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Design of end-on cyanato bridged trinuclear Cu(II) Schiff base complex with salen type Schiff base ligand: Synthesis, structural investigation and DFT study

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One ONNO-donor tetradentate Schiff base ligand LH₂ was derived from the condensation of salicylaldehyde and 1,3-diaminopropane and reacted with Cu(NO₃)₂·6H₂O and NaNCO to yield one trinuclear complex with molecular formula [Cu₃L₂($\mu_{1,1}$ -NCO)₂]. The synthesized complex was characterized by IR, Uv-vis spectroscopy and electrochemical analysis. Single-crystal X-ray diffraction study explores that the two terminal copper atoms adopt square pyramidal geometry, whereas the central copper atom situated at the inversion center is surrounded by four phenoxo oxygens and two *end-on* cyanato anions to adopt an octahedral geometry. The ONNO-tetradentate Schiff base ligand coordinates with the copper(II) ion via two oxygen atoms of the phenoxo-group and two nitrogen atoms from the imine moiety. A theoretical DFT calculation was also carried out to supplement the experimental results. All the DFT calculations were done in gas phase.

Keywords: Tetradentate Schiff base; Trinuclear copper complex; X-ray study; DFT Calculation

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1. Introduction

The construction of transition-metal Schiff base complexes having supramolecular arrays based on covalent or hydrogen-bonding interactions along with pseudohalide-bridging is an area of great research activity in inorganic chemistry due to their interesting properties [1, 2]. Their physical, optical, and electronic properties have been explored in different coordination environments with organic chelators, blockers, and suitable bridging units [3-5]. In a few multicopper enzymes, it has been established by X-ray crystallography [6], MCD spectroscopy [7] and magnetic studies [8] that a trinuclear array of copper centers may be the essential functional unit of the cofactors which catalyze the 4e⁻/4H⁺ reduction of dioxygen to water. The key factor that leads the researchers to synthesize such type of complexes is the exchange coupling between paramagnetic centers and possible magneto-structural correlation in molecular systems, which develops a few new functional molecular-based materials [9-12].

Pseudohalide anions $(N_3^-, SCN^-, NCO^-, etc.)$ are versatile ligands for obtaining multinuclear 1D, 2D or 3D coordination networks. These bridging ligands also play an important role in the magnetic exchange pathways between paramagnetic centers and, in general, show various magnetic interactions which are attributed to the diversity of coordination modes and to their ability to transmit magnetic interaction between metal centers [13, 14]. The cyanate anion, like the most widely studied azide, can also act as a bridging ligand between two metal ions. The most common bridging modes are: end-to-end (a) and end-on fashion (b, c) (scheme 1). The most comprehensive literature refers to azide bridging ligand: the end-to-end bridging mode creates antiferromagnetic coupling [15] and the end-on mode results in ferromagnetic coupling [16]. But, these behaviors are not so clear for the cyanato bridging ligands as the number of reported complexes that have been fully characterized is too low to permit magneto-structural correlations [14]. The study of the ability of cyanato ligand as a super-exchange pathway between copper(II) ions is difficult as most of the published compounds for which structural and magnetic data are available also have another type of bridge in their structures. It is difficult to separate the contribution of the cyanato ligand to the total coupling constant. Only four such compounds are bridged exclusively by cyanato ligands, $[Cu_2(\mu_{1,1}-NCO)_2)(terp)_2(H_2O)_2](PF_6)_2$, $[Cu_2(\mu_{1,3}-NCO)(L^1)](ClO_4)_3 \cdot MeCN \cdot 1.5EtOH, [Cu_2(\mu_{1,3}-NCO)_2(EtMe_4dien)_2](ClO_4)_2 and$ $[{CuL(\mu_{1,3}-NCO)}_n]$ [17a-d]. Magnetic data for these complexes prove the high versatility of the

cyanato ligand in its super-exchange pathway. Also a few trinuclear copper complexes of LH_2 are reported in the literature [18] and in all the cases the ligand acts as tetradentate N_2O_2 -donor. The common factor between the structures is that they mainly consist of $Cu_3N_2O_4$ core regardless the factor of counter anion.



Herein, we describe the synthesis of a newly designed trinuclear copper(II) complex having molecular formula $[Cu_3L_2(\mu_{1,1}-NCO)_2]$ (1), where LH₂ is the 2:1 condensation product of salicylaldehyde and 1,3-diaminopropane. The complex has been characterized by elemental analysis, IR, UV-vis spectroscopy and cyclic voltammetry. The crystal structure of the synthesized complex has been determined by single-crystal X-ray diffraction study. Theoretical density functional theory (DFT) study has also been carried out to supplement the experimental data.

2. Experimental

2.1. Materials

Salicylaldehyde, 1,3-diaminopropane and copper nitrate were purchased from Sigma-Aldrich (USA) and used without purification. All solvents were AR grade and used as received.

2.2. Physical measurements

The infrared spectrum of the investigated complex was recorded on a Perkin–Elmer Spectrum 2 FT-IR spectrophotometer with KBr discs (4000–400 cm⁻¹). Elemental analyses (C, H and N) were carried out using a Perkin–Elmer 2400 II elemental analyzer. Ground-state absorptions for the complex were recorded at 300 K with a Perkin–Elmer Lambda-35 (UV–vis) spectrophotometer using HPLC grade acetonitrile. Cyclic voltammetric study was carried out on

CH 660E electrochemistry system using tetrabutylammonium perchlorate as supporting electrolyte at scan rate of 50 mV sec⁻¹ in acetonitrile. A platinum working electrode, one platinum wire auxiliary electrode and saturated calomel electrode (SCE) were used as standard three electrode configurations.

2.3. Synthesis of the ligand and complex

2.3.1. Synthesis of LH₂. LH₂ was synthesized by refluxing 2 mmol of salicylaldehyde (0.21 mL) and 1 mmol of 1,3-diaminopropane (0.08 mL) for 1 h in methanol and was used without purification [18a].

2.3.2. Synthesis of $[Cu_3L_2(\mu_{1,1}$ -NCO)_2] (1). Cu(NO₃)₂·6H₂O (0.2813 g, 1.5 mmol) and LH₂ (0.268 g, 1 mmol) were dissolved in 25 mL acetonitrile and then an aqueous solution (5 mL) of sodium cyanate (0.651 g, 1 mmol) was added dropwise to the solution. The green mixture was then stirred for 30 min and the resulting solution was filtered and kept for slow evaporation. After a couple of weeks green needle-shaped crystals appeared and were found suitable for X-ray diffraction study. Yield: 42% (0.351 g). Anal. Calc. for $[C_{36}H_{32}Cu_3N_6O_6]$: C, 51.71; H, 3.86; N, 10.05. Found: C, 51.63; H, 3.93; N, 10.18%.

2.4. X-ray crystallography

To collect the X-ray diffraction data single-crystal of the complex was mounted on an Oxford Diffraction Gemini diffractometer equipped with graphite monochromated Mo $K\alpha$ ($\lambda = 0.71069$ Å) fine-focus sealed tubes. Intensity data were collected at 100(1) using φ and ω scans. Crystal data were collected using a Gemini (Oxford Diffraction, 2006). Data refinement and reduction were performed using CrysAlis RED [19], (Oxford Diffraction, 2002) software. Multiscan absorption corrections were applied empirically to the intensity values ($T_{min} = 0.46$ and $T_{max} = 0.90$) using SADABS [20]. The structures were solved by direct methods using the program SIR-97 [21] for the complex and refined with full-matrix least-squares based on F^2 using program CRYSTALS [22]. All non-hydrogen atoms were refined anisotropically. C-bound hydrogen atoms were placed geometrically and refined using a riding model approximation. The molecular graphics and crystallographic illustrations for the complex were prepared using CAMERON [23] and ORTEP [24]. All relevant crystallographic data and structure refinement parameters for the complexes are summarized in table S1.

2.5. Computational details

The gas-phase geometry of the investigated complex was optimized without any symmetry/ restrictions with spin-unrestricted DFT calculations using the hybrid DFT (B3LYP [25] and PBEPBE [26]) methods and several basis sets (6-31G* and 6-311+G* [27]) with the Gaussian 09 software package [28]. The initial structure of the complex was generated from its X-ray crystallographic data. No constraint was applied in the calculations and all atoms were free to optimize. The charge distribution in the complex has been computed using the Mulliken method [29] for deriving atomic charges at the B3LYP/6-311+G* level of theory. We have also computed the chemical hardness using the equation proposed in the literature at the B3LYP/6-311+G* level of theory [30]. That is, $\eta = \frac{1}{2} \times (I-A)$, where I and A are the vertical ionization potential and vertical electron affinity, respectively. On the basis of the optimized ground and excited state geometries, the absorption and emission spectral properties in acetonitrile (CH₃CN) were calculated by the time-dependent density functional theory (TD-DFT) [31] approach associated with the conductor-like polarizable continuum model (CPCM) [32]. We computed the lowest forty singlet-singlet transitions and forty singlet-triplet transitions in absorption and emission processes, respectively, and the results of the TD calculations were qualitatively similar to the observed spectra. GaussSum program version 2.2 was used to calculate the molecular orbital contributions from groups or atoms [33].

3. Results and discussion

3.1. Synthesis

LH₂ was synthesized using commercially available reagents following the process described earlier [18]. In recent years, our group has reported a number of trinuclear complexes using ONNO donor Schiff base ligands and in most of the cases the central metal atom is copper [18a, 34]. Interestingly, most of the trinuclear complexes reported so far contain an additional anion bridge. For example, in such studies, we synthesized two trinuclear copper(II) complexes using the same type of ligands as that of LH₂ with copper(II) acetate [34c] and Cu(II) bromide [18a]. When we used acetate, it behaves as a bridging chelating ligand [34c] but when we used bromide [18a] it acted as a monodentate ligand as bromide is devoid of any bridging ability. Keeping all this in mind, we used sodium cyanate to understand the role of cyanate in the final nuclearity of the synthesized copper(II) complex with one compartmental ligand LH₂ to furnish the trinuclear complex $[Cu_3L_2(\mu_{1,1}-NCO)_2]$ (1), where the desired square-pyramidal – octahedral – square-pyramidal topology of the triad is achieved with the support from cyanato bridging co-ligand which acted in a monodentate bridging mode.

3.2. Crystal structure descriptions

ORTEP diagram of the complex with atom numbering scheme of the trimeric asymmetric unit is presented in figure 1. Selected bond lengths and angles are given in table 1. The centrosymmetric complex shows a linear trinuclear array of three Cu(II) ions, where two μ -phenolato oxygen atoms of the deprotonated Schiff base ligand and one monoatomic bridging $\mu_{1,1}$ -NCO⁻ anion bridge each terminal copper atom with the central copper atom. Both the cyanato bridges for the terminal Cu1 and central Cu2 centers are in a *syn-syn* fashion but are mutually *trans* to each other, due to inversion symmetry.

The equatorial plane of the central Cu2 is formed by two bridging phenoxo-oxygen atoms (O21 and its symmetry-related counterpart O21') from two Schiff base ligands and two nitrogen atoms (N31 and N31') from two bridging cyanates, while the axial positions of the octahedron are occupied by two bridging phenoxo-oxygen atoms O1 and O1' (symmetry related counterpart). As the central Cu2 atom is located on an inversion center, all three *trans* angles are very close to 180° (actual values: 179.994°, 179.994° and 179.995° for N31'-Cu2-N31, O21-Cu2-O21' and O1-Cu2-O1', respectively). In the coordination sphere of Cu2 in the complex, the equatorial Cu2-O21(phenoxo) and Cu2-N31(cyanato) bond lengths are 2.003(4) Å and 1.957(5) Å, respectively, which are distinctly shorter than the axial Cu2-O1(phenoxo) distance of 2.409(4) Å (table 1). The coordination geometry of the central Cu(II) ion has typical Jahn-Teller distortion, as it is expected for a Cu(II) d⁹ system, from ideal octahedral geometry [35].

In the complex, two terminal copper atoms are five-coordinate, bearing identical environments, due to the presence of crystallographic inversion symmetry. The coordination number five for Cu(II) is very common, where it may possess either square-pyramidal (SP) or trigonal-bipyramidal (TBP) geometry [36]. For a five-coordinate metal center, the distortion of structure from SP to TBP can be evaluated by the Addison distortion index, τ defined as the ratio

of the mean in-plane Cu-L bond distance to the out-of-plane Cu-L bond distance [37], = $[|\theta - \theta|]$ Φ [/60], where θ and Φ are the two largest coordination angles and τ is 0 for perfect SP and 1 for ideal TBP geometry [38]. The calculated τ value for the complex is 0.326 which clearly suggests a distorted SP geometry for the terminal copper atoms in the complex. The basal plane of each of the two equivalent terminal copper centers is formed by the two imine nitrogen atoms (N9 and N13) and two phenolic oxygen atoms (O1 and O21). Cu1 is displaced from the mean equatorial plane constructed by two imine nitrogen atoms and two phenolic oxygen atoms of the Schiff base ligand by 0.244(3) Å, toward the apical nitrogen (N31). The two six-membered CuONC₃ chelate rings possess half-chair conformation, while the CuN₂C₃ chelate ring has a pronounced boat conformation. Cu-O equatorial bond lengths around the terminal Cu1 ions are 1.927(4) Å to 1.937(4) Å, while the Cu1-N equatorial distances are 1.935(5) Å and 1.978(5) Å. All the four bond distances are much shorter than the axial Cu1-N31 bond distance of 2.682(5) Å. The Cu1-imine nitrogen and Cu1-phenolic oxygen bond distances are in the ranges observed for similar systems [39]. Sorrel and Jameson have pointed out that the linear N-Cu-N bond enjoys a strong σ -overlapping between the ligand and the copper orbitals [40]. The extent of such overlap is determined by the steric demands of the participating ligands. In the present study, the Cu2-N31 distance is fairly high. This could be attributed to the presence of steric interference of the coordinating linear cyanato ligand, which is expected to participate in stronger σ -overlapping in the OCN-Cu(II)-NCO links. Interestingly, bridging –NCO group coordinates to the central Cu2 along equatorial plane via N-atom, whereas it occupies the axial position of the terminal Cu1 atom. The distortion from ideal square pyramidal geometry is also reflected from the difference in *cis*-angles lie in the basal plane which vary from 82.44(17)° to 92.99(18)° and angles in trans position vary from 158.83(19)° to 163.23(19)°.

The Cu1····Cu2 distance is 2.954 Å, which is comparable to similar type systems [41]. Packing diagrams of the complex are shown in figures 2 and S1. None of the intramolecular H-bonds were detected in the trimer. But the weak intermolecular non-classical interactions C14-H141···O33 = 2.44 Å along with C16-H161···O1 = 2.56 Å and C19-H191···N31 = 2.62 Å and stacking interaction propagate the molecule along the *c*-axis.

3.3. FT-IR spectrum

The infrared spectrum (figure S2) of the complex is very much consistent with the structural data. In the title complex, a strong and sharp absorption band at 2100 cm⁻¹ in the spectrum of the complex is due to v(NCO) and a band around 1615 cm⁻¹ may be assigned to the imine stretching frequency *i.e.* coordination of the nitrogen atom of the imine group to the metal ions [41, 42]. The phenolic v(Ar-O) band is observed in the frequency region 1178-1184 cm⁻¹, providing evidence for coordination to the metal ions through the deprotonated phenolic oxygen atoms [43]. Sharp bands at ~498 cm⁻¹ and ~423 cm⁻¹ correspond to the Cu-N and Cu-O stretching frequencies, respectively. A characteristic peak for v(C=C) is located at 1545 cm⁻¹ [43].

3.4. Electronic spectrum

The electronic spectrum of 1 was measured in acetonitrile and is depicted in figure 3. Multiple transitions are the characteristics of the spectrum for 1 and the bands are attributed primarily to the charge-transfer transitions within the tri-coordinated Schiff base ligand with varying amounts of anionic coligand-p orbital and metal-d orbital participation. To gain deeper insight into the electronic properties of the transitions involved in the optical absorption processes, we investigated 1 by means of TD-DFT in acetonitrile. The most relevant transitions involved, along with their energy, character, oscillator strengths of 1 are listed in table 2. The spectrum shows two strong absorption bands in the region 233 nm and 269 nm. These bands are clearly chargetransfer in origin [44]. The band around 382 nm is assigned to the $n-\pi^*$ transition of the azomethine group. The visible spectrum of the complex displays a single broad band at 673 nm. These spectral features are consistent with the five-coordinate geometry of the Cu(II) complex. In general, typical five-coordinate Cu(II) complexes of SP or distorted SP geometries exhibit a band in the range 550–660 nm, whereas the corresponding TBP complexes usually show a band at $\lambda > 800$ nm with a higher-energy shoulder [45]. This indicates that the solution spectrum of the complex is adequately explained by a d-d transition for the Cu(II) ion in a distorted SP geometry where the absorption band observed in the visible region results from a ${}^{2}E \rightarrow {}^{2}B_{1}$ transition. Based on TD-DFT analysis for 1, lower-energy transition around 673 nm is computed at 714 nm (1.7344 eV, f = 0.0177) as $\pi(L1) + \pi(L2) + 3d_{vz}(Cu3) + \pi(NCO2) \rightarrow 3d_z^2(Cu3) +$ π^* (L2) ²ILCT/²LMCT transition. The transition near 382 nm (3.2024 eV, f = 0.0228, $\lambda_{theo} =$

387 nm) is computed as $\pi(L1) + \pi(L2) + \pi(NCO1) + \pi(NCO2) \rightarrow 3d_z^2(Cu3) + \pi^*(L2)$ ILCT/LLCT transition.

3.5. Electrochemical study

Cyclic voltammogram of 1 (figure 4) shows two quasi-reversible reductive responses on the negative side of SCE at -0.219 and -1.04V, respectively, and one irreversible oxidative response on the positive side of SCE at 0.49 V. When the complex is cathodically scanned (0.0 to -1.5 V), the reduction peak at $E_{pc}^{1} = -0.219$ V and the peak at $E_{pc}^{2} = -1.04$ V are observed. When the sweep is reversed at -1.5 V in the anodic direction we can observe an oxidation wave (E_{pa}^{2}) corresponding to a one-electron redox process. Moreover, the first reaction ($E_{1/2}^{1} = -0.219$ V) is a single peak with a peak current intermediate between those of single-step 1e⁻¹ and 2e⁻¹ reactions; it therefore demonstrates the process of two one-electron steps that correspond to the redox process of the two terminal copper(II) ions.

The electrochemical behavior of the trinuclear copper(II) complexes can be interpreted according to the following scheme:

Positive potential, $Cu^{II}Cu^{II}Cu^{II} \longrightarrow Cu^{II}Cu^{II}Cu^{II}$; negative potential, $Cu^{II}Cu^{II}Cu^{II} \longrightarrow Cu^{II}Cu^{II}Cu^{II} \longrightarrow Cu^{I}Cu^{I}Cu^{I}Cu^{I}$. This is similar to the other trinuclear copper(II) complexes [46].

At Positive Potential: $Cu^{II}Cu^{II}Cu^{II} \xrightarrow{-e^{-1}} Cu^{II}Cu^{II}Cu^{II}$ At Negative Potential: $Cu^{II}Cu^{II}Cu^{II} \xrightarrow{+e^{-1}} Cu^{II}Cu^{II}Cu^{II} \xrightarrow{+2e^{-1}} Cu^{I}Cu^{I}Cu^{I}$

3.6. Geometry optimization, charge distribution and electronic structure

The geometry of **1**, as derived from X-ray crystallography, was optimized without any symmetry restrictions by spin-unrestricted DFT calculations using the hybrid DFT (B3LYP and PBEPBE) methods with several basis sets (figure 5) and the GAUSSIAN 09 software package [28] (figure 5). The calculated bond lengths and angles are in agreement with the values based upon the X-ray crystal structure data (table 1). A difference between the experimental and theoretical studies is that computations were done in the gas phase, whereas the X-ray data were obtained in the solid phase for the complex under consideration. The main differences are found in the Cu1-N31ⁱ (i = 1-x, 1-y, 1-z) and Cu2-O1 distances that are overestimated using the DFT

methods. This is likely due to crystal packing effects that are not considered in the theoretical calculations. Regarding the coordination angles, the level of theory that provides better agreement is the B3LYP/6-311+G*, especially in the O21-Cu1-N9 angle (table 1).

All the nitrogen and oxygen atoms in the complex bear negative charges, while the carbon atoms and the copper center bear positive charges. The calculated charges on the copper atoms in the complex are +1.058 e for Cu1 and +1.029 e for Cu2 which are considerably lower than the formal charge +2, that confirms a significant charge donation from the ligands. In the compound, the calculated Mulliken atomic charges for the atoms N31, O1 and O31 are less than -1: -0.522, -0.433 and -0.420 e, respectively. So, all the electron density in valence 3s and 3p orbitals is lower than the predicted values. Similarly, the electron density of these atoms is lower than expected values. All these results indicate electron transfer from the donor atoms to the central metal. Calculated highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) frontier orbitals of the synthesized complex are shown in figures 6 and 7, respectively, and they show relevant differences. In fact, in the complex the HOMO is mainly localized on one of the Schiff base phenyl rings and terminal Cu, while in the LUMO, major contributions come from the metal and, to a lesser extent from the terminal Schiff base. Since the fimaj electron transfer occurs from the HOMO to LUMO, it can be inferred that the first electron-transfer in the complex is related to be LMCT. The HOMO-LUMO energy separation is useful for estimating the kinetic stability of molecules. A large HOMO-LUMO gap can be associated with high kinetic stability and low chemical reactivity [47]. The orbital energy level analysis for the complex at the B3LYP level shows that the HOMO–LUMO gap is 2.7 eV for α -spin and 2.4 eV for β -spin, which suggests that this complex is stable.

3.7. Frontier molecular orbital compositions

The partial frontier molecular orbital (FMO) compositions of **1** along with the HOMO–LUMO energy gap are listed in tables 3 and 4. The complex was grouped according to the following scheme: *i*) O1, C2-C8, N9, C10-C12, N13, C14-C20, O21 as L1; *ii*) the remaining Schiff base molety as L2; *iii*) N31, C32, O33 as NCO1 and *iv*) N31^{*i*}, C32^{*i*}, O33^{*i*} as NCO2. In the ground state the HOMO, HOMO-1, HOMO-2 and HOMO-3 of **1** mainly consist of π orbitals from the Schiff base ligand moleties. Whereas, LUMO consists of $3d_z^2$ (Cu3) with a considerable participation of π^* (L2) and LUMO+1 to LUMO+3 consist of alternating contributions from the ligands (L1 and L2) in the α -spin state. But, the scenario for the- β state is quite different. The ground state of HOMO and HOMO-1 consist of π (L1) and d_{yz} (Cu3). The HOMO-2 consist of π (L2) and d_{yz} (Cu3) and HOMO-3 mainly of π (L1). It is worth noting that LUMO of 1 are alike to $3d_z^2$ of Cu1. LUMO+1 consist of π^* (NCO1) and $3d_z^2$ (Cu3). LUMO+2 are composed of π^* (L1) and LUMO+3 consist of $3d_z^2$ (Cu3).

4. Conclusion

Using the cyanate anion as one of the bridging ligands, we have synthesized and structurally characterized one rare *end-on* cyanato bridged trinuclear copper(II) Schiff base complex. Elemental analyses, IR, electronic spectra and cyclic voltammogram are in agreement with the structure of the complex. The ONNO-tetradentate Schiff base ligand coordinates with the copper(II) ion via two oxygens of the phenoxo-group and two nitrogens from the imine moiety. The large value of Cu2-N31 distance shows the presence of steric interference of the coordinating linear cyanato ligand. DFT calculations were used for calculating structural, electronic and orbital properties of the complex and all values correlate with the structural data. All the DFT calculations were done in gas phase.

Appendix A. Supporting Information

Supplementary information contains crystallographic data for **1** having CCDC No. 882002 along with other necessary tables and figures. These data can be obtained free of charge via www.ccdc.cam.ac.uk.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure 1. ORTEP diagram of **1** with atom numbering scheme (Thermal ellipsoids are plotted at 40% probability level).





Figure 3. UV-vis spectrum of 1 in acetonitrile.









Figure 6. Molecular orbital surfaces and energy level for the HOMO of 1 (Computed at B3LYP level; $E_{HOMO} = 8.55 \text{ eV}$).



Figure 7. Molecular orbital surfaces and energy level for the LUMO of 1 (Computed at B3LYP level; $E_{LUMO} = 3.30 \text{ eV}$).

	X-ray	B3LYP/6-31G*	B3LYP/6-311+G*	PBEPBE/6-311+G*
Cu1-O1	1.928(4)	1.911	1.976	1.963
Cu1-O21	1.937(5)	1.896	2.054	2.033
Cu1-N9	1.936(5)	1.926	2.018	1.989
Cu1-N13	1.978(5)	1.899	2.033	2.011
Cu1-N31 ⁱ	2.682(5)	2.281	2.475	2.382
Cu2-O1	2.409(3)	2.717	2.718	2.718
Cu2-O21	2.003(4)	1.944	2.096	2.097
Cu2-N31	1.957(4)	1.923	1.971	1.949
O1-Cu1-O21	82.45(16)	83.30	80.54	79.98
O1-Cu1-N9	93.00(17)	90.55	91.40	91.63
O1-Cu1-N13	158.83(19)	165.39	165.57	163.25
O1-Cu1-N31 ⁱ	79.49(16)	81.49	87.92	89.84
O21-Cu1-N9	163.24(19)	152.50	165.57	171.24
O21-Cu1-N13	91.86(18)	93.45	87.92	89.49
N9-Cu1-N13	97.81(19)	98.60	97.89	98.08
N9-Cu1-N31 ⁱ	94.92(17)	92.37	100.65	100.32
N13-Cu1-N31 ⁱ	117.39(17)	113.98	108.52	106.56
O1-Cu2-O21	69.83(17)	70.34	64.01	62.96
O1-Cu2-O1 ⁱ	180.00	179.94	177.45	178.83
O21-Cu2-N31	95.3(2)	94.13	85.29	85.06
O21-Cu2-O21 ⁱ	180.00	179.89	179.45	179.49
O21 ⁱ -Cu2-N31	84.8(2)	85.77	81.40	80.75

Table 1. Important bond lengths (Å) and angles (°) for 1. The calculated distances and angles correspond to the B3LYP/6-311+G* level of theory.

Symmetry code: i= [3666.00]= 1-x, 1-y, 1-z.

Table 2. Main calculated vertical transitions with compositions, vertical excitation energies and oscillator strength of 1 in acetonitrile based on the lowest lying triplet excited state.

Composition	E (eV)	Oscillator strength (f)	λ_{theo} (nm)	Assignment	λ_{exp} (nm)
$H - 4 \rightarrow L (14\%)$	3.2024	0.0228	387.15	ILCT/LLCT	382
$H - 13 \rightarrow L (19\%)$				LMCT	\searrow
$H - 11 \rightarrow L (15\%)$				ILCT/LMCT	7
$H - 6 \rightarrow L (10\%)$	3.1624	0.0145	392.05	LLCT/LMCT	
$H - 4 \rightarrow L (53\%)$				ILCT/LLCT	
$H - 13 \rightarrow L (30\%)$	3.0316	0.0127	408.96	LMCT	
$\mathrm{H}-11 \rightarrow \mathrm{L}~(23\%)$				ILCT/LMCT	
$H - 12 \rightarrow L (46\%)$	2.9677	0.0116	417.77	ILCT/LMCT	
$H - 10 \rightarrow L (19\%)$				ILCT/LMCT	
$\mathrm{H-6} \rightarrow \mathrm{L}~(20\%)$			\nearrow	LLCT/LMCT	
$H - 2 \rightarrow L (58\%)$	1.7344	0.0177	714.84	ILCT/LMCT	673
$H - 3 \rightarrow L (16\%)$				ILCT/LMCT	

Orbital	a- MO	Energy	Contribution (%)							Main Rond Type
(eV)		(eV)	Cu1	Cu2	Cu3	L1	L2	NCO1	NCO2	
204	L+5	0.25	24	44	22	5	4	0	0	$3d_z^2(Cu1) + 3d_z^2(Cu2) + 3d_z^2(Cu3)$
203	L+4	-1.37	0	0	1	3	96	0	0	π*(L2)
202	L+3	-1.42	0	0	0	96	3	0	0	π*(L1)
201	L+2	-1.6	0	0	2	0	97	0	0	π*(L2)
200	L+1	-1.63	2	0	0	98	0	0	0 (π*(L1)
199	LUMO	-2.55	0	0	61	0	38	0	0	$3d_z^2(Cu3) + \pi^*(L2)$
198	НОМО	-5.25	0	1	2	13	83	1	0	$\pi(L1) + \pi(L2)$
197	H-1	-5.35	1	1	0	83	13	0	μ>	$\pi(L1) + \pi(L2)$
196	H-2	-5.6	0	1	1	12	75	8	2	$\pi(L1) + \pi(L2)$
195	H-3	-5.65	1	0	0	77	13	1	8	$\pi(L1) + \pi(L2)$
194	H-4	-6.06	3	4	4	13	12	37	28	$\pi(L1) + \pi(L2) + \pi(NCO1) + \pi(NCO2)$
193	H-5	-6.21	4	4	1	24	Y	40	21	$\pi(L1) + \pi(NCO1) + \pi(NCO2)$
HOMO - LUMO gap = -2.7 eV										

Table 3. Frontier molecular orbital composition (%) in the excited state of 1 for α -spin.

Orbital	<i>β</i> - MO	Energy	Contri	bution ((%)	Main Bond Type				
	(eV)	Cu1	Cu2	Cu3	L1	L2	NCO1	NCO2	Wall Bold Type	
203	L+5	-1.38	0	0	85	14	0	0	0	$\pi^{*}(L1) + 3d_{z}^{2}(Cu3)$
202	L+4	-1.41	0	0	14	85	0	0	0	$\pi^{*}(L1) + 3d_{z}^{2}(Cu3)$
201	L+3	-1.59	0	0	96	1	0	2	0	$3d_z^2(Cu3)$
200	L+2	-1.62	0	2	2	97	0	0	0	π*(L1)
199	L+1	-2.52	5	0	37	1	1	55		$\pi^*(\text{NCO1}) + d_z^2(\text{Cu3})$
198	LUMO	-2.85	59	0	9	7	9	7	9	$3d_z^2(Cu1)$
197	НОМО	-5.25	1	0	74	24	0	2	0	$\pi(L1) + 3d_{yz}(Cu3)$
196	H-1	-5.33	1	1	22	73	1	$\phi \rightarrow$	1	$\pi(L1) + 3d_{yz}(Cu3)$
195	H-2	-5.58	0	0	84	2	Th	2	1	$\pi(L2) + 3d_{yz}(Cu3)$
194	H-3	-5.62	1	1	2	84	V	0	11	$\pi(L1) + \pi(NCO2)$
193	H-4	-6.1	3	3	8	19	42	2	22	$\pi(L1) + \pi(L2) + \pi(NCO2)$
192	H-5	-6.21	2	9	4	53	1	0	32	$\pi(L1) + \pi(NCO2)$
HOMO - LUMO gap = -2.4 eV										

Table 4. Frontier molecular orbital composition (%) in the excited state of 1 for β -spin.

Graphical abstract

