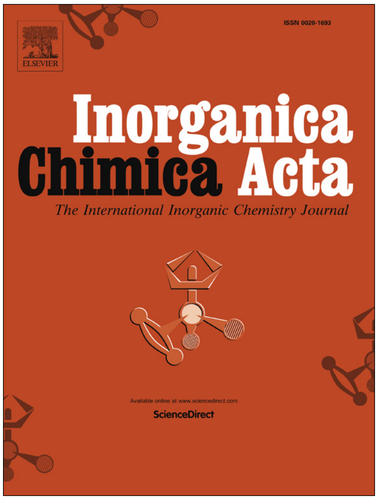

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A combined experimental and computational study of supramolecular assemblies in two photoluminescent cadmium(II) complexes with halosalicylaldimine Schiff bases

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Abstract

Two new cadmium(II) complexes, $[Cd(L^1)(OOCCH_3)(OH_2)]$ (**1**), $[Cd_2(L^2)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$ (**2**), have been synthesized using two halosalicylaldimine Schiff bases, HL^1 and HL^2 {where HL^1 = 2-(2-(ethylamino)ethyliminomethyl)-4-bromophenol, and HL^2 = 2-(2-(dimethylamino)ethyliminomethyl)-4-chlorophenol}, respectively. Both complexes have been characterized by elemental and spectral analysis and their structures have been confirmed by single crystal X-ray diffraction studies. Complex **1** is mononuclear and the cadmium(II) centre is apparently coordinated by a tridentate Schiff base, a water molecule and a bidentate chelating acetate. The acetate group could also be thought of as a single entity occupying just one stereochemical site as evident from the small value of chelate bite angle. Complex **2** is dinuclear and contain octahedral cadmium(II) bridged by double end-to-end thiocyanates. Supramolecular interactions in both complexes were also explored. The theoretical study, carried out using density functional theory (DFT) calculations, is devoted to the analysis of the interesting supramolecular assemblies in the solid state of the structures, paying special attention to hydrogen bonding interactions involving the coordinated solvent molecules.

Keywords: Cadmium(II); Schiff base; Hydrogen bonding; Photoluminescence; DFT study.

1. Introduction

Transition and non-transition metal complexes containing Schiff base ligands are of great interest since long for their catalytic activity [1-5], utility in modeling the multi metal active sites of metalloproteins [6,7] and potential use in nano-science [8,9]. They have also played an important role in the development of coordination chemistry related to enzymatic reactions, magnetism and molecular architectures [10-14]. Focusing on zinc, a group 12 metal, the functions of several hydrolytic enzymes, (Carboxypeptidases, Alcohol dehydrogenase, Leucine aminopeptidases, Carbonic anhydrase) etc are found to dependent on the presence of zinc in their active site structures [15-17]. Indeed, zinc is a very important metal in biology and several zinc(II) complexes have been used to model the active site of the enzyme glycerophosphodiesterase [18]. In the contrary, cadmium (the successor of zinc) is not common in metalloproteins and metalloenzymes. Cadmium was thought as an extremely toxic element for long and was often correlated with mercury and lead as biologically harmful metals [19,20]. However, interest in the coordination chemistry of cadmium complexes is currently growing due to the increased recognition of its role in biological organisms [21,22], and due to its rich structural chemistry [23-26]. Recent discovery of a carbonic anhydrase from a marine diatom, *Thalassiosira weissflogii*, has shown the presence of cadmium in the active site [27], and there is many other reports regarding the biological relevance of cadmium [28-30]. However, its potential as an analogue for zinc(II) in metalloenzymes is relatively less investigated. In this context, synthesis and characterization of several new cadmium(II) complexes is an important research topic.

Water-bridged dinuclear cationic complexes are important in model studies of metallohydrolases and metallocatecholase [31,32]. Both bridging and coordinated water molecules have a significant role in the mechanism of action during bridge cleavage and ligand substitution reactions. In model complexes, these loosely bound water molecules may lose a proton to provide hydroxo bridges or may be replaced by other monodentate ligands. Several other solvent molecules may also serve the same purpose [33-35]. At the time of substituting the water molecules by anions, cluster-like metal-organic assemblies can be obtained, and several recent reports report the successful employment of anions as a template in the formation of organic and metal-organic assemblies [36-39]. Mononuclear complexes with a coordinated water molecule are also important because they can be used to produce water bridged dimers.

On the other hand, construction of supramolecular assemblies via various non-covalent interactions as binding forces is another important area of research in chemistry. Understanding the formation of assemblies through varieties of cooperative non-covalent interactions is crucial to gain knowledge in this field. Several well established noncovalent interactions, such as hydrogen bonding [40-42], π-stacking [43], cation···π [44,45], and C-H···π forces [46-48], have been used to govern the organization of multicomponent supramolecular assemblies. Moreover, other less established forces, such as lone-pair···π [49,50] and anion···π interactions [51-53], have opened new possibilities in supramolecular recognition. Supramolecular chemistry is a new concept in anion transport, anion-sensing and anion-recognition chemistry [54-57] catalysis [58-61]. Relatively less common halogen bonding and halogen···halogen contacts have also been reported as important tools in crystal engineering [62]. In the present work, we have used two halosalicylaldimine Schiff bases to prepare two cadmium(II) complexes, $[Cd(L^1)(OOCCH_3)(OH_2)]$ (**1**), and $[Cd_2(L^2)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$ (**2**) {where HL^1 = 2-(2-(ethylamino)ethyliminomethyl)-4-bromophenol, and HL^2 = 2-(2-(dimethylamino)ethyliminomethyl)-4-chlorophenol}. Complex **1** forms a supramolecular dimer via Br···Br interactions. Both complexes contain coordinated solvent molecules which are involved in strong hydrogen bonding interactions. Herein, we report the synthesis, spectroscopic characterization and X-ray crystal structures of these two new complexes. In addition we would also like to shed light on the formation mechanism of the assemblies by means of density functional theory (DFT) calculations, estimating the contribution of each interaction to the formation of the assembly using several theoretical models.

2. Experimental

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

2.1. Preparations

*2.1.1 Synthesis of $[Cd(L^1)(OOCCH_3)(OH_2)]$ (**1**)* { HL^1 = 2-(2-(ethylamino)ethyliminomethyl)-4-bromophenol}

A methanol solution of 5-bromosalicylaldehyde (1 mmol, 0.201 g) and N-ethyl-1,2-diaminoethane (1 mmol, 0.105 mL) was refluxed for 1 h to prepare a tridentate N_2O donor Schiff base, {2-(2-(ethylamino)ethyliminomethyl)-4-bromophenol} (HL^1). The Schiff base was not isolated was used directly for the preparation of complex **1**. A methanol solution of cadmium(II) acetate dihydrate (1 mmol, 0.266 g) was added to the methanol solution of Schiff base and refluxed for 1 h. X-ray quality single crystals of complex **1** were obtained after few days on slow evaporation of the solution in open atmosphere.

Yield: 0.32 g {70%, based on Cd(II)}. Anal. Calc. for $C_{13}H_{19}CdN_2O_4Br$ (FW 459.61): C, 33.97; H, 4.17; N, 6.09; Found: C, 33.91; H, 4.13; N, 6.15 %. IR (KBr, cm^{-1}): 1650 ($\upsilon_{C=N}$), 2972-2874 (υ_{CH}), 3100-3390 ($\upsilon_{OH}/\upsilon_{NH}$). UV-Vis, λ_{max} (nm), [ε_{max} (L mol^{-1} cm^{-1})] (DMSO), 262 (6.4×10^4), 336 (4.4×10^3). ^{1}H NMR (DMSO-d_6) δ ppm: 8.225 (s, 1H, -C**H**=N); 7.199 (s, 1H, Ar-**H**); 7.083 (d, 1H, J = 5.8 Hz, Ar-**H**); 6.417 (d, 1H, J = 6.2 Hz, Ar-**H**); 3.68 (s, 2H, -O**H**$_2$); 3.591 (s, 1H, -N-**H**); 3.468 (q, 2H, -C**H**$_2$CH$_3$); 3.415 (m, 2H, -C**H**$_2$CH$_2$-); 2.712 (m, 2H, -CH$_2$C**H**$_2$-); 2.330 (s, 3H, -C**H**$_3$); 1.299 (t, 3H, J = 7 Hz, -CH$_2$C**H**$_3$).

*2.1.2. Synthesis of $[Cd_2(L^2)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$ (**2**)* { HL^2 = 2-(2-(dimethylamino)ethyliminomethyl)-4-chlorophenol}

A methanol solution of 5-chlorosalicylaldehyde (1 mmol, 0.156 g) and N,N-dimethyl-1,2-diaminoethane (1 mmol, 0.104 mL) was refluxed for 1 h to prepare a tridentate N_2O donor Schiff base, {2-(2-(dimethylamino)ethyliminomethyl)-4-chlorophenol} (HL^2). The Schiff base was not isolated and was used directly for the preparation of complex **2**. A methanol solution of cadmium(II) nitrate tetrahydrate (1 mmol, 0.308 g) was added to the methanol solution of Schiff base and refluxed for 1 h. A methanol solution of sodium thiocyanate (1 mmol, 0.81 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: 0.29 g {71%, based on Cd(II)}. Anal. Calc. for $C_{26}H_{34.52}Cl_2Cd_2N_6O_4S_2$ (FW 854.96): C, 36.53; H, 4.07; N, 9.83. Found: C, 36.46; H, 4.02; N, 9.90 %. IR (KBr, cm^{-1}): 1637 ($\upsilon_{C=N}$), 2112, 2077 (υ_{SCN}), 3443 (υ_{OH}), 2995-2839 (υ_{CH}). UV-Vis, λ_{max} (nm), [ε_{max} (L mol^{-1} cm^{-1})] (DMSO), 262 (8.7×10^4), 334 (8.5×10^4). ^{1}H NMR (DMSO-d_6) δ ppm: 8.214 (s, 1H, -C**H**=N); 7.118 (d, 1H, Ar-**H**); 7.025 (dd, 1H, J = 5.8 Hz, Ar-**H**); 6.527 (d, 1H, J = 6.4 Hz, Ar-**H**); 4.081 (q, 1H, J = 5.6 Hz, -O**H**-CH_3); 3.541 (m, 2H, -C**H**$_2$$CH_2$-); 3.156 (d, 3H, J = 5.9 Hz, -OH-C**H**$_3$); 2.570 (m, 2H, -CH_2C**H**$_2$-); 2.319 (s, 6H, -N(C**H**$_3$)$_2$).

2.2. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra in KBr (4500-500 cm^{-1}) were recorded using a PerkinElmer FT-IR spectrum two spectrometer. Electronic spectra in DMSO (200-800 nm) were recorded on a PerkinElmer Lambda 35 UV-Vis spectrophotometer. Fluorescence spectra in DMSO were obtained on a Hitachi F-7000 Fluorescence spectrophotometer at room temperature. ^{1}H NMR spectra were measured at room temperature using Bruker DPX-400 MHz NMR spectrometer. 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 spectra were recorded in a 2θ range of 5-50° using 1-D Lynxeye detector at ambient conditions.

2.3. X-ray crystallography

Single crystals of complexes, **1** and **2**, having suitable dimensions, were used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) at 150 K. The molecular structure was solved by direct method and refined by full-matrix least squares on F^2 using SHELXL-97 [63]. There is a disorder in C(3) in complex **2** and two sets of positions {C(3A) and C(3B)} were refined with occupancies of x and 1-x with x converging to 0.631(9). Non hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to oxygen and nitrogen 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 [64]. A summary of the crystallographic data is given in Table 1.

2.4. Computational methods

All calculations were carried out using the TURBOMOLE version 7.0 [65] using the BP86-D3/def2-TZVP level of theory. To evaluate the interactions in the solid state, we have used the crystallographic coordinates. This procedure and level of theory have been successfully used to evaluate similar interactions [66-69]. The interaction energies were computed by calculating the difference between the energies of isolated monomers and their assembly. Some weak interactions (< 1 kcal/mol) have been also evaluated using a higher level of theory (MP2/def2-TZVP) to provide more accurate results. The interaction energies were corrected for the Basis Set Superposition Error (BSSE) using the counterpoise method [70]. The calculation of the Molecular Electrostatic Potential surfaces was done using the Spartan program [71].

2.5. Hirshfeld Surface Analysis

Hirshfeld surfaces [72-74] and the associated two-dimensional (2D) fingerprint [75-77] plots were calculated using Crystal Explorer, [78] with bond lengths to hydrogen atoms set to standard values [79]. 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

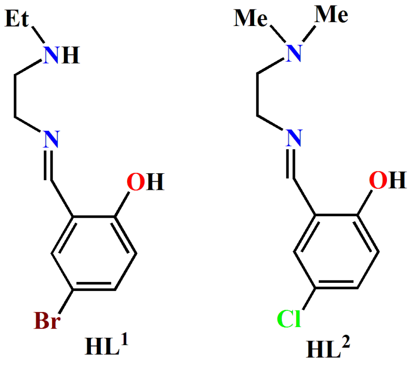
$$d_{norm} = \frac{\left(d_i - r_i^{vdw}\right)}{r_i^{vdw}} + \frac{\left(d_e - r_e^{vdw}\right)}{r_e^{vdw}}$$

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 [80] and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

3. Results and discussions

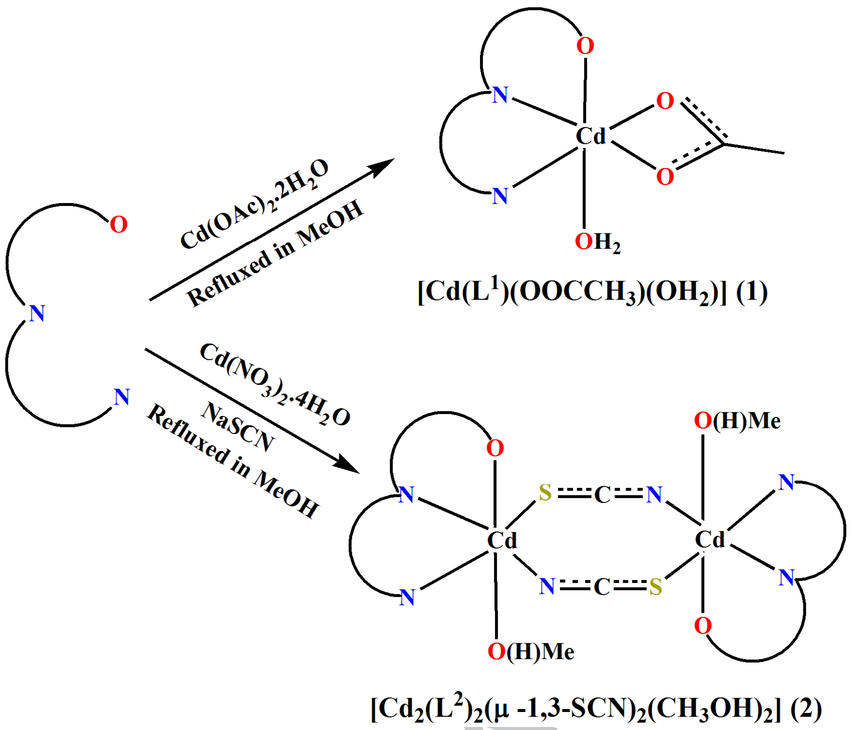
3.1. Synthesis

The tridentate Schiff base ligand, HL^1, was synthesized by the condensation of N-ethyl-1,2-diaminoethane with 5-bromosalicylaldehyde in methanol, following the literature method [81,82]. Similarly, another tridentate Schiff base, HL^2, was produced on refluxing N,N-dimethyl-1,2-diaminoethane with 5-chlorosalicylaldehyde. The Schiff base ligands were not isolated and used directly for the preparation of complexes.



Scheme 1: The Schiff base ligands, used in the present work.

Methanol solution of HL^1 was made to react with cadmium(II) acetate dihydrate under reflux to prepare the mononuclear complex, $[Cd(L^1)(OOCCH_3)(OH_2)]$ (**1**), in which cadmium(II) is coordinated by a depronated tridentate Schiff base, $(L^1)^-$ and oxygen atoms of an acetate and oxygen atom of one water molecule. On the other hand, addition of sodium thiocyanate to the methanol solution of HL^2 and cadmium(II) nitrate tetrahydrate, produced a dinuclear octahedral complex, $[Cd_2(L^2)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$ (**2**), in which, both cadmium(II) centres are in similar environment, being bonded to a depronated tridentate Schiff base, one nitrogen and one sulfur atom of two end-to-end thiocyanates. Methanol molecule coordinates in the sixth coordination site of each cadmium(II) to complete its distorted octahedral geometry. Formation of complexes is shown in scheme 2.



Scheme 2: Preparation of complexes **1** and **2**.

3.2. Description of structure

*3.2.1. [Cd(L^1)($OOCCH_3$)(OH_2)] (**1**)*

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. The ORTEP view of complex with selective atom numbering scheme is presented in Figure S1. The asymmetric unit consists of one cadmium(II), deprotonated form of one tridentate N_2O donor Schiff base, one water molecule and one acetate. The cadmium(II) centre, Cd(1), is apparently octahedrally coordinated by a phenoxo oxygen atom, O(1), amine nitrogen atom, N(1), imine nitrogen atom, N(2), from the deprotonated Schiff base ligand, $(L^1)^-$, an oxygen atom, O(2), from a water molecule and two oxygen atoms, O(3) and O(4), from a bidentate chelating acetate. The Schiff base ligand coordinates metal centre in meridional fashion. The Cd-N$_{imine}$ distance {2.284(3) Å} is shorter than the Cd-N_{amine} distance {2.362(3) Å}, as were also observed in similar systems [83]. The N(1)-Cd(1)-N(2) angle is 75.29(11)° and is typical of a five membered chelate ring [81]. The acetate ion is behaving as an unsymmetrical bidentate chelating ligand with unequal Cd(1)-O(3) and Cd(1)-O(4) distances [2.346(3) and 2.369(3) Å respectively]. The chelate bite angle, O(3)-Cd(1)-O(4) is 55.06(9)°. However, the small value of the angle may trace on the point that two oxygen atoms are sharing one site, i.e. the acetate group is better thought of as a single entity occupying just one stereochemical site in the coordination sphere of cadmium(II) instead of as a bidentate ligand. Thus the structure of the complex could be described as a distorted square pyramid with the value of Addison parameter [84], $\tau = 0.285$ { where, Addison parameter, $\tau = (\alpha-\beta)/60$, where α and β are the two largest Ligand-Metal-Ligand angles of the coordination sphere}. Selected bond lengths and bond angles are gathered in Tables S1 and S2, {Supplementary Information, (SI)} respectively.

Complex **1** shows significant hydrogen bonding interactions (Figure 1). The hydrogen atom, H(1), attached to amine nitrogen atom, N(1), creates a hydrogen bond with a symmetry related carboxylate oxygen atom, $O(3)^a$, (Symmetry transformation, ^{a} = 1+x,y,z) of a neighboring molecule. On the other hand, hydrogen atom, H(2S) linked to oxygen atom, O(2) of the coordinated water molecule, forms another hydrogen bond with identical symmetry related phenoxo oxygen atom, $O(1)^a$. Again, hydrogen atom, H(1S) of the same water molecule, forms an additional hydrogen bond with another symmetry related carboxylate oxygen atom, $O(4)^b$, (Symmetry transformation, ^{b} = 1-x,1-y,1-z) of a different neighboring molecule. Thus a double stranded hydrogen bonding chain is created. The details of hydrogen bonding interactions are given in Table 2.

An interesting feature in the complex is the presence of Br···Br interactions. Au···Au (aurophilicity) and Cu···Cu (cuprophilicity) interactions have long been well known in chemistry. The Br···Br interaction is also reported in the literature [23]. In complex, the Br···Br distance is 3.6135(7) Å, which is less than the sum of the van der Waals radii (1.9 Å). This Br···Br interaction creates a supramolecular dimeric structure as shown in Figure 2. There is no other significant supramolecular interaction present in the complex.

3.2.2. $[Cd_2(L^2)_2(\mu\text{-}1,3\text{-}SCN)_2(CH_3OH)_2]$ (**2**)

Complex **2** crystallizes in triclinic space group $P\bar{1}$. It features dual end-to-end thiocyanate bridged centrosymmetric dinuclear structure. The ORTEP view of complex with selective atom numbering scheme is presented in Figure S2. There is a disorder in C(3), and only one {C(3b)} of the two disordered positions (C3a, C3b) of C(3) is shown in Figure S2. The cadmium(II) is coordinated meridionally by one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), one phenoxo oxygen atom, O(1), of the tridentate deprotonated Schiff base, $(L^2)^-$ and one nitrogen atom, N(3), of coordinated thiocyanate and one oxygen atom, O(2), from a solvent methanol. The sixth coordination site of cadmium(II) is occupied by a symmetry related sulfur atom, $S(1)^c$, {Symmetry transformation ^{c} =1-x,1-y,1-z} of a thiocyanate to complete its octahedral geometry.

The saturated five membered chelate ring, Cd(1)-N(1)-C(3A)-C(4)-N(5), presents a half chair conformation with puckering parameters [85] q(2) = 0.497(5) Å, φ(2) = 230.0(6)°. The bridging thiocyanates are quasi-linear with the S-C-N angles being 179.6°(3). The Cd(II)···Cd(II) distance in the dinuclear moiety is 5.9023(2) Å. The Cd-N_{imine} distance {2.282(2) Å} is significantly shorter than the Cd-N_{amine} distance, {2.437(2) Å}, as were also observed in similar systems [83]. Selected bond lengths and angles are given in Tables S1 and S2, respectively.

Complex **2** shows significant intermolecular hydrogen bonding interactions (Table 2). Hydrogen atom, H(2), attached to the methanol oxygen atom, O(2), is participated in hydrogen bonding interaction with the symmetry related (1-x,2-y,1-z) phenoxo oxygen atom, O(1)^d to form a supramolecular chain as shown in Figure 3. There is no other significant supramolecular interaction present in the complex.

3.3. Theoretical results

Experimentally two new cadmium(II) complexes with two different N_2O ligands and anionic co-ligands have been synthesized and X-ray characterized (Figures S1 and S2). The theoretical study is devoted to the analysis of the interesting non-covalent interactions observed in the solid state of complexes **1** and **2**. In complex **1**, attention was given to the interactions involved in the formation of two dimers that are relevant to explain the crystal packing. First of all, molecular electrostatic potential surface (MEPS) of complex **1** has been computed (Figure 4A) in order to investigate the electrostatically favored interactions. As a result, the most positive part of the surface is located on hydrogen atoms of the cadmium(II)-coordinated water molecule. In addition, the coordinated oxygen atom of the anionic co-ligand (acetate) presents a strongly negative electrostatic potential. Therefore, the MEP surface explains the formation of the self-assembled dimer observed in the crystal packing where two symmetrically equivalent O-H···O hydrogen bonds are formed (Figure 4B). The interaction is very favored energetically (ΔE_1 = -22.1 kcal/mol) because the electrostatic potential value at the hydrogen atom is large (74 kcal/mol) due to the enhanced acidity of this hydrogen atom as a consequence of the coordination of the water to the cadmium(II) metal centre. In an effort to evaluate the influence to the metal coordination on the hydrogen bonding energy, an additional theoretical model has been computed where only one isolated water molecule is used (Figure 4C). As a result the interaction energy is reduced to ΔE_2 = -5.9 kcal/mol (compared to ½ × ΔE_1 = -11.1 kcal/mol) that confirms the large influence of the coordination of the water molecule to the cadmium(II) on the binding strength. It should be mentioned that a close examination of the MEP surface reveals the existence of a weak σ-hole on the extension of the C-Br bond (3 kcal/mol) that can be related to the formation of halogen bonded dimers in the solid state (Figure 4D). It is well known [86-88] that halogen atoms can form halogen···halogen contacts, which are generally divided into two major categories depending on their geometry, i.e. type I ($\theta_1 \simeq \theta_2$) and type II ($\theta_1 \simeq 180°$, $\theta_2 \simeq 90°$), where θ_1 and θ_2 are the C-X···X′ and C-X′···X angles (X, X′ = Cl, Br, I). Type II contacts involve an approach of the electrophilic region of one halogen atom to the nucleophilic region of the other, while in type I contacts two halogen atoms minimize repulsion by interfacing the neutral regions of their MEP surfaces. In complex **1**, the Br···Br contact is of type I ($\theta_1 \simeq \theta_2$ = 144º) and its interaction has been evaluated by computing the dimerization energy (Figure 4C) of the complex observed in the solid state. The interaction energy is almost negligible, (ΔE_3 = -0.1 kcal/mol, BSSE correction = 0.03 kcal/mol) which can be related to the small σ-hole and the directionality of the interaction. The influence of the ligand coordination to the cadmium(II) on the Br···Br interaction energy has also been evaluated. The dimerization energy of the same complex was computed (Figure 4D) where the cadmium(II) and co-ligands were eliminated and the ligand was protonated. As a result the interaction energy becomes slightly more favourable (ΔE_4 = -0.5 kcal/mol, BSSE correction = 0.04 kcal/mol). Since this energetic value is very small, this dimer has also been calculated using a higher level of theory (MP2/def2-TZVP) and the interaction energy is similar ΔE_4 = -0.7 kcal/mol (BSSE correction = 0.3 kcal/mol), giving reliability to the level of theory used in this manuscript and confirming the weak nature of the Br···Br interaction found in complex **1**.

The MEP surface of the dinuclear complex **2** has also been computed (Figure 5B) and the most positive part of the molecule corresponds to the hydroxyl hydrogen atom of the coordinated methanol molecule. Moreover, the coordinated oxygen atom of the organic ligand also exhibits a strongly negative electrostatic potential explaining the formation of infinite chains in the solid state stabilized by the formation of symmetrically equivalent O-H···O hydrogen bonds. This interaction has been evaluated energetically by computing one dimer of the chain (Figure 5A). As expected, the interaction energy is very large (ΔE_5 = -37.8 kcal/mol) due to the contribution of strong electrostatic effects caused by the coordination of the methanol to the cadmium(II) (enhanced acidic proton). A theoretical model also has been used (Figure 5C) where, the methanol is uncoordinated and the interaction is reduced to (ΔE_6 = -8.7 kcal/mol) thus confirming the strong influence of the metal coordination on the strength of the hydrogen bonds. The MEP surface also reveals that in this complex, the chlorine atom of the ligand does not exhibit a positive σ-hole on the extension of the C-Cl bond, which can be related to the absence of halogen bonding interaction in the solid state of complex **2**.

3.4. IR and NMR spectra

In IR spectra of complexes, distinct bands due to azomethine (C=N) stretching vibrations appears at 1650 and 1637 cm^{-1}, respectively. The asymmetric and symmetric stretching vibrations of the acetate group in complex **1** appear at 1558 and 1460 cm cm^{-1}, respectively. The difference between υ_{asym}(COO) and υ_{sym}(COO) ($\Delta\upsilon$ = 98 cm^{-1}), which is smaller than 164 cm^{-1} observed in ionic acetate, reflects the bidentate bridging coordination mode [89]. μ-1,3- mode of thiocyanate groups is confirmed by the splitting of absorption band corresponding to SCN-stretching vibration appearing at 2112 and 2077 cm^{-1} (indicating S- and N-coordination modes respectively). In addition, two medium bands are observed at 825 and 721 cm^{-1} related to ʋ(CS) [90-92]. Broad bands around 3374 and 3443 cm^{-1} are assigned as OH stretching vibrations in IR spectra of complexes, **1** and **2**, respectively. Bands in the range of 2995-2839 cm^{-1} due to alkyl C-H bond stretching vibrations are customarily noticed in the IR spectra of both complexes. IR spectra of complexes are given in Figure S3.

^{1}H NMR spectra for complexes **1** and **2** were recorded in DMSO-d$_6$ and summarized in experimental section. The imine protons (-CH=N) of complexes, **1** and **2**, appeared as a singlet at 8.225 ppm and 8.214 ppm, respectively whereas, aromatic protons of both complexes were customarily noticed in the range of 7.2-6.4 ppm. The methylene protons of diamine moiety of complexes **1** and **2** appeared as multiplet in the range of 3.5-2.6 ppm. The amine proton of diamine moiety and protons of coordinated water molecule in complex **1** were noticed as singlet at 3.59 and 3.68 ppm, respectively. In complex **2**, the proton of coordinated methanol molecule was appeared as quartet at 4.08 ppm. ^{1}H NMR spectrum of complex **2** is shown in Figure 6.

3.5. Electronic and fluorescence spectra

10^{-4} molar solution of complexes in DMSO were taken for the measurement of electronic spectra in the range 200-800 nm at room temparature. In both complexes, intense absorption bands are observed around 260 and 330 nm, respectively. All bands are assigned as intra ligand charge transfer transitions [81,93,94]. Luminescencent properties of complexes at 10^{-6} molar concentration in DMSO solution were investigated at room temperature. On exciting at 336 and 334 nm, emissions are observed around 393 nm for complexes **1** and **2**, respectively. For cadmium(II) complexes, emission originating from metal-centered MLCT/LMCT excited states are not expected, since cadmium(II) is difficult to oxidize or reduce due to its stable d^{10}

configuration. Thus, the emissions observed in the complexes are tentatively assigned to the (π-π^*) intraligand fluorescence [95,96]. Excitation and emission spectra of both complexes are shown in Figure S4.

Relative fluorescence quantum yields for both complexes were measured in DMSO using quinine sulfate (in 0.5 (M) H_2SO_4, $\Phi = 0.54$) as the quantum yield standard [97]. Fluorescence quantum yields of complexes **1** and **2** are 0.0311, 0.0744 respectively.

3.6. Powder X-ray diffraction

The experimental powder XRD patterns of bulk product of complexes are in good agreement with simulated XRD patterns from single crystal X-ray diffraction, confirming purity of the bulk samples (Figure 7). The simulated patterns were calculated from the single crystal structural data (cif file) using the CCDC Mercury software.

3.7. Hirshfeld surface analysis

Hirshfeld surfaces mapped over d_{norm}, shape index and curvedness, for the complexes **1** and **2**, is illustrated in Figure S5. The surfaces are shown as transparent to allow visualization of the molecular moiety around which they are calculated. The dominant interaction between O···H, X···H atoms { X = Br, (for complex **1**), X = Cl (for complex **2**)} can be seen in the Hirshfeld surfaces as red spots on the d_{norm} surface in Figure S5. Other visible spots in the Hirshfeld surfaces correspond to H···H contacts. The small extent of area and light color on the surface indicate weaker and longer contact other than hydrogen bonds. The intermolecular interactions O···H / H···O and X···H / H···X appear as distinct spikes in the 2D fingerprint plot (Figure S6). Complementary regions are visible in the fingerprint plots where one molecule acts as a donor ($d_e > d_i$) and the other as an acceptor ($d_e < d_i$). The fingerprint plots can be decomposed to highlight particular atom pair close contacts [98]. This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The proportions of O···H/ H···O interactions comprises 19.7 and 6.8 % of the Hirshfeld surfaces for each molecule of complexes **1** and **2**, respectively. On the other hand, X···H/H···X interactions {where, X = Br, (for **1**), X = Cl (for **2**)} contributes 12.4 and 14.8 % of the Hirshfeld surfaces for each molecule of complexes **1** and **2**, respectively. The O···H interaction is represented by a spike (d_i = 1.06, d_e = 0.66 Å in **1**, and d_i = 1.06, d_e = 0.67 Å in **2**) in the right (donor) area of the fingerprint plot (Figure S6). The H···O interaction is also represented by another spike (d_i = 0.70, d_e = 1.06 Å in **1**, and d_i = 0.67, d_e = 1.06 Å in **2**) in the left (acceptor) region of fingerprint plot and can be viewed as a bright red spots on the d_{norm} surface.

4. Summary

Synthesis and characterization of two new photoluminescent cadmium(II) complexes with halosalicylaldimine Schiff base ligands have been described in the present paper. The cadmium(II) centre in **1** is apparently octahedral being coordinated by a phenoxo oxygen atom, an amine nitrogen atom and imine nitrogen atom of the deprotonated Schiff base, an oxygen atom from a water molecule and two oxygen atoms from a bidentate chelating acetate. The small value of the chelate bite angle may trace on the point that two oxygen atoms are sharing one site, i.e. the acetate group could better be thought of as a single entity occupying just one stereochemical site in the coordination sphere of cadmium(II) instead of as a bidentate ligand. Thus the structure of the complex could be described as a distorted square pyramid. Complex **2** features double end-to-end thiocyanate bridged dinuclear structure. In both complexes, there are strong hydrogen bonding interactions. Moreover in complex **1**, weak type-I Br···Br contacts have been detected and studied by means of DFT calculations. In both complexes, the influence of the metal coordination of water and methanol molecules on their ability to form hydrogen bonding interactions has been analyzed theoretically.

Acknowledgement

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Appendix A. Supplementary data

CCDC 1062841 and 1062842 contain the supplementary crystallographic data for **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.

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

Complex	**1**	**2**
Formula	$C_{13}H_{19}CdN_2O_4Br$	$C_{26}H_{34.52}Cl_2Cd_2N_6O_4S_2$
Formula Weight	459.61	854.96
Temperature (K)	150	150
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a(Å)	5.5031(2)	8.3928(2)
b(Å)	9.7180(3)	9.0289(2)
c(Å)	16.4199(5)	11.8485(3)
α(°)	100.025(2)	110.675(1)
β(°)	95.487(2)	93.152(1)
γ(°)	97.843(2)	92.750(1)
Z	2	1
d_{calc} (g cm^{-3})	1.795	1.700
μ (mm^{-1})	3.649	1.596
F(000)	452	427
Total Reflections	12925	12701
Unique Reflections	3258	3188
Observed data [$I > 2\sigma(I)$]	2850	2999
No. of parameters	202	204
R(int)	0.032	0.022
R1, wR2 (all data)	0.0376, 0.0767	0.0253, 0.0600

R1, wR2 [$I > 2\sigma(I)$]	0.0307, 0.0722	0.0236, 0.0588

Table 2: Hydrogen bond distances (Å) and angles (º) of complexes **1** and **2**.

Complex	D–H···A	D–H	H···A	D···A	∠D–H···A
1	N(1)–H(1)···O(3)[a]	0.85	2.05	2.900(4)	173(3)
	O(2)–H(1S)···O(4)[b]	0.78	1.93	2.709(4)	178(7)
	O(2)–H(2S)···O(1)[a]	0.86	1.85	2.711(4)	173(4)
2	O(2)–H(2)···O(1)[d]	0.78	1.87	2.641(3)	173(4)

D, donor; H, hydrogen; A, acceptor. Symmetry transformations [a] = 1+x,y,z, [b] =1-x,1-y,1-z, [d] = 1-x,2-y,1-z.

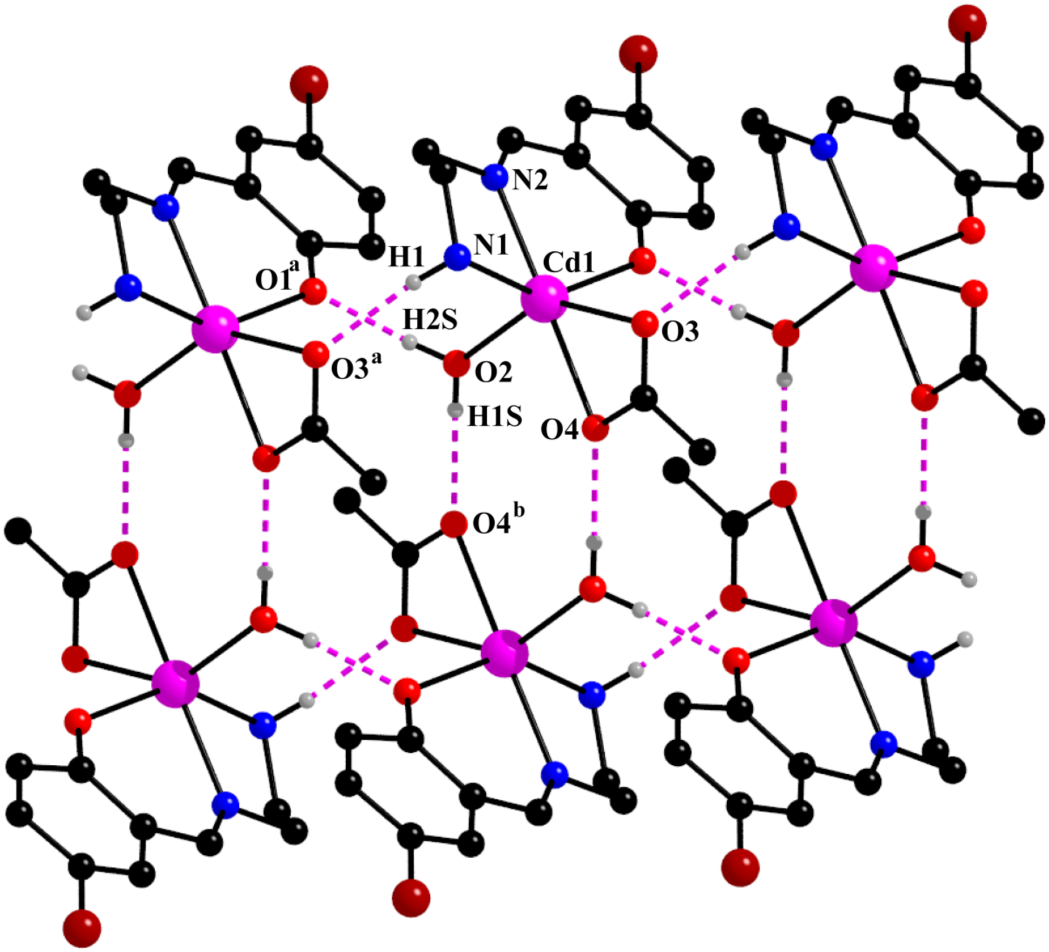


Figure 1: Hydrogen bonded chain in complex **1**. Selected hydrogen atoms are omitted for clarity. Symmetry transformations ^{a} = 1+x,y,z; ^{b} =1-x,1-y,1-z.

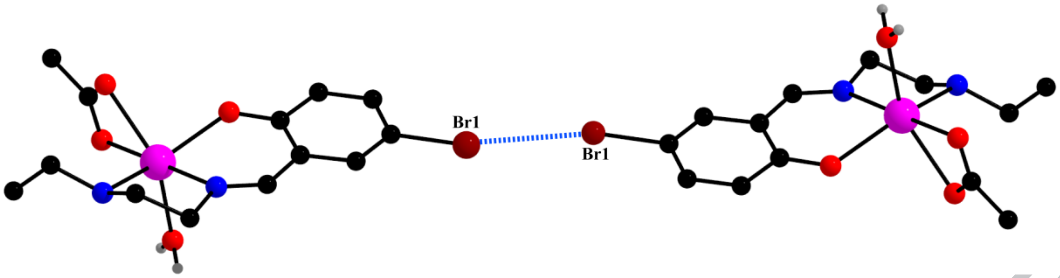


Figure 2: Br···Br interactions in complex **1**. Hydrogen atoms are not shown for clarity.

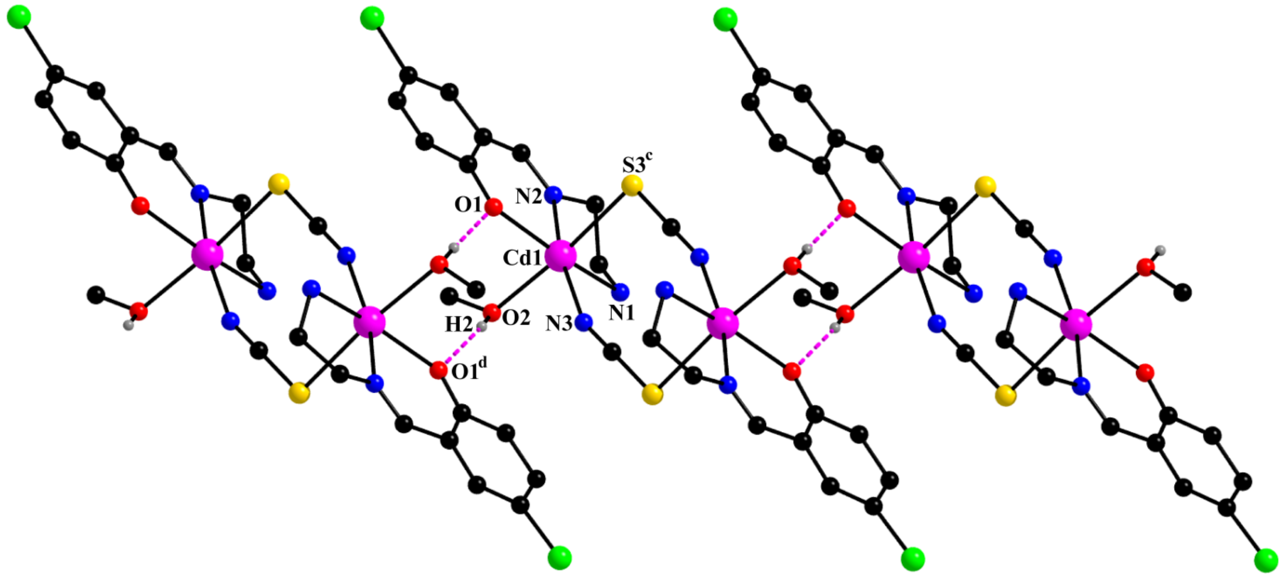


Figure 3: Supramolecular chain in complex **2**, generated through hydrogen bonding interactions. Methyl groups attached to amine nitrogens and selected hydrogen atoms are omitted for clarity. Symmetry transformations ^{c} =1-x,1-y,1-z; ^{d} = 1-x,2-y,1-z.

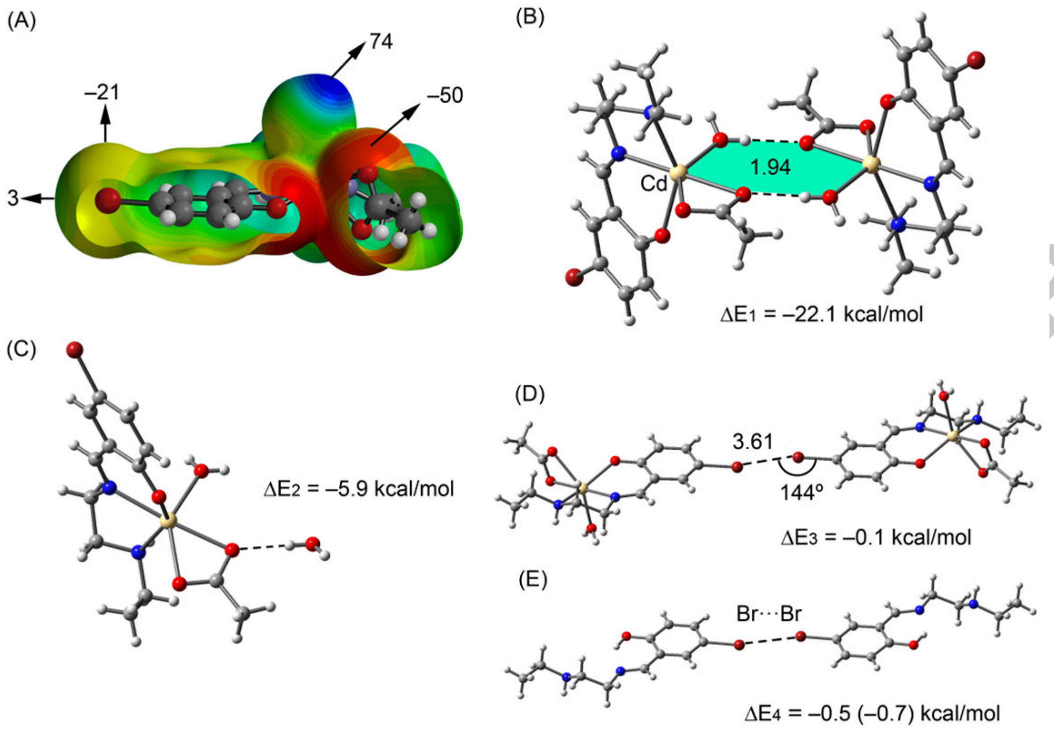


Figure 4: (A) MEP surface of complex **1**, the MEP values at selected points are given in kcal/mol. (B-E) Theoretical models used to evaluate the noncovalent interactions, distances in Å.

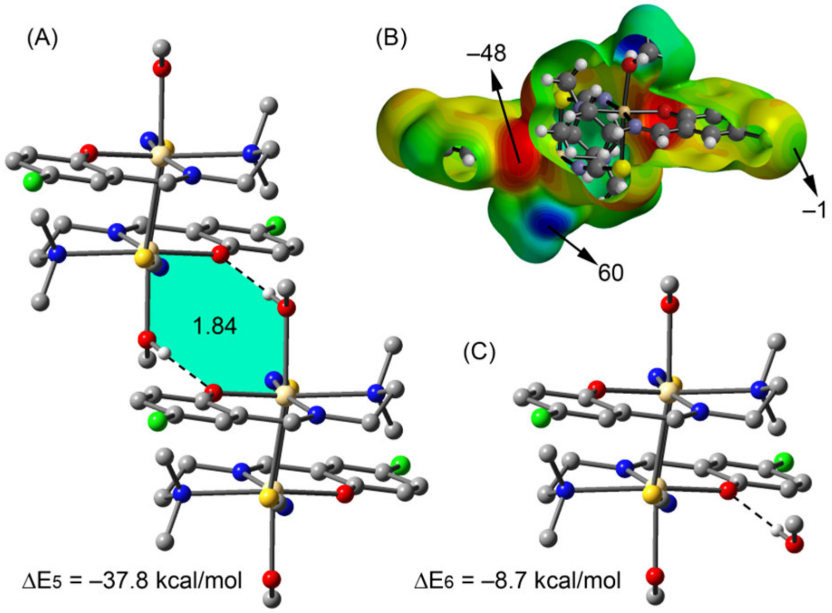


Figure 5: (A and C). Theoretical models used to evaluate the noncovalent interactions in complex **2**. Distances are in Å. Hydrogen atoms apart from the ones that participate in the hydrogen bonding interactions have been omitted for clarity. (B) MEP surface of complex **2**, the MEP values at selected points are given in kcal/mol.

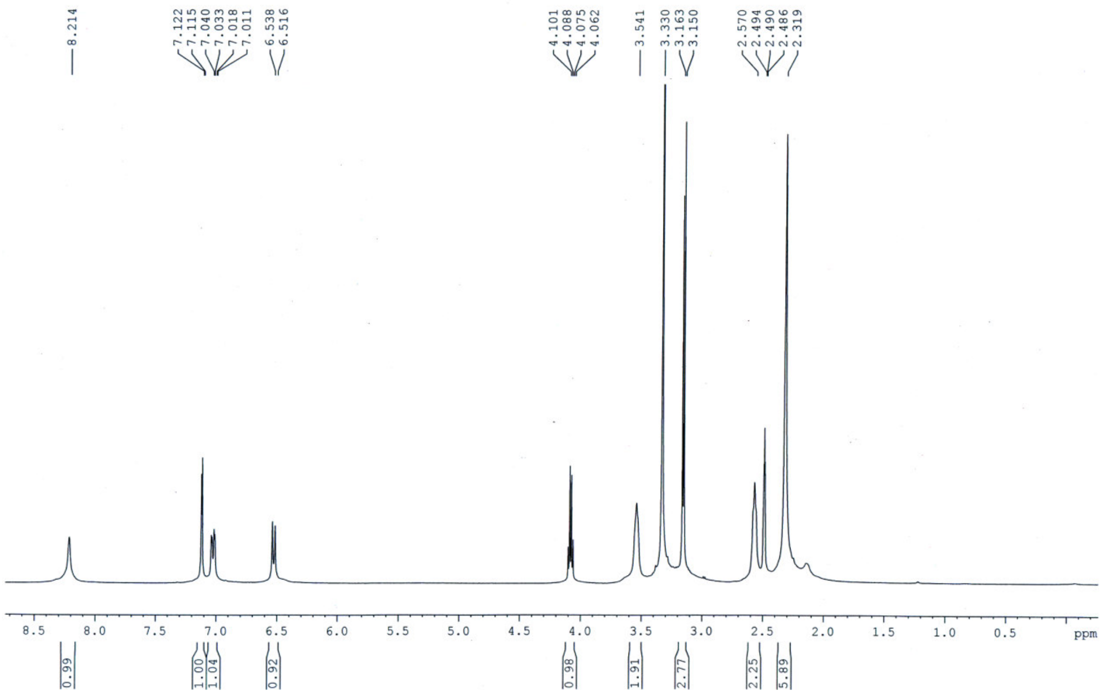


Figure 6: ^{1}H NMR spectrum of complex **2**.

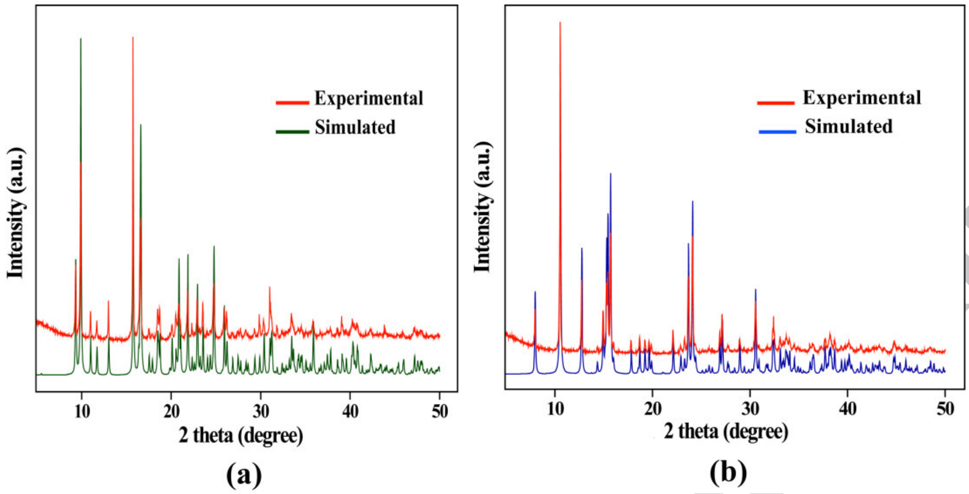


Figure 7: Experimental and simulated powder XRD patterns of complexes (a) **1**, (b) **2**, confirming the purity of the bulk materials.

Graphical Abstract (Synopsis)

A combined experimental and computational study of supramolecular assemblies in two photoluminescent cadmium(II) complexes with halosalicylaldimine Schiff bases

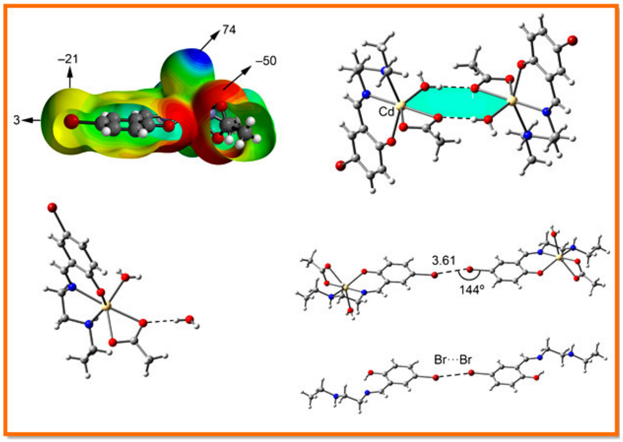
Sumit Roy, Antonio Bauzá, Antonio Frontera, Shouvik Chattopadhyay

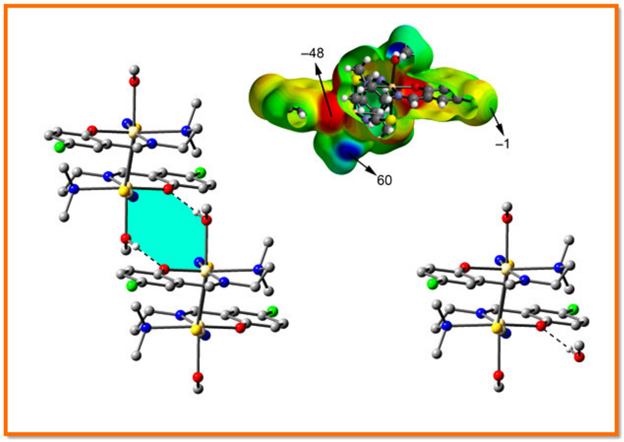
Two new photoluminescent cadmium(II) complexes with halosalicylaldimine Schiff bases have been synthesized and characterized. The structures have been confirmed by single crystal X-ray analysis. Supramolecular interactions in both complexes have been explored and analysed by means of DFT calculations.

Graphical Abstract (Pictogram)

A combined experimental and computational study of supramolecular assemblies in two photoluminescent cadmium(II) complexes with halosalicylaldimine Schiff bases

Sumit Roy, Antonio Bauzá, Antonio Frontera, Shouvik Chattopadhyay





A combined experimental and computational study of supramolecular assemblies in two photoluminescent cadmium(II) complexes with halosalicylaldimine Schiff bases

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Research Highlights

- Synthesis and characterisation of two photoluminescent cadmium(II) complexes with halosalicylaldimine Schiff base ligands.
- Molecular structures on the basis of X-ray crystallography
- Supramolecular dimer via Br···Br interactions
- DFT calculations of supramolecular interactions