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# Coordination behaviour and DFT studies of Copper(II) complexes of a novel chromone derived tetradentate Schiff base

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New Schiff base chelates of Copper(II) derived from the Schiff base ligand ethylenediaminobi(chromone-3-carbaldehyde) (FCED), *viz*., [Cu(FCED)Cl]Cl (**1**), [Cu(FCED)Br]Br (**2**), [Cu(FCED)($NO_3$)]($NO_3$) (**3**) and [Cu(FCED)]($ClO_4$)$_2$ (**4**) have been synthesized and characterized. Microanalytical data, molar conductance and magnetic susceptibility values have been obtained and IR, UV-Visible, EPR spectral studies, TG/DTA, and DFT studies have been carried out to suggest the tentative structures of the complexes. The ligand acts as a neutral tetradentate ONNO donor ligand and the bonding sites are Nitrogen atoms of azomethine groups and Oxygen atoms of carbonyl groups. A square pyramidal geometry is suggested for complexes **1**, **2** and **3** and a square planar geometry is suggested for **4**. The crystal data indicate that the complex **3** crystallizes in monoclinic P21/n space group with a distorted square pyramidal structure and the π-π stacking interactions results in polymeric chains in unit cell of the complex.

**Keywords**: Copper(II) complexes, Schiff base, Spectra, Magnetic susceptibility, Single crystal structures, π-π Stacking interactions, DFT studies

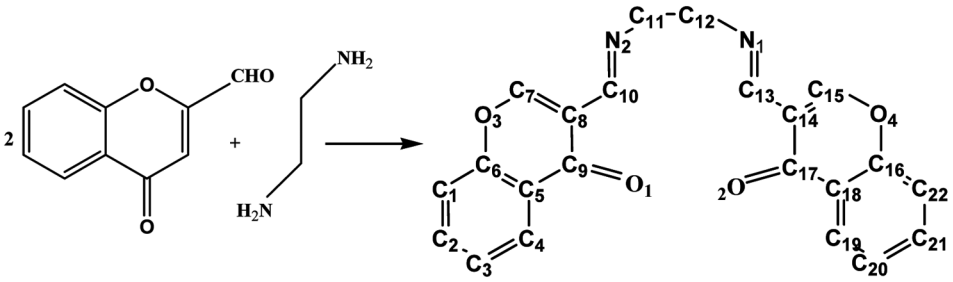
Schiff bases are well known as good ligands to coordinate metal ions. Schiff bases are very important materials for inorganic biochemists due to their diverse biological[1,2], pharmacological[3] and antitumor[4-6] activities and their excellent chelating ability. The most widely studied metal in this respect is copper(II)[7]. Tetradentate Schiff bases with four donor hetero-atoms have been extensively studied in literature due to their ability to stabilize many different metals in various oxidation states[8]. As a continuation of our contribution to the research on Schiff bases[9-11], we now report the complexes of copper(II) with ethylenediaminobi(chromone-3-carbaldehyde) (FCED).

## Experimental Section

### Materials and instrumentation

High purity 3- formylchromone, ethylenediamine (Aldrich,USA), copper(II) nitrate hexahydrate and copper(II) chloride hexahydrate (E. Merck, India) were purchased from respective concerns and used as such. Bromide and perchlorate of copper(II) were prepared by dissolving Analar Merck copper carbonate in the respective 50% acids and crystallizing the salts after concentrating the resulting solutions on a steam bath. All other chemicals and solvents were of AR grade.

The C, H and N contents in the complexes were determined on a Perkin-Elmer 240 CHN analyser. All the complexes were analyzed for their metal, halide and perchlorate contents by standard methods[12,13]. Molar conductivities were measured using freshly prepared $10^{-3}$ M solutions of dimethyl formamide, acetonitrile, nitrobenzene and methanol at room temperature using a Thoshniwal conductivity bridge with dip type conductance cell (cell constant 0.9741) which was calibrated with 0.01M KCl solution. The infrared spectra were recorded in the range 4000-100 $cm^{-1}$ on a Schimadzu IR 470 spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AV-400 spectrophotometer using acetone-$d_6$ as solvent. Solid state electronic spectra in the range 1100-200 nm were recorded using Schimadzu UV-VIS-2450 spectrometer. Magnetic susceptibility measurements were performed on pulverized samples at room temperature on a Sherwood Magway MSB MK1 balance. The diamagnetic corrections were calculated using Pascal's constants. The thermal studies were undertaken in a Perkin Elmer STA 6000 thermal analyser in nitrogen atmosphere in



Scheme 1 — Synthesis of ethylenediaminobi(chromone-3-carbaldehyde) (FCED)

temperature range 30-900°C with a heating rate 10°C $min^{-1}$. Single crystal X-ray data were collected using MoKα (k = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector.

Computational studies were performed using the Gaussian 09 software package, employing DFT/ B3LYP/6-311G(d,p) for geometry optimization and single-point energy calculations of the inhibitor. The molecular geometry for the studied compounds were fully optimized using the Gaussian 09 software package, employing Density functional theory B3LYP method, by implementing LANL2DZ basis set for the metal Cu and 6–311 + G(d,p) basis set for the ligand. No symmetry constrains were applied during the geometry optimization. Subsequently, the energies of the highest occupied molecular orbital ($E_{HOMO}$) and lowest unoccupied molecular orbital ($E_{LUMO}$), the energy gap (ΔE) between them, the dipole moment (μ), and global reactivity descriptors such as hardness (η), electronegativity (χ), and softness (S) were calculated based on Koopmans' theorem[14] and the corresponding equations.

$$Ionization\ potential\ (IP) = -E_{HOMO} \quad \text{... (1)}$$

$$Electron\ affinity\ (EA) = -E_{LUMO} \quad \text{... (2)}$$

$$Absolute\ Hardness\ (\eta) = \frac{IP-EA}{2} \quad \text{... (3)}$$

$$Absolute\ Electronegativity\ (\chi) = \frac{IP+EA}{2} \quad \text{... (4)}$$

$$Softness\ (S) = \frac{1}{2\eta} \quad \text{... (5)}$$

$$Chemical\ potential\ (\mu) = -\chi \quad \text{... (6)}$$

$$Electrophilicity\ index\ (\omega) = \frac{\mu^2}{2\eta} \quad \text{... (7)}$$

**Preparation of ethylenediaminobi(chromone-3-carbaldehyde) (FCED)**

An ice cold solution of 3-formylchromone (0.348 g, 2 mmol) in absolute ethanol (30 mL) was added dropwise to an ice cold solution of ethylenediamine (0.062 g, 1mmol) in absolute ethanol (10 mL). The mixture was stirred at this temperature for 24 h (Scheme 1). The white precipitate obtained was collected by filtration and washed several times with cold ethanol. It was then recrystallized from ethanol and dried. Yield 82%. m.p.188°C. Anal. Calcd for $C_{22}H_{16}N_2O_4$ (372): C, 70.96; H, 4.30; N, 7.52. Found: C, 70.93; H, 4.26; N, 7.46%. IR: 1643 (-C=O), 1587 $cm^{-1}$ (-CH=N-); $^1$H NMR: δ 8.162 (s,1H, -CH=N-), 7.01-7.93 (m, 2-Ph), 2.839 (s,4H, -$CH_2$-$CH_2$-); $^{13}$C NMR: δ 162.01 (C10, C13) UV-Vis ($\lambda_{Max/nm}$): 273 (π- π*), 372 (n- π*).

**Synthesis of metal complexes**

**[Cu(FCED)Cl]Cl (1)**: A solution of $CuCl_2.6H_2O$ in acetone (1mmol, 10 mL) was added to a hot solution of FCED in ethyl acetate (1mmol, 30 mL) and the mixture was refluxed for about 3 h. The precipitated bright green complex was filtered, washed repeatedly with ethyl acetate and dried under vacuum. Yield 0.423 g, 83.59%. Anal. Calcd for $C_{22}H_{16}N_2O_4Cl_2Cu$ (506.83): C, 52.13; H, 3.18; N, 5.52; Cl, 13.98; Cu, 12.53. Found: C, 52.06; H, 3.10; N, 5.45; Cl, 13.90; Cu, 12.48%. IR: 1615 [νC=O1, νC=O2], 1557 [ν-CH=N1, ν-CH=N2], 471 [νCu-N1, νCu-N2], 546 [νCu─O1, νCu─O2], 331 $cm^{-1}$ [Cu-Cl]; ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 62.3 (in DMF), 103 (in MeOH), 22.5 (Ph-$NO_2$); UV-Vis ($\lambda_{Max/nm}$): 333 (n - π*), 242 (π- π*), 593, 457 (d-d transitions), 396 (C-T transition); $\mu_{eff}$ = 1.80 BM.

**[Cu(FCED)Br]Br (2)**: A solution of $CuBr_2.4H_2O$ in acetonitrile (1 mmol, 10 mL) was added to a hot solution of FCED in ethyl acetate (1 mmol, 30 mL) and the mixture was refluxed for about 3 h. The

precipitated green complex was filtered, washed repeatedly with ethyl acetate and dried under vacuum. Yield 0.435 g, 73.05%. Anal. Calcd for $C_{22}H_{16}N_2O_4Br_2Cu$ (595.73): C, 44.35; H, 2.70; N, 4.70; Br, 26.82; Cu, 10.66. Found: C, 44.28; H, 2.61; N, 4.64; Br, 26.76; Cu, 10.57. IR: 1615 [νC=O1, νC=O2], 1557 [ν-CH=N1, ν-CH=N2], 477 [νCu─N1, νCu─N2], 549 [νCu─O1, νCu─O2], 328 $cm^{-1}$ [Cu-Br]; ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 104.9 (in DMF), 80 (in MeOH), 25 (Ph-$NO_2$); UV-Vis ($\lambda_{Max/nm}$): 240 (π- π*), 339 (n - π*), 440, 590 (d-d transitions), 398 (C-T transition); $\mu_{eff}$ = 1.82 BM.

**[Cu(FCED)($NO_3$)]($NO_3$) (3)**: A solution of $Cu(NO_3)_2.3H_2O$ in acetone (1 mmol, 10 mL) was added to a hot solution of FCED in ethyl acetate (1 mmol, 30 mL) and the mixture was refluxed for about 3 h. The precipitated blue complex was filtered, washed repeatedly with ethyl acetate and dried under vacuum. Yield 0.495 g, 88.50%. Anal. Calcd for $C_{22}H_{16}N_4O_{10}Cu$ (559.93): C, 47.19; H, 2.88; N, 10.00; Ni, 11.34. Found: C, 47.06; H, 2.75; N, 9.90; Ni, 11.27%. IR: 1614 [νC=O1, νC=O2], 1558 [νCH=N1, ν-CH=N2], 488 [νCu-N1, νCu-N2], 562 $cm^{-1}$ [νCu-O1, νCu-O2]; ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 67 (in DMF), 103 (in MeOH), 23 (Ph-$NO_2$); UV-Vis ($\lambda_{Max/nm}$): 243 (π-π*), 343(n - π*), 438, 592 (d-d transitions), 403 (C-T transition); $\mu_{eff}$ = 1.78 BM.

**[Cu(FCED)]($ClO_4$)$_2$ (4)**: A solution of $Cu(ClO_4)_2.6H_2O$ in acetone (1 mmol, 10 mL) was added to a hot solution of FCED in ethyl acetate (1 mmol, 30 mL) and the mixture was refluxed for about 3 h. The precipitated green complex was filtered washed repeatedly with ethyl acetate and dried under vacuum. Yield 0.506 g, 79.70%. Anal. Calcd for $C_{22}H_{16}N_2O_{12}Cl_2Cu$ (634.82): C, 41.62; H, 2.54; N, 4.41; $ClO_4$, 31.33; Cu, 10.01. Found: C, 41.56; H, 2.48; N, 4.35; $ClO_4$, 31.26; Cu, 9.94%. IR: 1614 [ν C=O1, ν C=O2], 1560 [ν -CH=N1, ν -CH=N2], 452 [ν Cu-N1, ν Cu-N2], 555 $cm^{-1}$ [ν Cu-O1, ν Cu-O2]; ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$): 225 (in acetonitrile), 172 (in MeOH), 58 (Ph-$NO_2$); UV-Vis ($\lambda_{Max/nm}$): 339 (n - π*), 240 (π- π*), 551 (d-d transition), 395 (C-T transition); $\mu_{eff}$ = 1.81 BM.

**Caution!** Perchlorate salts are potentially explosive and should be prepared in small quantities and handled with great care.

All the complexes were recrystallized from methanol-ethyl acetate mixture in the ratio 1:2 by slow diffusion of diethyl ether vapour from an adjacent container, but good quality crystals, suitable for X-ray crystallography, of only complex **3** was obtained.

### X-ray crystallographic study

The bright green block shaped crystals of [Cu(FCED)($NO_3$)]($NO_3$) (**3**) was directly picked up from the mother liquor attached to a glass fiber and transferred for data collection. X-ray single crystal data were collected using Mo Kα (k = 0.7107 Å) radiation on a BRUKER APEX II diffractometer equipped with CCD area detector. Unit cell refinement (Bruker, 2006)[15], data reduction (SAINT) and structure solution as well as refinement (SHELXL 97)[16] were carried out using software package of SMART APEX. All structures were solved by direct method and refinement in a routine manner. The molecular graphics were generated by using softwares Mercury 2.3 (Ref. 17), ORTEP 3 (Ref. 18) and Diamond 3 (Ref. 19). The details of X-ray crystal data and structure solution as well as refinement are given in Table 1.

## Results and Discussion

### General properties

The ligand and the complexes are stable at room temperature and are non-hygroscopic. The complexes are soluble in common organic solvents such as methanol, ethanol, dimethyl formamide and acetonitrile but insoluble in ethyl acetate, chloroform and acetone. The analytical data are in good agreement with theoretical values for proposed Cu(II) complexes as given in the experimental section.

The molar conductance data reveals that [Cu(FCED)Cl]Cl (**1**), [Cu(FCED)Br]Br (**2**) and [Cu(FCED)($NO_3$)]($NO_3$) (**3**) behave as 1:1 electrolytes whereas [Cu(FCED)]($ClO_4$)$_2$ (**4**) behave as 1:2 electrolyte.

### Infrared spectra

The free ligand FCED exhibits a strong ν(C=O) band at 1643$cm^{-1}$ (Ref. 20) and a ν(C=N) band at 1587 $cm^{-1}$ (Ref. 21) which provides a concrete evidence for the formation of Schiff base (FCED). However a relative decrease of ν(C=N) frequency to (1557-1560) $cm^{-1}$ supports the coordination of imine nitrogen atoms with metal ion in complexes[22]. In all the complexes shifting of ν(C=O) to lower frequencies (1614-1615) $cm^{-1}$ reveals the coordination of carbonyl oxygens[23]. Conclusive

Table 1 — Crystal data and structure refinement parameters of **3**

| Crystal parameters | **3** |
|---|---|
| CCDC No. | 1290 |
| Emperical formula | $C_{22}H_{16}CuN_4O_{10}$ |
| Formula weight | 559.936 |
| Crystal size (mm) | 0.30×0.20×0.20 |
| Crystal System | Monoclinic |
| Space group | P21/n |
| a(Å) | 11.930(5) |
| b(Å) | 8.987(5) |
| c(Å) | 21.076(5) |
| α(deg) | 90.000(5) |
| β(deg) | 104.172(5) |
| γ(deg) | 90.000(5) |
| Volume(Å)$^3$ | 2190.9(16) |
| Z | 4 |
| F(000) | 1140 |
| Temperature(K) | 293(2) |
| Rint | 0.0375 |
| Range of h,k,l | –14/14, –10/10, –25/25 |
| θ min/max(deg) | 2.23/25.00 |
| Reflections collected/unique /observed | 19408/3851 |
| Data/restraints /parameters | 3851/286/399 |
| Goodness of fit(GOF) in $F^2$ | 1.034 |
| Final R indices | $R_1 = 0.0363$, $wR_2 = 0.0910$ |
| R indices (all data) | $R_1 = 0.0517$ , $wR_2 = 0.1000$ |

evidence of bonding is also shown by the observation that the new bands appear in the complex at about 460 and 550 $cm^{-1}$ which are assigned to ν(Cu-O) and ν(Cu-N) stretching vibrations respectively[24]. Hence we can conclude that in all the complexes FCED acts as a tetradentate $N_2O_2$ donor chelating through two carbonyl oxygens and two imine nitrogens.

The nitrate complex exhibits vibrational frequencies of both coordinated and uncoordinated nitrate ions. A very strong band at 1397 $cm^{-1}$ and a medium band at 827 $cm^{-1}$ are attributed to $\nu_3$ and $\nu_2$ vibrations respectively of uncoordinated nitrate ion of $D_{3h}$ symmetry[25]. The presence of coordinated nitrate is indicated by two bands at 1499 and 1376 $cm^{-1}$due to $\nu_4$ and $\nu_1$ vibrations respectively of nitrate of $C_{2v}$ symmetry[26]. Since $\nu_4 - \nu_1 = 123$ $cm^{-1}$ the nitrate ion is coordinated in a monodentate fashion.

In the perchlorate complex the presence of very strong band at 1082 $cm^{-1}$ is attributed to $\nu_3$ vibration of uncoordinated perchlorate ion of $T_d$ symmetry[27].

The bands at 331 and 328 $cm^{-1}$ are due to the ν(Cu-Cl) and ν(Cu-Br) vibrations[28] respectively indicative of halogen coordination in complexes **1** and **2**.

## $^1$H and $^{13}$C NMR spectra

The $^1$H NMR spectrum of FCED exhibits a multiplet in the range 7.015-7.980 δ due to protons of phenyl ring. A four hydrogen singlet is observed at 2.839 δ due to $–CH_2 –CH_2$ protons. The azomethine proton appears as a singlet at δ 8.162 (Ref. 29).

The $^{13}$C NMR spectrum of FCED shows the presence of one keto, one azomethine, one ethyl, and nine aromatic signals for a total of 22 carbon atoms. The signals at 162.01 and 190.42 δ are attributed to azomethine and keto carbon atom respectively. The ten down field signals (111.21 -135.10) show the presence of aromatic carbon atoms. The signal at 29.83 δ is attributed to ethyl carbon atoms. The above results confirm the proposed structure of the ligand. Due to paramagnetic nature the $^1$H NMR and $^{13}$C NMR spectra of the complexes could not be studied.

## Electronic Spectra and Magnetism

The strong band at 273 nm due to π - π* transitions of FCED is blue shifted to 240-243 nm in all complexes. The band at 372 nm attributed to n - π* transition of FCED is also blue shifted to 333-343 nm in all the complexes. The reflectance spectra of the complexes **1, 2** and **3** shows two main bands in regions 438-457 nm and 590-593 nm due to the transitions $^2B_1 \rightarrow {}^2E_1$ and $^2B_1 \rightarrow {}^2A_1$ respectively corresponding to square pyramidal geometry[30]. The room temperature magnetic moments of complexes **1**, **2** and **3** are 1.80, 1.82 and 1.78 BM respectively which would be expected for square pyramidal geometry around copper(II) ion[31].

The complex **4** shows a band at 551 nm which is attributed to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition indicating a square planar geometry around copper(II) (Ref. 32,33). The magnetic moment is 1.81 BM which is also in good agreement with four coordinate copper(II) complexes with square planar geometry[34].

Furthermore the complexes show a strong band near 395 nm which can be assigned to charge transfer transition.

## ESR Spectra

The ESR spectrum of the complexes provides important information for studying the metal ion

environment. The ESR spectra of the complexes are given in Fig. 1. Trend $g_{\|} > g_{\perp} > 2.0023$, observed for complexes suggests $d_{x^2-y^2}$ ground state for Cu(II) ion[35]. For complexes **1**, **2** and **3** the greater the value of $g_{\|}$ compared to $g_{\perp}$ proposes a distorted square pyramidal structure and rules out the possibility of a trigonal bipyramidal structure which is expected to have $g_{\perp} > g_{\|}$. Also the observed $g_{\|}$ values of less than 2.3 for all complexes provide evidence for covalent character of bonding between Cu(II) ion and the ligand[36]. The fraction $\alpha^2$ for the present complexes lie in the range 0.67-0.91 supporting the covalent nature of the complexes. The EPR bonding parameters for the complexes is given in Table 2.

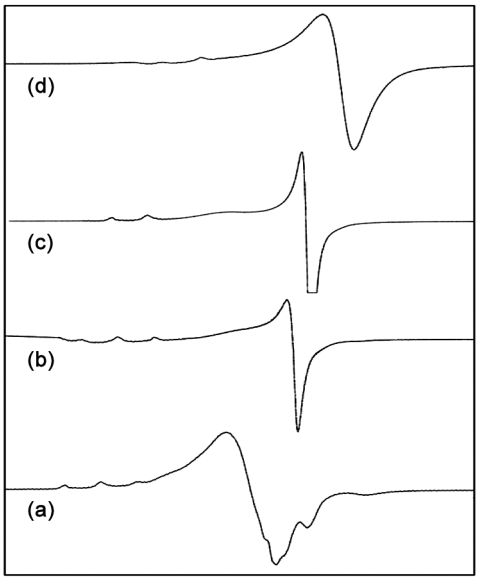



Fig. 1 — EPR spectra of A) **1** B) **2** C) **3** and D) **4** of copper (II) complexes

## Thermal analysis

The thermal decomposition behavior of all the complexes except **4** was studied. The TG and DTA data of the complexes are given in Table 3. Complexes **2** and **3** undergo decomposition in two stages while **1**undergoes three stage decomposition pattern with anhydrous CuO as final residue. There was a good agreement in mass loss between observed and calculated values. Complex **4** undergoes explosion when heated to high temperature and so its decomposition pattern cannot be studied.

## Crystal structure of $[Cu(FCED)(NO_3)]NO_3$ (3)

The crystals of **3** suitable for single crystal X-ray analysis were obtained by slow diffusion of diethyl ether vapour in to the methanol-ethyl acetate (2:1) solutions of the complex. The molecular structure of

Table 2 — EPR bonding parameters of copper(II) complexes

| Complex | $g_{\|}$ | $g_{\perp}$ | $A_{\|}$ | $A_{\perp}$ | $g_{iso}$ | $\alpha^2$ |
|---|---|---|---|---|---|---|
| [Cu(FCED)Cl]Cl (**1**) | 2.42 | 2.10 | 107.27 | 14.35 | 2.21 | 0.80 |
| [Cu(FCED)Br]Br (**2**) | 2.45 | 2.105 | 135.3 | 70.50 | 2.21 | 0.91 |
| $[Cu(FCED)(NO_3)](NO_3)$ (**3**) | 2.19 | 2.03 | 153.85 | 14.35 | 2.089 | 0.67 |
| $[Cu(FCED)](ClO_4)_2$ (**4**) | 2.28 | 2.06 | 107.66 | 43.56 | 2.13 | 0.64 |

Table 3 — Thermal data of Cu(II) complexes of FCED (**1-3**)

| Complex | Temp. range | DTA peak (°C) | Weight loss (%) Found(calculated) | Probable reaction | Composition of residue |
|---|---|---|---|---|---|
| [Cu(FCED)Cl]Cl (**1**) | 156-456 | 271.98 | 36.50(36.69) | Loss of half of FCED molecule | Anhydrous CuO |
| | 456-623 | 493.95 | 13.80(14.02) | Loss of two chloride ions | |
| | 623-849 | 806.80 | 36.45(36.69) | Loss of half of FCED molecule | |
| [Cu(FCED)Br]Br (**2**) | 170-323 | 220.00 | 26.50 (26.82) | Loss of two bromide ions | Anhydrous CuO |
| | 323-842 | 472.00 | 62.30 (62.44) | Loss of FCED molecule | |
| $[Cu(FCED)(NO_3)](NO_3)$ (**3**) | 195-291 | 270.93 | 33.30 (33.21) | Loss of half of FCED molecule | Anhydrous CuO |
| | 291-794 | 431.50 | 55.42 (55.36) | Decomposition of half of FCED molecule and two nitrate ions | |

Table 4 — Selected bond distances and angles of complex **3**

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| Cu ─ O(1) | 1.942(2) | N(2) ─ Cu ─ O(1) | 167.86(10) |
| Cu ─ O(2) | 1.946(2) | N(1) ─ Cu ─ O(2) | 172.82(10) |
| Cu ─ N(1) | 1.938(3) | N(2) ─ Cu ─ O(6) | 98.84(17) |
| Cu ─ N(2) | 1.954(3) | N(1) ─ Cu ─ O(6) | 102.36(12) |
| Cu ─ O(6) | 2.247(3) | O(1) ─ Cu ─ O(6) | 99.33(16) |
| C(10) ─ N(1) | 1.273(4) | O(2) ─ Cu ─ O(6) | 84.30(11) |
| C(13) ─ N(2) | 1.278(4) | N(1) ─ Cu ─ N(2) | 84.35(11) |
| | | O(1) ─ Cu ─ O(2) | 88.23(9) |

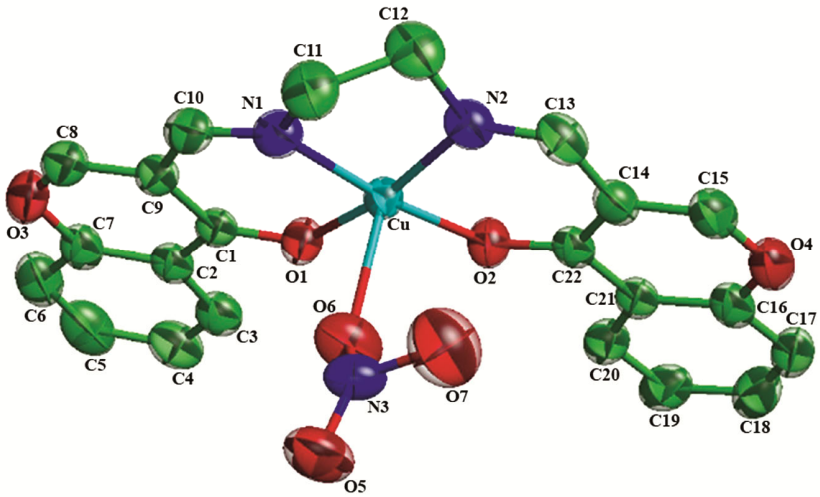



Fig. 2 — The ORTEP plot of **3** with atom labelling scheme. Atomic displacement parameters are shown at 50% probability level. Hydrogen atoms and ionic nitrate are omitted for clarity

the complex **3** with the atom labeling scheme are shown in Fig. 2. The crystallographic data are summarized in Table 1. Selected bond lengths and angles related to the metal coordination sphere for the structure are given in Table 4.

The complex **3** was crystallized in the monoclinic system with space group *P21/n*. Each copper atom is penta-coordinated with square pyramidal geometry. The copper(II) centre is coordinated by two carbonyl oxygen atoms (O1,O2) and two imine nitrogen atoms (N1,N2) of tetradentate chelating ligand FCED with trans angles ∠O1-Cu-N2 = 167.86 (10), O(2)-Cu-N(1) = 172.82(10) which are less than expected for perfect square pyramidal geometry[37], while the fifth position is occupied by monodentately coordinated nitrate ion (O6). Trigonal index defined as $\tau = (\beta - \alpha)/60$ (where β and α are largest angles in metal coordination sphere with $\beta > \alpha$) is only 0.083 indicating the existence of a distorted square pyramidal metal coordination sphere[38], taking in to account that this angular parameter has an ideal value 0 for square pyramidal geometry with $C_{2v}$ symmetry and 1 for trigonal bipyramidal geometry with $D_{3h}$ symmetry. Such type of distorted square pyramidal geometry was observed in similar type of Cu(II) complexes (τ=0.08-0.58). The C-N and C-O bond distances were comparable with similar Cu(II) complexes. The complex **3** is involved in weak π-π interactions with the carbon atoms present in the adjacent chromone ring *via* C(7)---C(17) interaction [C(7)---C(17) = 3.395 Å] resulting in the formation of a dimer[39] (Fig. 3). Each dimers extents to form 3D stacks through weak hydrogen bond interactions *via*

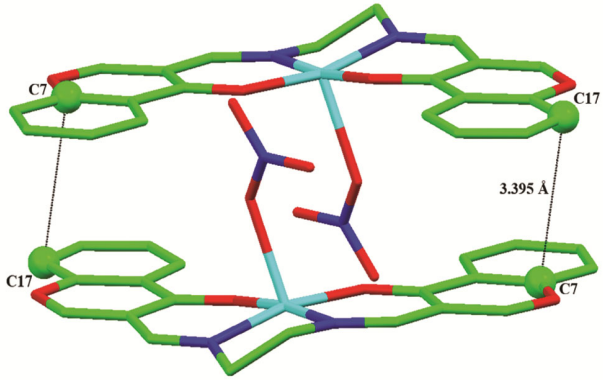



Fig. 3 — Dimer in complex **3** *via* weak π-π interactions

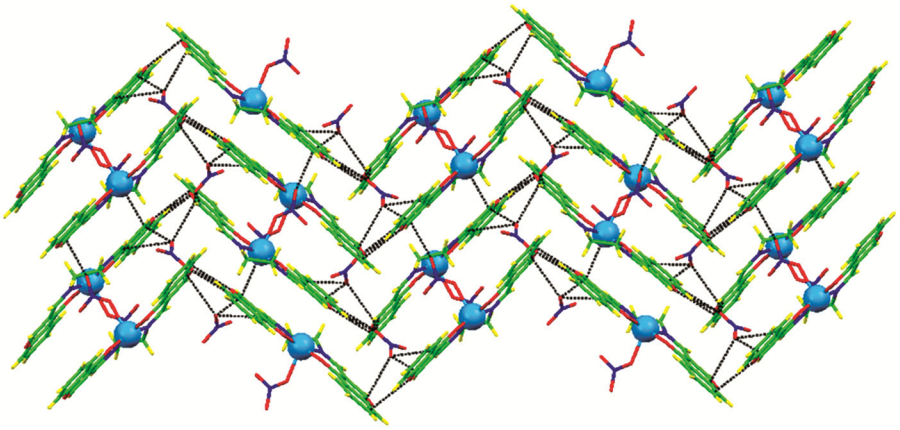


Fig. 4 — Each dimers in complex **3** extents to form 3D stacks which results in herringbone picking network

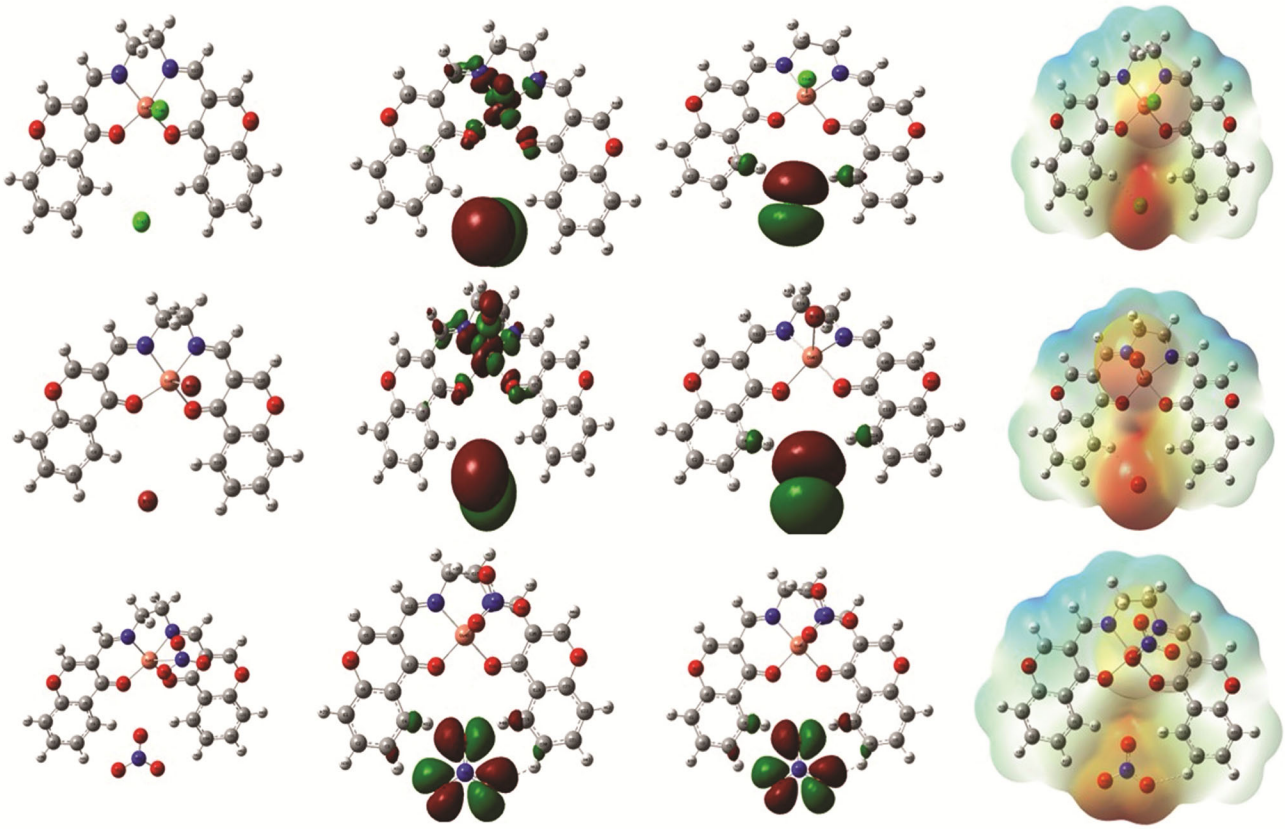


Fig. 5 — Optimised Geometry, HOMO, LUMO and MEP map of 1, 2, and 3

ionic as well as coordinated nitrates which results in herringbone picking network (Fig. 4).

**Frontier molecular orbitals (FMOs) analysis**

Optimized geometry, Frontier Molecular orbitals, Molecular electrostatic potential maps of the studied complexes are exhibited in Fig. 5. The dispersion of isodensities of HOMOs and LUMOs is almost similar in all complexes. In [Cu(FCED)Cl]Cl, [Cu(FCED) Br]Br , and [Cu(FCED)$NO_3$]$NO_3$ complexes, the metal ion chelates with the ligand FCED to form two six membered and one five membered ring with the sequences of A) O11,C7,C8,C12,N13, B) N16, C17, C26, C27, O28, and C) N13, C14, C15, N16. The values of the calculated quantum chemical parameters such as the energy of the highest occupied molecular orbital (EHOMO), energy of the lowest unoccupied molecular orbital (ELUMO), energy gap (ΔEgap), ionization potential (IP), electron affinity (EA), Absolute hardness (η), Absolute electronegativity (χ),

Table 5 — Quantum chemical parameters of Cu complexes

| Properties | [Cu(FCED)Cl]Cl | [Cu(FCED)Br]Br | [Cu(FCED)$NO_3$]$NO_3$ |
|---|---|---|---|
| $E_{HOMO}$ (eV) | –3.8390 | –3.8395 | –4.481 |
| $E_{LUMO}$ (eV) | –3.7908 | –3.7906 | –4.227 |
| ΔE (eV) | 0.0482 | 0.0489 | 0.2536 |
| IP (eV) | 3.8390 | 3.8395 | 4.481 |
| EA (eV) | 3.7908 | 3.7906 | 4.227 |
| χ (eV) | 3.8149 | 3.8150 | 4.354 |
| η (eV) | 0.0241 | 0.0244 | 0.1268 |
| S ($eV^{-1}$) | 20.75 | 20.49 | 3.9432 |
| μ | –3.8149 | –3.8150 | –4.3544 |
| ω | 301.9 | 298.24 | 74.76 |

softness (S), Chemical potential (μ), and Electrophilicity index (ω) are presented in Table 5. The value of the $E_{HOMO}$ determines the molecule's ability to donate electrons. A higher $E_{HOMO}$ value indicates a greater ease of donating electrons to the unoccupied orbitals of a receptor molecule. Conversely, a lower $E_{LUMO}$ value suggests a lower resistance to accepting electrons, making the molecule more capable of electron acceptance. The energy gap between HOMO and LUMO gives an idea about the reactivity of the complex. The complex [Cu(FCED)$NO_3$]$NO_3$ posess highest energy gap (ΔE = 0.2536eV) which shows its less reactivity and higher stability. Global descriptive parameters are calculated using ionization potential (IP) and electron affinity (EA). These descriptors are essential for explaining the reactivity and stability of the studied Cu complexes. [Cu(FCED)Cl]Cl has the lowest value of chemical hardness (0.0241 eV) and are less stable and more reactive. The order of hardness is [Cu(FCED)$NO_3$]$NO_3$ > [Cu(FCED)Br]Br > [Cu (FCED)Cl]Cl.The highest value of chemical potential obtained for [Cu(FCED)Cl]Cl indicates its ability to charge transfer in its ground state. [Cu(FCED) ($NO_3$)]$NO_3$ possesses the highest electronegativity value, indicating its superior ability to accept electrons[40-44].

Molecular electrostatic potential maps (MEP) were used as a visual tool to understand the electron density at different regions and to determine the more reactive centres in the studied Cu complexes. In MEP map the red color indicates the most negative electrostatic potential region and blue color for the most positive electrostatic potential region and the region of the zero electrostatic potential indicated by green color

## Conclusion

In this paper, we have explored the synthesis and coordination chemistry of a series of Copper(II) complexes of the Schiff base derived from 3-formylchromone and ethylenediamine. The complexes are characterized by elemental analysis, molar conductance studies, CHNS analysis, spectroscopic techniques, magnetic susceptibility measurements and thermal analysis data. Single crystal X-ray characterization of complex **3** has also been discussed. The ligand to metal ratio in all the complexes is found to be 1:1. The complexes **1**, **2**, and **3** have square pyramidal geometry with one of the anions as counter ion and **4** have square pyramidal geometry with both the anions as counter ions. In complexes Schiff base acts as a tetradentate ligand with ONNO donor sites forming chelate rings. The X-ray crystal analysis of **3** shows that the copper(II) ion is in a distorted square pyramidal environment with the metal atom ligated by $N_2O_2$ from the ligand at the equatorial positions and the fifth, apical donor is one oxygen atom from nitrate ion. The individual complex molecules are stacked together to form one dimensional infinite zig-zag molecular chains by intermolecular π-π stacking interactions between pairs of chromone rings. The FMO analysis showed the energies of HOMO and LUMO orbitals and these energies were used to find out the global descriptive parameters of the synthesised Copper(II) complexes.

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## Supplementary Information

CCDC 1290 contain the supplementary crystallographic data for complex **3**. The data can be

obtained free of charge from Cambridge Crystallographic Data centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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