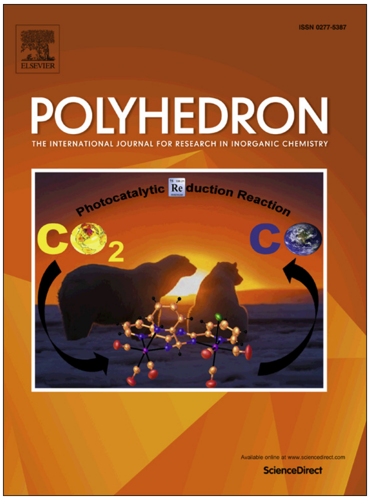

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Photocatalytic activity of a dinuclear thiocyanate bridged cadmium(II) Schiff base complex for the degradation of organic dye in visible light

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Abstract

A dinuclear centrosymmetric cadmium(II) Schiff base complex, $[Cd_2(L)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$, {HL = 2-(3-(methylamino)propyliminomethyl)-4,6-dichlorophenol} has been synthesized and characterized. X-ray crystallography has confirmed its structure. The complex crystallizes in monoclinic space group *C2/c* with cell dimensions, a = 26.161(1) Å, b = 8.9412(3) Å, c = 18.9687(8) Å, β = 129.202(1)°. Extended supra-molecular assemblies were generated through weak non-covalent interactions. The application of the complex as a photocatalyst for the decomposition of organic dye in visible light has been explored.

Keywords: Cadmium(II); Schiff base; End-to-end thiocyanate; Crystal structure; Photoluminescence; Photocatalyst.

1. Introduction

The environmental contamination caused by organic pollutants is a great problem nowadays. The synthesis and characterization of efficient, cheap and environment friendly photocatalysts is, therefore, a hot topic due to their applications to purify water and air by thoroughly decomposing organic compounds [1-4]. Methylene blue (MB) is one of the well-known dyes widely used in several industries and has caused serious pollution. A new emerging application of cadmium(II) complexes as photocatalyst for the degradation of organic dyes in UV light was established in recent years [5,6]. However, there is no report of the application of cadmium(II) Schiff base complexes in photocatalysis using visible light.

In the present work, a tridentate N_2O donor salicylaldimine Schiff base has been used to prepare a dinuclear cadmium(II) complex. The complex has been shown to have good photocatalytic activity to decompose methylene blue in visible light. Herein, we would like to report the synthesis characterization, self assembly and photocatalytic activity of a thiocyanate bridged dinuclear cadmium(II) Schiff base complex.

2. Experimental

Methylene blue was purchased from Loba Chemie and used without further purification. All other starting materials and solvents were commercially available, reagent grade, and used as purchased from Sigma-Aldrich without further purification. **Caution!!!** perchlorate salts are potentially explosive. Although no problem was encountered in the present study, only small amounts of the materials should be prepared and they must be handled with care.

2.1. Preparation

2.1.1. Synthesis of $[Cd_2(L)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$

A methanol solution of 3,5-dichlorosalicylaldehyde (1 mmol, 0.191 g) and N-methyl-1,3-diaminopropane (1 mmol, 0.103 mL) was refluxed for 1 h to prepare a tridentate N_2O donor Schiff base, {2-(3-(methylamino)propyliminomethyl)-4,6-dichlorophenol} (HL). The Schiff base was not isolated and was used directly for the preparation of complex. A methanol solution of cadmium(II) perchlorate hexahydrate (1 mmol, 0.419 g) was added to the methanol solution of Schiff base and refluxed for 1 h. A methanol solution of sodium thiocyanate (1 mmol, 0.081 g) was then added to it and refluxed further for ca. 1 h. Single crystals, suitable for X-ray diffraction, were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.69 g (73%). Anal. Calc. for $C_{26}H_{34}Cd_2Cl_4N_6O_4S_2$ (FW 925.31): C, 33.75; H, 3.70; N, 9.08 Found: C, 33.7; H, 3.6; N, 9.1 %. IR (KBr, cm^{-1}): 1631 ($\upsilon_{C=N}$), 2082 (υ_{SCN}), 3280 (υ_{NH}), 3444 (υ_{OH}), 3001-2850 (υ_{CH}). UV-Vis, λ_{max} (nm), (ε_{max} (L mol^{-1} cm^{-1})) (DMSO), 261 (1.2×10^4), 337 (6.4×10^3), 428 (2.2×10^3).

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a PerkinElmer 240C elemental analyzer. Infrared spectrum in KBr (4000-400 cm^{-1}) was recorded using a PerkinElmer Spectrum Two FTIR spectrophotometer. Electronic spectrum in DMSO (800-200 nm) was recorded on a PerkinElmer Lambda 35 UV-Vis spectrophotometer. Fluorescence spectrum in DMSO was obtained on a Hitachi F-7000 Fluorescence spectrophotometer at room temperature. The powder XRD data were collected on a Bruker D8 Advance X-ray diffractometer using Cu K_α radiation (λ = 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2θ range of 5-50° using 1-D Lynxeye detector at ambient conditions. Lifetime measurement was recorded using Hamamatsu MCP photomultiplier (R3809) and was analyzed by using IBHDAS6 software.

2.3. X-ray crystallography

A suitable single crystal of the complex was used for data collection using a Bruker D8 QUEST area detector diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 100 K. The molecular structure was solved by direct method and refined by full-matrix least squares on F^2 using SHELXL-2014 [7]. X-ray intensity data were measured. The frames were integrated with the Bruker SAINT Software package using a wide-frame algorithm. Non hydrogen atoms were refined anisotropically. Hydrogen atoms attached to oxygen and nitrogen were located by difference Fourier maps and were kept at fixed positions. Others hydrogen atoms were placed in their geometrically idealised positions and constrained to ride on their parent atoms. Numerical and/or multi-scan absorption corrections were applied to the data using the program SADABS [8]. The crystallographic and refinement data of the complex are summarized in Table 1.

2.4. Hirshfeld Analysis

Hirshfeld surfaces [9-11] and the associated two-dimensional (2D) fingerprint [12-14] plots were calculated using Crystal Explorer, [15] with bond lengths to hydrogen atoms set to standard values [16]. For each point on the Hirshfeld isosurface, two distances, d_e (the distance from the point to the nearest nucleus external to the surface) and d_i (the distance to the nearest nucleus internal to the surface), are defined. The normalized contact distance (d_{norm}) based on d_e and d_i is given by

$$d_{norm} = \frac{(\mathrm{d_i} - \mathrm{r_i^{vdw}})}{\mathrm{r_i^{vdw}}} + \frac{(\mathrm{d_e} - \mathrm{r_e^{vdw}})}{\mathrm{r_e^{vdw}}}$$

where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms. The value of d_{norm} is negative or positive depending on intermolecular contacts being shorter or longer than the van der Waals separations. The parameter d_{norm} displays a surface with a red-white-blue color scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique [17] and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

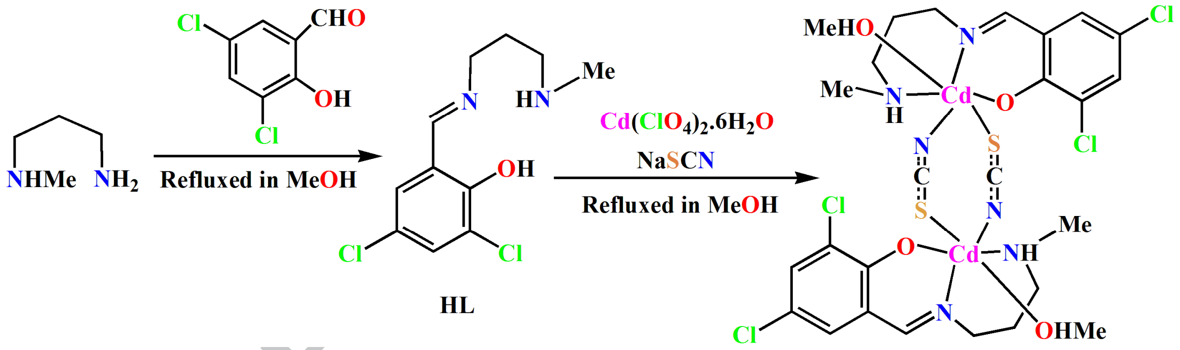
2.5. Photocatalytic Measurement

A photocatalytic experiment in aqueous solution was carried out in a typical process [5,18]. A 36 W Hg vapour lamp was used as the visible light source and the catalytic degradation was carried out with 100 mL of Methylene Blue solution (10 mg L^{-1}) with the complex using as catalyst. The mixture was stirred for 10 min in a dark environment to get a balance between adsorption and desorption. Then, the solution was stirred constantly. A 4 mL sample was taken from the reaction system in an interval of 5 min and the supernatant liquid obtained by centrifugation was used for collecting the UV-Visible spectrum. The characteristic peak for methylene blue at $\lambda = 607$ nm was employed to monitor the photocatalytic degradation.

3. Results and discussions

3.1. Synthesis

The tridentate Schiff base ligand (HL) was prepared by the condensation of N-methyl-1,3-diaminopropane with 3,5-dichlorosalicylaldehyde [19,20]. It was not isolated and used directly for the synthesis of the complex. The methanol solution of HL on reaction with cadmium(II) perchlorate hexahydrate followed by the addition of sodium thiocyanate under reflux produced the dinuclear complex, $[Cd_2(L)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$. Formation of the complex is shown in Scheme 1.



Scheme 1: Schematic representation of the preparation of the complex.

3.2. Description of structure

3.2.1. $[Cd_2(L)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$

The end-to-end thiocyanate bridged centrosymmetric dinuclear complex crystallizes in monoclinic space group, *C2/c*. A perspective view of the complex with selective atom-numbering scheme is shown in Figure 1. Selected bond lengths and angles are gathered in Tables

2 and 3, respectively. The X-ray crystal structure analysis reveals that the hexa-coordinated cadmium(II) is meridionally coordinated by one amine nitrogen atom, N(1), one imine nitrogen atom, N(5), one phenoxo oxygen atom, O(7), of the deprotonated tridentate Schiff base ligand (L^-), one nitrogen atom, N(1'), from a coordinated thiocyanate and one oxygen atom, O(1S) from a solvent methanol. An sulfur atom S(3')^a from a symmetry related {Symmetry transformation ^{a} = 1-x,1-y,1-z} bridging thiocyanate occupied sixth coordination site of each cadmium(II) to complete its octahedral geometry.

The bridging thiocyanates are almost linear with the value of S-C-N angle being 178.3°(2). S-Cd-N Angles (°), Cd-S and Cd-N distances (Å) of end-to-end bridging thiocyanates are 95.44(5)°, 2.7857(6) and 2.266(2)(Å) respectively and these values are more or less similar with other related cadmium(II) Schiff base complexes [21-28] (Table 4). In the dinuclear moiety, cadmium(II)···cadmium(II) distance is found to be 5.5736(5) Å. Cd(II)-O and Cd(II)-N distances fall within the range 2.325-2.337 Å and 2.222-2.345 Å respectively, as were also observed in similar systems [29-31]. The puckering parameters of the saturated six membered chelate ring, Cd(1)-N(1)-C(2)-C(3)-C(4)-N(5) are $q = 0.579(2)$ Å, $\theta = 20.7(2)°$ $\varphi = 160.6(6)°$ indicating an intermediate conformation between chair and half-chair [32].

There are significant intermolecular hydrogen bonding interactions in the solid state structure of the complex (Table 5). The hydrogen atom, H(1S), attached to the methanol oxygen atom, O(1S), is participated in hydrogen bonding interaction with the symmetry related phenoxo oxygen atom, O(7)^b {symmetry transformation ^{b} = 1-x,y,1/2-z}, to form a supramolecular chain, as shown in Figure 2. It also shows intermolecular C-H···π interaction with C···centroid distance being 3.643(2) Å. The hydrogen atom, H(4B), attached to C(4) is involved in C-H···π interaction with the symmetry related (1-x,y,1/2-z) phenyl ring, C(7)-C(8)-C(9)-C(10)-C(11)-C(12), producing a supramolecular chain as illustrated in Figure 3. There is no other significant supramolecular interaction present in the complex.

3.3. IR, electronic and fluorescence spectra

In the IR spectrum of the complex, a band corresponding to the azomethine (C=N) stretching vibration appears at 1611 cm^{-1} [29-31]. Sharp band corresponding to thiocyanate stretching vibration appears at 2082 cm^{-1} [33,34]. Broad bands in the range of 3001-2850 cm^{-1} are assigned as alkyl C-H bond stretching vibrations [35,36]. IR spectrum of the complex exhibits a sharp peak at 3280 cm^{-1}, which may attributed to the N-H stretching vibration [37,38]. Broad band due to O-H stretching vibration is customarily noticed around 3444 cm^{-1} in IR spectrum of the complex [39-41].

Electronic spectrum of the complex exhibits three bands of which the band at 261 nm may be attributed to ligand based π-π^* transition. On the other hand, bands at 337 and 428 nm may be assigned as n-π^* transitions [34,42,43]. The complex in DMSO, on exciting at 337 nm, exhibits luminescence at 395 nm. This may be assigned as intra-ligand (π-π*) fluorescence [35]. The lifetime of the excited state is 18.20 ns at room temperature (Table 6) and relative fluorescence quantum yield [42,43] for the complex is found to be 0.1082.

3.4. Photocatalytic activity

The distinct performance on the photocatalytic degradation of methylene blue (MB), an organic dye, was discovered in the complex in an aqueous solution under visible light irradiation. As shown in Figure 5, the residual concentration of the dye in an aqueous solution gradually decreased as a function of the increasing reaction time, indicating that the complex can degrade the organic dye. With increase in complex concentration, the rate of degradation was also increased (Figure 5). Again, as shown in Figure 6, it is shown that the intensity of the characteristic absorption peak of MB decreased with the increase of irradiation time in the degradation process.

The complex is highly efficient for the degradation of MB and the ratio of the degradation reaches about 64% using only 1 mg of the complex (Figure 5, curve **III**). Use of 2 and 3 mg of the complex, the ratio of the degradation reaches about 77 and 81%, respectively (Figure 5, curves **IV**,**V**). The ratio of the degradation reaches about 85% using 4 mg of the complex (Figure 5, curve **VI**). The reaction depends on 1st Order Kinetics and the details data on average rate constants for this degradation are given in Table 7. To prove the high photocatalytic efficiency of the complex to MB, comparative experiments without catalyst under visible light irradiation were performed, which showed only very little decomposition. We had also studied the photocatalytic activity of cadmium(II) perchlorate hexahydrate to MB under similar conditions (Figure 5, curve **II**), which showed that the rate of degradation was still very slow (only 13% using 4 mg of bare cadmium(II).

3.5. Powder X-ray diffraction

The experimental powder XRD patterns of the bulk product is in fine agreement with the simulated XRD patterns obtained from single crystal X-ray diffraction data (cif), confirming the purity of the bulk sample (Figure 7).

3.6. Hirshfeld surface analysis

The Hirshfeld surfaces of complex, mapped over d_{norm}, shape index and curvedness, is illustrated in Figure 8. The intermolecular interactions appear as distinct spikes in the 2D fingerprint plot (Figure 9). Details of Hirshfeld surfaces analysis are given in Electronic Supplementary Information (ESI).

4. Conclusion

In conclusion, a dinuclear thiocyanate bridged cadmium(II) Schiff base complex has been synthesized and characterized by elemental, spectral and single crystal X-ray diffraction analysis. The complex exhibits efficient photocatalytic ability in the decomposition of methylene blue under visible light. This is the first example of any X-ray characterized cadmium(II) Schiff base complex with photocatalytic application. These results provide an opening into a promising new field of efficient photocatalytic degradation of organic pollutant. We are now working hard to get better yield of the reaction and to synthesize other photocatalytic cadmium(II) complexes.

Acknowledgement

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Appendix A. Supplementary data

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC No 1062962. The data can be obtained free of charge from CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1: Crystal data and refinement details of the complex

Formula	$C_{26}H_{34}Cd_2Cl_4N_6O_4S_2$
Formula Weight	925.31
Temperature (K)	100
Crystal system	Monoclinic
Space group	*C2/c*
a(Å)	26.161(1)
b(Å)	8.9412(3)
c(Å)	18.969(1)
α(°)	(90)
β(°)	129.202(1)
γ(°)	(90)
Z	4
d_{calc} (g cm^{-3})	1.788
μ (mm^{-1})	1.711
F(000)	1840
Total Reflections	17214
Unique Reflections	3956
Observed data [I >2 σ (I)]	3539
No. of parameters	209
R(int)	0.033
R1, wR2 (all data)	0.0251,0.0441
R1, wR2 [I > 2 σ (I)]	0.01950.0425

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

Cd(1)–O(1S)	2.345(1)
Cd(1)–O(7)	2.222(2)
Cd(1)–N(1)	2.337(3)
Cd(1)–N(5)	2.325(2)
Cd(1)–N(1')	2.266(2)
Cd(1)–S(3')^{a}	2.786(1)

Symmetry transformation ^{a} =1-x,1-y,1-z.

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

O(1S)–Cd(1)–O(7)	97.78(6)
O(1S)–Cd(1)–N(1)	88.30(7)
O(1S)–Cd(1)–N(5)	89.59(5)
O(7)–Cd(1)–N(1)	166.82(5)
O(7)–Cd(1)–N(5)	78.83(6)
N(1)–Cd(1)–N(5)	89.58(7)
O(1S)–Cd(1)–N(1')	87.48(5)
S(3')^{a}–Cd(1)–O(1S)	173.39(6)
O(7)–Cd(1)–N(1')	94.11(7)
S(3')^{a}–Cd(1)–O(7)	87.95(4)
N(1)–Cd(1)–N(1')	97.85(8)
S(3')^{a}–Cd(1)–N(1)	85.42(4)
N(1')–Cd(1)–N(5)	171.92(8)
S(3')^{a}–Cd(1)–N(1')	95.44(4)
S(3')^{a}–Cd(1)–N(5)	88.28(4)

Symmetry transformation ^{a} =1-x,1-y,1-z.

Table 4: S-Cd-N Angle(°), Cd-S and Cd-N distances of bis-EE$(NCS)_2$ bridging moieties of some selected cadmium(II) Schiff base complexes

Complex	CSD Ref code	S-Cd-N Angle(°)	Cd-S (Å)	Cd-N	Centro-symmetric	Ref.
$[Cd_2(L)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$	-	95.44(5)	2.7857(6)	2.266(2)	Yes	This work
$[Cd_2(L^1)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$	UNAMIH	91.04(7)	2.7873(9)	2.228(2)	Yes	21
$[Cd(NCS)(\mu\text{-}1,3\text{-}SCN)(L^2)]_2$	FIBKUX	92.4(1)	2.616(8)	2.315(8)	Yes	22
$[Cd_2(L^3)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$	SASXAM	91.84(6)	2.7527(8)	2.244(2)	Yes	23
$[Cd_2(L^4)_2(NCS)_2(\mu\text{-}1,3\text{-}NCS)_2]$	IJOLOJ	90.77(5)	2.6679(6)	2.292(2)	Yes	24
$[Cd_2(L^4)_2(NCS)_2(\mu\text{-}1,3\text{-}NCS)_2]$	IJOLOJ01	91.14(5)	2.616(8)	2.315(8)	Yes	25
$[Cd_2(L^5)_2(NCS)_2(\mu\text{-}1,3\text{-}NCS)_2]$	OPUJUF	91.1(2)	2.849(2)	2.204(6)	Yes	26
$[Cd_2(L^6)_2(NCS)_2(\mu\text{-}1,3\text{-}NCS)_2]$	CESTOK	85.89(9)	*2.828(1)*	2.272(3)	Yes	27
$[Cd_2(L^7)(\mu\text{-}1,3\text{-}NCS)_2(NCS)_2]_n$	XIWMOG	93.8(1)	2.616(1)	2.387(5)	Yes	28

HL = 2-(3-(methylamino)propyliminomethyl)-4,6-dichlorophenol

HL^1 = 2-(2-(dimethylamino)ethyliminomethyl)-4-chlorophenol

L^2 = N,N-diethyl-N′-(1-pyridin-2-yl-ethylidene)-ethane-1,2-diamine

HL^3 = 4-nitro-2-(2-(dimethylamino)ethyliminomethyl)phenol

L^4 = (2-morpholino-N-(1-(2-pyridin-2-yl)ethylidene)ethanamine

L^5 = N′-(pyridine-2-yl)benzylidine)ethane-1,2-diamine

L^6 = N,N-dimethyl- N′-(1-pyridylmethylidene)-propane-1,3-diamine

L^7 = N-(1-pyridin-2-ylformylidene)-N-[2-(4-{2-[(1-pyridin-2ylformylidene) amino]ethyl}piperazin-1-yl)ethyl]-amine

Table 5: Hydrogen bond distances (Å) and angles (°) of complex.

D–H···A	D–H	H···A	D···A	∠D–H···A
O(1S)–H(1S)···O(7)^b	0.77	1.84	2.600(2)	175(4)

D, donor; H, hydrogen; A, acceptor. Symmetry transformation ^{b} = 1-x,y,1/2-z.

Table 6: The details data of the photoluminescence and time-resolved photoluminescence decay of complex.

λ_{ex}(nm)	λ_{em}(nm)	A_1(%)	τ_1(ns)	A_2(%)	τ_2(ns)	τ_{av}(ns)	χ^2
337	394	40.25	2.95	59.75	19.74	18.20	1.1416

Table 7: The details data of the rate constants for the degradation of organic dye.

Amount of complex (mg) taken in 10 mg L^{-1} aqueous solution of MB	Average rate constant
1	7.01×10^{-4}
2	8.87×10^{-4}
3	8.90×10^{-4}
4	9.29×10^{-4}

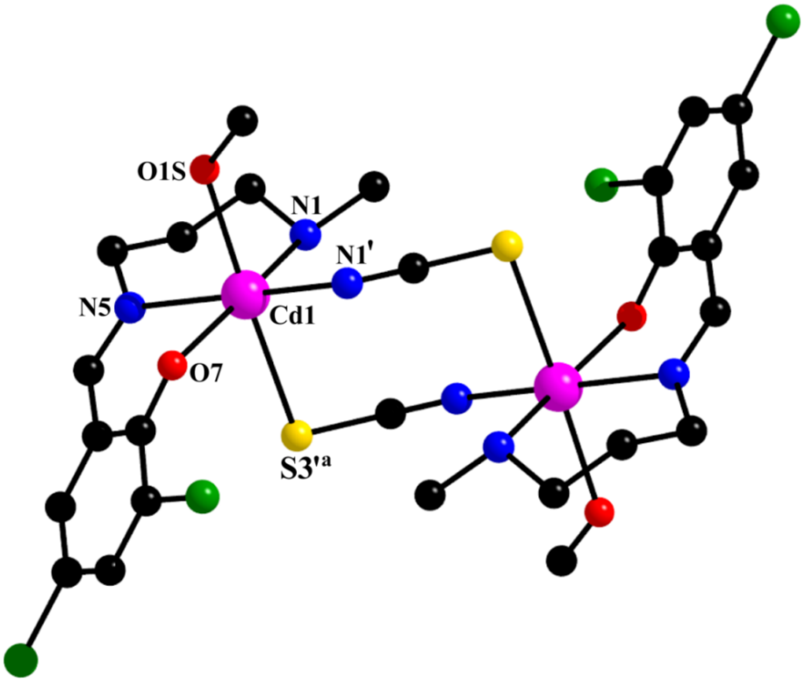


Figure 1: Perspective view of complex with selective atom-numbering scheme. Hydrogen atoms are omitted for clarity.

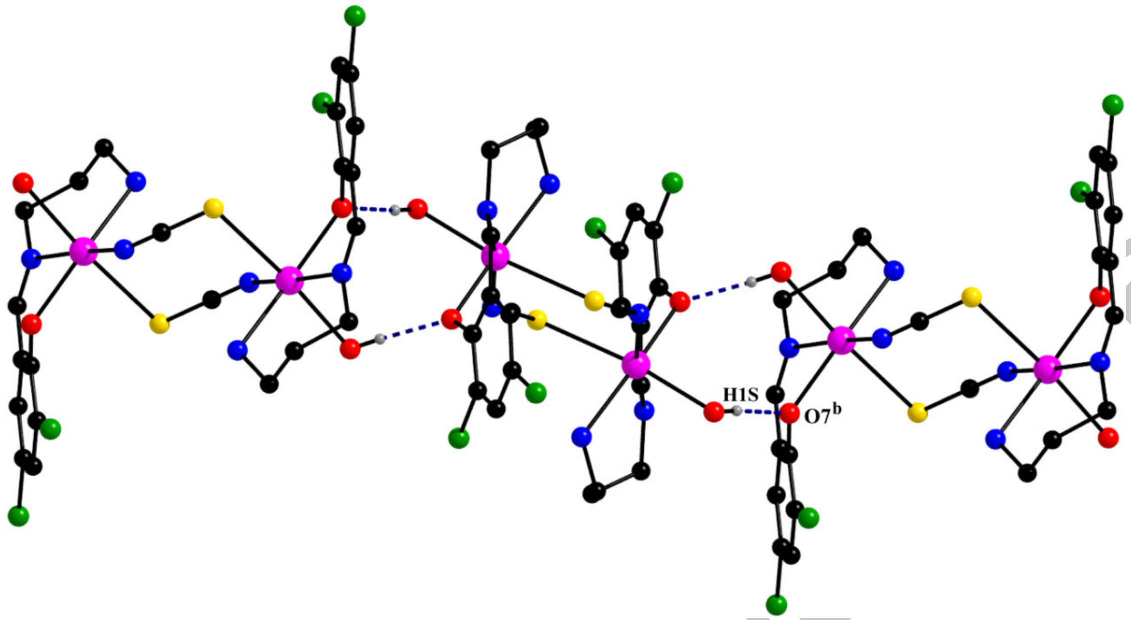


Figure 2: Supramolecular chain in complex, generated through hydrogen bonding interactions. Only relevant atoms are shown. Symmetry transformation ^{b} = 1-x,y,1/2-z.

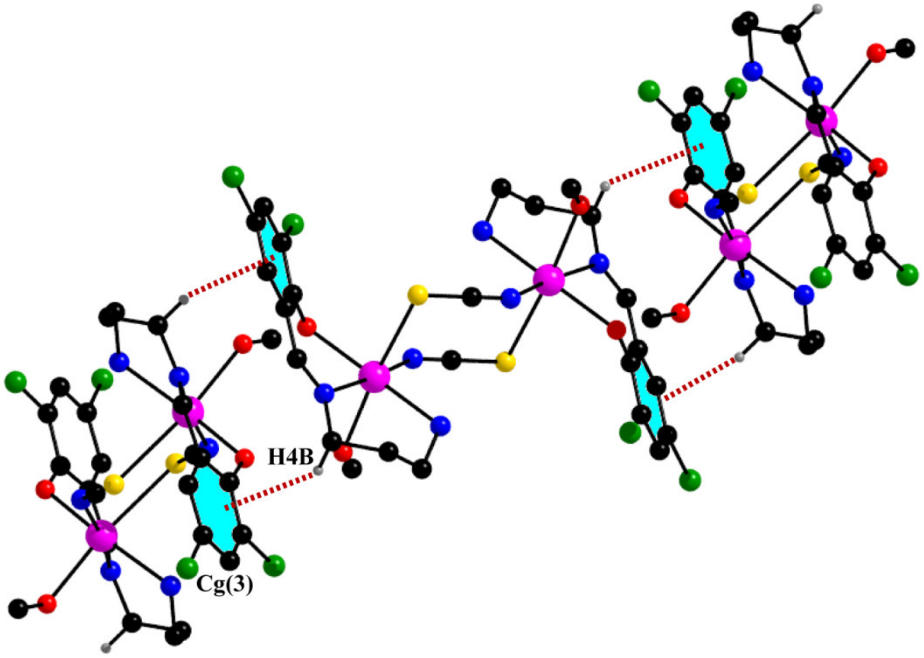


Figure 3: Supramolecular chain in complex, created through C-H···π interactions. Only relevant atoms are shown.

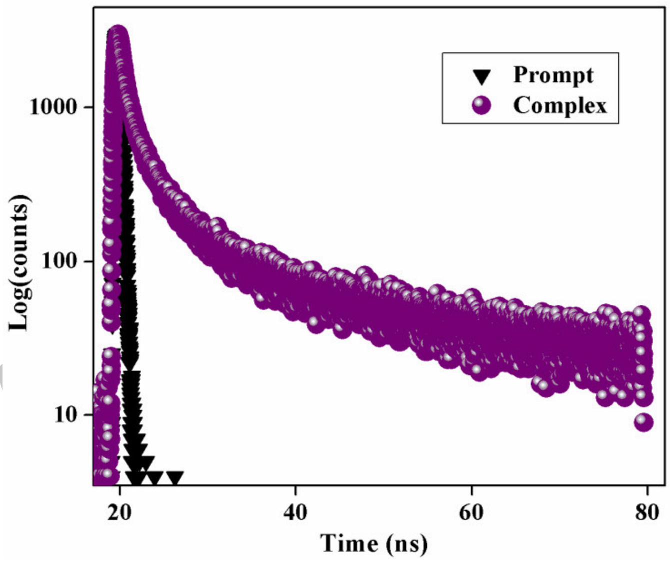


Figure 4: Lifetime decay profile of complex.

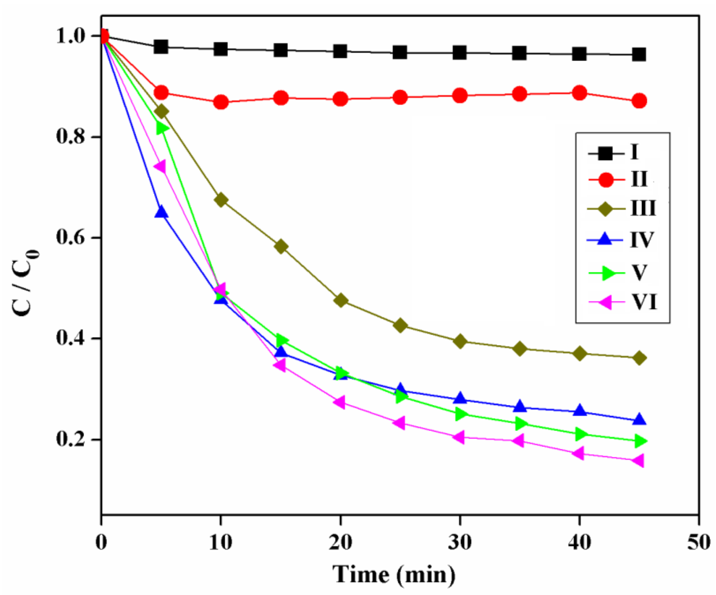


Figure 5: Changes in concentration of MB as a function of reaction time in the presence of different amount of complex (curves **III-VI**), without complex (curve **I**) and with Cadmium-salt (curve **II**) under visible light irradiation.

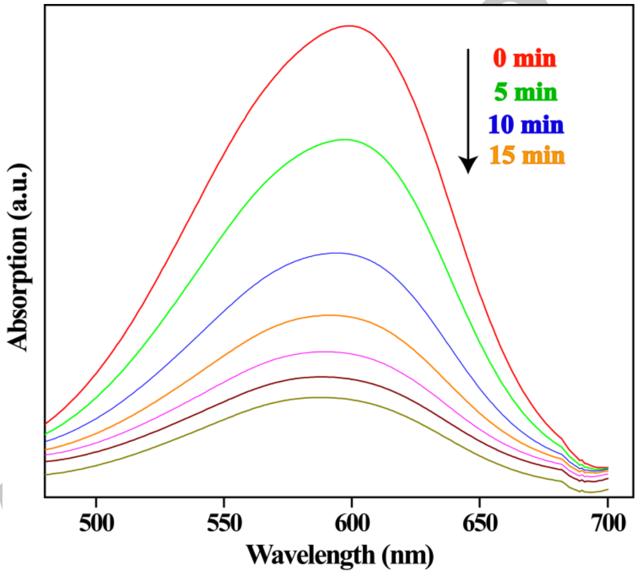


Figure 6: UV-VIS absorption spectra of MB solution with the complex (sample taken = 4 mg), used as a catalyst.

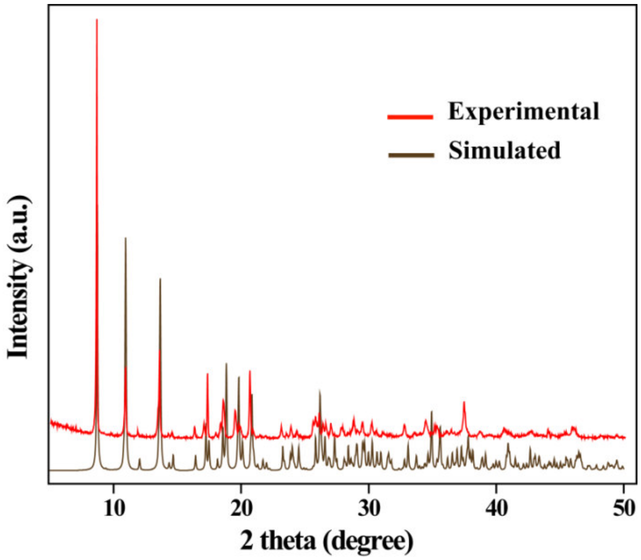


Figure 7: Experimental and simulated powder XRD patterns of complex

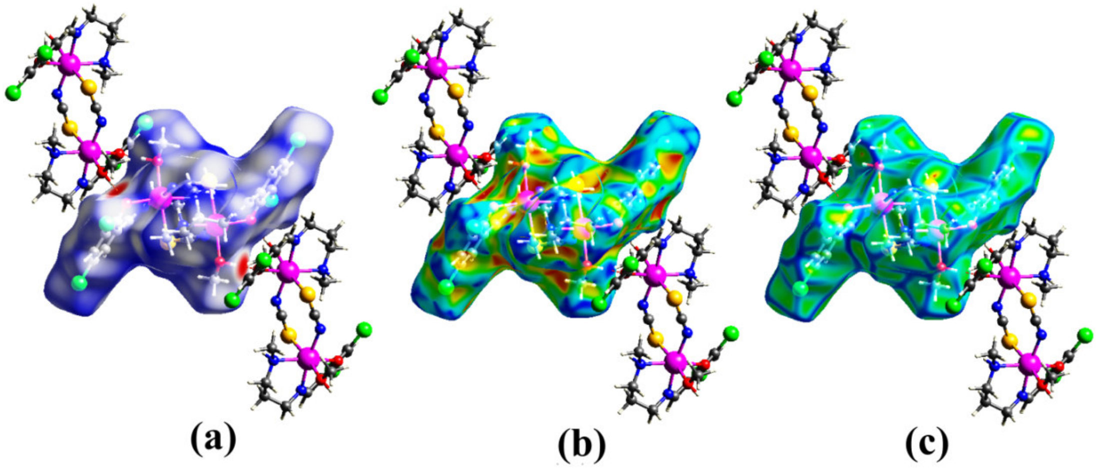
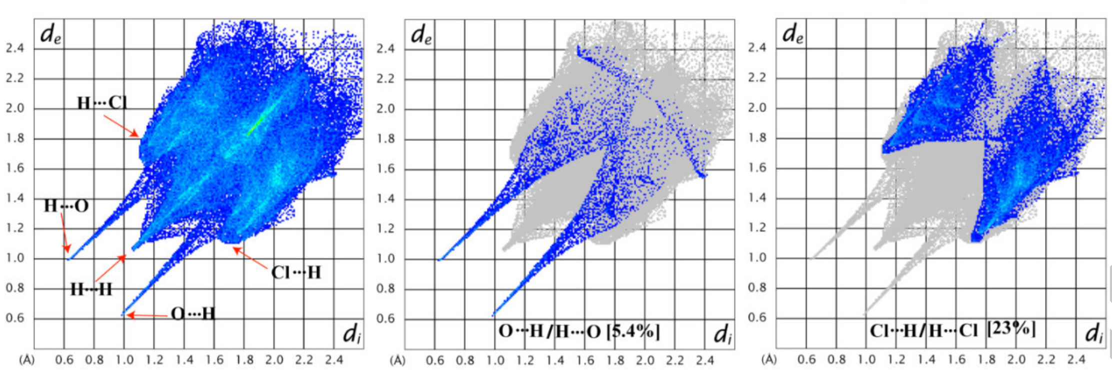


Figure 8: Hirshfeld surfaces mapped over d_{norm} (a), shape index (b) and curvedness (c) of the complex.



(a) **(b)** **(c)**

Figure 9: Fingerprint plots of the complex: full (a) and resolved into O···H/H···O (b) and Cl···H/H···Cl (c) contacts showing the percentages of contacts contributed to the total Hirshfeld surface area of the complex.

Graphical Abstract (synopsis)

Photocatalytic activity of a dinuclear thiocyanate bridged cadmium(II) Schiff base complex for the degradation of organic dye in visible light

Sumit Roy, Klaus Harms, Shouvik Chattopadhyay

One new photo-luminescent dinuclear cadmium(II) complex with salicylaldimine Schiff base ligand and thiocyanate as co-ligand has been synthesized and characterized. The structure has been confirmed by single crystal X-ray analysis. Under visible light irradiation, the complex can acts as a highly efficient photocatalyst for the decomposition of organic dye.