	11.1885(4)
α(deg)	90	106.675(4)
β(deg)	100.282(2)	100.107(3)
γ(deg)	90	104.824(4)
Z	4	2
d_{calc} (g cm-3)	1.902	2.415
μ(mm-1)	2.316	4.931
F(000)	540	818
Total Reflections	4383	8147
Unique Reflections	2330	4200
Observed data [I > 2 σ (I)]	1808	3711
R(int)	0.039	0.025
R1, wR2 (all data)	0.0684, 0.0982	0.0354, 0.0673
R1, wR2 [I > 2 σ (I)]	0.0460, 0.0910	0.0300, 0.0641
Largest diff. in peak and hole (eÅ^{-3})	0.79, -0.41	1.25, -0.93

Table 2: Selected bond lengths (Å) and bond angles (º) for complex **1**.

Bond lengths		Bond angels			
Cu(1)-O(1)	1.975(2)	O(1)-Cu(1)-N(1)	156.97(10)	N(1)-Cu(1)-N(3)*	102.36(10)
Cu(1)-N(1)	2.014(3)	O(1)-Cu(1)-N(2)	78.50(11)	N(1)-Cu(1)-N(5)	96.26(9)
Cu(1)-N(2)	1.962(3)	O(1)-Cu(1)-N(3)*	92.77(10)	N(2)-Cu(1)-N(3)*	104.22(10)
Cu(1)-N(3)*	2.375(3)	O(1)-Cu(1)-N(5)	99.31(9)	N(2)-Cu(1)-N(5)	159.62(10)
Cu(1)-N(5)	2.000(2)	N(1)-Cu(1)-N(2)	80.99(11)	N(3)*-Cu(1)-N(5)	96.11(10)

Table 3: Selected bond lengths (Å) and bond angles (º) for complex **2**.

Bond lengths		Bond angels			
Cu(1)-O(1)	2.154(3)	O(1)-Cu(1)-O(2)	89.24(12)	O(2)-Cu(1)-N(6)	73.50(13)
Cu(1)-O(2)	2.340(3)	O(1)-Cu(1)-N(1)	155.19(15)	N(1)-Cu(1)-N(2)	79.32(16)
Cu(1)-N(1)	2.077(4)	O(1)-Cu(1)-N(2)	76.54(14)	N(1)-Cu(1)-N(5)	97.05(13)
Cu(1)-N(2)	1.940(4)	O(1)-Cu(1)-N(5)	94.28(12)	N(1)-Cu(1)-N(6)	97.68(16)
Cu(1)-N(5)	2.237(3)	O(1)-Cu(1)-N(6)	106.35(14)	N(2)-Cu(1)-N(5)	104.11(15)
Cu(1)-N(6)	1.993(4)	O(2)-Cu(1)-N(1)	91.79(13)	N(2)-Cu(1)-N(6)	176.87(15)
-	-	O(2)-Cu(1)-N(2)	105.57(13)	N(5)-Cu(1)-N(6)	77.05(15)
-	-	O(2)-Cu(1)-N(5)	150.12(14)	-	-

Table 4: Hydrogen bond distances (Å) and angles (°) for complexes **1** and **2**.

Complexes	D–H···A	D–H	D···A	H···A	∠D–H···A
1	N(4)–H(4A)···O(1)*	0.80(4)	2.839(4)	2.07(4)	161(4)
	N(4)–H(4B)···N(7)$^{\Delta}$	0.79(4)	3.07(3)	2.30(5)	164(4)
2	N(3)–H(3)···O(6)	0.87(4)	2.815(6)	1.97(4)	162(4)
	N(4)–H(4A)···I(1)	0.85(5)	3.797(4)	2.99(4)	158(4)
	N(4)–H(4B)···O(5)	0.85(5)	3.095(6)	2.28(5)	162(5)
	N(7)–H(7)···O(4)$^{\text{☼}}$	0.85(4)	3.271(5)	2.57(4)	141(3)
	N(7)–H(7)···O(1)†	0.85(4)	2.904(6)	2.27(4)	131(3)
	N(8)–H(8A)···I(3)$^{\Diamond}$	0.85(4)	3.976(4)	3.16(3)	162(3)
	N(8)–H(8B)···O(4)$^{\text{☼}}$	0.85(4)	2.984(5)	2.19(4)	155(4)

Symmetry element *= -1/2+x,1/2-y,z; $^{\Delta}$ = 1-x,-y,-z; $^{\text{☼}}$ = -1+x,-1+y,1+z;† = -x,-y,2-z;$^{\Diamond}$ = -x,1-y,2-z; D, donor; H, hydrogen; A, acceptor.

Table 5: Geometrical parameters (distances in Å and angles in °) of the cation···π interactions in **1**.

Cg(I)····M(Cation)	Cg(I)····M (Å)	β (°)	M···Perp (Å)
Cg(2)···Cu(1)$^{\text{€}}$	3.698	20.26	3.469
Cg(3)···Cu(1)$^{\text{€}}$	3.753	21.38	3.753

β = Cg(I)···M vector and normal to plane of Ring(I); M···Perp = Perpendicular distance of M (Cation) on Ring(I); Cg(2) = centre of gravity of the ring $\mathbf{R^2}$ [Cu(1)–N(1)–C(5)–C(6)–N(2)], Cg(3) = centre of gravity of the ring $\mathbf{R^3}$ [N(1)–C(1)–C(2)–C(3)–C(4)–C(5)]. Symmetry element $^{\text{€}}$=1-x,-y,1-z.

Table 6: Geometric features (distances in Å and angles in °) of the C–H···π interactions in **1** and **2**.

Complexes	C–H····Cg(Ring)	H····Cg (Å)	C–H····Cg (°)	C····Cg (Å)
1	C(6)–H(6)···Cg(2)*	2.80	3.557(4)	137
	C(6)–H(6)···Cg(3)*	2.74	3.671(4)	167
2	C(1)–H(1)···Cg(2)	2.95	3.276(5)	102
	C(10)–H(10)···Cg(5)‡	2.85	3.765(5)	163

Cg(2) = centre of gravity of the ring **R^{2}** [Cu(1)–N(1)–C(5)–C(6)–N(2)], Cg(3) = centre of gravity of the ring **R^{3}** [N(1)–C(1)–C(2)–C(3)–C(4)–C(5)] for **1** and Cg(2) = centre of gravity of the ring **R^{2}** [Cu(1)–O(2)–C(14)–N(7)–N(6)], Cg(5) = centre of gravity of the ring **R^{3}** [N(1)–C(1)–C(2)–C(3)–C(4)–C(5)] for complex **1** for **2**. Symmetry element *= -1/2+x,1/2-y,z; ‡= -x,-y,1-z.

Table 7: Geometric features (distances in Å and angles in °) of the π···π stacking in **1** and **2**.

Complex	Cg(I)····Cg(J)	Cg····Cg	α	Cg(I)···Perp	Cg(J)···Perp	Slippage
1	Cg(1)···Cg(3)$^{\text{€}}$	3.369(2)	5.8(1)	3.325(1)	3.319(1)	-
	Cg(2)···Cg(2)$^{\text{€}}$	3.575(2)	0	3.446(1)	3.446(1)	0.951
	Cg(3)···Cg(1)$^{\text{€}}$	3.369(2)	5.8(1)	3.320(1)	3.325(1)	-
2	Cg(2)···Cg(4)†	3.586(2)	3.9(2)	3.157(2)	3.220(2)	-
	Cg(3)···Cg(3)$^{\Diamond}$	3.789(2)	0	3.269(2)	3.269(2)	1.917
	Cg(4)···Cg(2)†	3.586(2)	3.9(2)	3.220(2)	3.157(2)	-
	Cg(6)···Cg(6)‡	3.865(2)	0	3.639(2)	3.639(2)	1.301

α = Dihedral Angle between ring (I) and ring (J); Cg(I)···Perp = Perpendicular distance of Cg(I) on ring (J); Cg(J)···Perp = Perpendicular distance of Cg(J) on ring (I); Slippage = Distance between Cg(I) and perpendicular projection of Cg(J) on ring (I); Cg(1) = centre of gravity of the ring **R**^{1} [Cu(1)–O(1)–C(7)–N(3)–N(2)], Cg(2) = centre of gravity of the ring **R**^{2} [Cu(1)–N(1)–C(5)–C(6)–N(2)], Cg(3) = centre of gravity of the ring **R**^{3} [N(1)–C(1)–C(2)–C(3)–C(4)–C(5)] for **1** and Cg(2) = centre of gravity of the ring **R**^{2} [Cu(1)–O(2)–C(14)–N(7)–N(6)], Cg(3) = centre of gravity of the ring **R**^{3} [Cu(1)–N(1)–C(5)–C(6)–N(2)], Cg(4) = centre of gravity of the ring **R**^{4} [Cu(1)–N(5)–C(12)–C(13)–N(6)], Cg(6) = centre of gravity of the ring **R**^{6} [N(5)–C(8)–C(9)–C(10)–C(11)–C(12)] for **2**. Symmetry element $^{\text{€}}$=1-x,-y,1-z; † = -x,-y,2-z; ‡ = -x,-y,1-z; $^{\Diamond}$ = -x,1-y,2-z, ‡ = -x,-y,1-z.

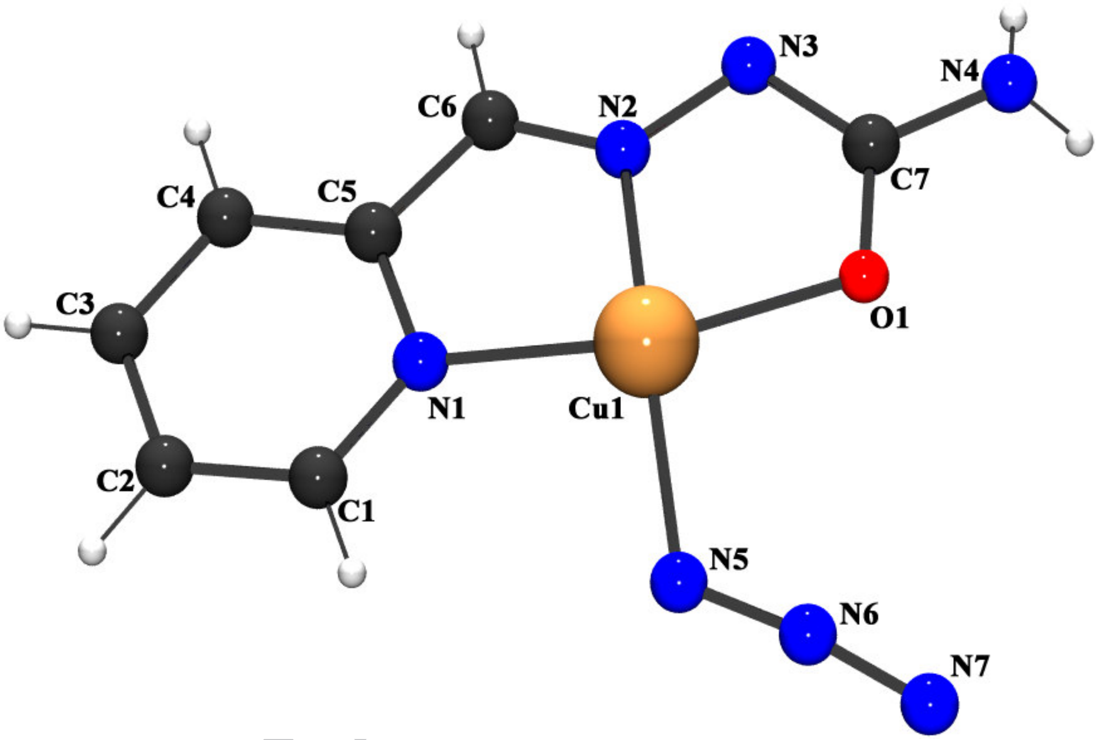

Figure 1: Perspective view of the asymmetric unit of **1** with selective atom labeling scheme. Hydrogen atoms are shown as spheres of arbitrary radius.

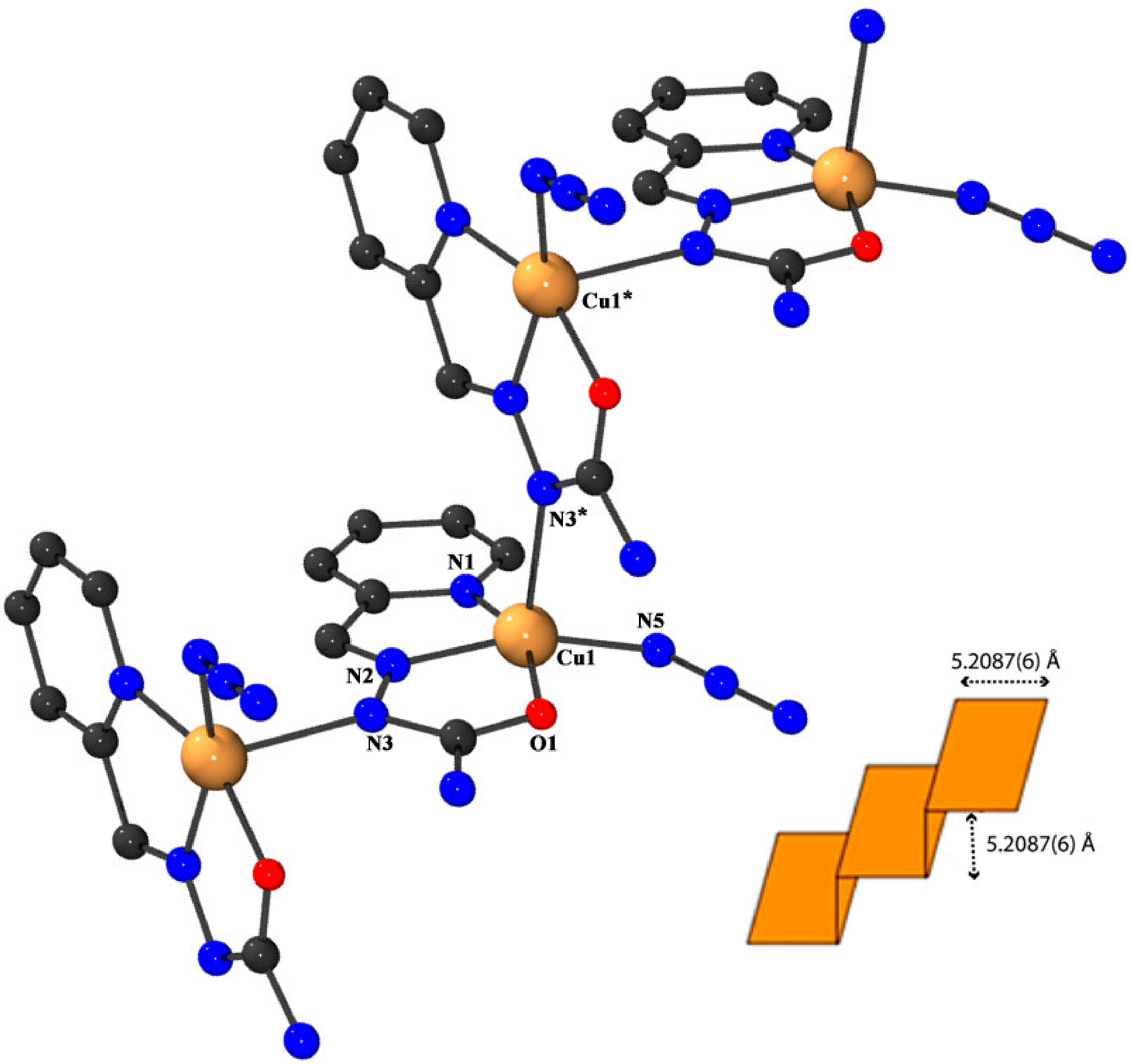

Figure 2: A perspective view of polymeric stair-like structure of complex **1**. Symmetry element: * = 1/2+x,1/2-y,z.

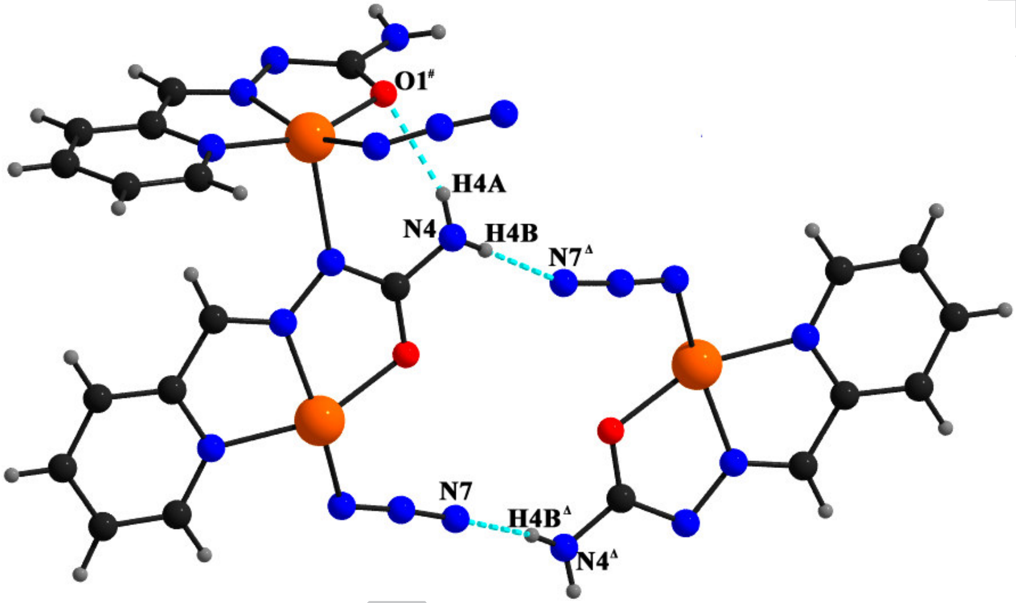

Figure 3: Hydrogen bonding interactions in **1**. Symmetry element *= -1/2+x,1/2-y,z; $^{\Delta}$ = 1-x,-y,-z;

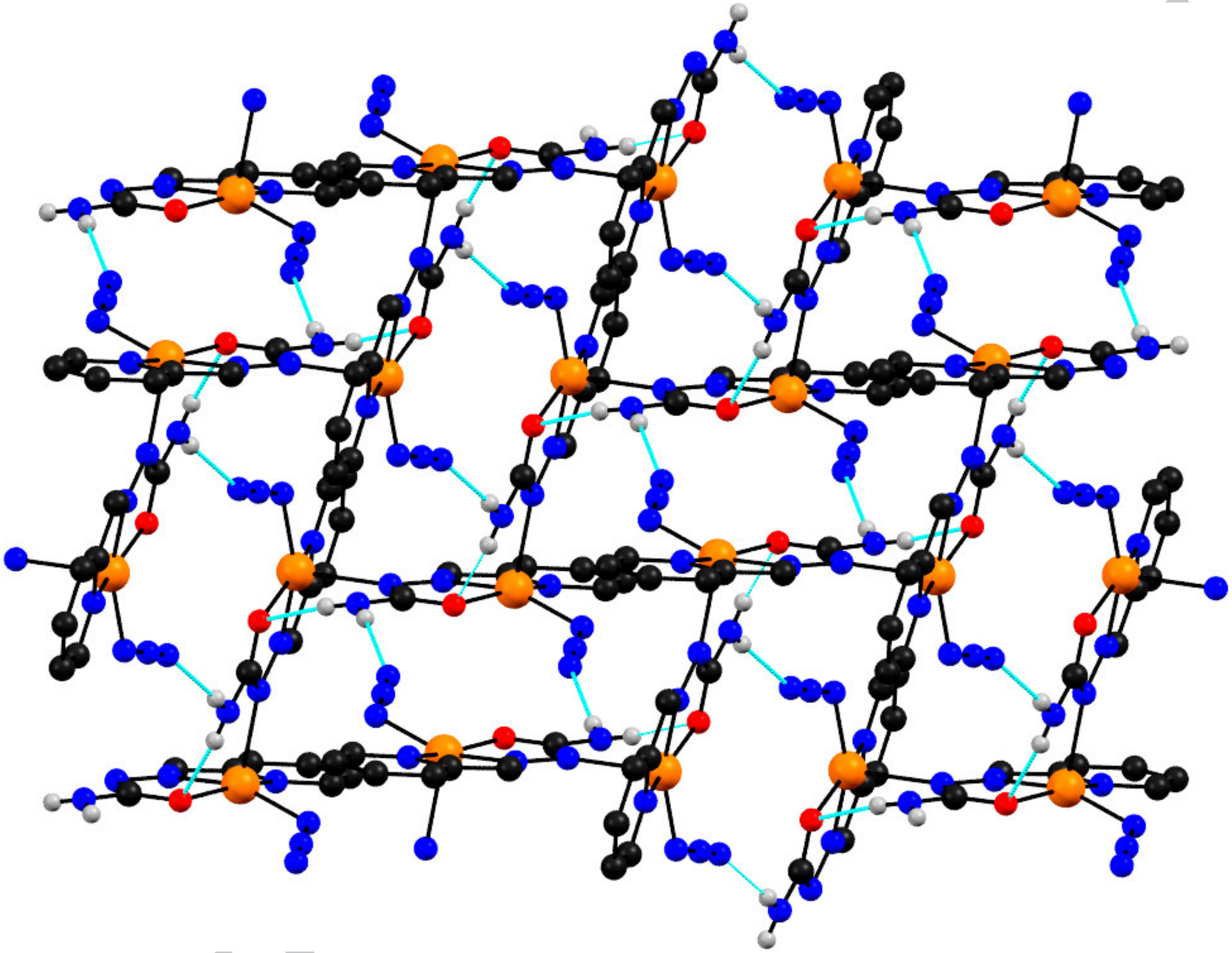

Figure 4: Perspective view of the two-dimensional hydrogen bonded self assembly in **1**. The hydrogen atoms participating in hydrogen bond have only been shown for clarity.

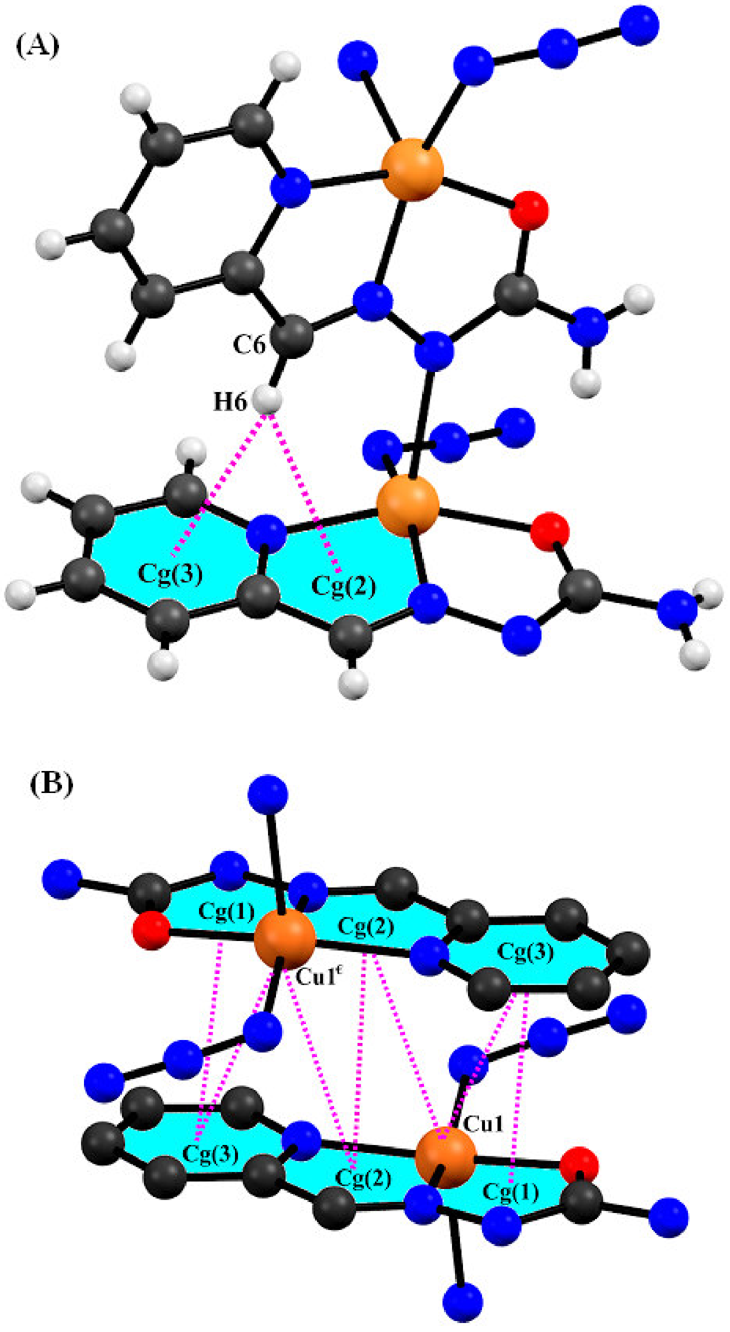

Figure 5: C-H···π interactions **(A)** and π···π stacking, cation···π interactions **(B)** in **1**. Symmetry element $^{\text{€}}$=1-x,-y,1-z.

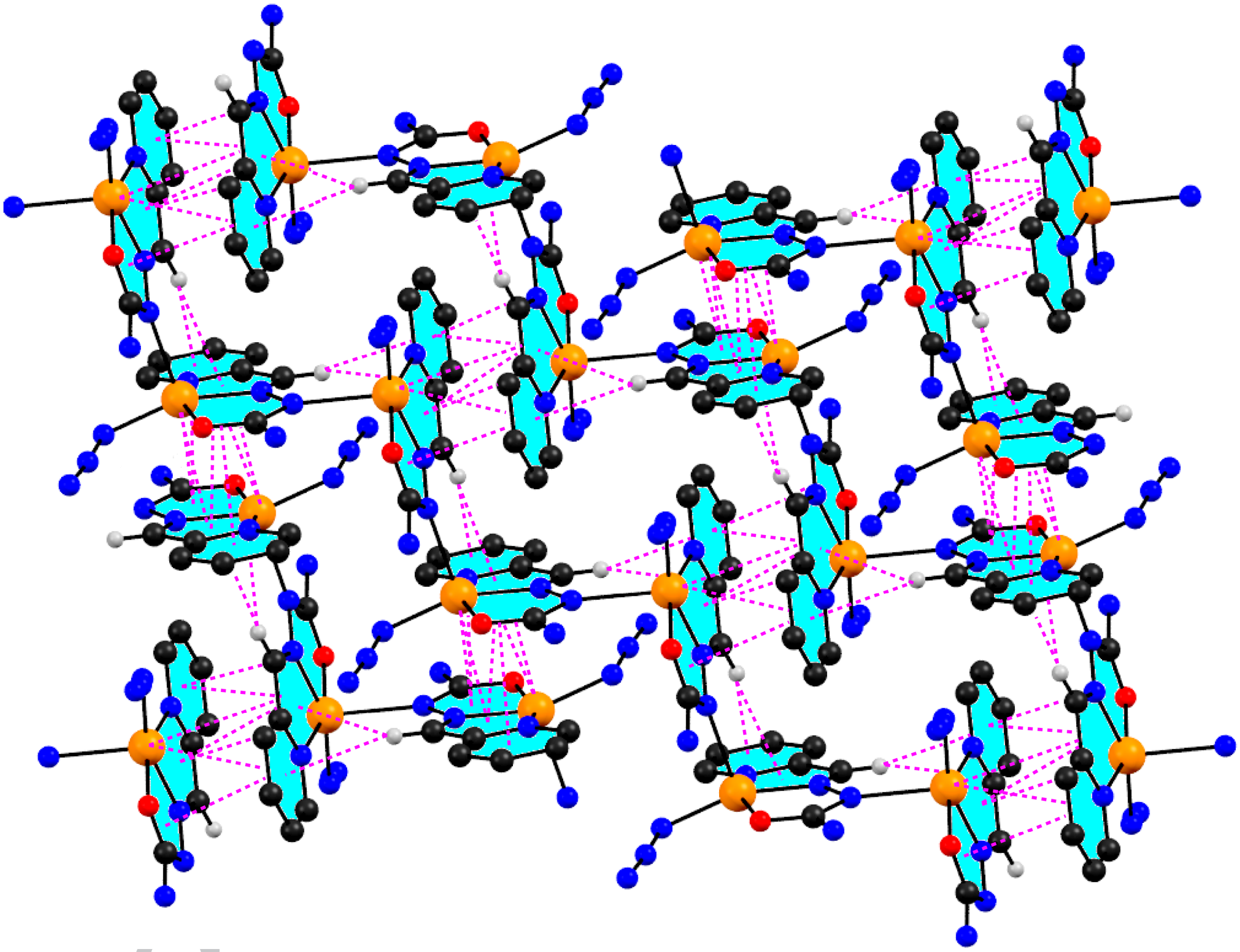

Figure 6: A perspective view of two-dimensional supramolecular self assembly in **1** highlighting π···π stacking, C-H···π and cation···π interactions. Hydrogen atoms participating in C-H···π interactions have only been shown for clarity.

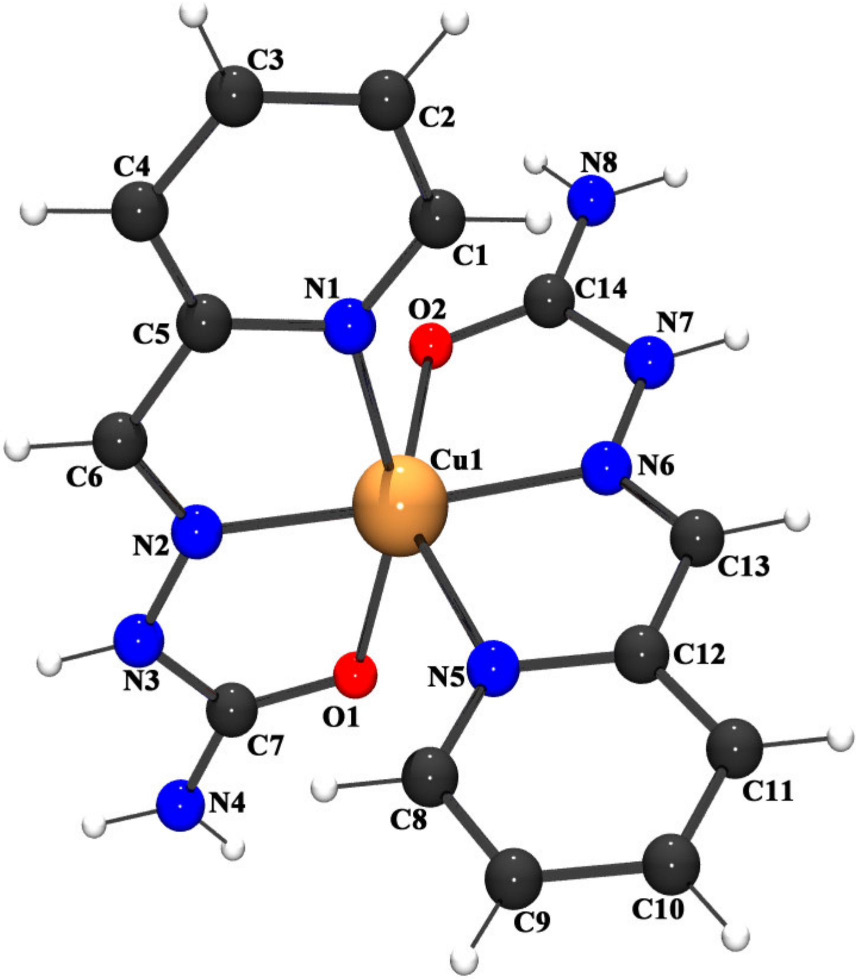

Figure 7: Perspective view of the asymmetric unit of **2** with selective atom labeling scheme. Counter anions have been omitted for clarity. Hydrogen atoms are shown as spheres of arbitrary radius.

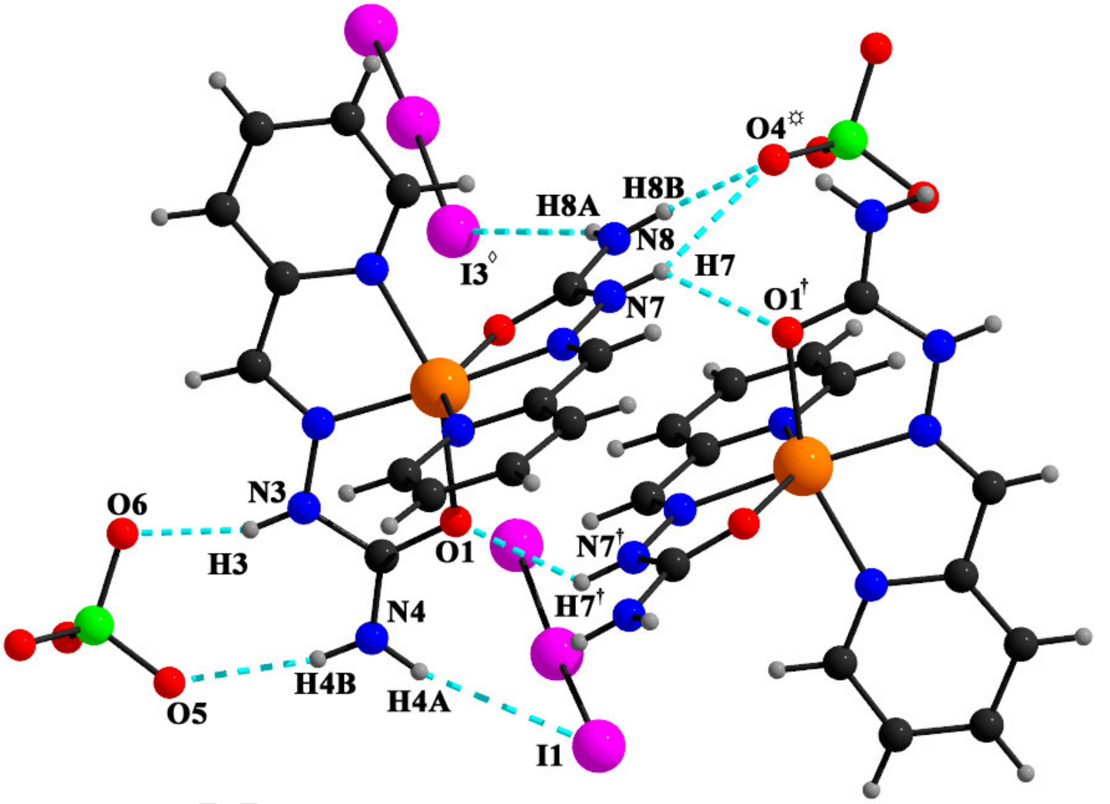

Figure 8: Hydrogen bonded interactions in **2**. Symmetry element: $^{☼}$ = -1+x,-1+y,1+z; † = -x,-y,2-z; $^{\Diamond}$ = -x,1-y,2-z.

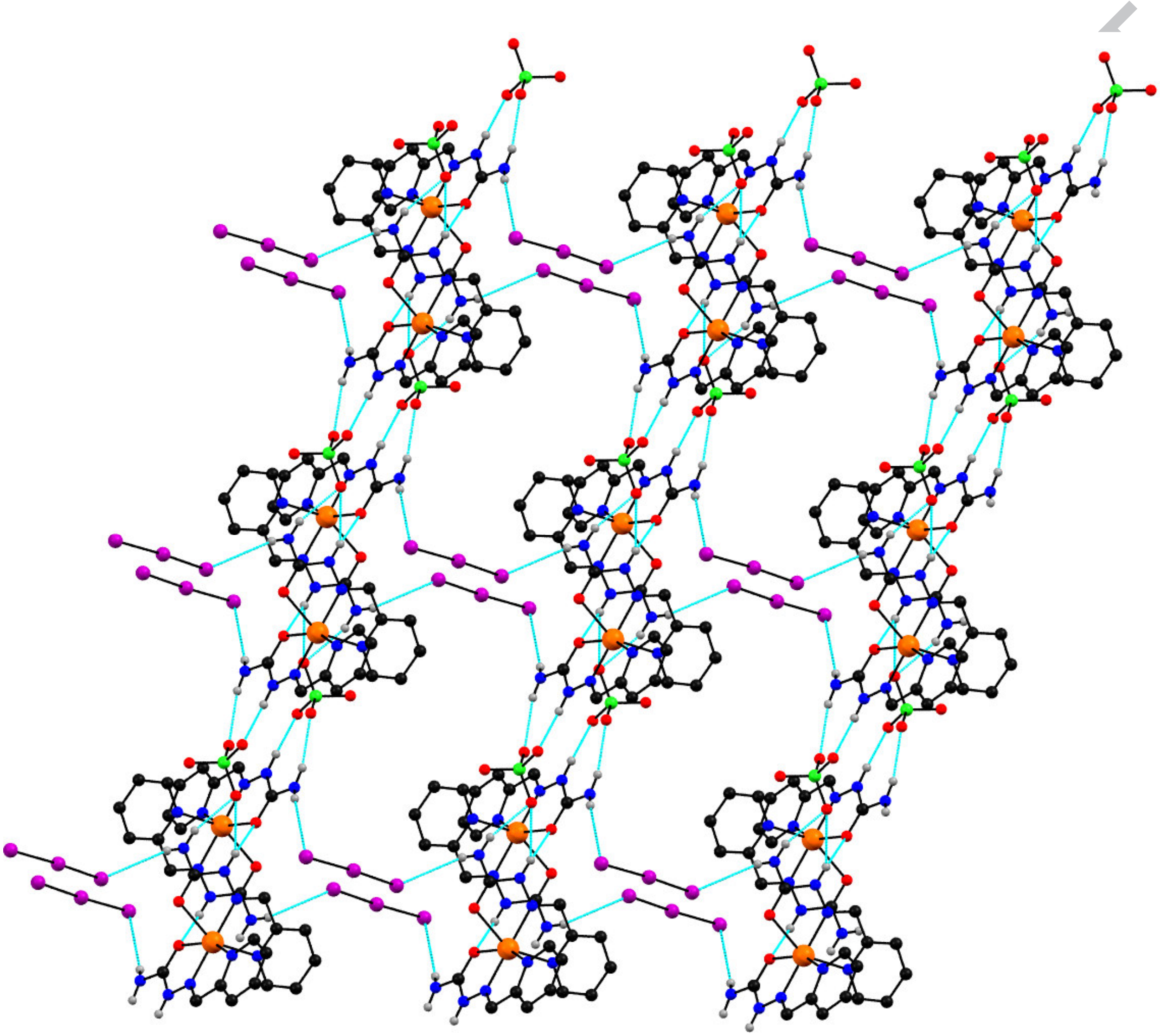

Figure 9: A perspective view of two-dimensional hydrogen bonded self assembly in **2**. The hydrogen atoms participating in hydrogen bonding have only been shown for clarity.

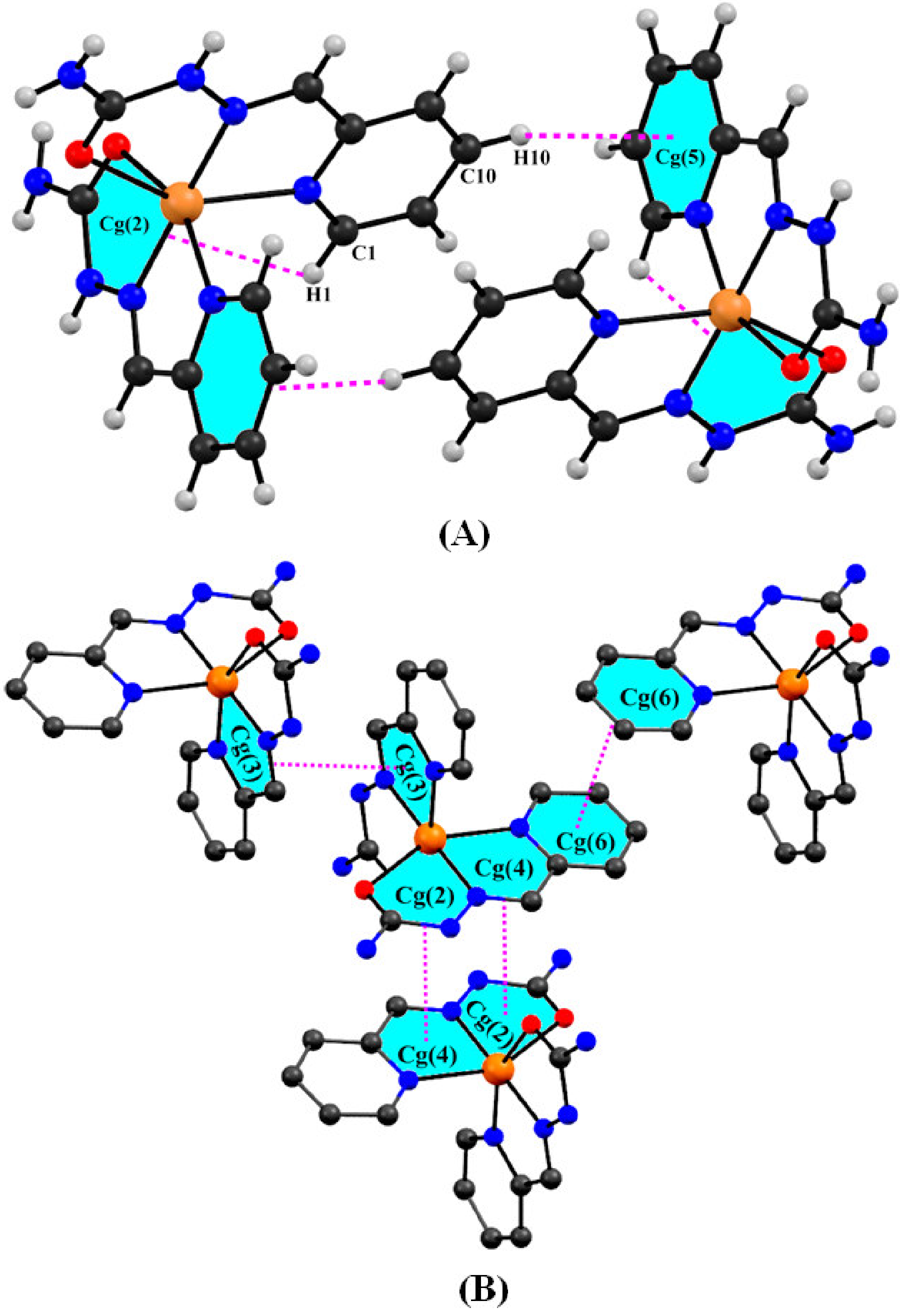

Figure 10: A perspective view of C-H···π interactions **(A)** and π···π stacking **(B)** in complex **2**.

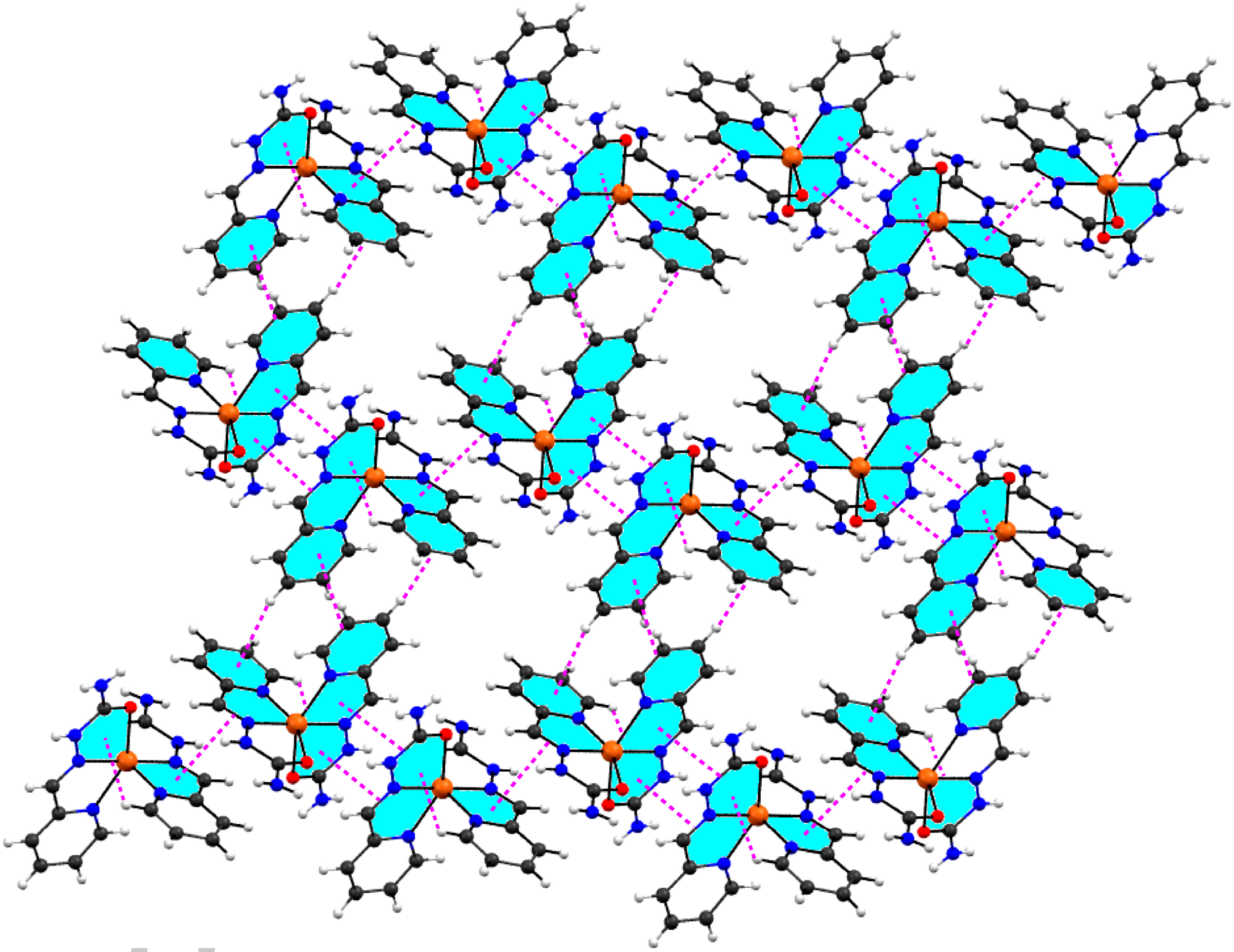

Figure 11: A perspective view of two-dimensional supramolecular self assembly of **2** highlighting π···π stacking and C-H···π interactions.

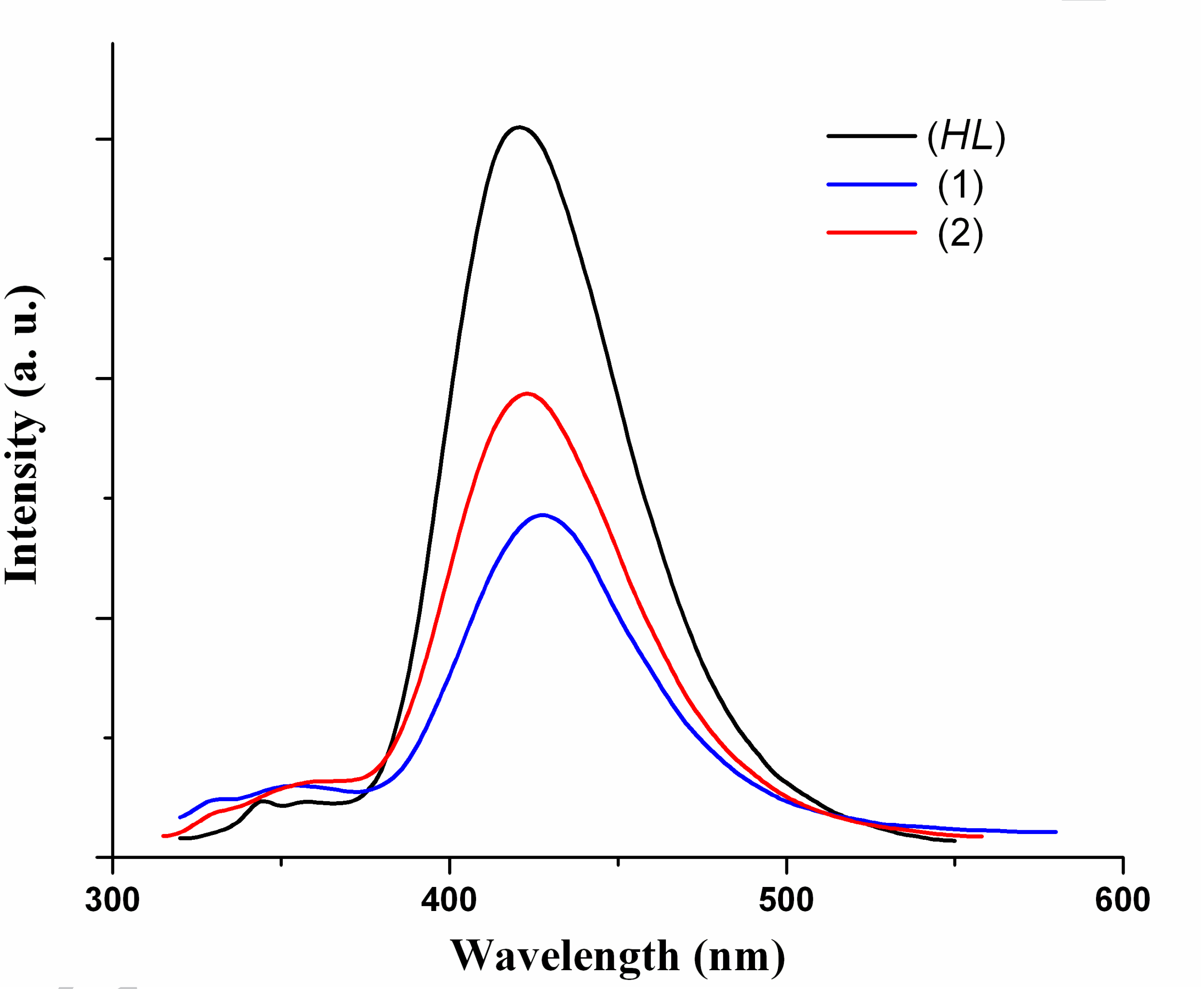

Figure 12: Photoluminescence spectra of **1**, **2** and ***HL*** in DMSO at room temperature.

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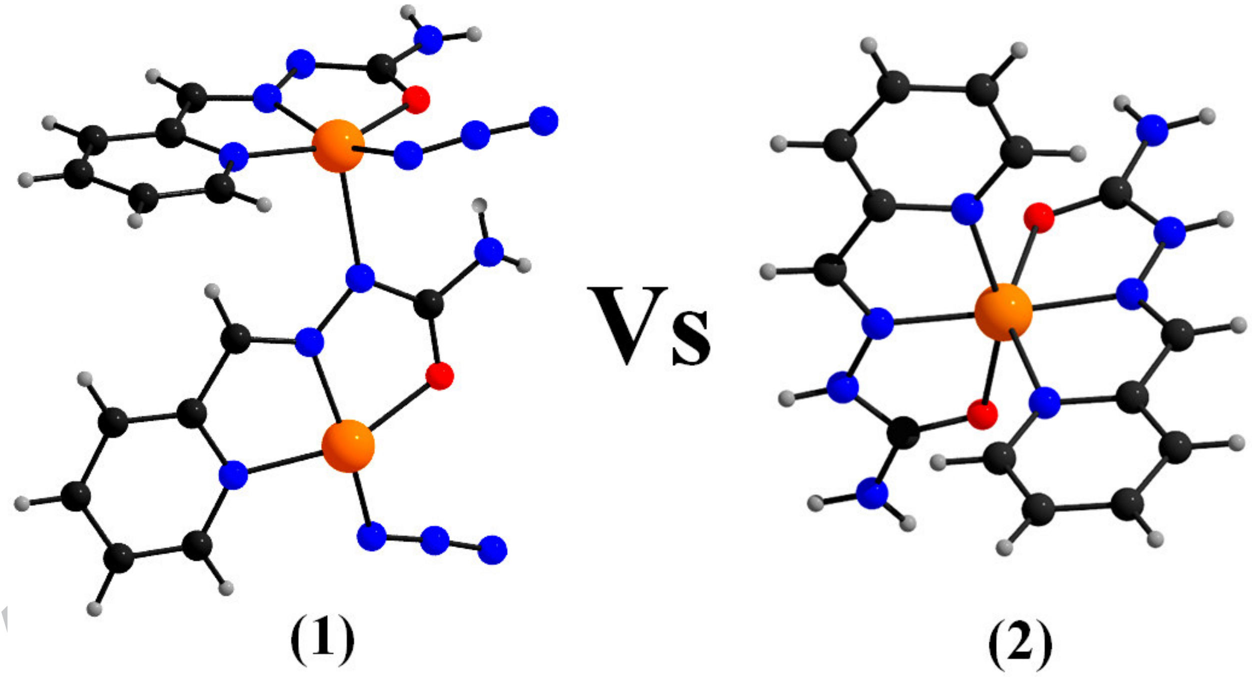

Anion modulated structural variations in copper(II) complexes with a semicarbazone Schiff base: Synthesis, characterization and self assembly

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Two copper(II) complexes have been prepared using a flexidentate semicarbazone Schiff base. The formation of the complexes with different stereochemistry could be controlled by the tactful choice of counter anions.