



Synthesis, Characterization, and Crystal Structure of New Binuclear Cu(II) PyrPzAmide Containing Schiff Base and Azide Bridging Complex: A Combined Experimental and Theoretical Density Functional Theory Computational Analysis

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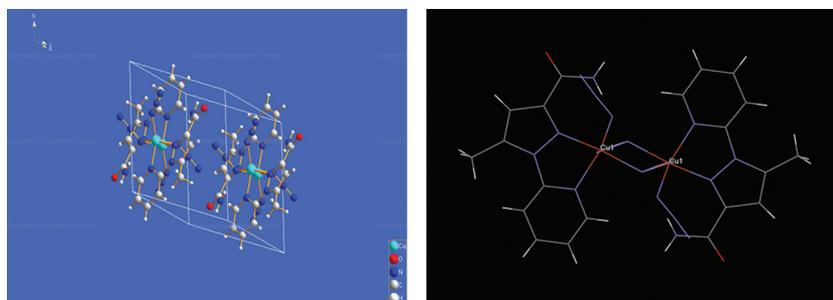
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ABSTRACT

The work in this paper lucidly represents the synthesis, characterization, crystal structure, and density functional theory (DFT) computational studies of one novel binuclear Cu(II) complex 1 $[\text{Cu}_2(\text{L}_1)_2(\text{N}_3)_4]$ using potentially chromophoric bidentate N,N-donor PyrPzAmide Schiff base ligand as well as incorporation of a versatile linker azide (N_3^-) ions. Complex 1 has been unambiguously characterized by common methods such as elemental analysis (carbon, hydrogen, and nitrogen), ultraviolet-visible, infrared spectroscopy, and single crystal X-ray diffraction. The Schiff base ligand L_1 is the bidentate N,N chelating donor of PyrPzAmide. Complex 1 crystallizes in the triclinic crystal system with space group P-1. In this novel binuclear structural framework, two Cu(II) centers are bridged by Schiff base PyrPzAmide N,N potential donor held together by two μ -1,1(end-on, EO) symmetric bridging azide ions. Each Cu(II) center in complex 1 is pentacoordinated and adopts a distorted square pyramidal geometry. DFT calculations have been performed using the UB3LYP level of theory and basis sets used LanL2DZ to obtain a clear geometry optimized model of complex 1. The geometry of complex 1 has been optimized in the singlet ground states by DFT calculation. Apart from, a theoretical DFT computational study has been carried out to supplement the experimental results such as bond distances and angles of complex 1 optimized structure.

Graphical abstract



Key words: Cu(II) binuclear Schiff base complex, N_3^- ions, X-ray crystal structure, Density functional theory study.

HIGHLIGHTS

- A new binuclear Cu(II) N,N donor PyrPzAmide Schiff complex 1 has been synthesized.
- Single X-ray crystallography has been performed for newly synthesized Cu(II) complex 1.
- Complex 1 geometry has been completely optimized in the singlet ground states by DFT calculations.
- Complex 1 crystal metrical parameters (bond distances and angles) have been compared with DFT computational method.

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1. INTRODUCTION

Today, synthetic inorganic chemistry has been explored to synthesizing Cu(II) bi or trinuclear complexes using chromophoric N,N chelating donor Schiff base ligand after incorporation of a suitable pseudohalides bridging such as versatile azide ions due to their versatile molecular topologies, structural variety, varied denticity [1-5], and wide biological applications such as antimalarial, antibacterial, antitumoral, and antiviral activities [6-11]. Hence, the prime strategy for designing and construction of the polynuclear Cu(II) complexes must be used a suitable bridging co-ligands. Although many different linkers, such as N_3^- , CN^- , NCS^- , NCO^- [12-15] and different metal ions have been employed for the construction of copper (II) polynuclear complexes and thus 1-D, 2-D, 3-D coordination polymer (CP) and supramolecular crystal system results. Due to this reason Cu(II)-azide, pseudohalides [16-19] system is one of the most popular among synthetic chemists. Hence, today, an azide ion (N_3^-) is one of the most prominent versatile bridging linker for construction of CP. The two most frequently observed diverse bridging modes with different metal ions are μ -1,1 (end-on, EO) and μ -1,3 (end-to-end, EE). Apart from other bridging modes μ -1,1,1, μ -1,1,3, μ -1,1,1,1, μ -1,1,3,3, and μ -1,1,1,3,3,3 (Scheme 1). Thus, due to steric and electronic demands of the azide co-ligands yielding various polynuclear complexes and 1-D, 2-D, 3-D species of different topologies depending on the metal ion and PyrPyzA Schiff base ligand used [20,21]. Binuclear and trinuclear azido-bridged copper(II) complexes have received great interest for biologists and bioinorganic chemists due to their model systems for the active sites in copper proteins [22]. We herein using copper perchlorate as the metal precursor, one new binuclear Cu(II) complex 1 [$Cu_2(L)_2(N_3)_4$] has been synthesized using novel PyrPzAmide N,N Schiff base and potential azide ions. In the present communication, we have carefully reported the complex 1 synthetic details, characterization, details X-ray crystal structure along with μ -1,1 azide bridging nature. Finally a combined theoretical and experimental density functional theory (DFT) analysis of fully optimized structure of complex 1 has been performed in a comparative approach.

2. EXPERIMENTAL

2.1. Materials

All research chemicals such as copper perchlorate, NaN_3 were of reagent grade, purchased from suitable commercial sources and finally used without further purification. CH_3CN and CH_3OH purchased from Sigma-Aldrich Chemical Company (USA). All common solvents (AR) also used without further purification. The synthetic reactions and work-up were done in open air.

Caution! Sodium azide and metal perchlorate compounds are potentially explosive, especially in the

presence of organic Schiff base ligands. Hence, only a small amount of the material should be prepared and it should be handled with care.

2.2. Physical Measurement

Elemental analyses (carbon, hydrogen, and nitrogen) of complex 1 have been determined with a Perkin–Elmer CHN analyzer 2400. Mass spectra of title complex 1 were done with a JEOLJMS-AX 500 mass spectrometer. IR spectra (KBr pellet, 400 – 4000 cm^{-1}) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. Absorption spectra in DMF solvent of complex 1 was measured using a UV-2450 spectrophotometer (Shimadzu) with a 1cm path length quartz cell. All spectra were corrected for the instrumental functions.

2.3. Computational Methods

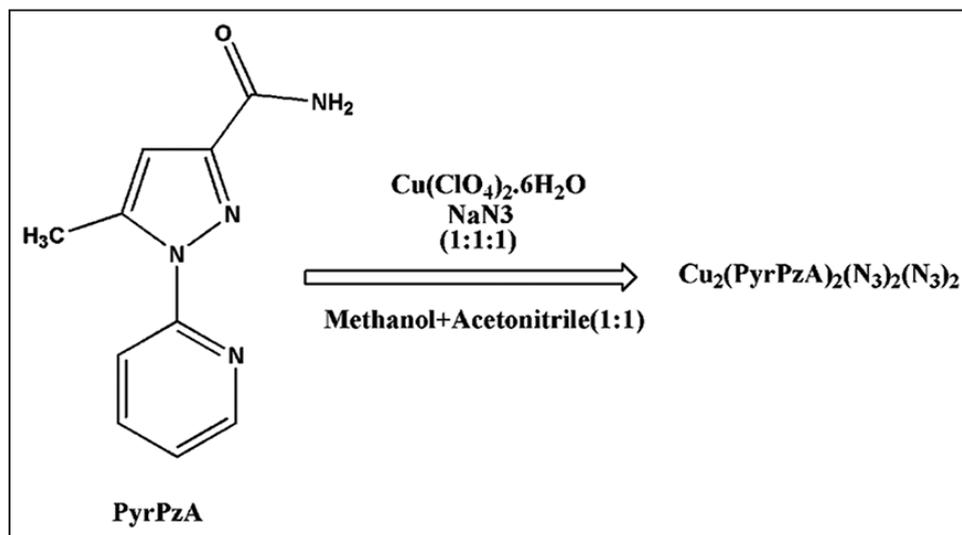
All computations of complex 1 were performed using the Gaussian 09 (G09) software package using the Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr nonlocal correlation functional (B3LYP) [23-25]. In the calculation, the LanL2DZ basis set was assigned to all elements [26]. The geometric structures of Cu(II) complex in the ground state (singlet) was fully optimized at the B3LYP level in acetonitrile using the conductor-like polarizable continuum model (CPCM).

3. SYNTHESIS OF COMPLEX 1

To a solution of PyrPzA (1.01 g, 5 mmol) in 1:1 methanol-acetonitrile (100 mL), $Cu(ClO_4)_2 \cdot 6H_2O$ (1.855 g, 5 mmol) taken in the same solvent was added dropwise with constant stirring. After 20 min aqueous NaN_3 (0.65 g, 10 mmol) dissolved in few drops of water was added and stirred for 2 h. X-ray quality brown color crystals are obtained by slow evaporation after 1 week (Scheme 2). Crystal was collected and air dried. The specific details of Cu(II) complex 1 and characterization data are given below. For complex 1, yield, 1.668 g (60%). Anal. Calc. for $C_{20}H_{20}Cu_2N_{20}O_2$: C, 34.34; H, 2.88; N, 40.04 Found: C, 34.33; H, 2.87; N, 40.05% IR (KBr, ν_{max}/cm^{-1}): 1606 ($\nu_{C=N}$), 1546 ($\nu_{C=N}$), 2064 (ν_{azide}). UV-vis (DMF): λ_{max}/nm : 265 nm.

4. X-RAY CRYSTALLOGRAPHIC STRUCTURE DETERMINATION OF COMPLEX 1

Binuclear Cu(II) complex 1 the data collections were made using a CCD area detector equipped with a graphite monochromated $Mo-K_{\alpha}$ ($K=0.71073\text{ \AA}$) source in the ω scan mode at 293 K. The molecular structure of complex 1 has been solved by direct methods and refinement by full-matrix least squares on F^2 using the SHELXS-97 package [27]. Nonhydrogen atoms were refined with anisotropic thermal parameters. H atoms were placed in their geometrically idealized positions and constrained to ride on their parent atom multi-scan empirical absorption corrected were applied to



Scheme 2: Synthesis of complex 1.

the data using the program SADABS [28,29]. During crystal data refinement common programs used are SHELXS-97 and ORTEP. Different crystallographic pictures are generated using software Mercury 3.8v, Diamond 4.2.2v, Crystal and Olex-2. A summary of the crystallographic data and structure refinement parameters of binuclear Cu(II) complex 1 is given in Table 1. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication nos. CCDC 1458007. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK: <http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi>, e-mail: data_request@ccdc.cam.ac.uk, or Fax: +44 1223-336033.

5. RESULTS AND DISCUSSION

5.1. Synthesis

A nice complexation behavior of N,N chelating donor PyrPzAmide Schiff base ligand L_1 was investigated toward Copper perchlorate in the presence of versatile linker N_3^- ions. Complex 1 was obtained by mixing the PyrPzAmide Schiff base ligand, Cu(II) perchlorate and sodium azide taken in 1:1:1 molar ratio in methanol and acetonitrile mixed solvent. X-ray quality brown colored crystal obtained after 6 days on slow evaporation of the reaction mixture at room temperature. Binuclear azide bridged Cu(II) complex 1 has been characterized by different physicochemical techniques and IR, UV-Vis, mass spectroscopic studies, and finally single X-ray diffraction. Complex 1 geometry has been completely optimized in the singlet ground states by DFT computational method. Complex 1 synthetic reaction is summarized in Scheme 2.

5.2. Characterization of Binuclear Cu(II) Complex 1

The IR spectra of PyrPzAmide Schiff base Cu(II) complex 1 is consistent with the data given in this

paper. A strong sharp peak at 2064 cm^{-1} for complex 1 is assigned as the μ -1,1 azide bridge [30]. The strong bands occurring at $\nu_{\text{C}=\text{N}}$ 1606 (pyr) and $1546\text{ (pz)}\text{ cm}^{-1}$ for complex 1, respectively, are shifted toward lower frequencies compared to that of PyrPzAmide Schiff base ligand, indicating coordinating bidentate fashion mode of N,N donor center of the respective ligand. DMF solution of complex 1 show ligand based transition at 265 nm and this is assignable to $\pi \rightarrow \pi^*$ transition [31,32].

6. X-RAY CRYSTAL STRUCTURE ANALYSIS OF COMPLEX 1

A common perspective view of complex 1 with the atom numbering scheme is shown in Figure 1a and b. Selected some crystal metrical parameters are lucidly given in Table 1. Complex 1 crystallizes triclinic crystal system in the space group P-1. The complete crystal structure of $[\text{Cu}_2(\text{L}_1)_2(\text{N}_3)_4]$ 1 is a noncentrosymmetric dimer as shown in Figure 2. The environment of each Cu metal is five-coordinate. The unit cell of complex 1 comprises one molecule. Since the Addison parameter (σ) [33] of the pentacoordinate Cu(II) is 0.314, that suggesting the PyrPzAmide Schiff base N,N chromophore formed Cu(II) complex 1 predominantly square-based pyramidal (SP) binuclear geometry (Figure 1). The crystal structure clearly reflects that one Cu(II) metal center are directly linked by N^1 , N^3 donor side of PyrPzAmide Schiff base along with end-on, EO bridging of azide co-ligands. Another crystal section of Cu(II) bonded in a similar fashion. It is worth to mention that any of the bridging azide nitrogen atoms occupies one equatorial position of one Cu^{II} center but the axial position of the second Cu^{II} metal ion, so the mode of the end-on azide in complex (1) is equatorial-axial in terms of the type of the coordination position it occupies. The bond distances of $\text{Cu}^1\text{-N}^1$ and $\text{Cu}^1\text{-N}^3$ are 2.023 (5) Å, 2.043 (6) Å, respectively. Again bond distances of end-on,

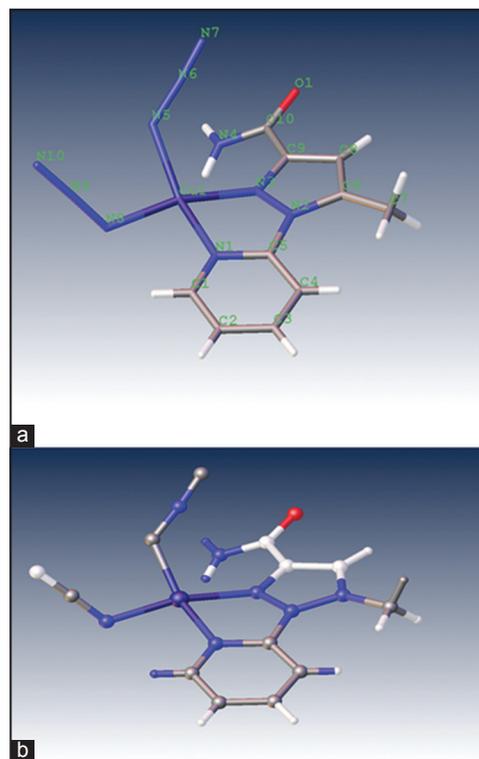
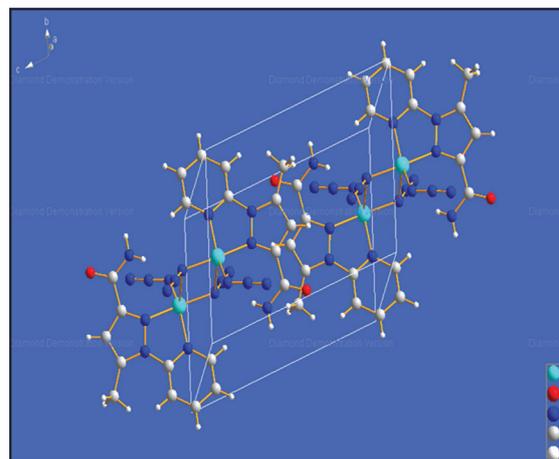
Table 1: Experimental data for crystallographic analysis of Cu (II) complex 1.

| | |
|------------------------------------------------------|--------------------------------------------------------------------------------|
| Empirical formula | C ₂₀ H ₂₀ Cu ₂ N ₂₀ O ₂ |
| Formula weight | 699.66 |
| Temperature (k) | 150 (2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | |
| a (Å) | 6.922 (9) |
| b (Å) | 9.463 (12) |
| c (Å) | 11.184 (14) |
| α (°) | 115.00 (3) |
| β (°) | 90.62 (4) |
| γ (°) | 94.85 (4) |
| Volume (Å ³) | 660.69 |
| Z | 1 |
| Density _{cal} (mg m ⁻³) | 1.758 |
| Absorption coefficient (mm ⁻¹) | 1.674 |
| F (000) | 354 |
| θ range (°) for data collection | |
| Index ranges | -7 ≤ h ≤ 7 -10 ≤ k ≤ 10 -12 ≤ l ≤ 12 |
| Goodness-of-fit on f ² | 1.136 |
| Completeness to theta | 23.99 |
| Independent reflections (r _{int}) | 1654 |
| Refinement method | Full-matrix least squares on f ² |
| Reflections collected | |
| Final r indices [i > 2σ(i)] | R ₁ =0.0566, ω ₂ =0.1147 |
| Largest difference peak and hole (eÅ ⁻³) | 0.095 and -0.503 |

EO azide bridging with respect to Cu(II) center are Cu^{II}-N⁸ and Cu^{II}-N⁵ 2.457 (5) Å, 1.936 (6) Å. The crystal structure of PyrPzAmide Schiff base copper complex can be best described as a 1D layer due to intermolecular hydrogen bonding (Figure 3). The structure is stabilized by a network of intermolecular hydrogen bonding via O1 versus N4 and N4 versus O1 of PzAmide unit. Apart from, a strong vander wall interaction has been strongly involved in complex 1 crystal structure (Figure 4, Appendix A).

7. DFT COMPUTATION OF CU(II) COMPLEX 1

The geometry of complex 1 as derived from X-ray crystallographic data has been optimized without any symmetry restrictions by means of DFT calculations using the hybrid DFT (B3LYP) method with the basis set LanL2DZ and the GAUSSIAN 09 software

**Figure 1:** (a and b) ORTEP view - An atom numbering scheme of complex 1.**Figure 2:** A complete noncentrosymmetric dimer structure of complex 1.

package. For the geometry-optimized DFT models of complex 1 (Figure 5), the input structures were acquired from the CIF data. The experimental results like selected bond distances, and angles were compared with the theoretical values in Table 2. According to this Table 2, the agreement between the most geometrical parameters calculated at the different DFT levels with LanL2DZ basis set used and the experimental data's fulfilled maximum satisfactory. Hence, DFT model should also be capable of producing a maximum reliable geometry of Cu(II) Schiff base binuclear complex 1. The slight

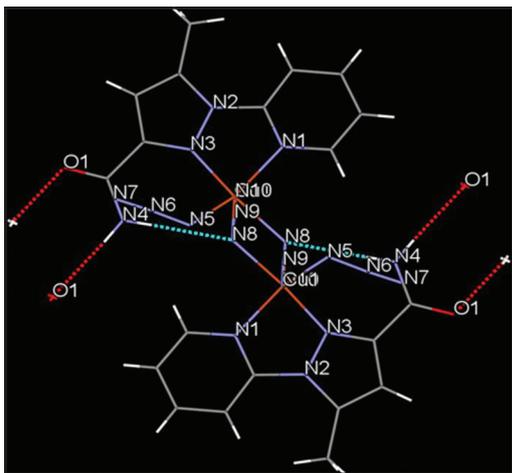


Figure 3: Details of H-bonding interaction in crystal structure 1.

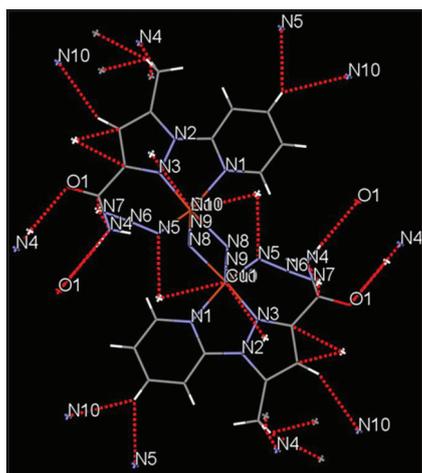


Figure 4: Details of van der Waals radii interaction in crystal structure 1.

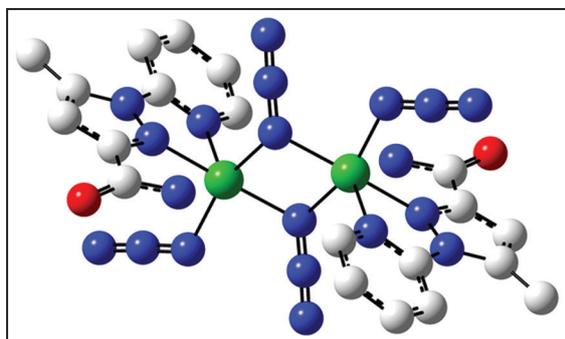


Figure 5: Density functional theory optimized structure of binuclear Cu(II) complex 1.

discrepancies with respect to bond distances, angles could be attributed to the fact that crystallographic X-ray measurement has been purely done only in solid state where lattice with interactions in the crystal structure takes place predominantly but the computed DFT method refers to the isolated gaseous phase. Mulliken charge distribution structure (Figure 6) of

Table 2: Experimental and theoretical bond distances and angles comparison via DFT computational method of complex 1.

| | Complex 1 | |
|----------------|--------------------|------------|
| | Experimental (sxd) | Calculated |
| Bond distances | | |
| Cu1-N5 | 1.936 (5) | 2.02054 |
| Cu1-N8 | 1.991 (5) | 2.06789 |
| Cu1-N1 | 2.023 (5) | 2.21841 |
| Cu1-N3 | 2.043 (5) | 2.10656 |
| Cu1-N8 | 2.458 (5) | 2.10700 |
| Bond angles | | |
| N5-cu1-N8 | 91.49 (18) | 89.76 |
| N5-cu1-N1 | 150.0 (2) | 156.11 |
| N8-cu1-N1 | 93.55 (16) | 94.46 |
| N5-cu1-N3 | 101.19 (18) | 98.64 |
| N8-cu1-N3 | 165.39 (17) | 159.31 |
| N1-cu1-N3 | 79.12 (16) | 75.80 |
| N5-cu1-N8 | 107.3 (2) | 100.08 |
| N8-cu1-N8 | 81.49 (18) | 73.81 |
| N1-cu1-N8 | 102.64 (16) | 103.25 |
| N3-cu1-N8 | 87.75 (15) | 91.92 |

DFT=Density functional theory

complex 1 has been derived from DFT computational study and strongly observed that Cu(II) metal center in complex 1 has been extensive charge reduction takes place by PyrPzAmide N,N donor Schiff base ligand. This is further supported that a strong binding takes place between Cu(II) metal center with N,N chelating donor Schiff base ligand along with versatile azide ions during complex 1 formation.

7.1. DFT Studies of Binuclear Cu(II) Complex 1

7.1.1. Energy and other physical properties of HL and model compound

| | |
|-------------------|-----------|
| Charge | 0 |
| Spin | Singlet |
| Energy (eV) | -65620.03 |
| Dipole moment (D) | 0.0014 |
| Point group | C1 |

8. CONCLUDING REMARKS

In our laboratory, PyrPzAmide chromophoric N,N bidentate chelating Schiff base ligand (L_1) was successfully used to synthesized one binuclear Cu(II) complex 1 with Copper perchlorate as the metal precursor and azide as a versatile bridging coligand. The Schiff base ligand form a square-based pentacoordinated complex via N,N donor center. Each Cu metal center in this complex satisfies completely

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***Bibliographical Sketch**



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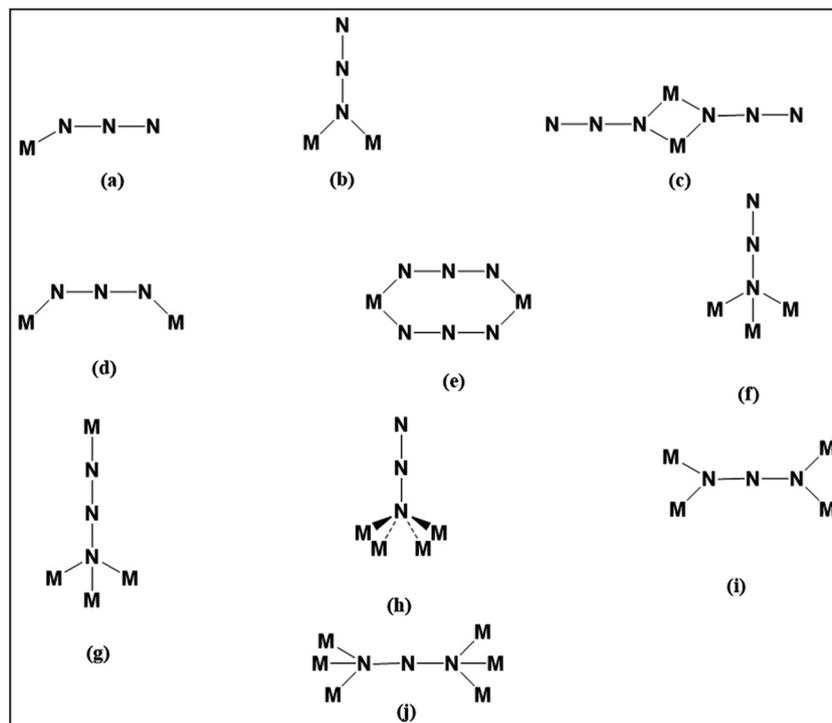


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APPENDIX

Appendix A: Supplementary data

CCDC 1458007 contains the supplementary crystallographic data (excluding structure factors) for Cu(II) complex. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or e-mail: Deposit@ccdc.cam.ac.uk. Azide ions versatile bridging modes are enclosed in Figure S1.



Scheme 1: Versatile binding modes of azide (N_3^-) ions.