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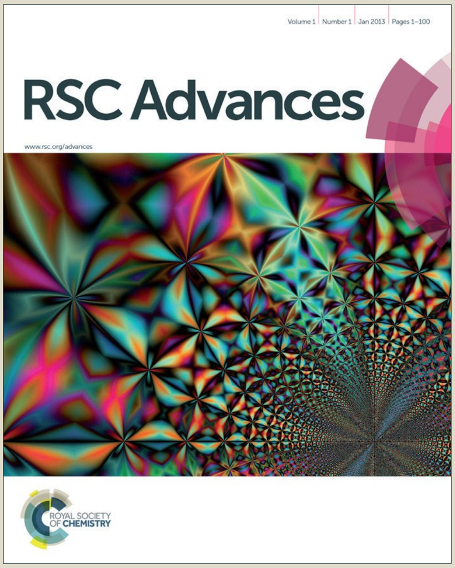

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A novel method for copper(II) mediated region-selective bromination of aromatic ring under mild condition

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Abstract

A tridentate N_2O donor Schiff base is used as the substrate and copper(II) perchlorate and potassium bromide have been used as reagents. In the resulting copper(II) Schiff base complex, the 4 position of the aromatic ring of the Schiff base moiety is brominated. X-ray single crystal diffraction study confirms the structure of the complex. In the conventional bromination of aromatic substrates with bromine as the reagent, a potential pollutant hydrobromic acid is produced as by-product. The present method provides an alternative environmentally friendly route for the bromination of activated aromatic ring. Regioselectivity of the bromination in the ligand have been studied the using DFT calculations.

Keywords: Copper(II); Schiff-base; crystal structure; bromination; supramolecular interactions.

Introduction

Nature has developed a variety of processes for regio- and stereo-selective halogenations of specific substrates using some halogenating enzymes.[1,2] The use of enzymes for the halogenation of small molecules is very expensive due to the purification procedure needed to recover the biocatalyst. The other available methods for halogenation of aromatic rings under mild conditions are relatively hard and poorly selective.[3] At the same time, conventional methods for the direct halogenation of aromatic systems involve the use of potentially hazardous elemental halogens[4] and expensive transition-metal based catalysts.[5] On the other hand, halogenated aromatic compounds are important components in biologically and pharmaceutically active molecules and also key intermediates in the synthesis of a number of organometallic species required for the preparation of natural products.[6] So, researchers have recently been developing a variety of alternative methods for the halogenations of aromatic compounds.[7] The development of new methodology for halogenation using non-polluting and less expensive reagents remains an important challenge till date. In a previous paper, we reported an efficient and novel method for the nucleophilic thiocyanation of activated aromatic compounds using sodium thiocyanate at ambient conditions.[8] Currently, we are concerned with attempts to perform halogenation on an aromatic ring following the same method.

Our study has focused on bromoarenes which are useful synthetic intermediates for the manufacture of pharmaceuticals, finechemicals, agrochemicals, and other specialty chemicals, such as flame retardants, pesticides, and herbicides.[9] They are also useful and important intermediates for cross-coupling reactions[10] and as precursors to organometallic reagents.[11] In addition, several aryl bromides are biologically active and potentially useful as antitumor, antibacterial, antifungal, antineoplastic, or antiviral agents.[12] In the conventional bromination of aromatic substrates with bromine as the reagent, the atom efficiency is effectively reduced to half, as one half of the bromine is lost as hydrobromic acid, which is corrosive, toxic, and a potential pollutant. Keeping this in mind, we report here a new approach to the bromination of activated aromatic ring with a more environmentally friendly catalytic process at ambient conditions. We have used a tridentate N_2O donor Schiff base as the substrate and copper(II) perchlorate and potassium bromide as reagents. At the end of the reaction, we obtain a copper(II) Schiff base complex, in which the phenyl ring of the Schiff base moiety is brominated. X-ray single crystal diffraction study confirms the structure of the complex. Herein, we also report the synthesis and characterization of this square planar copper(II) complex.

Experimental

Materials

N,N-diethyl-1,2-diaminoethane and 1-hydroxy-2-acetonaphthone were purchased from Merck and were of reagent grade. They were used without further purification.

Caution!!

Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. Only a small amount of the material should be prepared and they should be handled with care.

Synthesis of the complex

The tridentate Schiff base, H_2L, was synthesized by refluxing N,N-diethyl-1,2-diaminoethane (1 mmol, 0.14 mL) with 1-hydroxy-2-acetonaphthone (1 mmol, 0.186 g) in methanol for ca. 1 h. The ligand was not isolated and was used directly for the synthesis of the complex. A methanol solution (20 ml) of copper(II) perchlorate hexahydrate (1 mmol, 370 mg) was added to the methanol solution of the ligand (1 mmol) with stirring. A methanol solution (5 ml) of potassium bromide (2 mmol, 238 mg) was then added and stirred further for ca. 1h. The temperature of the system is maintained at 32°C. A deep green precipitate separated out and was collected by filtration. Diffraction quality single crystals were obtained after a few days on slow evaporation of a dark green acetonitrile solution of the complex in open atmosphere.

Yield: 0.24 g (47%), Anal. Calc. for $C_{18}H_{22}Br_2CuN_2O$ (FW 505.73): C, 42.75; H, 4.38; N, 5.54%; Found: C, 42.2; H, 4.6; N, 5.3%.IR (KBr, cm^{-1}) 1573 ($\nu_{C=N}$); UV -Vis, λ_{max} (nm) [ε_{max}(dm^3 mol^{-1} cm^{-1})] (acetonitrile) 223 (23575), 263 (16773), 330 (7360), 395 (4474). Magnetic moment: 1.73 BM.

Physical Measurements

Elemental analyses (carbon, hydrogen, and nitrogen) were carried out using a Perkin-Elmer 2400 II elemental analyzer. IR spectrum in KBr (4000-400 cm^{-1}) was recorded using a Parkin Elmer RXI FTIR spectrophotometer. Electronic spectrum in acetonitrile (1000–200 nm) was recorded in a Hitachi U-3501 spectrophotometer. Fluorescence spectrum in acetonitrile was recorded on a Shimadzu RF-5301PC Spectrofluorophotometer at room temperature. The PXRD data was collected on a Bruker D8 Advance X-ray diffractometer using with Cu Kα radiation (λ= 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2θ range of 2–50° using 1-D Lynxeye detector at ambient conditions. The magnetic susceptibility measurement was done with an EG&PAR vibrating sample magnetometer, model 155 at room temperature.

X-ray crystallography

Single crystals of the complex were used for data collection using an Oxford Diffraction X-Calibur System diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ= 0.71073 Å) at 150 K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 package.[13] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Empirical absorption corrections were applied using the ABSPACK program.[14] Other programs used included PLATON[15] and ORTEP.[16] CCDC reference number is 997024.

Theoretical methods

The calculations of the noncovalent interactions were carried out using the TURBOMOLE version 7.0[17] using the BP86-D3/def2-TZVP level of theory. To evaluate the interactions in the solid state, we have used the crystallographic coordinates. This procedure and level of theory have been successfully used to evaluate similar interactions.[18] The interaction energies were computed by calculating the difference between the energies of isolated monomers and their assembly. The interaction energies were corrected for the Basis Set Superposition Error

(BSSE) using the counterpoise method.[19] For the analysis of the regioselectivity of the bromination, we have fully optimized the geometries.

The NCI plot is a visualization index based on the electron density and its derivatives, and enables identification and visualization of noncovalent interactions efficiently. The isosurfaces correspond to both favorable and unfavorable interactions, as differentiated by the sign of the second density Hessian eigenvalue and defined by the isosurface color. NCI analysis allows an assessment of host-guest complementarily and the extent to which weak interactions stabilize a complex. The information provided by NCI plots is essentially qualitative, i.e. which molecular regions interact. The color scheme is a red-yellow-green-blue scale with red for ρ^{+}_{cut} (repulsive) and blue for ρ^{-}_{cut} (attractive). Yellow and green surfaces correspond to weak repulsive and weak attractive interactions, respectively.[20]

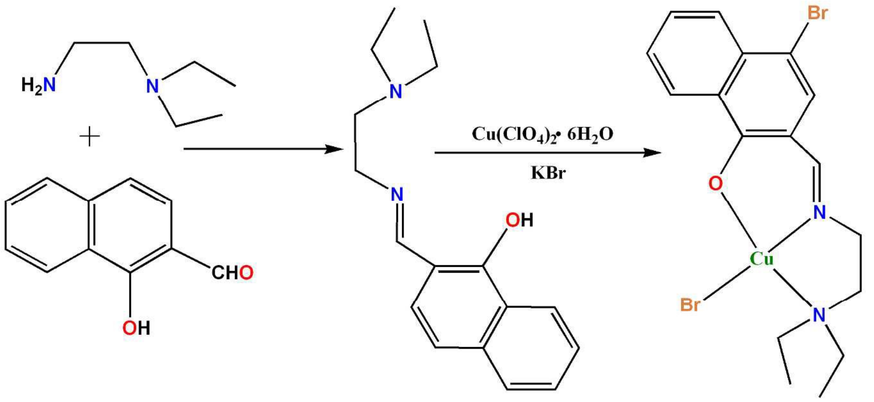
Results and discussion

Synthesis

The ligand (H_2L) was prepared by the condensation of N,N-diethyl-1,2-diaminoethane with 1-hydroxy-2-acetonaphthone in methanol following the literature method.[8] The methanol solution of the Schiff base ligand, thus prepared, was added to a methanol solution of copper(II) perchlorate hexahydrate and the solution was stirred for 1 h (at 32°C). A methanol solution of potassium bromide was then added to it with constant stirring (Scheme 1). Surprisingly, in the isolated product, bromine was found to have been substituted into the phenyl ring of the Schiff base to form a unique compound. We repeated the synthesis several times and found that this brominated complex is the sole product as confirmed by the elemental analysis, mass spectral analysis, PXRD and single crystal X-ray diffraction studies. There is no evidence of dibrominated compound, as confirmed by mass spectrometry of the reaction mixture and also by the elemental analysis of the final product (bulk material). Although bromination in the aryl ring is not a very common phenomenon at room temperature, a few reports of copper(II) mediated bromination could be found in literature.[21] In the present study, the most probable pathway of the reaction is as follows:

$$Cu^{2+} + 2Br^{-} = Cu(Br)_2;\ \ 2CuBr_2 + 2O_2 + 2H_2L = 2[Cu(L\text{-}Br)Br] + 4H_2O.$$

The reaction has also been performed under argon (inert) atmosphere, but no solid product could be isolated in that case. Mass spectrum of the reaction mixture did not support the formation of the non-brominated copper(II) complex. Non-brominated copper(II) complex intermediate could also not be isolated using low equivalent of KBr. In every case, the brominated complex is the sole product. Use of low equivalent of KBr reduced the yield only. Use of copper(II) bromide produced the same product, as characterized by elemental analysis and X-ray diffraction data.



Scheme 1: Schematic representation of the reaction

Description of structure

The complex crystallizes in monoclinic space group $P2_1/c$. A perspective view of the complex with selective atom numbering scheme is shown in Figure1. The copper(II) centre is coordinated by one phenoxo oxygen atom, O(11), one amine nitrogen atom, N(26), and one imine nitrogen atom, N(23), of the tridentate deprotonated Schiff base ligand and one bromide ion, Br(1). Deviations of the coordinating atoms, Br(1), O(11), N(23) and N(26), from the least-square mean plane through them are -0.0812(8), 0.098(5), -0.105(6),0.089(6) Å respectively and that of Cu(1) from the same plane is 0.1099(9) Å. The five membered chelate ring, {Cu(1)–N(23)–C(24)–C(25)–N(26)} assumes a half-chair conformation with puckering parameters Q(2) = 0.428(7) Å and $\phi(2)$ =118.6(8)^o.[22] The complex forms a 2D layer structure via supramolecular interactions (C–H···π, π···π, anion···π) as shown in Figure 2. The methyl hydrogen atom H(22C), attached to C(221), is involved in significant C–H···π interactions with the symmetry related(1-x,2-y,1-z) phenyl ring C(13)–C(14)–C(15)–C(16)–C(17)–C(18). Similarly, the hydrogen atoms H(30A), attached to C(30), and H(27B), attached to C(27), are involved in C–H···π interactions with the symmetry related (1-x,1/2+y,1/2-z) phenyl rings C(13)–C(14)–C(15)–C(16)–C(17)–C(18) and C(12)–C(13)–C(18)–C(19)–C(20)–C(21), respectively. The bromine atom, Br(19), attached to C(19), is involved in intermolecular anion···π interaction with symmetry related (1-x,1-y,-z) six member chelate ring, Cu(1)–O(11)–C(12)–C(21)–C(22)–N(23). The geometric features of all the aforementioned non-bonded interactions are given in table S1 (Supplementary Information). The phenyl ring C(12)–C(13)–C(18)–C(19)–C(20)–C(21), is involved in intermolecular π···π interactions with the symmetry related (-x,1-y,-z) phenyl ring C(12)–C(13)–C(18)–C(19)–C(20)–C(21) and the six membered chelate ring Cu(1)–O(11)–C(12)–C(21)–

C(22)–N(23). The geometric features of these π···π interactions are given in table S2 (Supplementary Information).

IR and electronic spectra

In the IR spectrum of the complex, a distinct band due to the azomethine (C=N) group was observed at 1573 cm^{-1}. The electronic spectrum of the complex in acetonitrile was recorded in the range of 200–1000 nm. The intense absorption bands at short wavelengths, at 223, 322 and 330 nm may be assigned to intra ligand (ILCT)/ligand to metal (LMCT) charge transfer bands. The absorption at 395 nm may be assigned as a d-d transition.

PXRD and magnetic moment

The experimental PXRD pattern of the bulk product is in good agreement with the simulated XRD pattern from single-crystal X-ray diffraction, indicating consistency of the bulk sample (Figure 3).

Room temperature magnetic susceptibility measurement for the complex showed that it has a magnetic moment close to 1.73 BM, as expected for the discrete magnetically non-coupled spin-only value for copper(II).

Regioselectivity of the Bromination

Experimentally, during the synthesis of the complex, a bromination of the aromatic ring of the ligand takes place at the C_{para} with respect to the phenoxide group. It is known that copper(II) bromide is a simple and efficient catalyst for mono bromination of electron rich aromatic compound,[23] and in general the mono-bromination takes place at the *para* position relative to the –OH, –OR or $-NR_2$ substituent and at the *ortho* position in case the *para* is blocked by an alkyl group. In case of inorganic complexes it is a rare phenomenon that the electrophilic aromatic substitution (S_EAr) takes place during the inorganic complex synthesis. Moreover, to our knowledge this phenomenon is unprecedented during the synthesis of coordination complexes involving naphtalene based ligands. We have studied the regioselectivity of the bromination in the ligand using DFT calculations. To analyze it, we have computed the ESP charges of several species that may exist in the reaction mixture upon the addition of the $CuBr_2$ reagent. They are shown in Figure 4 along with the charges at the six C atoms where the S_EAr may occur. In the three species considered where the Cu is not coordinated the activated carbon atom (more nucleophilic) is in *para* to the –OH group, and the other C atoms are either deactivated (C3 and C6 negligible charge) or are less nucleophilic (C5, C7 and C8). In the specie where the metal is coordinated to the ligand, the C5 is also the most nucleophilic. Taking into consideration the measured values of the charges at C4, the most reactive species toward a S_EAr reaction are the ceto form of the Schiff base ligand and the Cu(II) complex. Remarkably, the charge analysis of all species predicts the same regioselectivity (C4), which is the one observed experimentally. In case this position is blocked by a substituent, the subsequent most reactive position would be C5.

Study of the supramolecular interactions

The bromination of the ligand during the synthesis of the complex has some further effect on its the solid state architecture. In Figure 5 we show a fragment of the crystal structure where a self-assembled dimer is represented. This dimer is generated due to the formation of an intricate combination of noncovalent interactions. That is, two symmetrically related H-bonds, C–H···π and ancillary Br···Cu interactions (see dashed lines in Figure 2A) and a π···π stacking interaction. The ancillary Br···Cu interaction is established between the Cu(II) center and the Br atom that appears upon bromination. We have computed by means of DFT calculations (BP86-D3/def2-TZVP) this self-assembled dimer taken from the X-ray structure (using the crystallographic coordinates).The interaction energy of this dimer (ΔE_1 = –31.4 kcal/mol, Figure 2B) is very large due to the contribution of all aforementioned interactions and also other long range van der Waals (vdW) interactions. In an effort to estimate the contribution of the interactions where the Br participates (H-bonds, and ancillary Br···Cu), we have computed an additional model where both aromatic Br atoms have been replaced by H atoms (see small arrows in Figure 2C). As a result the interaction is significantly reduced to ΔE_2 = –22.8 kcal/mol that corresponds to the contribution of the π···π, C–H···π and other long range vdW interactions to the total dimerization energy. The contribution of both H-bonds and ancillary Br···Cu can be estimated by difference, which is –8.6 kcal/mol. Moreover, to estimate the contribution of the C–H···π interaction, we have computed an additional theoretical model where the methyl groups attached to the C=N imine bond have been replaced by H atoms (see small arrows in Figure 2D).As a result the C–H···π interactions are not present and, consequently, the interaction energy is reduced (with respect to ΔE_1) to ΔE_3 = –26.4 kcal/mol. Thus, the contribution of the C–H···π interactions is $\Delta E_1 - \Delta E_3$ = –5.0 kcal/mol (–2.5 kcal/mol each interaction), which is modest as expected for this type of noncovalent bonding.

In order to characterize the interactions shown in Figure 5, we have computed the noncovalent interaction (NCI) plot of this compound. The NCI plot is a visualization index that enables identification and visualization of non-covalent interactions efficiently. The NCI analysis allows an assessment of host–guest complementarity and the extent to which weak interactions stabilize a complex (see the Computational Methods section). The information provided is essentially qualitative, that is, which molecular regions interact. The representation of the NCI plot computed for compound **1** is shown in Figure 6. An extended region can be observed between the aromatic rings that reaches the Cu metal centers and Br atoms, thus characterizing both the ancillary Br···Cu and π–π interactions (the green surface corresponds to weak interaction). This extended isosurface also reaches the region between the π-system and the $–CH_3$ groups thus confirming the existence of C–H···π interactions.

Conclusion

In summary, we have synthesized a square planar copper(II) complex using a tridentate Schiff base ligand, copper(II) perchlorate hexahydrate and potassium bromide. During complex formation, copper(II) mediated bromination with a high selectivity for the 4-position on the aromatic ring of the Schiff base ligand has taken place. The bromination occurs under extremely mild conditions, i.e. in air and at room temperature. We did not have to use hazardous elemental Br_2 as the brominating agent in this method. Thus an efficient, rapid and environment friendly method for the regio-selective bromination of the aromatic ring is developed. DFT study has also been performed.

Further studies are necessary to elucidate the intimate mechanism of the selective activation of the 4-position of the aromatic ring, which is still poorly understood.

Acknowledgments

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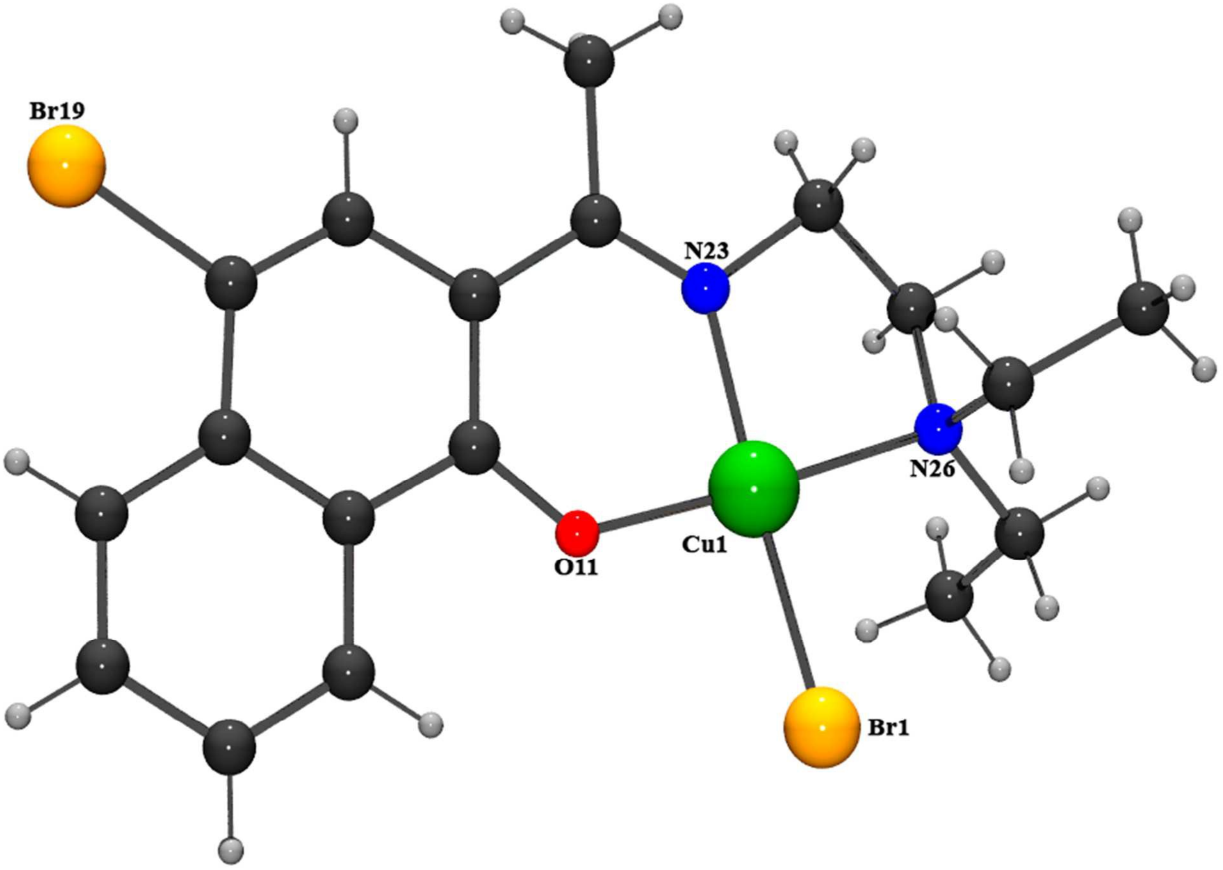

Figure 1: Perspective view of the complex with selective atom numbering scheme.

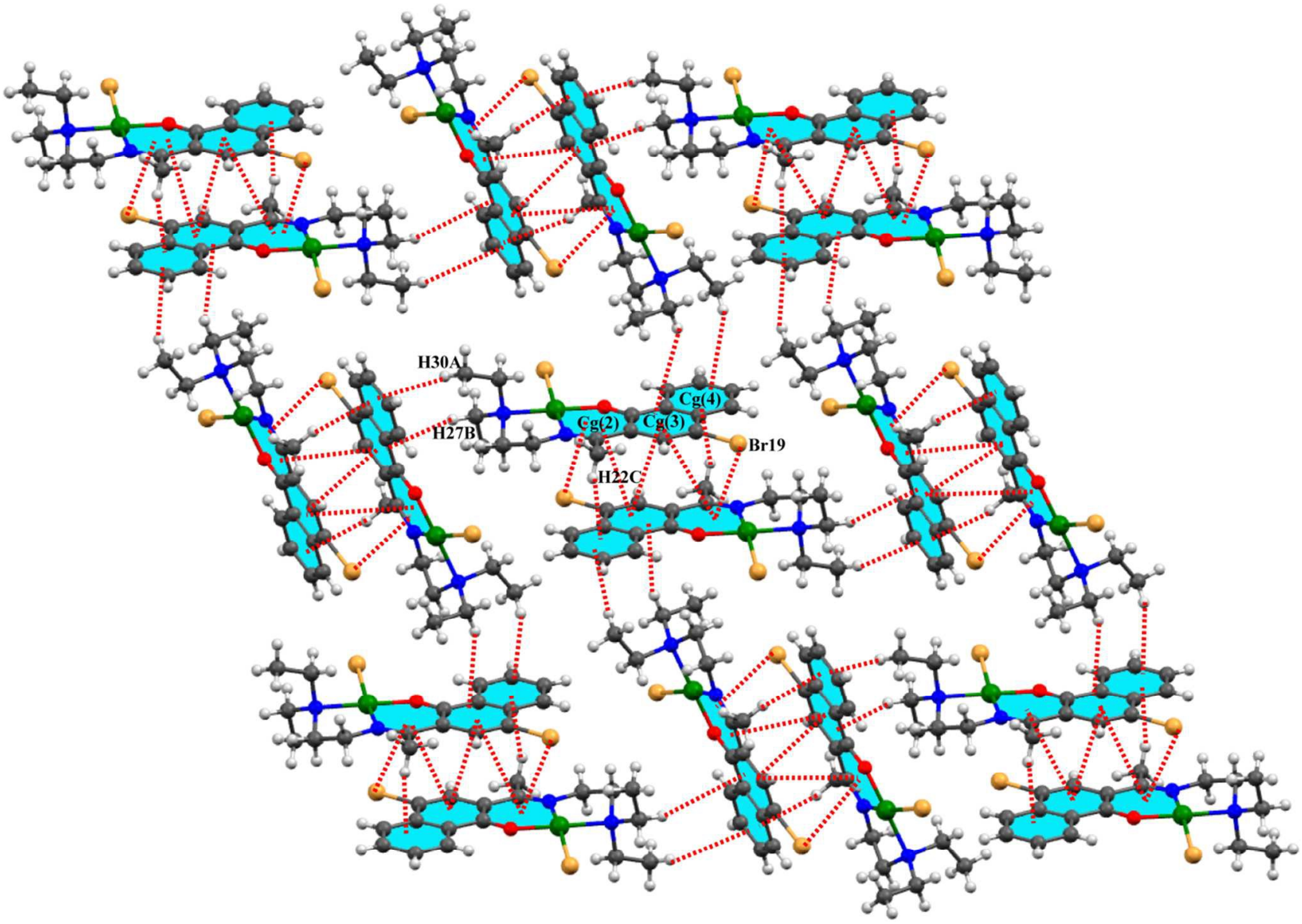

Figure 2: Two-dimensional sheet of complex along crystallographic bc plane formed via C–H···π interactions shown as dotted lines.

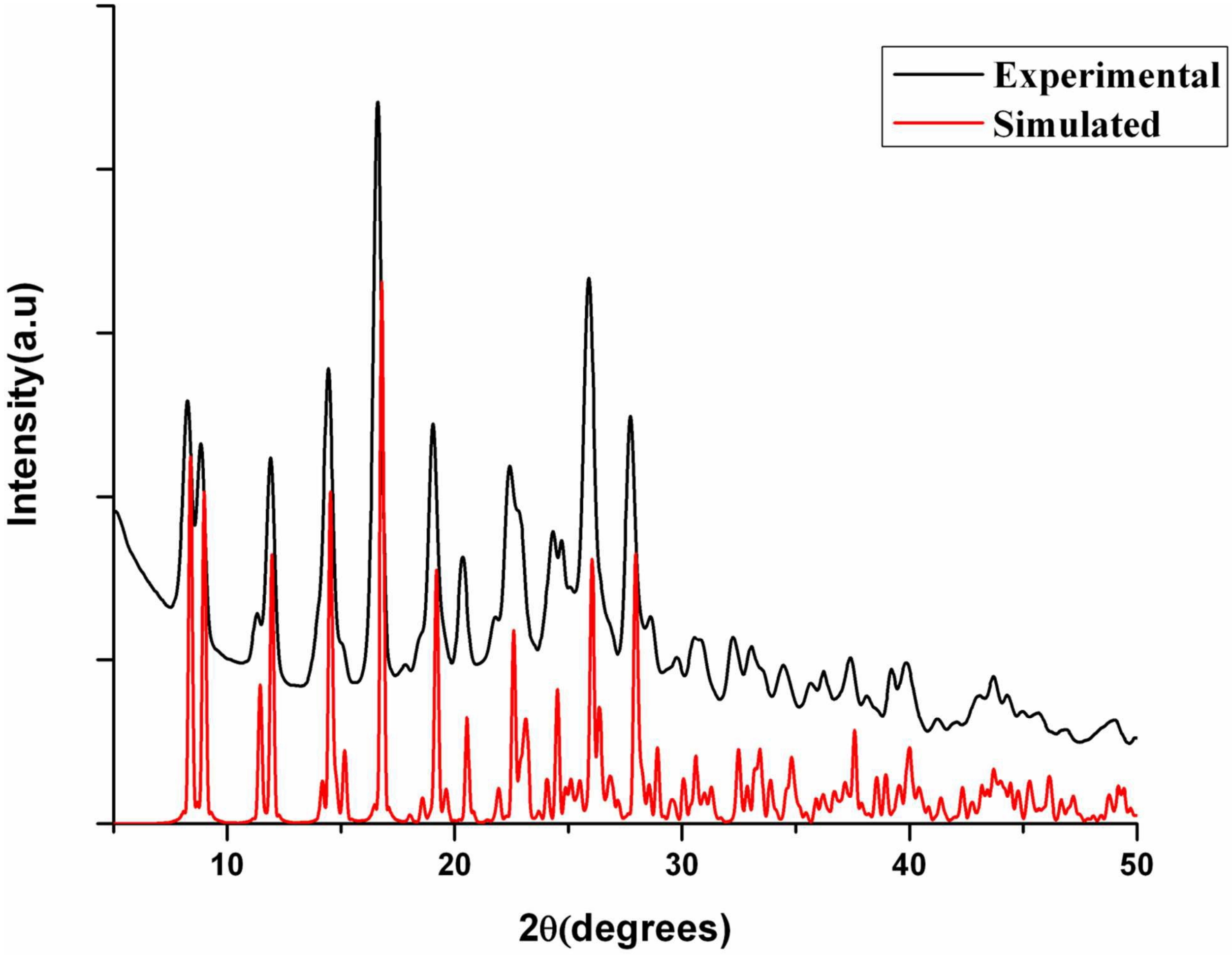

Figure 3: Experimental and simulated powder XRD patterns of the complex confirming the purity of bulk material.

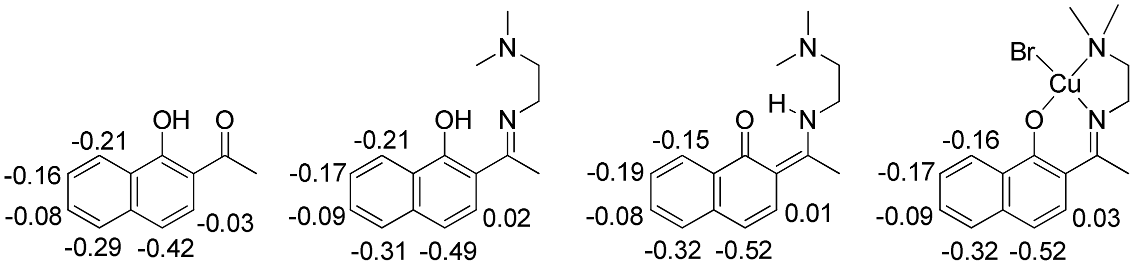

Figure 4: Merz-Kollman electron charges of several species that likely exist in the reaction mixture prior to bromination.

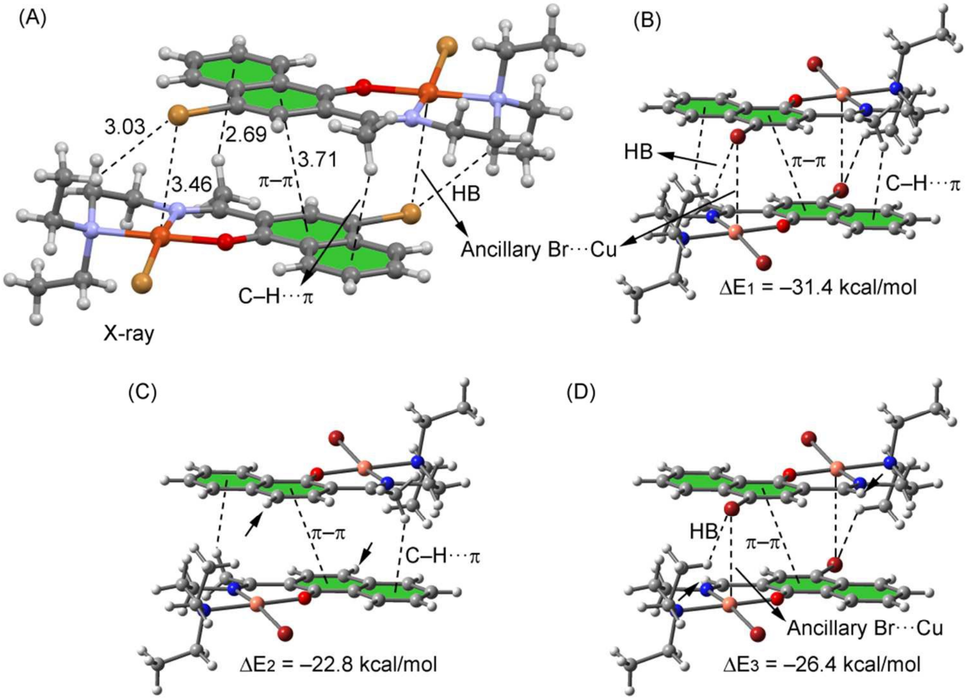

Figure 5: A) X-ray fragment of **1**. (B–D) Theoretical models used to evaluate the noncovalent interactions. Distances are in Å.

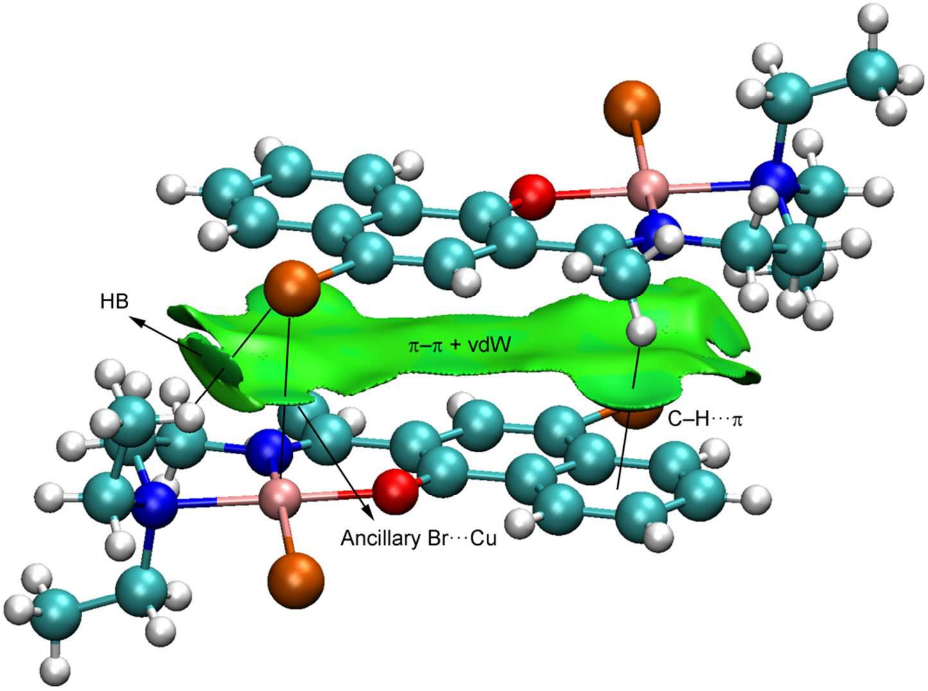

Figure 6: NCI plot of the self-assembled dimer of compound 1. NCI plot only shows the intermolecular interactions.

A novel method for copper(II) mediated region-selective bromination of aromatic ring under mild condition

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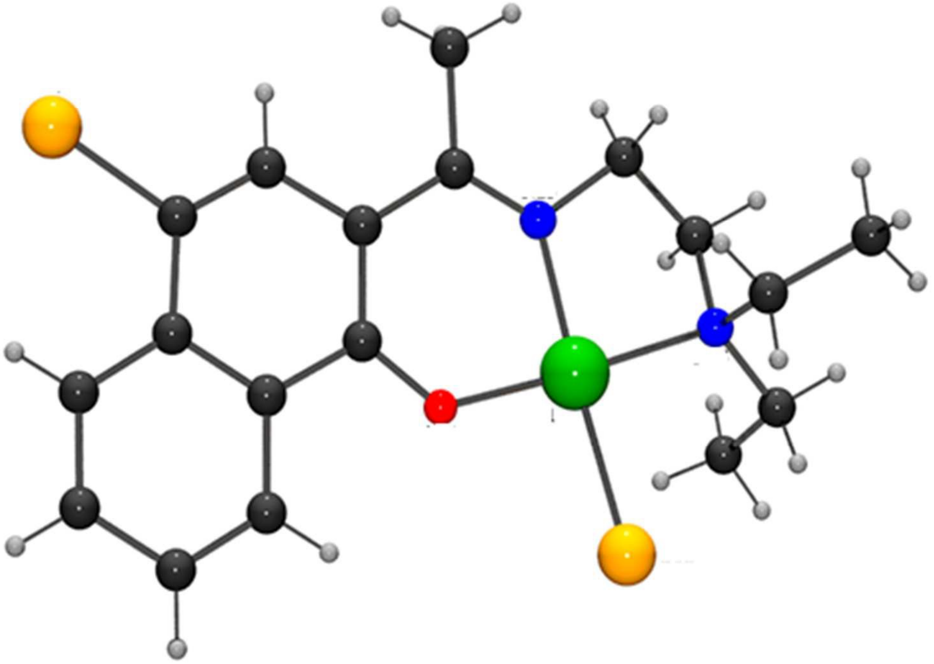

A square planar copper(II) complex has been synthesized using a tridentate Schiff base ligand H_2L and characterized. During complex formation, bromination at the 4 position of the aromatic ring of the Schiff base ligand has taken place. Regioselectivity of the bromination in the ligand have been studied the using DFT calculations.