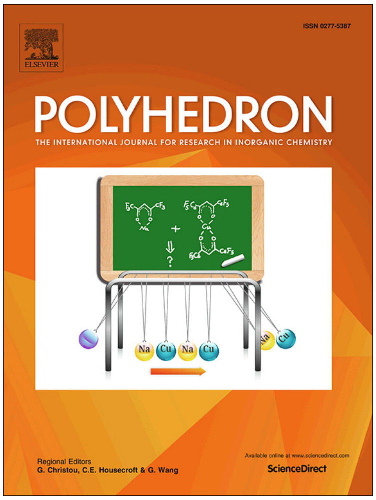


Schiff base and azido coordinated di-/poly-nuclear cadmium(II) complexes: Crystal structure, photocatalytic degradation of methylene blue and thermal analysis

Soumen Manna, Ennio Zangrando, Subal Chandra Manna

PII: S0277-5387(19)30741-7
DOI: https://doi.org/10.1016/j.poly.2019.114296
Reference: POLY 114296

To appear in: *Polyhedron*

Received Date: 30 August 2019
Revised Date: 15 November 2019
Accepted Date: 16 November 2019

Please cite this article as: S. Manna, E. Zangrando, S.C. Manna, Schiff base and azido coordinated di-/poly-nuclear cadmium(II) complexes: Crystal structure, photocatalytic degradation of methylene blue and thermal analysis, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.114296

Schiff base and azido coordinated di-/poly-nuclear cadmium(II) complexes: Crystal structure, photocatalytic degradation of methylene blue and thermal analysis

Soumen Manna,[a] Ennio Zangrando,[b] Subal Chandra Manna[a,]*

[a]*Department of Chemistry, Vidyasagar University, Midnapore 721102, West Bengal, India, E-mail: scmanna@mail.vidyasagar.ac.in, Fax: (91) (03222) 275329.*

[b]*Department of Chemical andPharmaceutical Sciences, University of Trieste, 34127 Trieste, Italy.*

Abstract

Two Schiff base coordinated cadmium(II) complexes, namely $[Cd(H_4L^1)(N_3)_2]_n$(**1**)and $[Cd_2(L^2)(N_3)_2]\cdot(H_2O)$ (**2**) (where H_4L^1=2-((2-hydroxy-3-methoxybenzylidene)amino)-2-(hydroxymethyl)-propane-1,3-diol; andH_2L^2 = bis((3-methoxysalicylidene)ethyl)ethylamine), were synthesized and characterized by X-ray single crystal diffraction. Both the complexes **1** and **2** crystallize in monoclinic system with space group $P\ 2_1/n$. Complex **1** is a 1D coordination polymer where $Cd(H_4L^1)$species are doubly connected by bridging μ-1,1 azide anions. Complex **2** is a discrete dinuclear compound where the double deprotonatedSchiff base $(L^2)^{2-}$ acts as a two compartmental ligandcoordinating two cadmium atoms. Photocatalytic activity of the complexes has been studied using UV-vis absorption spectroscopic technique and the results show that both the complexes are active for photocatalytic degradation of methylene blue (MB) in presence of UV light, and within180 min MB decomposed by 37.64% and 32.60% in presence of complexes **1** and **2**, respectively.

Keywords: Cadmium(II); Schiff base; Coordination polymer; Crystal structure; Photocatalyst

1. *Introduction*

The design and synthesis of coordination compounds of group 12 metal complexes are of great interest because of their functional behavior, due to their wide varieties of structures [1-2]and potential application in the area of material science [3-4]. In addition, these coordination compounds are well known in the literature for their interesting photophysical and photochemical properties which allow their potential use as luminescent probes, light emitting diodes and photovoltaic devices [5].For these purposes Schiff bases with different polydentate coreare potential ligands for the synthesis of cadmium(II) coordination compounds, andthe combined use of chelating Schiff base and linear bridging ligands is an efficient strategy for the design of polynuclear cadmium(II) species [6].

Removal of highly toxic organic pollutants from the wastewater is an important area of current research [7]. Organic dyes in the industrial waste water are very toxic since these pollutants remain in water for long time. Photocatalytic degradation of organic dye is a useful technique for the treatment of industrial wastewater. TiO_2 is well known photocatalyst for the degradation of organic dye in presence of UV-visible light. However, post separation of TiO_2catalyst is very difficult after treatment of wastewater, causing limitation of theuse of TiO_2 as catalyst [8]. Recently coordination compounds have attracted great interestfor the study of photocatalytic degradation of organic dyes in water and still represents a big challenge [9-10]. Literature survey reveals that Schiff base coordinated cadmium(II) species show photocatalytic activity for the degradation of organic dyes [6].

In the present contribution we have used two Schiff bases, namely2-((2-hydroxy-3-methoxybenzylidene)amino)-2-(hydroxymethyl)-propane-1,3-diol (H_4L^1) and bis((3-methoxysalicylidene)ethyl)ethylamine) (H_2L^2), in combination with azide ligands to synthesize two cadmium complexes, $[Cd(H_4L^1)(N_3)_2]_n$ (**1**) and $[Cd_2(L^2)(N_3)_2]\cdot(H_2O)$ (**2**). Both the compounds **1** and **2** are active for photocatalytic degradation of methylene blue in presence of visible light.

2. Experimental

2.1. Materials and physical measurements

Tris(2-aminoethyl)aminewas purchased from the Sigma-Aldrich and used as received. All other chemicals were of AR grade, and the reactions were performed under aerobic conditions. The solvents used for spectroscopic studies were purified and dried by standard procedures before use [11].

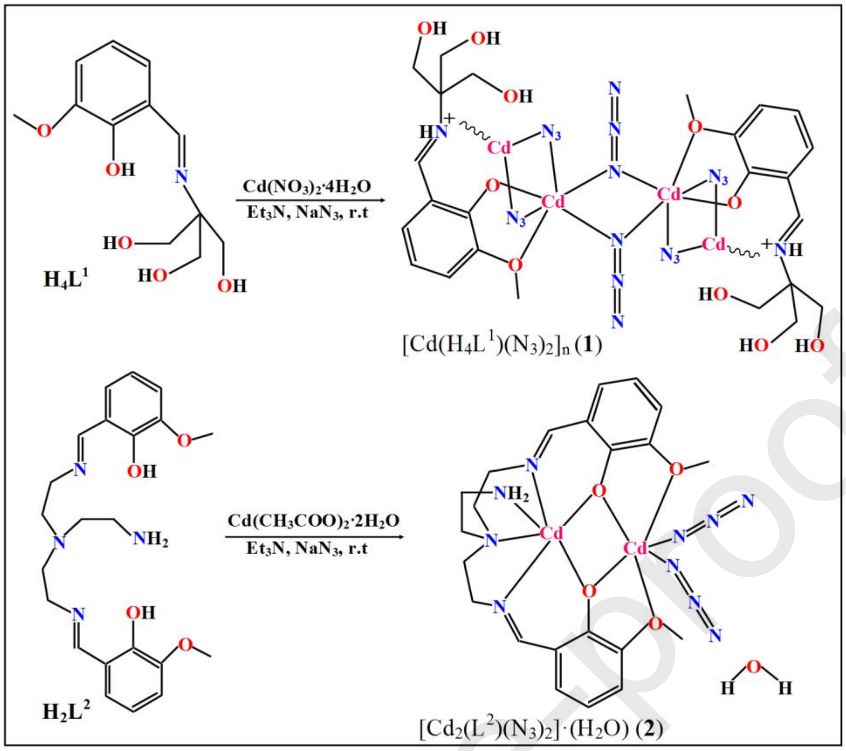
Elemental analyses (carbon, hydrogen, and nitrogen) were performed with a Perkin–Elmer 240C elemental analyzer. The IR spectra were recorded with samples as KBr pellets with a Bruker Vector 22 FTIR spectrophotometer operating in the wavenumber range from400 to 4000 cm^{-1}. The electronic absorption spectra were obtained at room temperaturewith aShimadzu UV-1601spectrophotometer. Quartz cuvette of 1 cm path length and 3 cm^3volume was used for all measurements. Emission spectra were recorded on a Hitachi F-7000 spectrofluorimeter. The X-ray powder diffraction (PXRD) data were collected from Bruker D2 phaser X-ray diffractometer (30 kV, 10 mA), employing Mo-Kα (λ=0.71073Å) radiation at room temperature. Thermogravimetric analyses (TGA) were carried out with a TGA Q50 V20.13 Build 39 instrument under N_2 atmosphere. Mass spectra of complexes **1** and **2** were performed using ultraflexTOF/TOF instrument in water.

2.2. Crystallographic Data Collection and Refinement

Intensity data collection for complexes **1-2** was carried out at room temperature with a Smart Apex-II, Bruker AXS diffractometer equipped with CCD and Mo-Kα radiation (λ = 0.71073 Å). Cell refinement, indexing and scaling of the data sets were done by using the Apex-II package [12]. The structures were solved by direct methods and subsequent Fourier analyses [13] and refined by the full-matrix least-squares method based on F^2 with all observed reflections [13]. The CH_2-OH groups of complex **1** have been refined with a constrained C-O distance of 1.43(1) Å due to the disorder detected in the oxygen atoms. In compound**2**a lattice water molecule was located in the Fourier map.Hydrogen atoms were placed at calculated positions. Publication material and calculations were performed by using WingX program Version 2013.3,[14] and Diamond [15].Crystal data and details of refinements for the two compounds are given in Table 1.

2.3. Synthesis

Complexes **1** and **2** have been synthesized adopting procedures which are schematically displayed in Scheme **1**.



Scheme **1**. Synthesis of complexes **1** and **2**.

*2.3.1. Synthesis of [Cd(H_4L^1)(N_3)$_2$]$_n$ (**1**)*

The polydentate ligand $H_4L^1$was prepared by refluxing 2-hydroxy-3-methoxy benzaldehyde (1 mmol, 0.152 g) and tris(hydroxymethyl)amino methane (1 mmol, 0.121 g) in methanol (10 mL) following the reported method [15]. A methanolic solution (10 mL) containing H_4L^1 (0.09 gm, 0.5 mmol) and Et_3N (0.05 gm, 0.5 mmol) was added to 10 mL of methanol containing $Cd(NO_3)_2.4H_2O$ (0.154 g, 0.5 mmol) under stirring condition. To this reaction mixture, 2 ml of aqueous solution of sodium azide (0.032 gm, 0.5 mmol) were added and stirred for additional 2 h. The yellow colored solution was filtered and left at room temperature. Yellow colored crystals suitable for X-ray diffraction were obtained after a few days. Yield: 66%. Anal. Calcd for $C_{12}H_{17}CdN_7O_5$ (451.74 g mol^{-1}): C, 31.90; H, 3.79; N, 21.70 %. Found: C, 31.92; H, 3.76; N, 21.73 %. Selected FTIR bands (KBr, cm^{-1}; vs = very strong, s = strong, m = medium, w = weak, br = broad): 3373 (br), 2946 (w), 2894 (w), 2038 (vs), 1632 (vs), 1545 (s), 1498 (vs), 1338 (s), 1288 (s), 1220 (vs), 1165 (s), 1039 (vs), 959 (w), 891 (s), 774 (vs), 733 (vs), 657 (s), 606 (s). UV-vis spectra [λ_{max}, nm (ε, L $mol^{-1}cm^{-1}$)] (CH_3OH solution) 227 (5.689×10^4), 236 (5.719×10^4), 266 (2.829×10^4), 292 (3.642×10^4), 416 (1.535×10^4).

2.3.2. Synthesis of $[Cd_2(L^2)(N_3)_2]\cdot(H_2O)$ ***(2)***

The Schiff base ligand $H_4L^2$was prepared by stirring a methanolic solution(20 mL) of 2-hydroxy-3-methoxybenzaldehyde (0.152 g, 1 mmol) and tris(2-aminoethyl)amine (0.073 g, 0.5 mmol) for 1 h at room temperature. Then $Cd(OAc)_2\cdot2H_2O$ (0.133 g, 0.5 mmol) dissolved in methanol was added to a methanolic solution of H_4L^2 (0.207 g, 0.5 mmol) and Et_3N (0.1 g, 1 mmol) and stirred for 2 hrs. To this resultant solution, 2 mlof aqueous solution of sodium azide (0.032 gm, 0.5 mmol) were added and the stirred for additional 1 h. The yellow colored solution was filtered and left at room temperature. Colorless crystals suitable for X-ray diffraction were obtained after a few days. Yield: 72%. Anal. Calcd for $C_{22}H_{30}Cd_2N_{10}O_5$ (739.37 g mol^{-1}): C, 35.73; H, 4.08; N, 18.94%. Found: C, 35.75; H, 4.10; N, 18.91%. Selected FTIR bands (KBr, cm^{-1}; vs = very strong, s = strong, m = medium, w = weak, br = broad): 3333 (s), 2896 (w), 2856 (w), 2039 (vs), 1631 (vs), 1598 (vs), 1549 (s), 1448 (vs), 1405 (s), 1333 (w), 1301 (vs), 1238 (vs), 1211 (vs), 1155 (w), 1074 (vs), 1030 (s), 959 (vs), 905 (s), 846 (vs), 782 (s), 739 (vs), 625 (vs), 509 (w). UV-vis spectra [λ_{max}, nm (ε, L $mol^{-1}cm^{-1}$)] (CH_3OH solution) 232 (1.818×10^5), 271 (8.338×10^4), 357 (3.552×10^4).

2.4. Photocatalytic Measurement

The photocatalytic activity of complexes **1** and **2** were studied out using 10 μM aqueous solution of methylene blue (MB). A 125 W mercury vapour lamp was used as the source of UV light and photocatalytic degradation experiment was carried out with a solution of MB where catalyst concentration is 1 gm L^{-1}. The mixture of solution containing MB and catalyst was stirred continuously under UV light and a 4 ml of the irradiated solution was taken after 20 mins interval, and recorded the absorption spectra. The characteristic electronic absorption band at 660 nm of MB was used to examine the photocatalytic degradation process.

3. Result and Discussion

3.1. Crystal structure description

3.1.1. $[Cd(H_4L^1)(N_3)_2]_n$(**1**)

The structural analysis of compound **1** shows a coordination polymeric complex where $Cd(H_4L^1)$ units are doubly connected by bridging μ-1,1 azide anions. The metal exhibits a highly distorted octahedral coordination sphere where the Schiff base chelates the Cd atom through the methoxy and phenolato oxygen donor, so that all the hydroxyl groups result uncoordinated (Fig.1). The ligand appears neutral in its zwitter ionic form, being the imino nitrogen protonated and not involved in coordination. An intramolecular hydrogen bond interaction (N7…O1 = 2.597 Å, N-H…O1 = 136.74°) can be seenfor**1**. Cd complexes with a 2-methoxy Schiff base that acts as chelating agent through methoxo and phenoxo oxygens and uncoordinated imino nitrogen have been reported [16].

The Cd-O bond lengths are significantly different, being the Cd-O1 (phenoxo) of 2.216(5) Å and that involving the methoxy oxygen of 2.487(5) Å. The Cd-N bond distances fall in the range 2.292(6) - 2.366(6) Å, in agreement with similar structures reported [16]. In the polymeric chain the Cd atoms are alternatively separated by 3.716Å and 3.734 Å with an intermetallic angle of 129.22°. The zig-zag arrangement of the chain and the bridging N_3^- anions lead to coordination bond angles far from ideal octahedral values (Table 2) and the smaller N(1)-Cd-N(1') and larger N(4)-Cd-O(2) values are 73.5(2)° and 149.7(2)°, respectively. A similar coordination polymer $[Cd(\mu\text{-}1,1\text{-}N_3)_2]_n$ [17] has been reported with metals coordinated by N,N-dimethyl-1,3-diaminopropane ligand having a Cd-Cd distance of 3.839 Å.

The crystal packing of present complex shows interdigitated polymers connected by short π-π interactions involving phenyl rings (alternated distance of 3.347(4)Å and 3.407(4) Å between centroids), and weak hydrogen bonds among the alcoholic groups O17-H and O15(at x-1, y, z) [O…O = 2.811 Å, O-H…O= 147.1°] although the high degree of thermal motion indicates a positional disorder of hydroxyl oxygen atoms(Fig. 2).

3.1.2. $[Cd_2(L^2)(N_3)_2]\cdot(H_2O)$ *(**2**)*

Tripodal Schiff base ligands having three equal groups attached to the tertiary amine nitrogen have been alreadyreported [18], but most of these have been employed to study properties of lanthanide complexes. Here an asymmetric tripodal molecule H_2L^2 (H_2L^2 = bis((3-methoxysalicylidene)ethyl)ethylamine) as target ligand was synthesized with the aim to react with Cd^{2+} ions.

Compound **2** crystallizes in monoclinic system, space group $P2_1/n$, as discrete dinuclear complexalong with a lattice water molecule. The anionic organic species $(L^2)^{2-}$ acts as a two compartmental ligand coordinating two cadmium atoms where phenoxo oxygen atoms act as bridging donors towards the metals that are separated by 3.638 Å (Fig.3). Both metals exhibit a six-coordination geometry.Cd1 is coordinated by the imino and amino nitrogen donors and by the phenoxy oxygens in highly distorted pentagonal pyramid coordination geometry where the amino nitrogen N4 is located at the apex. Cd2, beside the bridging phenoxo oxygens, is coordinated by the methoxy groups, and completes the distorted trigonal prismatic environment with azide anions.

The Cd1–N bond distances are in the range of 2.2701(18)-2.5707(18) Å and Cd1–O_{phen} are of2.2975(15)Å and 2.3187(15) Å. On the other hand, the Cd2-O bond lengths fall in between 2.2325(15)-2.5167(15) Å, and Cd2-N are of 2.210(2)Å and 2.199(2) Å, the latter is the shortest among those reported. The deviations from an octahedral geometry are clearly shown by the values of bond angles reported in Table 3. The Cd-O-Cd bridging angles average to 105.77°, while the terminal coordinated azides form a N-N-Cd2 angle of 125.79° (mean value). In order to accomplish coordination with all donor atoms, the ligand assumes a conformation where phenol moiety ringsareslightly bent to form a dihedral angle of 20.12° (Fig.4).These geometrical parameters are in agreement to those reported in the dinuclear complex $[Cd(L')_2Cd(N_3)_2]$ (HL´ = 2-((3-(dimethylamino)propylimino)methyl)-6-methoxyphenol) formed by two Schiff bases, but having a similar core and coordination set for the metals [17].

The crystal packing shows the metal complexes connected by H-bonds (Fig.5) involving nitrogens of symmetry related azide anions and the water molecule (O5…N5 = 2.947(3), O5-H…N5 = 166°, O5…N10 = 2.945(3) Å, O5-H…N5 = 167°). In addition,terminalazideatom N10 weakly interacts with amine group N4 of a symmetry related complex (N10…N4 = 3.072(4) Å).

*3.2. FTIR spectra of complexes **1** and **2***

The IR spectral band for **1** and **2**(Table 1S, Fig.1S)at 1632 cm^{-1} and 1631 cm^{-1}, respectively, is due to the azomethine (C=N) group. The band at 2946 cm^{-1} (for **1)** and 2896 cm^{-1} (for **2)**is due to aromatic C-H stretching vibration; while aliphatic ν(C-H) stretching vibration for **1** and **2** appears at 2894 and 2856 cm^{-1}, respectively. Bands at 1165 cm^{-1} (for **1**) and 1155 cm^{-1}(for **2**) are assigned to *ν*(O–CH$_3$) stretching vibration. Asymmetric structure vibration for azido group (ν$_{as}$(N$_3$)) appears at 2038 and 2039 cm^{-1} for complexes **1** and **2**, respectively. IR spectroscopic technique is an important tool to identify the types of bonding, end-on/end-to-end, present in a compound. It is to note that azido bridged cadmium compounds show major tendency to form end-on bridging mode in comparison to the end-to-end bridging mode. Like **1** and **2**, the reported complexes [Cd$_2$(MeDPA)$_2$(μ$_{1,1}$-N$_3$)$_2$(N$_3$)$_2$], [Cd(3-ampy)(μ$_{1,1}$-N$_3$)$_2$]$_n$, [Cd(8-aminoql)(μ$_{1,1}$-N$_3$)$_2$]$_n$ and [Cd(3,5-daba)(μ$_{1,1}$-N$_3$)$_2$]$_n$ [19]also exhibit end-on bonding modes and their ν$_{as}$(N$_3$) stretching vibrations are very close to the reported ionic azide in KN$_3$ (2039 cm^{-1}).

*3.3. Electronic and emission spectra of complexes **1** and **2***

The electronic absorption spectra of complexes **1** and **2** have been recorded in methanol (Table 2S, Fig.2S). Compound **1** shows significant transitions at 227 (5.689×10^4 L mol^{-1} cm^{-1}), 236 (5.719×10^4 L mol^{-1} cm^{-1}), 266 (2.829×10^4 L mol^{-1} cm^{-1}), 292 (3.642×10^4 L mol^{-1} cm^{-1}) and 416 (1.535×10^4 L mol^{-1} cm^{-1}) and compound **2** shows transitions at 232 (1.818×10^5 L mol^{-1} cm^{-1}), 271 (8.338×10^4 L mol^{-1} cm^{-1}) and 357 (3.552×10^4 L mol^{-1} cm^{-1}).

On excitation at 236 nm, compound **1** exhibits a luminescence band at 307 nm in methanol at room temperature and compound **2**, on excitation at 232 nm shows an emission band at 305 nm (Fig. 3S).

3.4. PXRD and Thermogravimetric Analysis

The powder X-ray diffraction (PXRD) patterns of complexes **1** and **2** are coincident with the simulated diffraction pattern obtained from the single crystal XRD data, suggesting that the bulk samples are same as the single crystals used for structural analysis. (Fig.4S-5S). The differences in intensity between synthesized compound and simulated pattern from single crystal of complexes may be due to favored orientation of the crystalline powder samples [20].

The thermogravimetric analysis (TGA) of **1**-**2**was investigated under a nitrogen atmosphere and shown in Fig.6.For complex **1**, initial weight loss begins at 202°C and continues in one step up to 246°C. The total weight loss over this range is 20.47%, which corresponds to the loss of organic component. TGA curve for complex **2** exhibits weight loss in two steps. In the first step the weight loss of 2.29% below 100°C is assigned to the loss of lattice water (calcd 2.43%). The second step of 13.56% weight loss in the range 265-296°C is attributed to loss of organic component present in the crystalline compound.

3.5. Photocatalytic activity

Photocatalytic activities of complexes **1** and **2** have been studied by photodegradation of methylene blue (MB). Methylene blue is an organic dye and it is widely used in industry for the synthesis of various textile and painting materials. The photo-catalytic degradation of methylene blue was studied using UV light and progress of the reaction studied using UV-vis absorption spectroscopic technique. Before irradiation, 10 μM, 50 μL aqueous solution of methylene blue (MB) was added to the aqueous solution of complexes **1** and **2**to maintain a catalyst concentration of 1g L^{-1}.Aqueous solution of methylene blue shows characteristic absorption band at 660 nm (Fig.6S). In presence of complexes **1** and **2**, the absorbance of 660 nm band of methylene blue gradually decreased with time. The change in the electronic absorption spectra of MB in presence of complexes under study after 180 min is shown in Figs.7-8.

To determine the kinetics of photocatalytic degradation of MB by complexes **1** and **2**, the UV-vis titration spectral data have been analyzed by using Langmuir-Hinshewood model as described by

$$\ln(C_t/C_0) = -K_{app}t$$

$$\text{or, } \ln(A_t/A_0) = -K_{app}t$$

Where C_t and C_0= concentration of dye at time t and at t=0, respectively, A_t and A_0 = absorbance of dye at time t, and at t=0, respectively, K_{app} = apparent rate constant.

The $\ln(C_0/C_t)$ vs t plot gives a straight line passing through origin, and the slope of the lines furnishes the value of apparent rate constant (Fig.9). Calculated values of rate constant for **1** and **2** are 2.63×10^{-3} and 2.45×10^{-3} min^{-1}, respectively.

Percentage of decomposition of dye was calculated using the equation

$$\text{Dye removal (\%)} = \frac{C_0-C_t}{C_0}\times 100$$

$$= \frac{A_0-A_t}{A_0}\times 100$$

Calculated results show that after 180 min, the dye decomposed by 37.64% and 32.60% in presence of complex **1** and **2**, respectively. It is worth of note that there is no noticeable change of intensity of MB band at 660 nm in absence of complexes **1** and **2**even after 180 min (Fig.9). This indicates that complexes **1** and **2** play a fundamental role for decomposition of the dye. A comparison (Table 4) of results of Cd(II) coordination compound catalyzed photocatalytic degradation of MB indicates that **1** and **2** are less efficient photo-catalyst in contrast to the previously reported compounds.

4. Conclusion

In summary, we have presented here the synthesis, crystal structure, thermal analysis and photocatalytic activities of two azido coordinated cadmium(II) complexes using 2-((2-hydroxy-3-methoxybenzylidene)amino)-2-(hydroxymethyl)-propane-1,3-diol (H_4L^1) and bis((3-methoxysalicylidene)ethyl)ethylamine) (H_2L^2). Cadmium(II)-azido in combination with H_4L^1 and H_2L^2results 1D coordination polymer (**1**) and discrete dinuclear compound (**2**). 2D supramolecular structure of complex **1** is formed with H-bonding and π-π interactions. On the other hand complex **2** forms1D supramolecular chain like structure with H-bonding interactions. Both the complexes are active for UV-light-driven photocatalytic degradation of methylene blue (MB).

Acknowledgements

The authors gratefully acknowledge the financial assistance given by the CSIR, Government of India, to Dr. Subal Chandra Manna (Project No. 01 (2743)/13/EMR-II). Dr. S. C. Manna thanks UGC-SAP and DST-FIST New Delhi and Vidyasagar University for infrastructural facilities.

Supplementary information

CCDC 1947104 and 1947105 contain the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail:

deposit@ccdc.cam.ac.uk. IR, photophysical parameters, UV-vis absorption spectra, PXRD patterns.

References

[1] Z. Su, K. Cai, J. Fan, S. -S. Chen, M.-S. Chen, W. -Y. Sun, *CrystEngComm* 12 (2010) 100-108.

[2] (a) J. -C. Dai, X. -T. Wu, Z. -Y. Fu, C. -P. Cui, S. -M. Hu, W. -X. Du, L. -M. Wu, H. -H. Zhang, R. -Q. Sun, *Inorg. Chem*. 41 (2002) 1391- 1396; (b) A. Bhunia, E. Zangrando, S. Mistri, S. C. Manna, *Inorg. Chim. Acta*, 409 (2014) 528 - 537.

[3] D. Singh, C. M. Nagaraja, *Cryst. Growth Des*. 15 (2015) 3356-3365.

[4](a) O. R. Evans, W. Lin, *Acc. Chem. Res*. 35 (2002) 511-522; (b) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev*. 38 (2009) 1450-1459.

[5] (a) R. Kumar, P. Bhargava, R. Srivastava, *Adv. Sci. Lett*. 20 (2014) 1001- 1004; (b) G. -Y. Wang, C. Song, D. -M. Kong, W.-J. Ruan, Z. Chang, Y. Li, *J. Mater. Chem*. A 2 (2014) 2213-2220; (c) Y. Wu, Y. Lin, F. Wei, M. Hu, L. Liu, P. Zhou, Q. Hu, J. *Nanosci. Nanotechnol*. 14 (2014) 3976-3982; (d) P. K. Santra, P. V. Kamat, *J. Am. Chem. Soc*. 135 (2013) 877-885.

[6] (a) S. Roy, K. Harms,A. Bauzá, A. Frontera, S. Chattopadhyay, *Polyhedron*, 121 (2017) 199-205; (b) S. Roy, K. Harms, S. Chattopadhyay, *Polyhedron*, 127 (2017) 471-477.

[7] (a) T. Wen, D. -X. Zhang, J. Zhang, *Inorg. Chem*. 52 (2013) 12-14; (b) A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J. -M. Herrmann, *Appl. Catal. B-Environ*. 31 (2001) 145-157; (c) Y. Lv, L. Yu, X. Zhang, J. Yao, R. Zou, Z. Dai, *Appl. Surf. Sci*. 257

(2011) 5715-5719; (d) W. Cui, W. An, L. Liu, J. Hu, Y. Liang, *J. Hazard. Mater*. 280 (2014) 417-427.

[8] (a) K. Nakata, A. Fujishima, *J. Photochem. Photobiol*. C, 13 (2012) 169-189; (b) A. Janczyk, E. Krakowska, G. Stochel, W. Macyk, *J. Am. Chem. Soc*. 128 (2006) 15574 -15575; (c) A. Y. Nosaka, E. Kojima, T. Fujiwara, H. Yagi, H. Akutsu, Y. Nosaka, *J. Phys. Chem*. B, 107 (2003) 12042-12044; (d) A. Fujishima, X. Zhang, D. A. Tryk, *Int. J. Hydrogen Energy*, 32 (2007) 2664-2672; (e) R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni,E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, *Nature*, 388 (997) 431 - 432.

[9] (a) C.-C. Wang, J.-R. Li, X.-L. Lv,Y.-Q. Zhang, G. Guo, *Energy Environ. Sci*. 7 (2014) 2831-286; (b) A. Kuila, N.A. Surib, N. S. Mishra, A. Nawaz, K. H. Leong, L. C. Sim, P.Saravanan, S. Ibrahim, *ChemistrySelect* 2 (2017) 6163-6177; (c) M. Li,L. Liu,L. Zhang,X. Lv,J. Ding,H. Hou,Y. Fan, *CrystEngComm*, 16 (2014) 6408-6416; (d) P. Mahata, G. Madras, S. Natarajan, *J. Phys. Chem*. B, 110 (2006) 13759-13768.

[10](a) L. Liu, J. Ding, C. Huang, M. Li, H. Hou, Y. Fan, *Cryst. Growth Des*. 14 (2014) 3035-3043; (b) J.-C. Jin, J. Wu,W.-C. Liu,A.-Q. Ma,J.-Q. Liu,A. Singh,A. Kumar, *New J. Chem.*, 42 (2018) 2767-2775; (c) W. Meng, Z. Xu, J. Ding, D. Wu, X. Han, H. Hou, Y. Fan, *Cryst. Growth Des*. 14 (2014) 730-738.

[11]D. D. Perrin, W. L. F. Armarego, D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1980.

[12]Bruker (2007). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

[13]Sheldrick, G.M. (2008). *ActaCryst*. A64, 112-122

[13]L. J. Farrugia, *J. Appl. Crystallogr*., 32 (1999) 837-838.

[14] Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

[15] S. Manna, A. Bhunia, S. Mistri, J. Vallejo, E. Zangrando, H. Puschmann, J. Cano, S. C. Manna,*Eur. J. Inorg. Chem*. 2017, 2585-2594.

[16](a) Zhong-Lu You, Xiao Han, Guang-Ning Zhang Z. *Anorg. Allg. Chem*., 634, 142-146, 2008; (b) Hua-Qiong Li, Hui-Duo Xian, Jian-Feng Liu, Guo-Liang Zhao *ActaCrystallogr*., Sect E, 64, m1482 and m1593, 2008; (c) Hua-Cai Fang, Ji-Qin Zhu, Li-Jiang Zhou, Hong-Yang Jia, Shan-Shan Li, Xue Gong, Shu-Bin Li, Yue-Peng Cai, P.K. Thallapally, Jun Liu, G.J. Exarhos,*Cryst. Growth Des*., 8, 2076–2079, 2008.

[17]S. Roy, P.K. Bhaumik, K. Harms, S. Chattopadhyay, *Polyhedron*, **75,** 57-63, 2014.

[18](a) J.-P. Costes, F. Dahan, F. Nicodeme, *Inorg. Chem*., 42, 6556-6563, 2003. (b) S.M. Cohen, M. Meyer, K.N. Raymond, *J. Am. Chem. Soc*., 120, 6277- 6286, 1998. (c) Min-XiaYao, Zhao-XiaZhu, Xing-Yun Lu, Xiao-Wei Deng, Su Jing,*Dalton Trans*., 45, 10689-10695, 2016. (d) ShuangLiu, Li-Wei Yang, S.J. Rettig, C.Orvig, *Inorg. Chem*., 32, 2773-2778, 1993. (e) Ka-LeungWong, Ga-Lai Law, Wai-Ming Kwok, Wing-TakWong, D.L.Phillips, *Angew. Chem., Int. Ed*., 44, 3436-3439, 2005.

[19] (a) F. A. Mautner,F. R. Louka, J. Hofer,M. Spell,A. Lefèvre, A. E. Guilbeau, and S. S. Massoud, *Cryst. Growth Des*. 2013, 13, 4518−4525; (b) Z. -L. Chen,C.-F. Jiang, W. -H. Yan, F. -P. Liang, S. R. Batten, *Inorg. Chem*. 2009,48, 4674−4684; (c) H. Xu, L.-F. Huang, L. -M. Guo, Y. -G. Zhang, X. -M. Ren,Y. Song, J. J. Xie, *Lumin*. 2008, 128, 1665−1672; (d) M. A. S. Goher, A. K. Hafez, M. A. M. Abu Youssef, A. M. A. Badr, C. Gspan, F. A. Mautner, *Polyhedron* 2004, 23, 2349−2356; (e) I. Agrell, *Acta Chem. Scand*. 1971, 25, 2965−2974.

[20] J. Sun, Y. –H. Wei, F. –L. Liu and D. Sun, *RSC Advances*, 2012, 2, 10189–10194.

[21] M. Li, L. Liu, L. Zhang, X. Lv, J. Ding, H. Hou, Y. Fan, *CrystEngComm* 16 (2014) 6408-6416.

[22] X. -L. Wang, Y. Xiong, G. -C. Liu, H. -Y. Lin, X. -T. Sha, J. Shao, *Polyhedron* 24 (2016) 590-596.

[23] Y. -J. Yang, D. Liu, Y. -H. Li, G. -Y. Dong, *Polyhedron* 156 (2018) 72-79.

[24] X. –X. Zhao, D. Liu, Y. –H. Li, G. –H. Cui, *Polyhedron* 156 (2018) 200-207.

[25] J. Gu, Y. Cai, M. Wen, Z. Shi, A. Kirillov, *Dalton Trans.*, 47 (2018) 14327-14339.

Table 1. Crystal data and details of structure refinement of complexes **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{12}H_{17}CdN_7O_5$	$C_{22}H_{30}Cd_2N_{10}O_5$
Formula mass, g mol^{-1}	451.72	739.36
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/n$	$P\ 2_1/n$
a, Å	6.7305(6)	15.3991(14)
b, Å	10.1895(9)	9.0213(12)
c, Å	23.972(3)	19.9725(15)
β, deg	96.428(9)	107.702(11)
V, $Å^3$	1633.7(3)	2643.2(5)
Z	4	4
$D_{(calcd)}$, g cm^{-3}	1.837	1.858
μ(Mo-Kα), mm^{-1}	1.378	1.663
F(000)	904	1472
Theta range, deg	3.07 - 28.87	1.99 - 26.41
No. of collected data	7427	20361
No. of unique data	3805	5364
R_{int}	0.0358	0.0208
Obs reflects [$I > 2\sigma(I)$]	2364	4935
Goodness of fit (F^2)	1.111	1.028
Parameters refined	228	354
*R*1, *wR*2 ($I > 2\sigma(I)$) [a]	0.0617, 0.1280	0.0205, 0.0472
*R*1, *wR*2 (all data)	0.1050, 0.1543	0.0232, 0.0484
Residuals, e $Å^{-3}$	0.995, –0.759	0.693, –0.481

Table 2. Coordination bond lengths (Å) and angles (°) for complex **1** (the Cd atom is located on a two-fold axis).

Cd-O(1)	2.216(5)	Cd-N(1')	2.292(6)
Cd-O(2)	2.487(5)	Cd-N(4)	2.307(6)
Cd-N(1)	2.367(6)	Cd-N(4")	2.366(6)
N(1)-Cd-N(1')	73.5(2)	N(4)-Cd-N(1)	96.5(2)
N(4)-Cd-N(4")	74.7(2)	O(1)-Cd-N(4")	110.8(2)
O(1)-Cd-O(2)	68.33(16)	N(1')-Cd-N(4")	94.4(2)
O(1)-Cd-N(1')	140.6(2)	N(1)-Cd-N(4")	159.9(2)
O(1)-Cd-N(4)	98.2(2)	N(1')-Cd-O(2)	85.0(2)
N(1')-Cd-N(4)	118.0(2)	N(4)-Cd-O(2)	149.7(2)
O(1)-Cd-N(1)	88.16(19)	N(1)-Cd-O(2)	109.6(2)
		N(4")-Cd-O(2)	84.72(19)

Symmetry codes: (') -x, -y, -z+1; (") -x+1, -y, -z+1.

Table 3. Coordination bond lengths (Å) and angles (°) for complex **2**

Cd(1)-O(2)	2.2975(15)	Cd(2)-O(1)	2.4534(15)
Cd(1)-O(3)	2.3187(15)	Cd(2)-O(2)	2.2325(15)
Cd(1)-N(1)	2.2701(18)	Cd(2)-O(3)	2.2779(15)
Cd(1)-N(2)	2.5707(18)	Cd(2)-O(4)	2.5167(15)
Cd(1)-N(3)	2.2948(18)	Cd(2)-N(5)	2.210(2)
Cd(1)-N(4)	2.306(2)	Cd(2)-N(8)	2.199(2)
N(1)-Cd(1)-N(3)	110.95(7)	N(8)-Cd(2)-N(5)	115.07(8)
N(1)-Cd(1)-O(2)	79.63(6)	N(8)-Cd(2)-O(2)	111.12(7)
N(3)-Cd(1)-O(2)	143.62(6)	N(5)-Cd(2)-O(2)	119.11(7)
N(1)-Cd(1)-N(4)	105.02(7)	N(8)-Cd(2)-O(3)	114.87(7)
N(3)-Cd(1)-N(4)	119.00(7)	N(5)-Cd(2)-O(3)	116.20(6)
O(2)-Cd(1)-N(4)	89.31(6)	O(2)-Cd(2)-O(3)	74.27(5)
N(1)-Cd(1)-O(3)	140.17(6)	N(8)-Cd(2)-O(1)	84.35(7)
N(3)-Cd(1)-O(3)	79.17(6)	N(5)-Cd(2)-O(1)	79.99(6)
O(2)-Cd(1)-O(3)	72.30(5)	O(2)-Cd(2)-O(1)	67.29(5)
N(4)-Cd(1)-O(3)	102.35(6)	O(3)-Cd(2)-O(1)	141.25(5)
N(1)-Cd(1)-N(2)	72.74(6)	N(8)-Cd(2)-O(4)	83.78(7)
N(3)-Cd(1)-N(2)	72.09(6)	N(5)-Cd(2)-O(4)	81.92(6)
O(2)-Cd(1)-N(2)	142.19(6)	O(2)-Cd(2)-O(4)	141.04(5)
N(4)-Cd(1)-N(2)	73.91(7)	O(3)-Cd(2)-O(4)	66.86(5)
O(3)-Cd(1)-N(2)	143.62(5)	O(1)-Cd(2)-O(4)	151.66(5)

Table 4. Photocatalytic activities of cadmium(II) coordination compounds for the degradation of methylene blue (MB).

Complex	Rate constant (min^{-1})	Efficiency (%)	Ref.
$[Cd(H_4L^1)(N_3)_2]_n$ (**1**)	2.63×10^{-3}	37.64	This work
$[Cd_2(L^2)(N_3)_2]\cdot(H_2O)$ (**2**)	2.45×10^{-3}	32.60	This work
$[\{CdL^3(\mu\text{-}1,1\text{-}N_3)\}_2Cd(\mu\text{-}1,1\text{-}N_3)_2\cdot1.76\ CH_3OH]_n$	3.56×10^{-3}	68.0	[6a]
$[Cd_2(L^4)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$	7.01×10^{-4}	64.0	[6b]
$\{[Cd_3(pbmb)_3(1,3,5\text{-}btc)_2(H_2O)]\cdot3H_2O\}_n$	-	37.0	[21]
$[Cd(pbmb)(1,2,4,5\text{-}btec)_{0.5}]_n$	-	46.0	[21]
$[Cd_2(3\text{-}pna)(mip)_2(H_2O)]\cdot2H_2O$	-	48.0	[22]
$[Cd(3\text{-}pna)(mip)]_2\cdot3H_2O$	-	42.0	[22]
$[Cd(L^5)(dctp)]_n$	1.10×10^{-3}	74.3	[23]
$\{[Cd(L^6)(Hbtc)(H_2O)]\cdot H_2O\}_n$	1.80×10^{-3}	86.0	[23]
$\{[Cd(L^7)(1,4\text{-}ndc)]_n$	2.35×10^{-2}	96.5	[24]
$\{[Cd(L^8)_{1.5}(bdc\text{-}Cl_4)]\cdot H_2O\}_n$	1.69×10^{-2}	93.9	[24]
$\{[Cd_3(\mu_4\text{-}dbba)_2(phen)_3]\cdot H_2O\}_n$	9.60×10^{-3}	78.3	[25]

H_4L^1=[2-((2-hydroxy-3-methoxybenzylidene)amino)-2-(hydroxymethyl)-propane-1,3-diol]; H_2L^2 = bis((3-methoxysalicylidene)ethyl) ethylamine); HL^3=2-(3-(dimethylamino) propyliminomethyl) -6- ethoxyphenol; HL^4=2-(3-(methylamino) propyliminomethyl)-4,6-dichlorophenol; L^5=1,3-bis(2-methylbenzimidazol-1-ylmethyl)benzene; L^6=1,2-bis(imidazol-1-ylmethyl)benzene; L^7=1,4-bis(benzimidazol-1-yl)butane; L^8=1,6-bis(benzimidazol-1-yl)hexane; 3-pna=3-pyridylnicotinamide; H_2mip=5-methylisophthalic acid; H_2dctp=2,5-dichloroterephthalic acid; H_3btc= 1,3,5-benzenetricarboxylic acid; 1,4-H_2ndc = 1,4-naphthalenedicarboxylic acid; H_2bdc-Cl_4 = 2,3,5,6-tetrachloroterephthalic acid; phen=1,10-phenanthroline; H_3dbba=2-(3,5-dicarboxylatobenzyloxy)benzoic acid; pbmb=1,1′-(1,3-propane)bis-(2-methylbenzimidazole); 1,2,4,5-H_4btec=1,2,4,5-benzenetetracarboxylic acid.

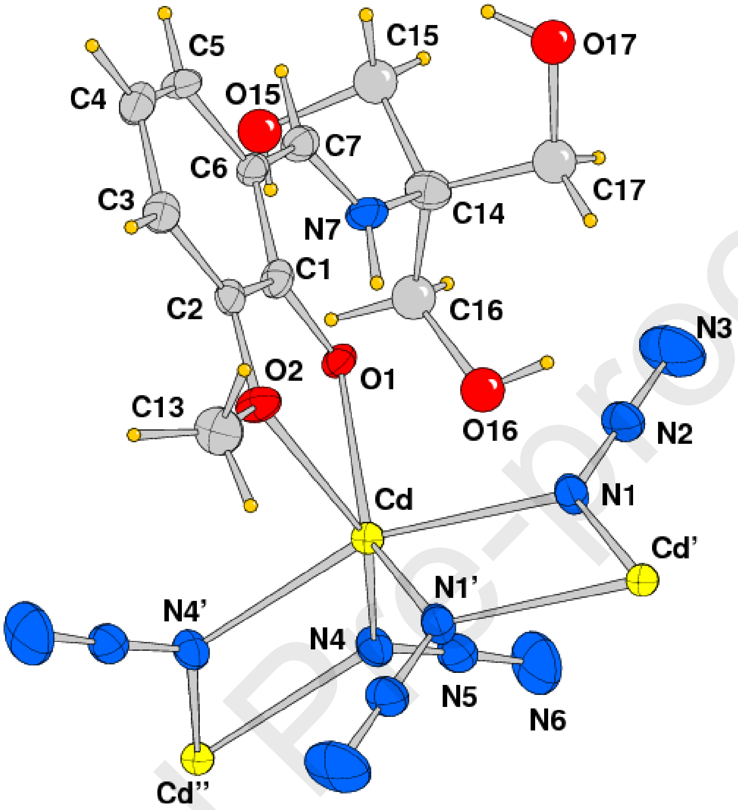


Fig. 1. ORTEP drawing (ellipsoid probability at 25%) of complex **1**with label scheme of the crystallographic independent unit. For clarity the -CH_2OH groups aredepicted as spheres due to the positional disorder of these groups.

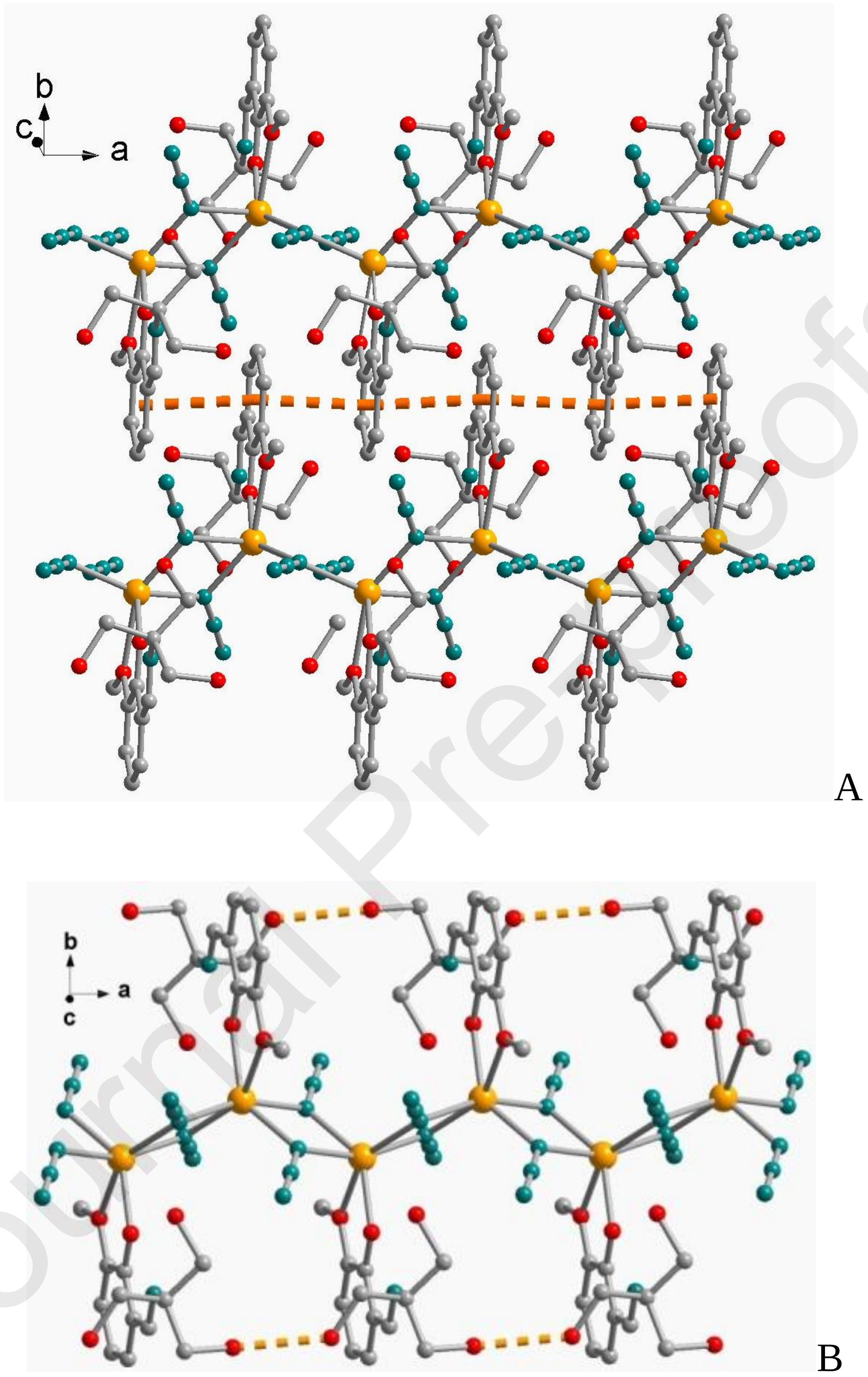


Fig. 2. (A) Packing diagram showing interdigitated polymers with indication π-π interactions in compound **1** and (B) intra-chain H bonds among the OH groups.

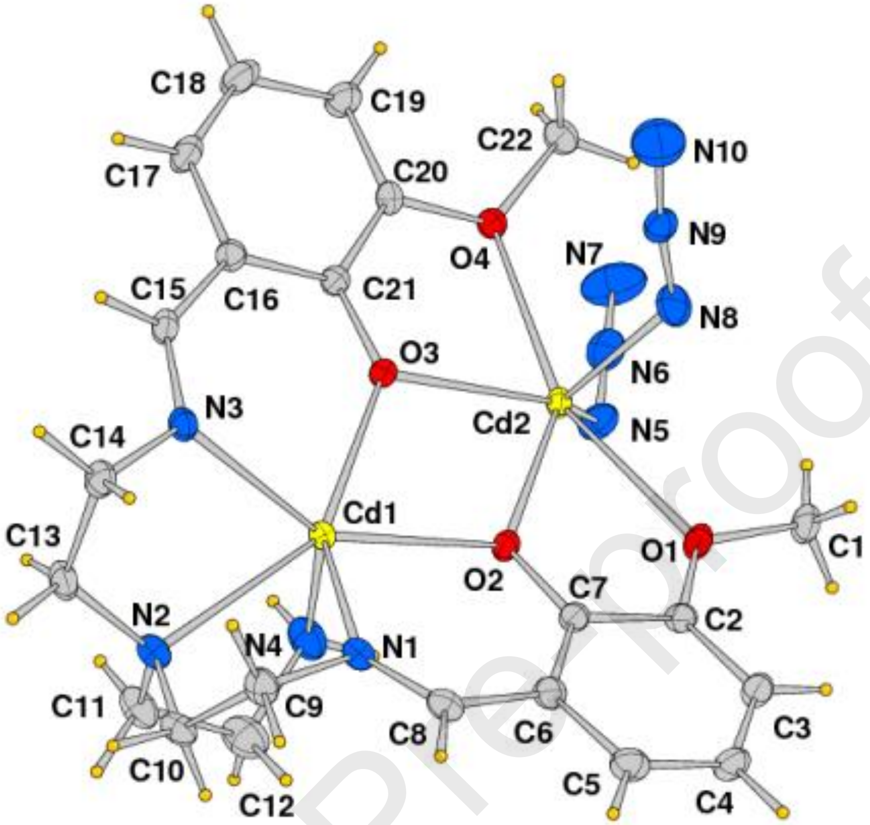


Fig. 3. Molecular structure of complex **2** (ORTEP drawing, ellipsoid probability at 50%) with atom labelling scheme.

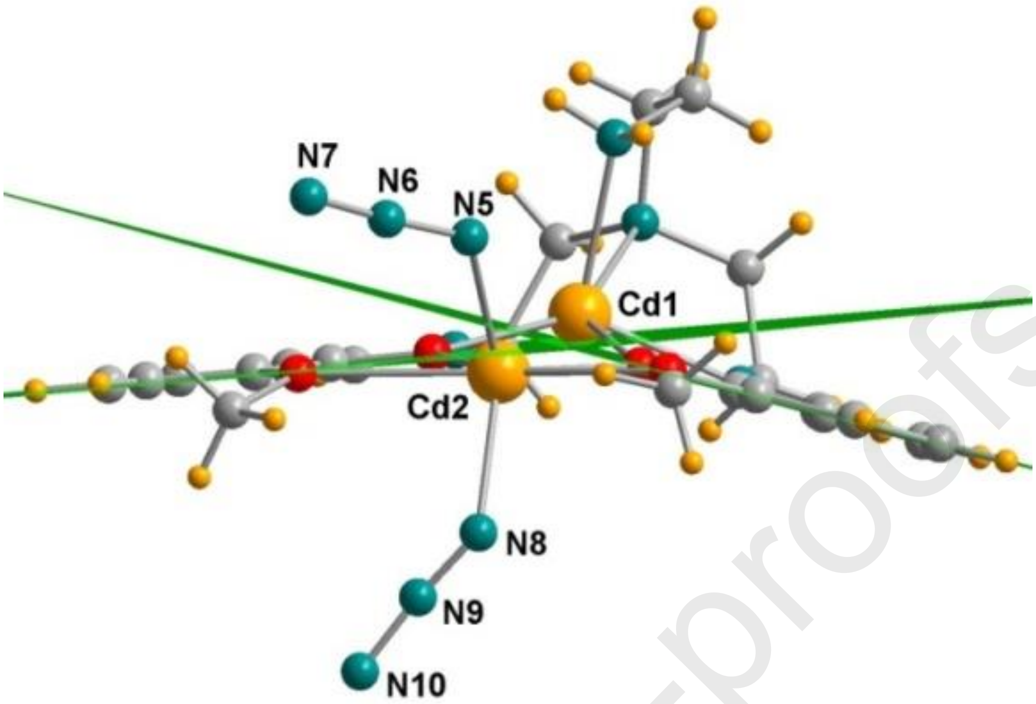


Fig. 4. Perspective view of the complex showing the conformation of the ligand with mean planes through phenol moieties forming a dihedral angle of 20.12°.

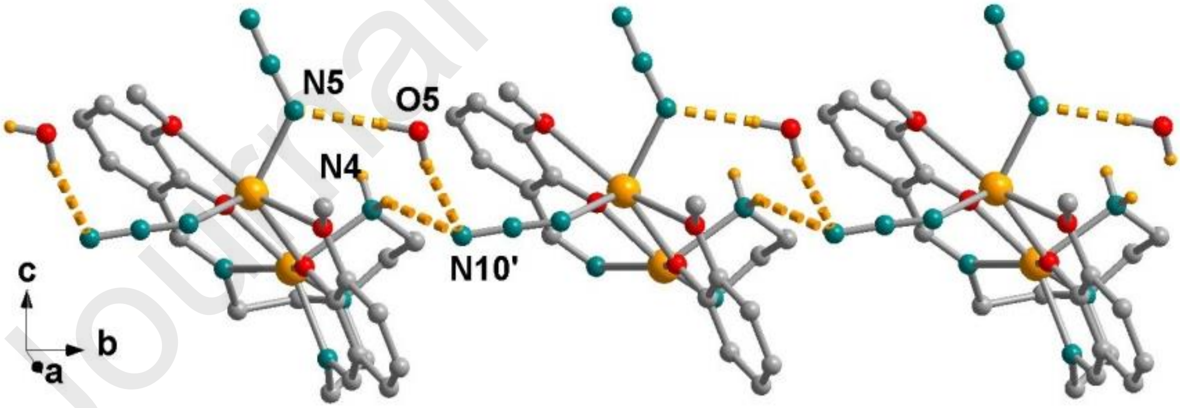


Fig. 5. Crystal packing of **2** showing Cd complexes connected by H-bonds though lattice water molecules (only hydrogen atoms involved in H-bonds are shown for sake of clarity).

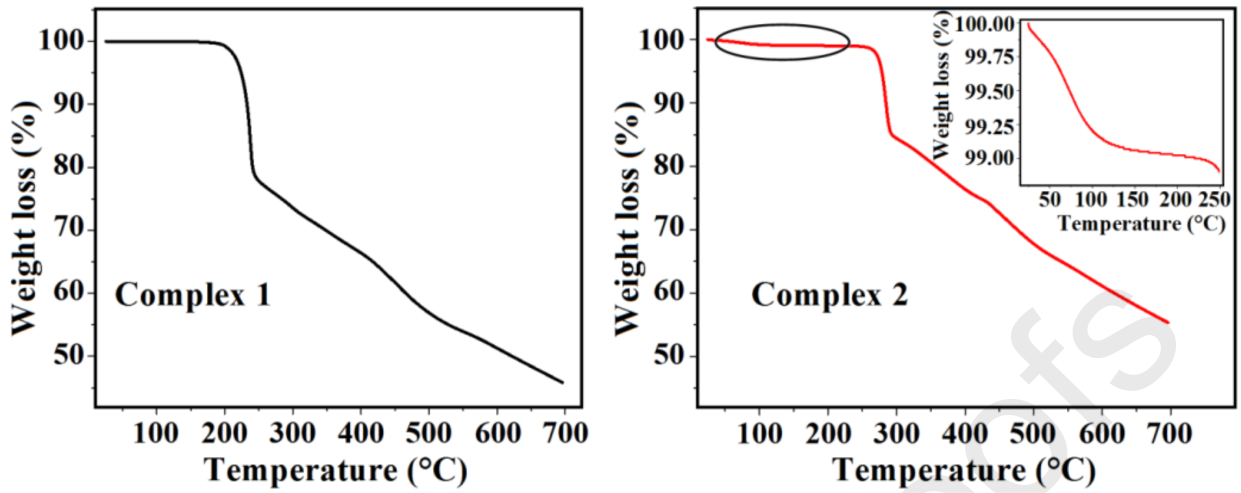


Fig. 6. TGA curve of complex **1** (left) and **2** (right).

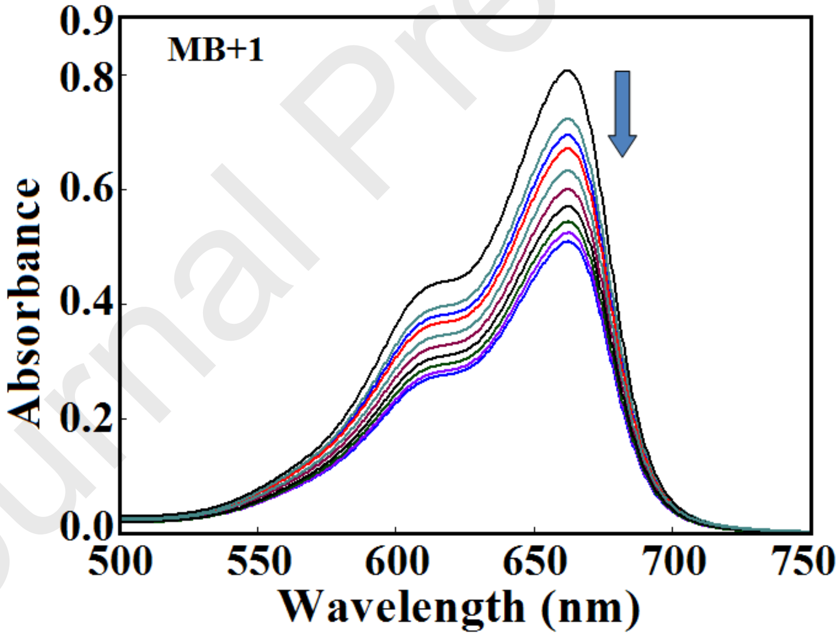


Fig.7. Absorption spectra of MB aqueous solution in presence of **1** during irradiation (thespectra were recorded atintervals of20 minutes).

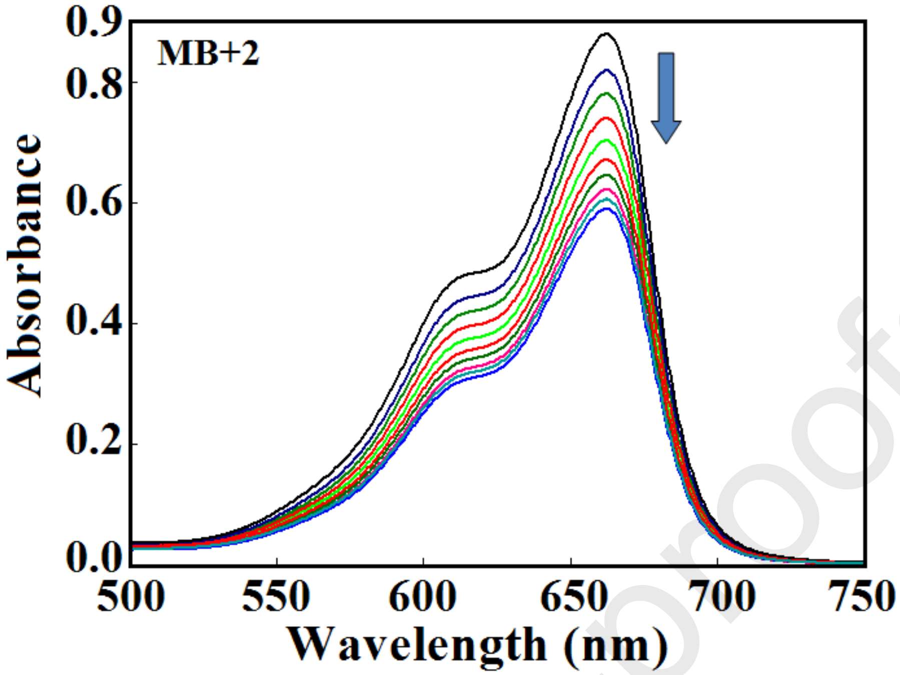


Fig.8. Absorption spectra of MB aqueous solution in presence of **2** during irradiation (the spectra were recorded at intervals of 20 minutes).

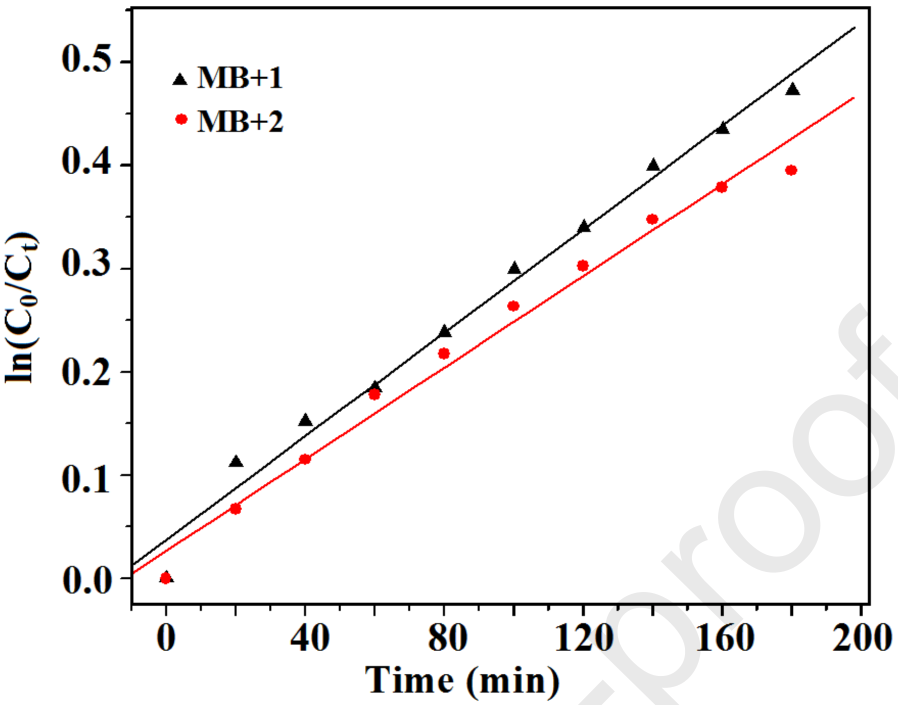
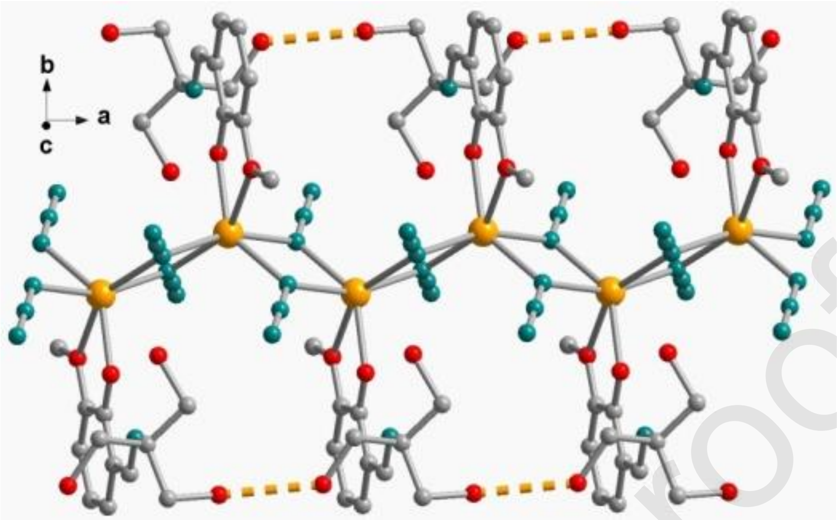


Fig.9. Plot of photocatalytic degradation kinetics of MB at different concentrations of complexes **1** and **2**.



Two cadmium(II)-azido complexes, [Cd(H_4L^1)$(N_3)_2$]$_n$ (**1**) and [Cd_2(L^2)$(N_3)_2$]·(H_2O) (**2**) (H_4L^1 = 2-((2-hydroxy-3-methoxybenzylidene)amino)-2-(hydroxymethyl)-propane-1,3-diol; and H_2L^2 = bis((3-methoxysalicylidene)ethyl)ethylamine) were synthesized and structurally characterized. Both the complexes are active for photocatalytic degradation of methylene blue (MB) in presence of UV light.