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# Photocatalytic ability of two hetero-tetranuclear complexes with CuO<sub>2</sub>Cd cores to degrade methylene blue: Influence of their structures on activity

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Abstract: Two centrosymmetric hetero-tetranuclear copper(II)/cadmium(II) complexes,  $(\mu_{LI})$ - $N_{3}_{2}[(H_{2}O)Cu(L^{R})Cd(N_{3})]_{2} \cdot 2CH_{3}OH$  (1) and  $(\mu_{1,1}-NCS)_{2}[CuL^{R}Cd(SCN)]_{2} \cdot 2CH_{3}OH$  (2), have been prepared with a compartmental reduced Schiff base ligand,  $H_2L^R=2, 2'-[(2, 2-dimethyl-1, 3-dimethyl-1, 3-d$ propanediyl)bis(iminomethylene)]bis[6-methoxy-phenol]. Both complexes have been characterized elemental and spectral analyses. Structures of both complexes have been confirmed by single crystal X-ray diffraction technique. Both complexes contain CuO<sub>2</sub>Cd cores. Here the bridging mode of azide and thiocyanate is quite different. Complex 1 contains  $\mu_{-1}$  azide bridges between two cadmium(II) centres whereas in complex 2,  $\mu_{-1}$  thiocyanate bridges occur between copper(II) and cadmium(II) centres. The ability of both complexes to be used as photo-catalyst in degrading methylene blue (MB) has been explored. The difference in photocatalytic performance may be correlated with their structures. Complex 1 shows better catalytic activity compared to complex 2, and can degrade almost 62% MB in 18 minutes. Comparative IR studies (before and after the photocatalytic degradation process) confirmed the stability of both catalysts.

**Keywords:** Compartmental reduced Schiff base; Hetero-tetranuclear complexes; Copper(II); Cadmium(II); Photocatalytic degradation.

#### 1. Introduction

Different groups of coordination chemists were synthesizing varieties of homo and hetero polynuclear complexes of transition and non-transition metals with salen type di-Schiff base ligands (prepared by the condensation of several diamines with salicylaldehyde) for long [1-5]. In this method, the ability of phenoxo oxygen atoms of salicylaldimine Schiff bases was utilized to bridge different metal centres [6-11]. Our group was also engaged in the synthesis and characterization of such complexes [12-14]. Several 'half salen' type mono-condensed Schiff bases have also been used to prepare such complexes [15-18]. Ability of many of these complexes in mimicking several enzymes, e.g. phosphatase, phenoxazinone synthase, catechol oxidase etc was investigated [19-25]. Opto-electronic properties of few such complexes were explored [26, 27]. Few complexes were found effective to degrade methylene blue under visible light irradiation [28-30]. The denticity of these 'salen' type Schiff bases may be increased by using 3-alkoxysalicylaldehyde instead of salicylaldehyde [31-33]. In this method, 'salen' type hexadentate N<sub>2</sub>O<sub>4</sub> donor compartmental Schiff bases were produced affording a facile synthetic route to multimetallic complexes with greater ease. N,N'-bis(3-methoxysalicylidene)-2,2dimethylpropane-1,3-diamine is a well known compartmental Schiff base, containing inner N<sub>2</sub>O<sub>2</sub> and outer O<sub>4</sub> compartments. We have prepared many heterometallic complexes with this ligand [34, 35]. Many other groups were also used this ligand to prepare hetero-metallic complexes [36-38]. Usually, transition metals are placed in the inner  $N_2O_2$  compartment as their radii matches well with the radius of this compartment. On the other hand, non-transition metals of larger size usually fit well in the outer  $O_4$  compartment [39-43].

In this work, we have reduced the Schiff base ligand with borohydride to get a more flexible reduced Schiff base ligand which was then used to prepare tetranuclear heterometallic

copper(II)/cadmium(II) complexes,  $(\mu_{1,1}-N_3)_2[(H_2O)Cu(L^R)Cd(N_3)]_2 \cdot 2CH_3OH$  (1) and  $(\mu_{1,1}-NCS)_2[CuL^RCd(SCN)]_2 \cdot 2CH_3OH$ , where  $H_2L^R=2,2'-[(2,2-dimethyl-1,3-propanediyl)bis(iminomethylene)]bis[6-methoxy-phenol]. Both complexes were characterized with single crystal X-ray diffraction analysis. Both complexes could be used as photo-catalyst to degrade methylene blue under visible light irradiation, although complex 1 was found to be better catalyst than complex 2. Methylene blue is an organic dye pollutant released by textile industries and it is necessary to destroy methylene blue from industrial waste to minimize environmental pollution [44-46]. A probable mechanistic pathway for the photocatalytic degradation of the organic dye by these complexes has been proposed. The difference in their photocatalytic performance has also been correlated with their structures.$ 

#### 2. Experimental

All starting materials and solvents were commercially available, reagent grade, and used as purchased from Sigma-Aldrich without further purification.

**Caution!!!** Although no problem was encountered in this work, azide complexes are potentially explosive. Only a small amount of the materials should be prepared and they must be handled with care.

#### 2.1. Preparation

2.1.1. Preparation of the ligand, 2,2'-[(2,2-dimethyl-1,3-propanediyl)bis(iminomethylene)]bis[6methoxy-Phenol] ( $H_2L^R$ )

A hexadentate Schiff base ligand,  $H_2L$  [N,N'-Bis(3-hydroxysalicylidene)-2,2-dimethyl-1,3-propanediamine], was synthesized by refluxing of 2,2-dimethyl-1,3-propanediamine (0.2

mL, 2 mmol) with 3-methoxysalicylaldehyde (~610 mg, 4 mmol) in methanol solution (10 mL) for ca. 2 h. The Schiff base was not purified but used directly for the preparation of the reduced Schiff base ligand,  $H_2L^R$ . The methanol solution (10 mL) was then cooled to 0°C and solid sodium borohydride (8 mmol, 310 mg) was added to it slowly with constant stirring. Then the resulting solution was acidified with glacial acetic acid (2 mL) and stirred for 10 minutes. The solution was evaporated to dryness under reduced pressure in a rotary evaporator (~60°C). The residue was dissolved in water (15 mL) and extracted with dichloromethane (15 mL). The organic phase was dried over anhydrous sodium acetate and the solvent i.e. dichloromethane was evaporated under reduced pressure using a rotary evaporator to give the reduced Schiff base ligand,  $H_2L^R$ .

### 2.1.2. Preparation of the complex $(\mu_{-1,1}N_3)_2[(H_2O)Cu(L^R)Cd(N_3)]_2 \cdot 2CH_3OH(1)$

A methanol solution (5 mL) of copper(II) acetate monohydrate (~400 mg, 2 mmol) was added to the methanol solution (10 mL) of the reduced Schiff base ligand  $H_2L^R$ , with constant stirring. A methanol (10 mL) solution of cadmium(II) acetate dihydrate (~540 mg, 2 mmol) was then added to it and the stirring was continued for about 2h. A methanol–water (2:1) solution (10 mL) of sodium azide (260 mg, 4 mmol) was added and the resulting mixture was refluxed for ca. 2h. Crystalline product was obtained after few days on very slow evaporation. Single crystals, suitable for X-ray diffraction, were isolated from the crystalline product.

**Yield:** 914 mg (~67%) based on copper(II). Anal. Calc. for  $C_{44}H_{68}Cd_2Cu_2N_{16}O_{12}$  (FW: 1365.06): C, 39.88; H, 4.46; N, 17.72. Found: C, 39.7; H, 4.3; N, 17.9 %, FT-IR (KBr, cm<sup>-1</sup>): 3412 ( $v_{O-H}$ ), 3246-3166 ( $v_{N-H}$ ), 2972-2835 ( $v_{C-H}$ ), 2060 ( $v_{\mu-1,1-N3}$ ), 2035 ( $v_{N3}$ ). UV–Vis,  $\lambda_{max}$  (nm), [ $\varepsilon_{max}$  (L mol<sup>-1</sup> cm<sup>-1</sup>)] (DMF): 242 (1.5 × 10<sup>4</sup>), 280 (7.9 × 10<sup>3</sup>), 336 (8.9 × 10<sup>2</sup>), 414 (1.0 × 10<sup>3</sup>), 591 (2.2 × 10<sup>2</sup>).

2.1.3. Preparation of the complex  $(\mu_{-1,1}NCS)_2[CuL^RCd(SCN)]_2 \cdot 2CH_3OH(\mathbf{2})$ 

Complex 2 was prepared in a similar method to that of complex 1, except that sodium thiocyanate (~330 mg, 4 mmol) was added instead of sodium azide. Crystalline product was obtained after few days on very slow evaporation. Single crystals, suitable for X-ray diffraction, were isolated from the crystalline product.

**Yield:** 905 mg (~65%) based on copper(II). Anal. Calc. for  $C_{48}H_{64}Cd_2Cu_2N_8O_{10}S_4$  (FW: 1393.23): C, 41.57; H, 4.25; N, 8.43. Found: C, 41.3; H, 4.1; N, 8.6%, FT-IR (KBr, cm<sup>-1</sup>): 3220-3145 ( $v_{N-H}$ ), 2972-2835 ( $v_{C-H}$ ), 2081 ( $v_{\mu-1,1-NCS}$ ), 2017 ( $v_{SCN}$ ). UV–Vis,  $\lambda_{max}$  (nm), [ $\epsilon_{max}$  (L mol<sup>-1</sup> cm<sup>-1</sup>)] (DMF): 240 (1.8 × 10<sup>4</sup>), 280 (1.0 × 10<sup>4</sup>), 336 (1.1 × 10<sup>3</sup>), 410 (1.3 × 10<sup>3</sup>), 595 (2.7 × 10<sup>2</sup>).

#### 2.2. Physical measurement

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr (4500-500 cm<sup>-1</sup>) were recorded with a Perkin-Elmer Spectrum Two spectrophotometer. Electronic spectra were recorded on a JASCO J-630 spectrophotometer.

#### 2.3. X-ray crystallography

Suitable crystals of both complexes were used for data collection using a 'Bruker D8 QUEST area detector' diffractometer equipped with graphite-monochromated Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). The molecular structures were solved by direct method and refined by full-matrix least squares on  $F^2$  using the SHELXL-18/1 package [47]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to nitrogen and oxygen atoms were located by difference Fourier maps and were kept at fixed positions. All

other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [48]. The details of crystallographic data and refinements have been given in Table 1. Important bond lengths and angles have been listed in Tables 2 and 3, respectively.

#### 2.4. Photocatalytic measurement

The photocatalytic experiment in aqueous solution has been carried out in usual process [49]. The catalytic degradation has been carried out separately with 100 mL of Methylene Blue (MB) solution (20 mg L<sup>-1</sup>) with the complex using as catalyst. The mixture has been stirred for 10 min in a dark environment to get a balance between adsorption and desorption. The solution has been then stirred constantly. A 3 mL sample has been taken from the reaction system in an interval of 3 min and the supernatant liquid obtained by centrifugation has been used for collecting the UV–Vis spectrum. The characteristic peak for methylene blue (~600 nm) has been employed to monitor the photocatalytic degradation.

### 3. Results and discussion

#### 3.1. Synthesis

2,2-dimethyl-1,3-diaminopropane was refluxed with 3-methoxysalicylaldehyde in a 1:2 ratio to form a N<sub>2</sub>O<sub>4</sub> donor compartmental Schiff base ligand,  $H_2L$ , following a literature method and NaBH<sub>4</sub> was used as a reducing agent to prepare reduced Schiff base ligand ( $H_2L^R$ ) [50, 51]. This reduced Schiff base ( $H_2L^R$ ) on reaction with copper(II) acetate monohydrate followed by the addition of cadmium(II) acetate dihydrate and sodium azide in methanol gave rise to complex 1. The complex 2 was synthesized in similar method to that of complex 1, except that sodium

thiocyanate is used instead of sodium azide. Synthetic route to the formation of both complexes **1** and **2** have been shown in Scheme **1**.



Scheme 1: Synthetic route to complexes 1 and 2

#### 3.2. Description of structures

### 3.2.1. $(\mu_{1,1}-N_3)_2[(H_2O)Cu(L^R)Cd(N_3)]_2 \cdot 2CH_3OH(1)$

Structure determination reveals that complex 1 crystallizes in the monoclinic space group  $P2_1/c$ . The complex is a centrosymmetric zigzag tetramer and is build up of two dinuclear units,  $[(H_2O)Cu(L^R)Cd(N_3)]$ , connected through two end-on azide bridges. A perspective view of the complex with selective atom numbering scheme has been shown in Fig. 1. In the asymmetric

unit, the copper(II) centre, Cu(1), and cadmium(II) centre, Cd(1), respectively occupy the inner N<sub>2</sub>O<sub>2</sub> and outer O<sub>4</sub> sites of a potential compartmental reduced Schiff base  $H_2L^R$ , with a Cu(1)…Cd(1) distance of 3.378(6) Å.

Copper(II) centre is penta-coordinated being bonded to two amine nitrogen atoms, N(1) and N(2), and two phenoxo oxygen atoms, O(1) and O(2), of the deprotonated reduced Schiff base ligand,  $(L^R)^{2-}$  and one oxygen atom, O(5), from a coordinated water molecule. The geometry of any penta-coordinated metal centre may conveniently be measured by the Addison parameter ( $\tau$ ) [52]. The geometry of copper(II) centre is slightly distorted square pyramidal with  $\tau = 0.06$  ( $\tau = 0$  indicates perfect square pyramid). On the other hand, cadmium(II) centre, Cd(1), is hepta-coordinated and its geometry is distorted pentagonal bipyramidal. Cd(1) is coordinated by two phenoxo oxygen atoms, O(1) and O(2), two methoxy oxygen atoms, O(3) and O(4), and one nitrogen atom, N(3), of an end-on bridging azide, which constitute the pentagonal plane. The sixth site is occupied by a nitrogen atom, N(6), from a terminal azide. The seventh coordination site is occupied by another nitrogen atom, N(3), from an end-on bridging azide, which bridges Cd(1) and its symmetry {'= 1-x,1-y,1-z} related counterpart, Cd(1'). The saturated six-membered chelate ring [Cu(1)–N(1)–C(9)–C(10)–C(13)–N(2)] has envelope conformation with puckering parameters, q = 0.523(6) Å;  $\theta = 23.0(5)^\circ$ ;  $\phi = 177.6(14)^\circ$  [53, 54].



Fig. 1. Perspective view of complex 1 with selective atom numbering. Hydrogen atoms and the lattice methanol molecule have been omitted for clarity.

# 3.2.2. $(\mu_{1,1}$ -NCS)<sub>2</sub>[CuL<sup>R</sup>Cd(SCN)]<sub>2</sub>·2CH<sub>3</sub>OH (2)

Complex 2 crystallizes in triclinic space group,  $P\overline{1}$ . It is basically a centrosymmetric cyclic tetramer with [-Cd-( $\mu_{1,1}$ -NCS)CuO<sub>2</sub>Cd( $\mu_{1,1}$ -NCS)-Cu-] core, in which two hetrerodinuclear [CuL<sup>R</sup>Cd(SCN)] units are linked through two end-on thiocyanate bridges. A perspective view with selective atom numbering scheme has been shown in Fig. 2. Cu(1)···Cd(1') {symmetry transformation '= 1-x,1-y,1-z} distance in the tetrameric unit is 3.617(9) Å.

Copper(II) centre, Cu(1), is square pyramidal being coordinated equatorially by two amine nitrogen atoms, N(1) and N(2), and two phenoxo oxygen atoms, O(1) and O(2), of the deprotonated reduced Schiff base,  $(L^R)^{2-}$ . The fifth position is occupied by a nitrogen atom, N(3'), of the bridging thiocyanate. The square pyramidal geometry of copper(II) centre is confirmed by  $\tau$ , here  $\tau = 0.01$  [52]. On the other hand, the coordination geometry of cadmium(II) centre, Cd(1),

is distorted octahedral, where two phenoxo oxygen atoms, O(1) and O(2), and two methoxy oxygen atoms, O(3) and O(4), of the reduced Schiff base constitute the equatorial plane. One axial site is occupied by a sulfur atom, S(1), from terminal thiocyanate and another axial site is occupied by nitrogen atom, N(3), from thiocyanate which is act as a bridge between the cadmium(II) centre, Cd(1) and the symmetry related copper(II) centre, Cu(1'). The saturated sixmembered chelate ring [Cu(1)–N(1)–C(9)–C(10)–C(13)–N(2)] has envelope conformation with the puckering parameters, q = 0.524(6) Å;  $\theta = 148.2(5)^{\circ}$ ;  $\varphi = 2.6(11)^{\circ}$  [53, 54].



Fig. 2. Perspective view of complex 2 with selective atom numbering. Hydrogen atoms and the lattice methanol molecule have been omitted for clarity.

#### 3.3. Comparison of structures of 1 and 2

It is interesting to note here that in complex **1**, cadmium(II) centre of one asymmetric unit is connected with a cadmium(II) centre of a symmetry related counterpart via end-on azide bridges. This makes the copper(II) centres free to be used in any catalytic reaction. On the other

hand, cadmium(II) centre of one asymmetric unit in complex **2** is connected with a copper(II) centre of a symmetry related dinuclear unit via end-on thiocyanate bridges. Thus both copper(II) and cadmium(II) are confined in a cyclic tetrameric unit, making copper(II) less available to take part any catalytic reaction.

#### 3.4. Supramolecular interactions

Solid state structures of both complexes are stabilized through significant non-covalent interactions such as hydrogen bonding and C–H $\cdots\pi$ . Complex 1 shows five significant hydrogen bonding interactions. The hydrogen atom, H(1), attached to amine nitrogen atom, N(1), involve in hydrogen bonding interaction with the symmetry related (x, 1.5-y, -0.5+z) oxygen atom, O(6<sup>j</sup>), of the lattice methanol molecule. Another hydrogen atom, H(5C), attached to oxygen atom, O(5), of coordinated water molecule participate in hydrogen bonding interaction with the symmetry related (1-x, 1/2+y, 3/2-z) azide nitrogen atom N(8<sup>i</sup>). These two intermolecular hydrogen bonding interactions form a two dimensional layer structure. On the other hand, the oxygen atom, O(6), of the lattice methanol molecule forms hydrogen bond with the hydrogen atom, H(5D), attached with the oxygen atom, O(5), of the coordinated water molecule. Again, hydrogen atom, H(6), of the same lattice methanol molecule, forms an additional hydrogen bond with azide nitrogen atom, N(6). Another hydrogen atom, H(2), attached to amine nitrogen atom N(2), participates in hydrogen bond formation with the azide nitrogen atom, N(5). Two dimensional layer structure of the complex has been shown in Fig. 3 and selected small part of the two dimensional structure of hydrogen bonding has been shown in Fig. 4. Details of the hydrogen bonding interactions have been given in Table 4.

The hydrogen atom, H(22A), attached to the carbon atom, C(22), of the lattice methanol molecule, is involved in a C–H··· $\pi$  interaction with the symmetry related (x,1.5-y,0.5+z) phenyl ring [C(2)–C(3)–C(4)–C(5)–C(6)–C(7)]. Two dimensional layer structure of C–H··· $\pi$  interaction has been shown in Fig. 5 and selected small part of C–H··· $\pi$  interaction with specific atom numbering has been shown in Fig. 6. Details of the geometric feature of the C–H··· $\pi$  interaction have been given in Table 5.



**Fig. 3.** Hydrogen bonded layer structure of complex **1**. Only the relevant hydrogen atoms have been shown.



Fig. 4. Selected small part of hydrogen bonded structure of complex 1. Only the relevant hydrogen atoms have been shown. Symmetry transformation i = x, 1.5 - y, 0.5 + z, j = 1 - x, 0.5 + y, 1.5 - z



Fig. 5. Two dimensional supramolecular C–H··· $\pi$  interactions in complex 1. Only the relevant hydrogen atoms have been shown for clarity. Symmetry transformation: #= x,1.5-y,0.5+z.



Fig. 6. Selected small part of C–H··· $\pi$  interactions of complex 1. Only the relevant hydrogen atoms have been shown. Symmetry transformation #= x,1.5-y,0.5+z.

Three types of supramolecular interactions have been observed in complex 2 (H-bonding, C-H··· $\pi$  and  $\pi$ ··· $\pi$  interactions). The hydrogen atom, H(2N), attached to amine nitrogen atom, N(2), of the reduced Schiff base is engaged in intramolecular hydrogen bonding interaction with the same symmetry related oxygen atom, O(5), of lattice methanol molecule, as shown in Fig. 7. Details of the hydrogen bonding interaction have been gathered in Table 4.

The hydrogen atom, H(24B), attached to the carbon atom, C(24), of lattice methanol involved molecule is in the  $C-H\cdots\pi$ interaction with phenyl a ring [C(15)-C(16)-C(17)-C(18)-C(19)-C(20)]. The C-H··· $\pi$  interaction of the complex has been shown in Fig. 8. Detail of the C-H $\cdots\pi$  interaction has been given in Table 5. Complex 2 shows a significant  $\pi \cdots \pi$  stacking interaction (Fig. 9) between an aromatic ring [C(2)–C(3)–C(4)–C(5)– C(6)-C(7) with a symmetry-related (1-x,1-y,1-z) aromatic ring [C(15)-C(16)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(17)-C(18)-C(1C(19)–C(20)]. Details of the  $\pi$ ··· $\pi$  interaction have been given in Table 6.



Fig. 7. Hydrogen bonding structure of complex 2 with lattice methanol molecule. Only the



relevant hydrogen atoms have been shown.

Fig. 8. C–H··· $\pi$  interaction of complex 2 with lattice methanol molecule. Only the relevant

hydrogen atoms have been shown.



Fig. 9. Intramolecular  $\pi \cdots \pi$  stacking interactions in complex 2. Hydrogen atoms and lattice methanol molecules have been omitted for clarity.

#### 3.5. Hirshfeld surfaces analysis

The Hirshfeld surfaces of both complexes mapped over  $d_{norm}$  (range -0.1 Å to 1.5 Å), shape index and curvedness have been shown in Fig. 10. Red spots on these surfaces denote the dominant interactions. Analysis of Hirshfeld surfaces indicates that there are interactions mainly between nitrogen and hydrogen atoms in complex 1, whereas, there are significant interactions between sulphur and hydrogen atoms in complex 2. Other visible spots in Hirshfeld surfaces correspond to C…H and H…H contacts. The intermolecular interactions appear as distinct spikes in the 2D fingerprint plot (Fig. S1).



Fig. 10. Hirshfeld surfaces of both complexes 1 and 2 mapped over d<sub>norm</sub> (left), shape index (middle), curvedness (right).

#### 3.6. IR and electronic spectra

In the IR spectrum of complex **1**, a sharp peak at 2060 cm<sup>-1</sup> and an associated small peak at 2036 cm<sup>-1</sup> indicate the presence of bridging and terminal azides [55-57]. In IR spectrum of complex **2**, there are two successive strong peaks observed at 2081 and 2017 cm<sup>-1</sup>, indicating the presence of terminal (S-bonded) and end-on bridged thiocyanates (N-bonded), respectively [58]. A moderately strong band due to stretching vibration of N–H bond appears around 3213-3166 cm<sup>-1</sup> for both complexes [59]. A broad peak around 3412 cm<sup>-1</sup> indicates the presence of coordinating water molecule in complex **1** [60]. Bands near the range of 2972–2835 cm<sup>-1</sup> are due to alkyl C–H bond stretching vibrations, which are customarily noticed in the IR spectra of both complexes [61]. The IR spectra of both complexes have been shown in Fig. **S2** (Electronic Supplementary Information, ESI).

Electronic spectrum of each complex in DMF displays one absorption band in the visible region around 590 nm which may be considered as  ${}^{2}T_{2g}(D) \leftarrow {}^{2}E_{g}(D)$  transition for copper(II) [35,60]. Bands around 410 nm (407 nm for complex 1 and 414 nm for complex 2) may be attributed to LMCT transition from the N donor centres of Schiff base to copper(II) [62, 63]. Another bands around 335 nm (for both 1 and 2) may be attributed to LMCT transition from the O donor centres of Schiff base to cadmium(II) [64]. The high intensity band occur at 242 (for 1) and 240 (for 2) nm is attributed to  $\pi \rightarrow \pi^*$  transition of the ligand. Another intense band observe in the region of 275-285 is correspond to  $n \rightarrow \pi^*$  transition for both complexes [62, 65]. The UVvis spectra of both complexes have been shown in Fig. 11 and Fig. S3 (ESI), respectively.



Fig. 11. UV-vis spectra of complex 1. Inset shows the visible range spectrum.

#### 3.7. Photocatalytic activity

The ability of both complexes (1 and 2) to be used as photo-catalyst for the degradation of organic dye, viz. methylene blue (MB), has been investigated under visible light irradiation. The degradation efficiencies are defined as  $C/C_0$ , where C and  $C_0$  represent the residual and initial concentration of organic dyes, respectively. The degradation efficiencies (C/C<sub>0</sub>) is calculated by the following equation:-

Degradation efficiencies (%)=  $(C_0-C)/C_0 \times 100$ .

As shown in Fig. 12, the residual concentration of the dye in an aqueous solution gradually decreased as a function of the increasing reaction time, indicating that both complexes degrade organic dyes. Both complexes are efficient for the degradation of MB and the ratio of the degradation reaches around 62% (for complex 1) and 30% (for complex 2) using 10 mg of complexes.

To prove the photocatalytic efficiency of both complexes to MB, comparative experiments without catalyst under visible light irradiation have been performed, which showed only very little decomposition. The photocatalytic activity of cadmium(II) acetate and copper(II) acetate have also been studied to MB under similar conditions (mentioned in the Fig. 13), which showed that the rate of degradation was still very slow using 10 mg of bare cadmium(II) as well as bare copper(II). It is revealed that the intensity of the characteristic absorption peak of MB decreased with the increase of irradiation time in the degradation process. Kinetic plots of both complexes have been shown in Fig. 13.



Fig. 12: UV–Vis absorption spectra of MB solution with both complexes (sample taken = 10



**Fig.13.** Degradation efficiency of MB in presence of complex 1 and complex 2. Experimental condition [MB]= 20 mg/L.

In order to verify whether both complexes are capable of maintaining its structural integrity during photocatalytic decomposition of MB, IR experiments for both complexes were performed during the course of photocatalytic reactions. The IR experiments indicated that the

patterns are nearly identical when compared with the pure complex. Hence the IR experiments imply that both complexes maintain their structural integrity even after getting involved in the photocatalytic reactions. IR spectra of both complexes 1 and 2 (before and after degradation) have been shown in Fig. 14 and S4, respectively.



Fig.14: IR spectra of complex 1 before (blue) and after (red) photodegradation process.

The first step of the process is excitation of electrons from the valence band to the conduction band which creates equal amounts of positives vacancies or holes in valence band. It is well-established that holes act as powerful oxidants and electrons as powerful reductants. The second step is adsorption of oxygen or water on the surfaces of catalyst. Electrons in the conduction band is scavenged by oxygen molecule to produce  $O_2^{+-}$  anion radical, which provides peroxide radical ('OOH) and then decomposed to active hydroxyl radical ('OH). On the other hand, the holes in the valence band interact with H<sub>2</sub>O or  $^{-}OH$  to produce highly active hydroxyl

radical ('OH). Finally, the effective degradation of methylene blue is occurred by these generated hydroxyl radicals ('OH).

#### 3.8. Structure-activity relationship

The photocatalytic degradation study has been carried out with visible light irradiation. So the degradation process must be initiated with visible light absorption. Absorption spectra of both complexes contain peaks around 590 nm in the visible region, originating from copper(II)-based  ${}^{2}T_{2g}(D) \leftarrow {}^{2}E_{g}(D)$  transition. Thus copper(II) centres may be considered as the initiator of the degradation process. As already mentioned, copper(II) centre in complex 1 is relatively more free to take part in any reaction for its open zigzag structure. High efficiency of complex 1 to degrade the dye (MB) is therefore justified from its structure. On the other hand, copper(II) is rigidly imprisoned in a cyclic tetranuclear skeleton in complex 2 and is less free to take part in reaction. This explains the less catalytic efficiency of complex 2 compared to complex 1.

A comparative study has also been done to compare the degradation efficiency of these complexes with all reported complexes, which has been characterized structurally. The comparative study has been shown in Table 7. This indicates our complexes are good enough to be explored in industrial chemistry, although better complexes are also known in literature. However, it should be noted that many of the previously reported catalysts have been prepared using Schiff bases as ligands and therefore their application in aqueous medium is limited (Schiff bases are susceptible to hydrolysis). Our complexes are containing reduced Schiff bases as ligands and may, therefore, be used in aqueous medium without any problem related to destruction of the ligands via hydrolysis.

#### 4. Concluding remarks

Synthesis and X-ray characterization of two new hetero-tetranuclear copper(II)cadmium(II) complexes with same reduced Schiff base ligand have been described in this paper. In both complexes 1 and 2, copper(II) and cadmium(II) resides on N<sub>2</sub>O<sub>2</sub> and O<sub>4</sub> donor sites, respectively. The bridging mode in complex 2 is quite different than that of complex 1. In complex 1, two cadmium(II) centres are bridged by end-on bridging azide whereas in complex 2, the copper(II) and cadmium(II) is bridged by end-on bridging thiocyanate instead of two cadmium(II) centres. Both complexes show significant supramolecular interactions in their solid state structures. Photocatalytic degradation study of both complexes gives a reliable result as it is the first report of the degradation study for heterometallic complexes with reduced Schiff base ligands. Both complexes have catalytic ability for the degradation of organic pollutant, MB, under visible light irradiation. Complex 1 shows a good catalytic degradation property than complex 2. The structural variation upon the degradation process has also been rationalized. Finally, efficient catalytic ability of both complexes for the photo-degradation of organic pollutant under visible light irradiation indicates the potential application of the complex in industrial chemistry.

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#### **Appendix A. Electronic Supplementary Information**

UV-VIS spectrum of complex **2** and Hirshfeld surface analysis and IR spectrum of both complexes **1** and **2** are given in the electronic supplementary information part. CCDC 1891988–1891989 contains the supplementary crystallographic data for both complexes **1** and **2**, respectively.

### Reference

- [1] T. K. Ghosh, S. Jana, A. Ghosh, Inorg. Chem. 57 (2018) 15216-15228.
- [2] S. Dutta, S. Jana, P. Mahapatra, A. Bauzá, A. Frontera, A. Ghosh, CrystEngComm 20 (2018)6490–6501
- [3] P. Mahapatra, S. Giri, M. G. B. Drew, A. Ghosh, Dalton Trans. 47 (2018) 3568–3579
- [4] P. Mahapatra, M. G. B. Drew, A. Ghosh, Inorg. Chem. 57 (2018) 8338-8353
- [5] S. Maity, S. Ghosh, P. Mahapatra, A. Ghosh, Inorg. Chim. Acta 482 (2018) 807-812.
- [6] M. Mousavi, V. Bereau, J.-P. Costes, C. Duhayon, J.-P. Sutter, CrystEngComm 13 (2011) 5908–5914.
- [7] A. Hazari, L. Kanta Das, A. Bauzá, A. Frontera, A. Ghosh, Dalton Trans. 45 (2016) 5730– 5740.
- [8] P. Seth, A. Figuerola, J. Jover, E. Ruiz, A. Ghosh, Inorg. Chem. 53 (2014) 9296–9305.
- [9] V. Bereau, S. Dhers, J.-P. Costes, C. Duhayon, J.-P. Sutter, Eur. J. Inorg. Chem. (2018) 66– 73.

- [10] C. Biswas, M. G. B. Drew, E. Ruiz, M. Estrader, C. Diaz, A. Ghosh, Dalton Trans. 39 (2010) 7474–7484.
- [11] J. Mukherjee, R. Mukherjee, Inorg. Chim. Acta 337 (2002) 429-438.
- [12] S. Chattopadhyay, G. Bocelli, A. Musatti, A. Ghosh, Inorg. Chem. Commun. 9 (2006)1053-1057.
- [13] S. Chattopadhyay, M. G. B. Drew, A. Ghosh, Eur. J. Inorg. Chem. 2008, 1693-1701.
- [14] A. Bhattacharyya, S. Sen, K. Harms, S. Chattopadhyay, Polyhedron 88 (2015) 156-163.
- [15] X. Pang, R. Duan, X. Li, Z. Sun, H. Zhang, X. Wang, X. Chen, Polym. Chem. 5 (2014)6857–6864.
- [16] R. Duan, B. Gao, X. Li, X. Pang, X. Wang, H. Shao, X. Chen, Polymer 71 (2015) 1-7
- [17] D. J. Darensbourg, O. Karroonnirun, S. J. Wilson, Inorg. Chem. 50 (2011) 6775-6787.
- [18] M. Mandal, U. Monkowius, D. Chakraborty, New J. Chem. 40 (2016) 9824--9839.
- [19] S. K. Barman, T. Mondal, D. Koley, F. Lloret, R Mukherjee, Dalton Trans. 46 (2017) 4038–4054.
- [20] C. Belle, I. G.-Luneau, L. Karmazin, J.-L. Pierre, S. Albedyhl, B. Krebs, M. Bonin, Eur. J. Inorg. Chem. (2002) 3087–3090.
- [21] O. V. Amirkhanov, O. V. Moroz, K. O. Znovjyak, T. Yu. Sliva, L. V. Penkova, T. Yushchenko, L. Szyrwiel, I. S. Konovalova, V. V. Dyakonenko, O. V. Shishkin, V. M. Amirkhanov, Eur. J. Inorg. Chem. (2014) 3720–3730.

- [22] S. Albedyhl, D. Schnieders, A. Jancso, T. Gajda, B. Krebs, Eur. J. Inorg. Chem. (2002) 1400–1409.
- [23] S. K. Dey, A. Mukherjee, Coord. Chem. Rev. 310 (2016) 80-115.
- [24] M. Mahato, D. Mondal, H. P. Nayek, ChemistrySelect 1 (2016) 6777 6782.
- [25] P Kar, MGB Drew, A Ghosh, Inorg. Chim. Acta 405 (2013) 349-355.
- [26] V. Stavila, A. A. Talin, M. D. Allendorf, Chem. Soc. Rev. 43 (2014) 5994-6010.
- [27] N. Hoshino, F. Iijima, G. N. Newton, N. Yoshida, T. Shiga, H. Nojiri, A. Nakao, R. Kumai,
- Y. Murakami, H. Oshio, Nat. Chem. 4 (2012) 921-926.
- [28] H.-H. Wang, J. Yang, Y.-Y. Liu, S. Song, J.-F. Ma, Cryst. Growth Des. 15 (2015) 4986–4992.
- [29] S. Farhadi, M. M. Amini, M. Dusek, M. Kucerakova, F. Mahmoudi, J. Mol. Struct. 1130(2017) 592-602.
- [30] T. Basak, M. G. B. Drew, S. Chattopadhyay, Inorg. Chem. Commun. 98 (2018) 92–98.
- [31] M. Andruh, Chem. Commun. 47 (2011) 3025–3042.
- [32] A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, Inorg. Chim. Acta, 202 (1992) 157-171.
- [33] U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, C. Benelli, Inorg. Chim. Acta, 207(1993) 39-58
- [34] P. Seth, A. Figuerola, J. Jover, E. Ruiz, A. Ghosh, Inorg. Chem. 53 (2014) 9296-9305

- [35] A. Hazari, L. Kanta Das, A. Bauzá, A. Fronter, A. Ghosh, Dalton Trans. 43 (2014) 8007– 8015
- [36] T. Kajiwara, M. Nakano, K. Takahashi, S. Takaishi, M. Yamashita, Chem. Eur. J. 17 (2011) 196–205.
- [37] T. Kajiwara, K. Takahashi, T. Hiraizumi, S. Takaishi, M. Yamashita, Polyhedron 28 (2009)1860–1863.
- [38] Z.-X. Wang, L.-F. Wu, X.-K. Hou, M. Shao, H.-P. Xiao, M.-X. Li, Z.Anorg.Allg.Chemie.640 (2014) 229-235.
- [39] T. Ishida, R. Watanabe, K. Fujiwara, A. Okazawa, N. Kojima, G. Tanaka, S. Yoshii and H. Nojiri, Dalton Trans. 41 (2012) 13609–13619.
- [40] X.-C. Huang, X.-H. Zhao, D. Shao, X.-Y. Wang, Dalton Trans., 46 (2017) 7232–7241.
- [41] J.-P. Costes, F. Dahan, A. Dupuis, Inorg. Chem. 39 (2000) 165-168.
- [42] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, New J. Chem. (1998) 1525-1529.
- [43] V. Bereau, H. Bolvin, C. Duhayon, J.-P. Sutter, Eur. J. Inorg. Chem. (2016) 4988–4995.
- [44] V.K. Garg, M. Amita, R. Kumar, R. Gupta, Dyes Pigm. 63 (2004) 243-250.
- [45] V. K. Gupta, Suhas, I. Ali, V. K. Saini, Ind. Eng. Chem. Res. 43 (2004) 1740-1747.
- [46] P. M. K. Reddy, B. R. Raju, J. Karuppiah, E. L. Reddy, C. Subrahmanyam, Chem. Eng. J.217 (2013) 41–47.
- [47] G.M. Sheldrick, Acta Crystallogr., Sect. C 71 (2015) 3-8.

- [48] G. M. Sheldrick, SADABS, V2014/5, Software for Empirical Absorption Correction, University of Göttingen, Institute fur Anorganische Chemieder Universitat, Gottingen, Germany, 1999–2003.
- [49] T. Basak, A. Bhattacharyya, K. Harms, S. Chattopadhyay, Polyhedron 157 (2019) 449-457.
- [50] A. Hazari, T. K. Ghosh, C. J. G.-García, A. Ghosh, Inorg. Chimi. Acta 471 (2018) 168-175.
- [51] A. Hazari, L. K. Das, R. M. Kadam, A. Bauzá, A. Frontera, A. Ghosh, Dalton Trans. 44(2015) 3862–3876.
- [52] A. W. Addison, T. N. Rao, J. Reedijk, J. V. Rijn, G. C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349-1356.
- [53] D. Cremer, J. A. Pople, J. Am. Chem. Soc. 97 (1975) 1354–1358.
- [54] D. Cremer, Acta Crystallogr., Sect. B: Struct. Sci. 40 (1984) 498–500.
- [55] M. A. S. Goher, N. A. Al-Salem, F. A. Mautner, K. O. Klepp, Polyhedron 16 (1997) 825-831.
- [56] F. A. Mautner, M. Scherzer, C. Berger, R. C. Fischer, R. Vicente, S. S. Massoud, Polyhedron 85 (2015) 329–336.
- [57] F. A. Mautner, M. Traber, R. C. Fischer, K. Reichmann, R. Vicente, Polyhedron 144 (2018)30–35.
- [58] F. A. Mautner, M. Scherzer, C. Berger, R. C. Fischer, R. Vicente, S. S. Massoud, Polyhedron 85 (2015) 20–26.

[59] S. Chattopadhyay, M. S. Ray, S. Chaudhuri, G. Mukhopadhyay, G. Bocelli, Inorg. Chimica Acta 359 (2006) 1367-1375.

[60] P. Chakraborty, I. Majumder, H. Kara, S. K. Chattopadhyay, E. Zangrando, D. Das, Inorg. Chim. Acta 436 (2015) 139–145.

[61] M. A. Khan, A. A. Alqadami, M. Otero, M. R. Siddiqui, Z. A. Alothman, I. Alsohaimi, M. Rafatullah, A. E. Hamedelniel, Chemosphere 218 (2019) 1089–1099.

[62] S. Ghorai, A. Sarmah, R. K. Roy, A. Tiwari, C. Mukherjee, Inorg. Chem. 55 (2016) 1370–1380.

[63] A. Biswas, L. K. Das, M. G. B. Drew, C. Diaz, A. Ghosh, Inorg. Chem. 51 (2012) 10111-10121.

[64] A. Golcu, M. Tumer, H. Demirelli, R. A. Wheatley, Inorg. Chim. Acta 358 (2005) 1785– 1797.

[65] S. Roy, A. Bauzá, A. Frontera, S. Chattopadhyay, Inorg. Chim. Acta 453 (2016) 51-61.

[66] S. Roy, K. Harms, A. Bauzá, A. Frontera, S. Chattopadhyay, Polyhedron, 121 (2017) 199–205.

[67] X. Wei, Y. Li, Z. Qin, G. Cui, J. Mol. Struct. 1175 (2019) 253-260.

[68] X. Zhao, Z. Qin, Y. Li, G. Cui, Polyhedron, 153 (2018) 197-204.

[69] S. Roy, K. Harms, S. Chattopadhyay, Polyhedron 127 (2017) 471–477.

[70] X. Zhao, Z. Qin, Y. Li, G. Cui, Polyhedron, 146 (2018) 65-72.

[71] T. Liu, T. Hu, C. Hu, J. Lang, Inorg. Chem. Commun. 90 (2018) 26-28.

- [72] L. Liu, J. Ding, C. Huang, M. Li, H. Hou, Y.Fan, Cryst. Growth. Des. 14 (2014) 3035–3043.
- .y, J. Organo [73] K. Ghosh, K. Harms, A. Franconetti, A. Frontera, S. Chattopadhyay, J. Organomet. Chem.

 Table 1: Crystal data and refinement details of complexes 1 and 2.

	Complex	1	2
	Formula	$C_{44}H_{68}Cd_2Cu_2N_{16}O_{12}$	$C_{48}H_{64}Cd_2Cu_2N_8O_{10}S_4$
	Formula Weight	1365.06	1393.23
	Temperature (K)	273	273
	Crystal system	Monoclinic	Triclinic
	Space group	<i>P</i> 2 <sub>1</sub> /c	Pī
	a(Å)	10.5544(9)	11.6584(13)
	b(Å)	18.0146(14)	11.6797(12)
	c(Å)	15.1340(11)	12.7556(14)
	α	90	108.983(3)
	β	103.804(2)	99.804(3)
	γ	90	116.542(3)
	Z	2	1
	$d_{\rm calc} ({ m g  cm^{-3}})$	1.622	1.697
	μ (mm <sup>-1</sup> )	1.573	1.755
	F(000)	1388	706
	Total Reflections	31902	15213
	Unique Reflections	5032	4851
	Observed data [I >2 σ (I)]	4343	4271
-	No. of parameters	353	347
	R(int)	0.030	0.044
	R1,wR2 (all data)	0.0437, 0.1294	0.0499, 0.1360

Complex	1	2	
Cd(1)–O(1)	2.287(3)	2.256(3)	
Cd(1)–O(2)	2.307(3)	2.262(2)	2
Cd(1)–O(3)	2.471(4)	2.511(3)	
Cd(1)–O(4)	2.472(4)	2.496(4)	
Cd(1)–N(3)	2.354(5)	2.201(5)	
Cu(1)–O(1)	1.956(3)	1.964(3)	
Cu(1)–O(2)	1.953(3)	1.968(4)	
Cu(1)–N(1)	2.028(4)	2.022(4)	
Cu(1)–N(2)	2.032(4)	2.017(4)	
Cd(1)–N(6)	2.259(5)		
Cd(1)–N(3')	2.341(4)		
Cu(1)–O(5)	2.317(4)		
Cd(1)–S(1)		2.636(2)	
Cu(1)–N(3')		2.626(5)	

 Table 2: Selected bond lengths (Å) of complexes 1 and 2.

Symmetry transformation: '= 1-x, 1-y, 1-z.

AC

Complex 1 2 O(1)-Cd(1)-O(2)66.97(10) 66.46(10) 68.20(9) O(1)-Cd(1)-O(3)67.19(15) O(1)-Cd(1)-O(4)134.87(10) 132.15(11) 136.20(14) O(1)-Cd(1)-N(3)90.02(12) O(2)-Cd(1)-O(3)135.15(11) 133.63(14) 67.98(12) O(2)-Cd(1)-O(4)66.41(11) O(2)-Cd(1)-N(3)85.43(13) 136.67(15) O(3)-Cd(1)-O(4)156.56(11) 158.23(15) O(3)-Cd(1)-N(3)95.93(16) 80.21(13) 94.09(16) O(4)-Cd(1)-N(3)81.70(14) O(1)-Cu(1)-O(5)99.67(18) 78.70(13) O(1)-Cu(1)-N(1)90.59(15) 91.68(14) O(1)-Cu(1)-N(2)165.34(13) 170.44(16) O(2)-Cu(1)-N(1)168.94(13) 169.80(12) O(2)-Cu(1)-N(2)92.04(14) 92.07(14) O(1)-Cd(1)-N(6)96.86(12) O(1)-Cd(1)-N(3') 143.99(14) O(2)-Cd(1)-N(6)100.24(15) O(2)-Cd(1)-N(3')141.12(15) O(3)-Cd(1)-N(6)83.85(18) O(3)-Cd(1)-N(3')82.14(18) O(4)-Cd(1)-N(6)83.69(17) O(4)-Cd(1)-N(3')82.05(14) N(3)-Cd(1)-N(6)172.41(13) N(3)-Cd(1)-N(3')74.31(15)

 Table 3: Selected bond angles (°) of complexes 1 and 2.

N(3')-Cd(1)-N(6)	98.17(15)		
O(1)–Cu(1)–O(2)	80.15(13)		
O(2)–Cu(1)–O(5)	92.80(15)	—	
O(5)-Cu(1)-N(1)	94.72(16)	-	
O(2)–Cu(1)–N(2)	92.04(14)	-	
N(1)-Cu(1)-N(2)	95.65(15)	97.37(16)	
S(1)-Cd(1)-O(1)	-	101.08(11)	
S(1)-Cd(1)-O(2)	_	101.46(10)	
S(1)-Cd(1)-O(3)	_	85.74(9)	
S(1)-Cd(1)-O(4)	_	85.09(10)	
S(1)-Cd(1)-N(3)	-	106.13(13)	
O(1)-Cu(1)-N(3')		88.88(13)	
O(2)-Cu(1)-N(3')		89.83(15)	
N(1)-Cu(1)-N(3')		93.41(16)	
N(2)-Cu(1)-N(3')		93.63(14)	
O(5)-Cu(1)-N(2)	93.04(18)	—	

Symmetry transformation: '= 1-x, 1-y, 1-z.

Complex	D–H…A	D–H	Н…А	D…A	∠D–H…A
1					
	$N(1)-H(1)-O(6^{i})$	0.9800	2.0800	3.039(5)	167.00
	N(2)-H(2)-N(5)	0.9800	2.4800	3.182(6)	129.00
1	O(6)-H(6)-N(6)	0.8200	2.0200	2.831(5)	169.00
			C		
	O(5)-H(5C)-N(8)	0.88(9)	2.20(9)	2.926(8)	140(7)
	O(5)-H(5D)-O(6)	0.82(8)	2.22(10)	2.915(7)	143(10)
2	N(2)-H(2N)-O(5)	0.87(6)	2.16(6)	3.027(9)	171(5)

<b>Γable 4:</b> Hydrogen bond distances (	Å) and angles	(°) of complexes	1 and 2.
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Symmetry transformation: i = x, 1.5 - y, 0.5 + z.

**Table 5:** Geometric features (distances in Å and angles in °) of the  $C-H\cdots Cg$  interactions for complex 1 and 2.

Complex	C−H···Cg (Ring)	H···Cg (Å)	$C-H\cdots Cg(^{\circ})$	$C\cdots Cg(Å)$	Symmetry
1	C(22)-H(22A)····Cg(4)#	2.89	164	3.825(9)	x, 3/2-y, 1/2+z
2	C(24)-H(24B)····Cg(8)	2.85	125	3.499(11)	<i>x, y, z</i>

Symmetry transformation: = x, 1.5-y, 0.5+z. Cg(4) = centre of gravity of the ring [C(2)-C(3)-C(4)-C(5)-C(6)-C(7)] and Cg(8) = centre of gravity of the ring [C(15)-C(16)-C(17)-C(18)-C(19)-C(20)].

Cg(I)···Cg(J)	Cg…Cg (Å)	α	Cg(I)…Prep (Å)	Cg(J)…Prep (Å)
Cg(8)···Cg(7) <sup>i</sup>	3.735(3)	11.1(3)	3.467(2)	3.468(2)

**Table 6:** Geometric parameters (Å) for the  $\pi \cdots \pi$  interactions for the complex **2.** 

Symmetry transformations: i= 1-x, 1-y, 1-z; a= dihedral angle between ring I and ring J,  $Cg(I) \cdots$  Perp. = perpendicular distance of Cg(I) on ring J,  $Cg(J) \cdots$  Perp. = perpendicular distance of Cg(J) on ring I. Cg(7) = centre of gravity of the ring [C(2)-C(3)-C(4)-C(5)-C(6)-C(7)] and Cg(8) = centre of gravity of the ring [C(15)-C(16)-C(17)-C(18)-C(19)-C(20)] for the complex **2**.

**Table 7:** Kinetic studies for the degradation of methylene blue by some previously reported compounds and the present complexes.

Complex	Degradation time (min)	Degradation percentage	Refs.
$[Zn(\mu_{1,1}-N_3)_2\{Zn(L^a)(N_3)\}_2]$	18	90%	[30]
$[Zn(\mu_{-1,1}-N_3)_2{Zn(L^a)(N_3)}_2] \cdot 0.5CH_3OH$	60	90%	[49]
$[\{CdL^{a}(\mu_{-1,1}-N_{3})\}_{2}Cd(\mu_{-1,1}-N_{3})_{2}\cdot 1.76CH_{3}OH]_{n}$	40	99%	[66]
$[Zn(DCTP)(L^b)]_n$	120	96.9%	[67]
$[Zn(L^c)(DCTP)]_n$	120	81.4%	[67]
$[Cd_2(L^d)_2(hfpd)]_n$	180	94.1%	[68]

$[Zn(L^d)(tbta)]_n$	180	93.9%	[68]
$[Cd_2(L^e)_2(\mu_{-1,3}\text{-}SCN)_2(CH_3OH)_2]$	40	85%	[69]
$[Co(L^{f})(tbta)]\cdot H_{2}O]_{n}$	135	82.8%	[70]
$[Co(L^d)(nip)]_n$	135	84.7%	[70]
[Fe(L <sup>g</sup> )]	75	96.5%	[71]
${[Cd_{3}L^{h}_{2}(H_{2}O)_{5}] \cdot H_{2}O}_{n}$	180	88.7%	[72]
${[Cd_{3}L^{h}_{2}(hbmb)(H_{2}O)_{2}] \cdot 2.5H_{2}O}_{n}$	180	65.9%	[72]
$\{[Cd_3L^h_2(btbb)(H_2O)_2]\cdot 2EtOH\cdot 1.5H_2O\}_n$	180	85.8%	[72]
${[Cd_6L^h_4(bipy)_2(H_2O)_6] \cdot 3H_2O\}_n}$	180	63.8%	[72]
$[(N_3)L^iCo^{III}L^iCo^{III}L^i]$	90	55%	[73]
$(\mu_{-1,1}-N_3)_2[(H_2O)Cu(L^R)Cd(N_3)]_2\cdot 2CH_3OH$	18	62%	Complex 1
$(\mu_{-1,1}-NCS)_2[CuL^RCd(SCN)]_2\cdot 2CH_3OH$	18	32%	Complex 2

 $L^{a}$ =[2-((3-(dimethylamino)propylimino)methyl)-6-ethoxyphenol];  $L^{b}$ =1,3-bis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene;  $L^{c}$ =1,4-bis(benzimidazol-1-ylmethyl)benzene];  $L^{d}$ =1,5-bis(2-methylbenzimidazol-1-yl)pentane;  $L^{e}$ =2-(3-(methylamino)propyliminomethyl)-4,6-dichlorophenol;  $L^{f}$ =1,5-bis(benzimidazolyl)pentane;  $L^{g}$ =porphyrin 5-(2-(N-benzoyl-5-carboxyl)-

1-amino)-10,15,20-triphenyl porphyrin;  $L^{h}=3,4$ -bi(4-carboxyphenyl)-benzoic acid;  $L^{i}=2$ -((1-hydroxybutan-2-ylimino)methyl)-4-bromophenol;  $L^{i}=2$ -amino-1-butanol

H<sub>2</sub>DCTP=2,5-ichloroterephthalic acid; H<sub>4</sub>hfpd = 4,40-(hexafluoroisopropylidene)diphthalic acid, H<sub>2</sub>tbta=tetrabromoterephthalic acid. H<sub>2</sub>tbta=tetrabromoterephthalic acid; H<sub>2</sub>nip=5nitroisophthalicacid; hbmb=1,1'-(1,6-hexane)bis(2-methylbenzimidazole), btbb=1,4-bis(2-(4thiazolyl)benzimidazole-1-ylmethyl)benzene, 4,4'-bipy=4,4'-bipyridine.



Two new tetra-nuclear copper(II)/cadmium(II) complexes with CuO<sub>2</sub>Cd cores have been synthesized and characterized. Their ability to act as photo-catalyst in degrading methylene blue has been explored. The difference in their photocatalytic performance may be correlated with their structures.

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