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Formation of a water mediated assembly of two neutral copper(II) Schiff base fragments with $Cu_2(NCS)_4$ moiety: Exploration of noncovalent C-H···π(bimetallo ring) interactions

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Abstract: A water molecule is encapsulated in a dimeric assembly of a copper(II) Schiff base complex with a Cu₂(NCS)₄ moiety. The structure has been confirmed by single crystal X-ray diffraction analysis. Thermo-gravimetric analysis has been performed to check the stability of the enclathrated water molecule. The theoretical study is devoted to analyze the stabilization of the H₂O in the cavity generated by the formation of the supramolecular dimer of the copper(II) Schiff base moiety in the solid state. Cu₂(NCS)₄ moiety exists as a bimetallic eightmembered ring, which behaves as a π -system establishing C-H… π interactions with two neighbouring copper(II) Schiff base moieties. The molecular electrostatic energy (MEP) surface of the complex has been computed to rationalize the interaction from an electrostatic point of view.

Keywords: Copper(II); Multimetallic; Schiff base; Enclathrated water; C-H···π interactions; DFT studies.

Introduction

Mononuclear transition metal complexes with various salen type Schiff bases were prepared by our group and many other groups since long.¹ Many of such complexes were found application in biological modelling experiment e.g. to mimic catechol oxidase, phenoxazinone synthase, catalase etc.² DNA binding and DNA cleavage activities of such complexes were also explored.³ Non-covalent interactions (e.g. C-H··· π , π ··· π , cation··· π , anion··· π etc.) in many such complexes were investigated using various theoretical calculations.⁴ These mononuclear complexes were used as ligand (i.e. metalloligand) by various groups to form many homo and hetero polynuclear complexes.⁵ Presence of inner N₂O₂ and outer O₄ cavities, capable of accommodating different metal ions, made N₂O₄ donor salen type compartmental Schiff bases more attractive for preparing polynuclear complexes in recent past.⁶ Several mixed valence complexes were also prepared with these salen type compartmental ligands.⁷ Mononuclear transition metal complexes with various potential N₂O₄ donor salen type compartmental Schiff bases could also be assembled by ammonium ion or water molecule, placed in the O₄ cavity of the ligand.⁸ However, this area has not been explored in detail till date.

In the present work, a potential N₂O₄ donor compartmental Schiff base [N,N'-bis(3ethoxysalicylidene)propane-1,3-diamine] has been used to prepare a copper(II) complex using Published on 15 February 2018. Downloaded by University of Windsor on 18/02/2018 21:00:01

copper(II) acetate monohydrate. The Schiff base ligand encompasses a copper(II) ion in its N_2O_2 donor inner compartment, and two of these "ligand complexes"⁹ provide an octadentate crown ether type coordination set (through the outer O_4 compartments) to encapsulate a water molecule. The complex crystallizes with a discrete $Cu_2(NCS)_4$ moiety.

The energetic features of H₂O encapsulation via dimer formation have been studied by means of DFT calculations and the Bader's theory of atoms-in-molecules. Theoretical calculations are important in terms of finding many unconventional and rare interactions which can be very important in stabilizing the complex. The energy of C-H… π interaction between the hydrogen atoms of the ligand and the π -system of the bimetallic eight-membered planar ring of the Cu₂(NCS)₄ moiety has also been investigated. To our knowledge, this is the first study dealing with this unconventional C-H… π interaction that involves the π -system of a ring formed by two $\mu_{1,3}$ -pseudohalide ligands and two copper(II) centers.

Results and Discussion

Synthesis

1,3-diaminopropane was refluxed with 3-ethoxysalicylaldehyde in 1:2 ratio to form a potential N₂O₄ donor Schiff base ligand, H₂L, following the literature method.¹⁰ This Schiff base, (H₂L) on reaction with copper(II) acetate monohydrate and nickel(II) thiocyanate tetrahydrate, respectively formed the complex, [(CuL)₂ \subset (H₂O)][Cu₂($\mu_{1,3}$ -NCS)₂(NCS)₂], in which copper(II) is placed in the inner N₂O₂ compartment of the ligand and a water molecule is trapped in the O₄ compartments of two adjacent CuL moieties. Formation of the complex is shown in Scheme 1. On the other hand, use of copper(II) acetate monohydrate and sodium thiocyanate produced a

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trinuclear Cu/Na/Cu cationic unit and copper(I) thiocyanate anionic counterpart, the structure of which was reported by a different group.¹¹



Scheme 1: Preparation of the ligand and the complex.

The ligand has been used by various groups to prepare varieties of di, tri and tetranuclear complexes of the types $[(TrL)M]^{+x}$, $[(TrL)M(LTr)]^{+y}$ or $[(TrL)_2M_2)]^{+z}$ {Tr= any transition metal M = any metal} (Table 1).^{11,12} However, in no case, water molecule or any other non-metallic cation is trapped in the outer O₄ cavity of the ligand. Scheme 2 gathers all such X-ray characterized complexes.^{11,12} On the other hand, the present complex also possesses a dinuclear cyclic Cu₂(NCs)₄ unit in it. Formation of bimetallic eight-membered ring (Cu-N-C-S-Cu-N-C-S-) of Cu₂(NCs)₄, therefore, deserves special attention from both synthetic inorganic chemists and theoretical chemists as well and lead us to estimate the energy of C-H… π interaction between the hydrogen atoms of the ligand and the π -system of this bimetallic eight-membered planar ring.

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| Table 1: X-ray characterized di, tri and tetranuclear complexes of the types [(TrL)M] ^{+x} , |
|---|
| $[(TrL)M(LTr)]^{+y}$ or $[(TrL)_2M_2)]^{+z}$ {Tr= any transition metal, M= any metal} retrieved from |
| Cambridge Structural Database (CSD), version 5.38 updates (November 2016). $H_2L = [N,N'-bis(3-D)]$ |
| ethoxysalicylidene)propane-1,3-diamine]. |

| Complex | CCDC code | Ref |
|---|-----------|-----|
| [(SCN)ClCd(L)Ni(DMF) ₂] | LAVWEN | 12a |
| $[(SCN)(CH_3CO_2)Cd(L)Ni(CH_3OH)_2]$ | LAVWIR | 12a |
| [(CH ₃ CN)Cu(L)(UO ₂)(NO ₃) ₂] | YILHEI | 12b |
| $[Zn_2L(NCS)(OOCCH_3)(CH_3OH)_2]$ | VIRJAJ | 12c |
| [CuLZnCl ₂] | EXASIG | 12d |
| [CuLZnBr ₂] | EXATON | 12d |
| $[Na(CuL)_2][Cu_2(\mu_{1,3}-NCS)_3]_n$ | KEYWOC | 11 |
| $[(CH_3CO_2)_2Ni_2(L)_2Cd_2(NCS)_2]$ | ESOSAI | 4 |
| $[(DMSO)_2Ni(L)Cd(NCS)(_{\mu1,3}-SCN)Ni(DMSO)(L)Cd(NCS)_2]$ | ESOSEM | 4 |
| $[{(CH_3)_2CO}Cu(L)Gd(NO_3)_3]$ | FAKLOT | 12e |

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Scheme 2: X-ray characterized di, trinuclear and tetranuclear complexes with ligand H₂L, where,

H₂L = [N,N'-bis(3-ethoxysalicylidene)propane-1,3-diamine].

Structure description

Single crystal X-ray diffraction analysis reveals that the complex crystallizes in triclinic space group P1. The molecular formula of the complex is $[(CuL)_2 \subset (H_2O)][Cu_2(\mu_{1,3}-NCS)_2(NCS)_2]$. It is to be noted here that an investigation has been done whether the crystallography could be used to determine whether the three metal atoms could be identified as copper or nickel. We Published on 15 February 2018. Downloaded by University of Windsor on 18/02/2018 21:00:01.

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refined the structure with four combinations and obtained the following wR2 values (all data); Cu1, Cu2, Cu3: 0.0998; Cu1, Cu2, Ni3: 0.1032; Ni1, Ni2, Cu3: 0.1008 and Ni1, Ni2, Ni3: 0.0985. The R1 values with I > 2*sigma(I) are 0.0551, 0.0564, 0.0557, 0.0551 respectively. Clearly the metal assignation from these values is problematic though it seems likely that the metal atoms are either all copper or all nickel. However, tricoordinated nickel(II) is very much unusual, especially with non-bulkier ligand, and therefore, all metal centres are identified as copper(II).

The moiety $[(CuL)_2 \subset (H_2O)]$ consists of two neutral [CuL] parts which are strongly hydrogen bonded with a water molecule encapsulated between the two. The hydrogen atoms of the enclathrated water molecule are disordered and three sets of positions were used to refine both hydrogen atoms with occupancies of 0.33(1) for each site. A perspective view of the complex is shown in Figure 1. Important bond lengths and bond angles are listed in Table 2 and Table 3 respectively.

| Table 2: Selected bond lengths (| (Å) | of the complex. |
|----------------------------------|-----|-----------------|
|----------------------------------|-----|-----------------|

| Cu(3)-S(2) | 2.417(2) | Cu(2)-N(23) | 1.970(2) |
|-------------------------|----------|-------------|----------|
| Cu(3)-N(1) | 1.871(3) | Cu(1)-N(53) | 1.986(3) |
| Cu(3)-N(2) ^a | 1.891(3) | Cu(1)-O(41) | 1.914(2) |
| Cu(2)-O(11) | 1.913(2) | Cu(1)-N(49) | 1.968(2) |
| Cu(2)-O(31) | 1.916(2) | Cu(1)-O(61) | 1.928(2) |
| Cu(2)-N(19) | 1.974(2) | - | - |

Symmetry transformations: ^a = -x, -y, 2-z.

Table 3: Selected bond angles (°) of the complex.

| S(2)-Cu(3)-N(1) | 112.06(9) | O(31)-Cu(2)-N(23) | 90.55(9) |
|------------------------------|------------|-------------------|-----------|
| S(2)-Cu(3)-N(2) ^a | 104.14(9) | O(41)-Cu(1)-O(61) | 81.43(8) |
| N(1)-Cu(3)-N(2) ^a | 143.78(12) | O(41)-Cu(1)-N(49) | 91.31(10) |

| O(11)-Cu(2)-O(31) | 81.58(8) | O(41)-Cu(1)-N(53) | 170.30(10) |
|-------------------|-----------|-------------------|------------|
| O(11)-Cu(2)-N(19) | 92.24(9) | O(61)-Cu(1)-N(49) | 169.60(10) |
| O(11)-Cu(2)-N(23) | 169.62(9) | N(49)-Cu(1)-N(53) | 96.64(10) |
| N(19)-Cu(2)-N(23) | 96.41(10) | O(61)-Cu(1)-N(53) | 91.36(9) |
| O(31)-Cu(2)-N(19) | 170.37(9) | - | - |
| | | | |

Symmetry transformations: ^a = -x, -y, 2-z.

 H_2L is a potential N_2O_4 donor compartmental Schiff base having inner N_2O_2 and outer O_4 compartments with copper(II) occupying the inner N_2O_2 cavity. The outer O_4 compartment remains vacant. Different small molecules (acting as guests) may be encapsulated (with the help of hydrogen bonding interaction) in this vacant O_4 compartment (acting as host). Thus interesting host-guest complexes may be formed.¹³ In the present case, the outer O₄ cavities of two CuL moieties behave as host site to encapsulate water molecule (guest) leading to the formation of a host-guest complex, [(CuL)₂ \subset (H₂O)]. In this unit, both copper(II) centers assume square planar geometry. They [Cu(1) and Cu(2)] are coordinated with two imine nitrogen atoms [N(49), N(53) for Cu(1) and N(19), N(23) for Cu(2)] and two phenoxo oxygen atoms [O(41), N(53)]O(61) for Cu(1) and O(31),O(11) for Cu(2) of the deprotonated Schiff bases. The copper(II) centers are located almost exactly on the mean basal plane of the ligand cavity (deviation of only 0.008Å for Cu(1) and 0.007Å for Cu(2)]. The trans angles O(61)-Cu(1)-N(49) and O(41)-Cu(1)-N(53) are 169.6(1)° and 170.3(1)° respectively for Cu(1). For Cu(2), the trans angles O(11)-Cu(2)-N(23) and O(31)-Cu(2)-N(19) are 169.6(1)° and 170.3(1)° respectively. These values indicate slight distortion from perfect square planar geometry around copper(II) centers. Saturated six membered chelate ring [Cu(1)–N(49)–C(50)–C(51)–C(52)–N(53)] has envelope conformation with puckering parameters q = 0.567(4) Å; $\theta = 56.4(3)^{\circ}$; $\phi = 166.6(4)^{\circ}$.¹⁴ Another

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saturated six membered chelate ring [Cu(2)-N(19)-C(20)-C(21)-C(22)-N(23)] has half-chair conformation with puckering parameters q = 0.614(3) Å; $\theta = 116.3(3)^\circ$; $\phi = 30.5(3)^\circ$.¹⁴

The moiety, $[Cu_2(\mu_{1,3}-NCS)_2(NCS)_2]$, contains an eight-membered metallacyclic loop, $[Cu(3)-S(2)-C(2)-N(2)-Cu(3)^a-S(2)^a-C(2)^a-N(2)^a]$ {symmetry transformation; a = -x, -y, 2-z}. The copper(II) centers [Cu(3) and $Cu(3)^a]$ assume trigonal planar geometry being coordinated by one nitrogen and one sulphur atom, [N(1) and S(2) for Cu(3) and $N(1)^a$ and $S(2)^a$ for $Cu(3)^a]$ of two thiocyanate anions and one nitrogen atom $[N(2)^a$ for Cu(3) and N(2) for $Cu(3)^a]$ of a symmetry related thiocyanate anion. The distance between two copper(II) centers is 5.127(7) Å.



Figure 1: Perspective view of the complex with selective atom numbering scheme. Hydrogen atoms (except the water hydrogens) have also been omitted for clarity. Only one fraction of each disordered hydrogen atom of the enclathrated H₂O is shown for clarity. Symmetry

transformations: ^a = -x, -y, 2-z.

Theoretical Study

The theoretical study is devoted to analyze the stabilization of the H₂O molecule in the cavity generated by the formation of the supramolecular dimer of the CuL complex in the solid state. The molecular electrostatic energy (MEP) surface of the complex has been computed first to rationalize the interaction from an electrostatic point of view (Figure 2). As expected the surface shows a red colored isocontour at the region of the four coplanar oxygen atoms of the ligand, indicating the MEP value is large and negative (–80 kcal/mol). Since the MEP values are plotted onto the van der Waals surface, the plot also reveals that the size of the cavity is too small to accommodate the H₂O molecule. The most positive region are located at the axial positions of the square planar copper(II) atom (+33 kcal/mol).





As aforementioned, the complex forms a supramolecular dimer that is able to encapsulate H_2O . The interaction energy of this assembly has been computed considering first

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the formation of the dimer and then the interaction of the water (Figure 3) in order to evaluate the different contributions separately. The dimerization energy is -8.5 kcal/mol and both CuL moieties interact by means of π ··· π interactions involving both the aromatic and chelate rings, along with other long range van der Waals interactions. The interaction of the water with the dimer is weak (-0.9 kcal/mol) due to the compensating effect of (i) the energetically favourable hydrogen bonds and the (ii) electrostatic repulsion between the lone pairs at the oxygen atom and the negative surfaces of the CuL moieties. It should be mentioned that in the crystal structure, the water molecule is disordered because the hydrogen atoms of H₂O may establish hydrogen bonds with any of the eight oxygen atoms of the cavity. For the calculations, only one of both orientations has been considered as shown in Figure 3c.



Figure 3: (a) Dimerization of the CuL complex. (b) Detail of the stacking interaction between two CuL moieties (c) Interaction energy of H_2O with the CuL dimer. The water molecule has been represented in space-filled model. Distance in Å.

The AIM analysis, has been used to study the complexion of the H₂O with the dimer. The distribution of bond critical points (CP) and bond paths are represented in Figure 4, where the ring and cage CPs have been omitted for the sake of clarity. The existence of a bond CP and bond path connecting two atoms is an unambiguous evidence of interaction. The AIM

distribution shows that four bond CPs connect both hydrogen atoms of water to four oxygen atoms of the ligand, thus characterizing the bifurcated hydrogen bonds. Moreover, several atoms of the aromatic ring of one CuL complex are inter-connected to the copper(II)-chelate ring of another complex and vice-versa via five bond CPs, thus confirming the existence and participation of this unconventional π ··· π (chelate ring) in the formation of the supramolecular dimer.



Figure 4: AIM distribution of bond CPs (red spheres) and bond paths in the assembly of the complex. Some bond CPs and bond paths involving the ethyl arms have been omitted for clarity. The full distribution is shown in the ESI (Figure S1).

The role of the $[Cu_2(NCS)_4]$ moiety in the solid state of the complex has also been analyzed. Interestingly, it establishes C-H··· π interactions with two neighbouring CuL moieties (Figure 5a) where the π -system is a bimetallic eight-membered $[Cu(3)-S(2)-C(2)-N(2)-Cu(3)^{a}-S(2)^{a}-C(2)^{a}-N(2)^{a}]$ (symmetry transformation; $^{a} = -x$, -y, 2-z} ring. Remarkably, two hydrogen atoms of each organic ligand point to the middle of the ring leading to the formation of

supramolecular trimers. To our knowledge, this is the first report describing this type interaction involving two metal centers and two $\mu_{1,3}$ -bridging pseudohalide ligands. The interaction energy for the 1:1 complex is -3.5 kcal/mol (Figure 5b), which is remarkable for this type of bonding. Moreover, the C-H… π distances are very short (2.43 and 2.99 Å, measured from the hydrogen atoms to the mean plane). Finally, the AIM analysis of CPs and bond paths in this C-H… π supramolecular complex has also been computed. It reveals that four hydrogen atoms participate in the interaction that are connected to the sulfur and copper atoms of the bimetallic ring and confirming the existence of the C-H… π (bimetallo ring) noncovalent bonding. The interaction is further characterized by the presence of one ring CP (yellow sphere) as a consequence of the formation of a supramolecular ring.



Figure 5: (a) X-ray fragment of the complex. Distances in Å. (b) AIM distribution of bond and ring CPs (red and yellow spheres, respectively) and bond paths in the model of the complex. The interaction energy is also indicated.

Spectral and magnetic properties

A sharp band around 1610 cm⁻¹ due to azomethine (C=N) group is routinely noticed in the IR spectrum of the complex.¹⁵ Two strong bands at 2083 cm⁻¹ and 2112 cm⁻¹ in IR spectrum of the complex indicate the presence of end-to-end bridged thiocyanate.¹⁶ Band around 2929 cm⁻¹ in the IR spectrum of the complex is observed due to alkyl C-H bond stretching.¹⁷ A broad band around 3432 cm⁻¹ in the IR spectrum of the complex is observed due to O-H bond stretching of water molecule.¹⁸

Electronic spectrum of the complex consists of four bands around 235 nm, 281 nm, 372 nm and 606 nm respectively. In general, square planar copper(II) complex is expected to exhibit three bands corresponding to ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}$, ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$ transitions.¹⁹ But in many cases, the long tail of strong inter-ligand charge transfer transitions hides some or all of these bands. Broad absorption band around ~600 nm may be assigned to two superimposed transitions ${}^{2}B_{2g} \leftarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$ and ${}^{2}E_{g} \leftarrow {}^{2}B_{1g}$.¹⁹ The broad absorption ~372 nm may be assigned as ligand to metal charge transfer transitions.²⁰ Bands ~281 nm and ~235 nm may be assigned as ligand centered $\pi^{*} \leftarrow n$ and $\pi^{*} \leftarrow \pi$ transitions respectively.²¹ Lack of any electronic transition at longer wavelengths (over 650 nm) indicates a large crystal-field splitting as expected for Schiff base complexes.²²

X-ray diffraction of powdered sample

The experimental PXRD pattern of the bulk product is in good agreement with the simulated XRD pattern from single crystal X-ray diffraction results, indicating consistency of the bulk sample. The simulated pattern of the complex is calculated from the single crystal

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structural data (cif) using the CCDC Mercury software. The experimental and simulated PXRD patterns of the complex are shown in Figure 6.



Figure 6: Experimental and simulated PXRD patterns of the complex confirming purity of the bulk material.

Thermo-gravimetric analysis

The thermal behaviour of the complex has been studied in a dynamic nitrogen atmosphere (100 mL min⁻¹) at a heating rate of 10°C min⁻¹ using thermo-gravimetric (TG) technique. The thermo-gravimetric plot for the complex is given in Figure 7. The complex is stable up to ~60 °C. A weight loss of 1.73% for the complex in the temperature range of 70-100°C corresponds to loss of the enclathrated water molecule (calc. 1.82%). An exothermic

peak is also observed in the corresponding DTA curve for the complex, as expected. The dehydrated complex then decomposes ~250°C as indicated by huge weight loss in the TG curve.



Figure 7: Thermal analysis of the complex. Inset shows the highlighted blue rectangle.

Hirshfeld surface analysis

Hirshfeld surfaces of the complex, mapped over d_{norm} (range of -0.1 to 1.5 Å), shape index and curvedness, are illustrated in Figure 8. Red spots on the d_{norm} surface (Figure 8) indicate the interaction between sulphur and hydrogen atoms. O…H and N…H contacts are also observed in the Hirshfeld surfaces as smaller visible spots of light colour indicating weaker and longer contact. The intermolecular interactions appear as distinct spikes in the 2D fingerprint plot are shown in Figure 9.



Figure 8: Hirshfeld surfaces mapped with dnorm (left), shape index (middle) and curvedness



(right) of the complex.

Figure 9: Fingerprint plot: Full (top left), resolved into H…S/S…H (top right), H…O/O…H (bottom

left) and H…N/N…H (bottom right) contacts contributed to the total Hirshfeld Surface area of

the complex.

Concluding Remarks

Synthesis and characterization of a multi-metallic complex, $[(CuL)_2 \subset (H_2O)][Cu_2(\mu_{1,3} - NCS)_2(NCS)_2]$, has been described in this paper. This complex is unique in the sense that two molecules of a simple Cu-salen type monomeric complex (CuL) are utilized in this complex to trap a water molecule by strong H-bonding interactions. The energetic features of the dimer formation and water molecule encapsulation have been studied by means of DFT calculations. Bader's theory of atoms-in-molecules has been used to characterise the interactions. On the other hand, the π -system of the bimetallic eight-membered planar ring (Cu-N-C-S-Cu-N-C-S-Cu) of the moiety $[Cu_2(\mu_{1,3}-NCS)_2(NCS)_2]$ is also linked with the hydrogen atoms of CuL moieties by unconventional C-H… π interaction. The energetic features of this interesting C-H… π interaction has also been analysed with the help of DFT calculation. Remembering the various roles of water in chemical and biological systems, the present findings may serve as a prototype for synthesizing and stabilizing enclathrated water molecules in many other complexes.

Experimental Section

Nickel(II) thiocyanate tetrahydrate was prepared in our laboratory following the literature method.²³ All other materials were commercially available, reagent grade and used as purchased from Sigma-Aldrich without further purification.

Synthesis

Synthesis of the complex $[(CuL)_2 \subset (H_2O)][Cu_2(\mu_{1,3}-NCS)_2(NCS)_2]$

A potential N_2O_4 donor ligand, H_2L , was prepared by refluxing 3-ethoxysalicylaldehyde (332 mg, 2 mmol) and 1,3-diaminopropane (0.13 mL, 1 mmol) in methanol for ca. 1 h. The ligand was not isolated and used directly for the synthesis of the complex. A methanol (10 mL) solution of copper(II) acetate monohydrate (200 mg, 1.01 mmol) was added to the methanol solution (20 mL) of H₂L. The resulting solution was stirred for 15 min. A methanol (20 mL) solution of nickel(II) thiocyanate tetrahydrate (500 mg, 2.02 mmol) was added to the methanol solution (20 mL) of H₂L. The resulting solution was stirred for 2 hr. Single crystals, suitable for X-ray diffraction, were obtained after 3-4 days on slow evaporation of the solution in open atmosphere.

Yield: 274 mg (52%); based on copper(II). Anal. Calc. for $C_{44}H_{50}N_6Cu_3O_9S_2$ (FW = 1061.67): C, 44.51; H, 4.06; N, 9.03; Found: C, 44.7; H, 3.8; N, 9.2%. FT-IR (KBr, cm⁻¹): 1610 (C=N); 2083, 2112 (NCS); 3432 (O-H); 2929 (C-H). UV-VIS $[\lambda_{max}(nm)]$ $[\epsilon_{max}(Lmol^{-1}cm^{-1})]$ (acetonitrile): 235 (2.4×10⁵); 281 (6.7×10⁴); 372 (19.9×10³); 606 (5.9×10²). ESI-MS (positive ion mode, acetonitrile) m/z: 454.09 $[Cu(L)Na]^+$, 886.19 $[{Cu(L)}_2Na]^+$.

Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. IR spectrum in KBr (4500-500 cm⁻¹) was recorded with a Perkin Elmer Spectrum Two spectrophotometer. Electronic spectrum in acetonitrile was recorded on a Perkin Elmer Lambda 35 UV-visible spectrophotometer. Steady state photoluminescence spectrum in acetonitrile was obtained in Shimadzu RF-5301PC spectrofluorometer at room temperature. Time dependent photoluminescence spectrum was recorded using Hamamatsu MCP photomultiplier (R3809) and was analyzed by using IBHDAS6 software. The emission in the complex was tentatively attributed to intra-ligand transitions modified by metal coordination. Intensity decay profile was fitted to the sum of exponential series $I(t) = \sum_{i} \alpha_i \exp(\frac{-t}{\tau_i})$, where

 α_i was a factor representing the fractional contribution to the time resolved decay of the component with a lifetime of τ_i . A bi-exponential function was used to fit the decay profile of the complex, with obtaining χ^2 close to 1. The intensity-averaged lifetime (τ_{av}) was determined

from the result of the exponential model using $\tau_{av} = \frac{\sum_{i} \alpha_i \tau_i^2}{\sum_{i} \alpha_i \tau_i}$, where α_i and τ_i are the pre-

exponential factors and excited state luminescence decay time associated with the *i*-th component, respectively. The instrument was calibrated using metallic nickel. Powder X-ray diffraction measurement was obtained on a Bruker D8 instrument with Cu K_{α}, (λ =1.5406 Å) radiation. In this process, the complex was ground with a mortar and pestle to fine powders which were then dispersed with alcohol onto a zero background holder (ZBH). The alcohol was allowed to evaporate to provide an even coating of powder adhered to the sample holder. Mass spectrum was recorded in acetonitrile on an XEVO G2QTof spectrometer (Waters) with an electron spray ionization source. The TGA/DTA curves of the complex was recorded using a SDT Q600 TA instruments, with nitrogen as purge gas at a flow rate of 100 ml min⁻¹. The complex was heated from 20 to 500 °C at a rate of 10 °C min⁻¹.

X-ray crystallography

Suitable single crystal of the complex was picked, mounted on a glass fibre and diffraction intensities were measured with an Oxford Diffraction XCalibur diffractometer equipped with Mo K_{α} radiation (λ =0.71073 Å, 50 kV, 40 mA) at an ambient temperature (150

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K). Data collection and reduction were performed with the Crysalis software.²⁴ The structure of the complex was solved by direct methods and refined by full-matrix least squares on *F*², using the SHELXL-2016/6 package.²⁵ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached with oxygen atoms were located by difference Fourier maps. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Programs used included PLATON,²⁶ DIAMOND,²⁷ ORTEP²⁸ and MERCURY.²⁹ Details of crystallographic data and refinement are given in Table 4.

Table 4: Crystal data and refinement details of the complex.

| Formula | $C_{44}H_{50}N_6Cu_3O_9S_2$ |
|-------------------------------|-----------------------------|
| Formula Weight | 1061.67 |
| Temperature(K) | 150 |
| Crystal system | Triclinic |
| Space group | ΡĪ |
| <i>a</i> (Å) | 12.4225(7) |
| b(Å) | 13.0816(9) |
| <i>c</i> (Å) | 15.8045(9) |
| lpha(deg) | 66.690(6) |
| β(deg) | 72.340(5) |
| γ(deg) | 84.193(5) |
| Z | 2 |
| $d_{calc}(g \text{ cm}^{-3})$ | 1.569 |
| μ(mm⁻¹) | 1.562 |
| F(000) | 1094 |
| Total Reflections | 16054 |

| Unique Reflections | 12604 |
|---------------------------------------|----------------|
| Observed data [$l > 2\sigma(l)$] | 9609 |
| No. of parameters | 599 |
| R(int) | 0.028 |
| R1, wR2 (all data) | 0.0803, 0.0998 |
| <i>R</i> 1, <i>wR</i> 2 [I > 2 σ (I)] | 0.0551, 0.0921 |

Theoretical methods

The calculations of the non-covalent interactions were carried out using the Turbomole 7.0³⁰ and the M06-2X/def2-TZVP level of theory. The interactions in the solid state were evaluated using the crystallographic coordinates. This procedure and level of theory were successfully used to evaluate similar interactions.³¹ The interaction energies were computed by calculating the difference between the energies of isolated monomers and their assembly. The interaction energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys–Bernardi counterpoise technique.³² The molecular electrostatic potential surfaces were computed using the SPARTAN software.³³ The Bader's "atoms-in-molecules" analysis were performed at the same level of theory, using the AIMAII program.³⁴

Hirshfeld surfaces

The Hirshfeld surface³⁵ of the complex was determined using Crystal Explorer.³⁶ The normalized contact distance (d_{norm}) based on d_e and d_i was given by,

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where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms. d_e and d_i represent the distances from the point to the nearest nucleus external and internal to the surface respectively. The d_{norm} values were mapped on to the Hirshfeld surface, where red colour is used to highlight shorter contacts, white colour is used for contacts at distances around the vdW separation and blue colour is used for longer contacts. 2D-fingerprint plots of Hirshfeld surface were also shown as plots of d_i against d_e .

Notes and References

CCDC 1561200 contains the supplementary crystallographic data for the complex.

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Formation of a water mediated assembly of two neutral copper(II) Schiff base fragments with $Cu_2(NCS)_4$ moiety: Exploration of noncovalent C-H···π(bimetallo ring) interactions

Sourav Roy, Michael G. B. Drew, Antonio Bauzá, Antonio Frontera, Shouvik Chattopadhyay



The energetic features of dimer formation and water encapsulation in an interesting copper(II) Schiff base complex, $[(CuL)_2 \subset (H_2O)][Cu_2(\mu_{1,3}-NCS)_2(NCS)_2]$ have been studied by means of DFT calculations. An unconventional C-H… π interaction involving the π -system of the bimetallic eight-membered planar ring has also been explored.