Structural and luminescent properties of a tetranuclear cage-type cadmium(II) carboxylate cluster containing a V-shaped water trimer

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ABSTRACT
The structural characterization of tetranuclear cage-type cadmium(II) carboxylate \[\text{[Cd}_4(2\text{-cpida})_2(2,2'\text{-bpy})_6\text{-CIO}_4\text{-3H}_2\text{O}}\] (1) (2-H\text{3}cpida = N-(2-carboxyphenyl)iminodiacetic acid, 2,2'-bpy = 2,2'-bipyridine) is described. H-bonding interactions between three lattice water molecules form a V-shaped trimer (H\text{2}O)\text{3}, which is stabilized by 1. In addition, luminescence investigations revealed that 1 shows enhanced emissions as compared with free 2-H\text{3}cpida in the liquid state.

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1. Introduction

Inorganic–organic hybrid compounds with extended structures have intriguing structural motifs, bio-chemistries, and interesting electro-conductive, optical, and magnetic properties [1]. Metal carboxylates have been extensively studied because the carboxylate can bind to metal ions in various modes, such as monodentate, bidentate, and bridging [2]. Recent studies have focused on complexes with multidentate ligands such as the N-(carboxyphenyl)iminodiacetic acid (H₃cpida) series, which has two important features: (a) the iminodiacetate is more flexible than other carboxylate groups (e.g. benzene-tricarboxylate) and can, thus adopt different coordination modes and (b) the aromatic rings can offer additional π–π interactions that may stabilize frameworks. With two or more coordinated groups, polytopic ligands can be utilized for the construction of molecular architectures with specific magnetic or optical properties owing to various ways they can interact with metal ions [3, 5, 6].

Forces that influence the structure and properties of host–guest systems are hydrogen bonding interactions involving water molecules. Hence, characterization of small hydrogen-bonded water clusters not only help in understanding bulk water, but also provide clues to better understand how such aggregates influence, stabilize, or functionize the overall structure of the surrounding host lattices in the design of new materials. A series of water clusters such as (H₂O)ₙ (n = 3–6, 8, 10–12, 14–18, 45) with 1-D chain, 2-D layer, and 3-D structures have been found in supramolecular networks [7]. A water trimer is the smallest water cluster in the class. The cluster exhibits three-body interactions and plays a central role in efforts to develop non-additive potentials to bulk water [8]. Extensive theoretical investigations have been performed on cyclic water trimer [9], and the first solid state evidence to support the theoretically established cyclic geometry of the isolated water trimer was provided by MacGillivray and Atwood [10]. Surprisingly, an experimental investigation on a V-shaped water trimer, which is also one of the isomers of water trimers apart from the cyclic one is very rare [9(b), 11]. The first V-shaped water trimer was found crystallographically by Ghosh et al. in 2005, which coexisted with a water nonamer [9(b)]. In the same year, Liao et al. found a V-shaped water trimer in the structure of a metal-organic framework, wherein the water trimer (one coordinated water and two crystallization waters) was found to play an important role in the formation of a 3-D supramolecular structure [11(a)]. Zhou et al. observed an isolated V-shaped water trimer and protonated diethylenetriamine molecules can coexist in the crystal lattice of ferrous molybdenum(V) phosphate that formed an unprecedented 1-D strip-like arrangement via hydrogen bonding interactions [12]. Recently, we reported a mixed Ni(II) ion complex [13] which contains a V-shaped water trimer.

Few reports on cage-type tetranuclear clusters based on cadmium carboxylates have been published. In 2004, Kim et al. reported a tetranuclear cadmium carboxylate cluster, which was the first metal–organic analog of fluorite (CaF₂) [14]. Rowan et al. described a tetranuclear cadmium carboxylate cluster and its dynamic properties were studied by variable temperature (VT) ¹H NMR spectroscopy [6]. Recently, Huo et al. reported the hydrothermal synthesis and photoluminescence properties of a cadmium tetranuclear complex based on 2-substituted-8-hydroxyquinoline [15]. The introduction of an ancillary ligand like 2,2′-bipyridine (2,2′-bpy) has been widely used to impede the aggregation of metal centers, owing to the excellent chelating mode of this ligand as well as its ability to provide potential supramolecular contact (π–π stacking interactions) [16]. Polynuclear d¹⁰ metal (Zn(II), Cd(II)) coordination compounds have attracted interest because of their photoluminescent properties [17]. There is no report on a tetranuclear cadmium carboxylate cluster with 2,2′-bpy as a co-ligand. Inspired by the aforementioned considerations, we present the synthesis, structural characterization, stabilization of water trimer through hydrogen bonding interactions and its luminescent properties.

2. Experimental

2.1. Instruments and methods

All starting materials and products were stable towards moisture and air, and hence no specific precautions were taken to exclude air during the manipulation. Elemental analyses were performed on a
Perkin-Elmer 2400 Series Elemental Analyzer at IIT Madras. Infrared spectra were recorded on a Perkin Shimadzu spectrometer Spectrum One as KBr disks. UV–vis spectra were recorded using JASCO UV–vis NIR and methanol as solvent. Thermal analysis was carried out on a Perkin Elmer thermal analysis system. Commercial grade solvents were purified using conventional procedures and distilled prior to use [18]. Commercially available starting materials, cadmium acetate tetrahydrate (S.D. Fine), chloroacetic acid (S.D. Fine), 2-aminobenzoic acid (S.D. Fine), sodium perchlorate (Aldrich), and 2,2'-bipyridine (Aldrich) were used as received. N-(2-carboxyphenyl)iminodiacetic acid (2-H3cpida) was synthesized as described previously [19].

**Caution!** Perchlorate salts of metal complexes with organic ligands should be handled with care as they can cause an explosion.

### 2.2. Synthesis of [Cd4(2-cpida)2(2,2'-bpy)6]·(2,2-bpy)·(ClO4)·3H2O (1)

A solution of 2,2'-bipyridine (0.312 g, 2.0 mmol) in methanol (10 mL) was added to a methanol solution (20 mL) containing Cd(OAc)2·2H2O (0.266 g, 1 mmol). The solution was stirred at 40 °C for 2 h, followed by 2-H3cpida (0.166 g, 0.66 mmol) in methanol (10 mL) added dropwise. To the above solution, a saturated aqueous solution of NaClO4 (2 mL) was added. The colorless clear solution was filtered and kept for crystallization at room temperature. Colorless crystals formed after one week, were filtered and washed with ethanol and dried in vacuo (yield: 54%) m.p.: 210–212 °C (dec). Anal. Calcd for C92H82Cd4Cl2N16O26: C, 50.30; H, 3.58; N, 10.20%. Found: C, 50.97; H, 3.75; N, 10.74%. IR (KBr, cm −1): 3432 s, 3075 w, 2925 w, 1594 s, 1475 s, 1438 s, 1388 s, 1401 s, 1315 m, 1280 m, 1247 m, 1095 s, 1014 s, 925 w, 848 w, 763 s. UV–vis: λmax(CH3OH)/nm 206, 235, 285, 307: Fluorescence: λex 285 nm (CH3OH)/nm 325, 402.

### 2.3. Crystal structure determination

Compound 1 was obtained as white crystals by slow evaporation using methanol solvent. Crystal measurement was made on a Bruker Kappa Apex II coupled with a CCD area detector with graphite-monochromated with Mo-Kα radiation and wavelength of 0.71073 Å. The crystal, with approximate dimensions of 0.40 × 0.35 × 0.30 mm was mounted on a glass loop. The structure was solved by direct methods and expanded using Fourier techniques. All calculations were performed using the Crystal Structure Crystallographic software package X shell. The structure solution was achieved by direct methods as implemented in SHELXS-97. Final refinement of the structures was carried out using least-squares on $F^2$ using SHELXS-97 [20]. The crystal and refinement data are collected in table 1.

### 3. Results and discussion

#### 3.1. Synthesis and spectral characterizations

We obtained crystals of 1 in the reaction between 2-H3cpida and 2,2'-bpy with cadmium acetate in methanol solvent. The synthetic route to 1 is shown in scheme 1. Compound 1 was obtained in an analytically pure form and characterized by FT-IR, UV–vis absorption, emission spectroscopy, and single-crystal XRD analysis. H3cpida is a bifunctional bridging ligand that possesses six carboxylate oxygens, which serve as a bridging multidentate ligand. One nitrogen of the imine group also coordinates with cadmium, which leads to the tetranuclear clusters.

The FT-IR spectrum of 1 showed a broad absorption at 3400 cm−1, which was ascribed to the O–H stretch and suggested the presence of free water molecules. The emergence of peaks at 1400–1500 cm−1 confirmed the presence of –CH2 bending vibrations. The strong peaks of carboxyl groups appeared at 1594 cm−1 due to antisymmetric stretching vibrations and 1315–1475 cm−1 corresponding to symmetric stretching vibrations. No peaks were observed at 1700 cm−1, indicating complete deprotonation of the carboxylic acid groups in 1 (figure S1) [21].
3.2. Crystal structure of \([\text{Cd}_4(2\text{-cpida})_2(2,2\text{'-bpy})_6\text{(2,2-bpy)\cdot(ClO}_4\text{)}\cdot3\text{H}_2\text{O}}\) (1)

Compound 1 crystallizes in the triclinic P-1 space group (table 1). As shown in figure 1, there are two crystallographically independent Cd(II) centers in the asymmetric unit along with a perchlorate, a non-coordinated 2,2′-bpy, and three lattice waters.

The Cd(1) is six-coordinate with a distorted octahedral geometry, which is achieved by two carboxylate oxygens \([\text{Cd}(1)–\text{O} = 2.251–2.269 \text{ Å}]\) and four nitrogens \([\text{Cd}(1)–\text{N} = 2.382–2.392 \text{ Å}]\) from 2,2′-bpy ligands. Cd(2) is also six-coordinate with an octahedral geometry, surrounded by three carboxylate oxygens \([\text{Cd}(2)–\text{O} = 2.251–2.268 \text{ Å}]\), one nitrogen from 2-cpida ligand \([\text{Cd}(2)–\text{N}(7) = 2.443 \text{ Å}]\) and two nitrogens from 2,2′-bpy ligands \([\text{Cd}(2)–\text{N} = 2.228–2.310 \text{ Å}]\).

Two types of coordination modes of 2-cpida are present in the structure: (a) monodentate through one oxygen from phenylcarboxylate of 2-cpida and (b) four oxygens of two acetate groups, which adopt bidentate bridging modes (syn–syn). In addition, \(\pi–\pi\) aromatic stacking interactions between the 2,2′-bpy ligands (interplanar distances \(d(C(13)⋯C(27)) = 3.351 \text{ Å}\)) give a cage-type tetranuclear Cd(II) cluster, as shown figure 2(a) and 2(b). Two different Cd–Cd distances are present in 1 (Cd1–Cd1 8.768 Å and Cd2–Cd2 6.058 Å, figure 2(c)), which are longer than similar Cd(II) analogs [15, 22(b), (c)] and shorter than one [22(a)], which may be due to aromatic steric hindrance present in the ligands.

![Scheme 1. Synthesis of 1.](image)

### Table 1. Crystal data and structure refinement parameters of 1.

| Parameter                        | Value                  |
|----------------------------------|------------------------|
| Empirical formula                | \(\text{C}_{92}\text{H}_{82}\text{Cd}_4\text{Cl}_4\text{N}_6\text{O}_{26}\) |
| \(\text{FW}\)                    | 2348.24                |
| Temp. (K)                        | 293(2)                 |
| Wavelength (Å)                   | 0.71073                |
| Crystal system                   | Triclinic              |
| Space group                      | P-1                    |
| \(a\) (Å)                        | 13.6900(5)             |
| \(b\) (Å)                        | 14.1180(7)             |
| \(c\) (Å)                        | 14.5410(7)             |
| \(α\) (°)                        | 113.34(2)              |
| \(β\) (°)                        | 92.3360(10)            |
| \(γ\) (°)                        | 111.16(10)             |
| \(V\) (Å³)                      | 2350.38                |
| \(Z\)                            | 1.00                   |
| \(D(\text{Calcld})\) (Mg/m³)    | 1.498                  |
| Abs. coeff. (mm⁻¹)               | 1.036                  |
| \(F(000)\)                       | 1180                   |
| Crystal size (mm³)               | \(0.20 \times 0.10 \times 0.10\) |
| \(θ\) range (°)                  | 2.12–25.00             |
| Data/restraints/parameters       | 8206/49/659            |
| Goodness-of-fit on \(R^2\)       | 1.081                  |
| \(R_1\) [\(I > 2\sigma(I)\)]   | 0.0268                 |
| \(R_2\) [\(I > 2\sigma(I)\)]   | 0.0342                 |
Other bond lengths and angles lie in the normal range for octahedral Cd(II) complexes and are listed in table 2 [2(a)].

The lattice water molecules form a V-shaped water trimer by intermolecular hydrogen bonds, as shown in figure 3 [11(a), 12]. The average O⋯O distance in the trimeric water is 2.866 Å, which is slightly greater than the corresponding values in ice Ih (2.759 Å) and very close to those in liquid water (2.854 Å). The O⋯O⋯O angle is 130.9°, which differs somewhat from that of hexagonal ice (109.3°) [23]. This is likely caused by a lack of further hydrogen bonding to a neighboring molecule, which makes water molecules more linear than in hexagonal ice. The observed O⋯O⋯O angle (> 130°) evidently is caused by the water molecules occupying “free” space between complex molecules, with the geometry of the water clusters being dictated not only by hydrogen bonding but also the geometries of the occupied interstices. Intramolecular hydrogen bonding is observed between oxygen of acetate of 2-cpida and –CH of 2,2′-bpy [C(21)⋯O(1) 3.498 Å, ∠C(21)–H21⋯O(1) 163.1°] and intermolecular hydrogen bonding occurs between the water trimer with non-coordinated oxygen of phenylcarboxylate [O(5)⋯O(116)]

Figure 1. A view of 1 showing the atom-numbering scheme (C–H, hydrogens have been omitted for clarity).

Figure 2. (a) Coordination modes in 1. (b) Intramolecular π–π aromatic stacking interactions between the 2,2′-bpy ligands in 1. (c) Representation of the coordination geometry and Cd⋯Cd distances in 1.
Table 2. Selected bond lengths (Å) and angles (°) for 1.

| Bond lengths (Å) | Bond angles (°) |
|------------------|-----------------|
| Cd(1)–Cd(2) 5.260(3) | O(1)–Cd(1)–O(3) 105.80(7) |
| Cd(2)–Cd(2) 6.058(3) | O(3)#2–Cd(1)–N(2) 83.36(8) |
| Cd(1)–Cd(1) 8.768(2) | O(3)#2–Cd(1)–N(3) 84.94(9) |
| Cd(1)–O(1) 2.251(3) | O(1)–Cd(1)–N(1) 83.87(8) |
| Cd(1)–O(3) 2.269(3) | N(2)–Cd(1)–N(4) 68.54(9) |
| Cd(1)–O(4) 2.269(3) | N(2)–Cd(1)–N(3) 92.14(9) |
| Cd(1)–O(6) 2.251(3) | N(2)–Cd(1)–N(4) 53.85(9) |
| Cd(1)–N(1) 2.369(3) | N(3)–Cd(1)–N(4) 69.01(9) |
| Cd(1)–N(2) 2.382(3) | O(1)–Cd(1)–O(3) 105.80(7) |
| Cd(1)–N(3) 2.384(5) | O(3)#2–Cd(1)–N(4) 83.36(8) |
| Cd(1)–N(4) 2.384(5) | N(3)–Cd(1)–N(4) 92.14(9) |
| Cd(1)–N(5) 2.384(5) | N(3)–Cd(1)–N(1) 151.41(9) |
| Cd(1)–N(6) 2.443(3) | N(4)–Cd(1)–N(1) 145.99(9) |
| Cd(1)–N(7) 2.310(3) | O(6)–Cd(2)–O(4) 83.77(9) |
| Cd(2)–O(2) 2.251(3) | O(6)–Cd(2)–O(6) 103.86(9) |
| Cd(2)–O(4) 2.251(3) | N(5)–Cd(2)–N(6) 163.99(10) |
| Cd(2)–O(6) 2.251(3) | O(2)–Cd(2)–N(7) 78.60(8) |
| Cd(2)–N(5) 2.282(3) | O(2)–Cd(2)–N(7) 71.39(8) |
| Cd(2)–N(6) 2.244(3) | O(2)–Cd(2)–N(7) 123.17(9) |
| Cd(2)–N(7) 2.310(3) | O(2)–Cd(2)–N(7) 71.39(8) |
| Cd(2)–N(8) 2.310(3) | O(2)–Cd(2)–N(7) 123.17(9) |

Figure 3. Detailed representation of hydrogen bonding interaction and V-shaped water trimer in 1. Observed hydrogen bond lengths (Å) and angles (°): O(116)–H(11C)⋯O(5) 1.34.8(4), D-H 1.232(1), H⋯A 2.164(4), D⋯A 2.751(8); O(116)–H(11D)⋯O(115) 151.9(5), D-H 0.850(2), H⋯A 1.980(4), D⋯A 2.760(1); O(117)–H(11A)⋯O(115) 152.5(1), D-H 0.850(2), H⋯A 2.192(3), D⋯A 2.973(6); C(24)–H(24)⋯O(115) 152.7(9), D-H 0.931(1), H⋯A 2.498(6), D⋯A 3.352(2); C(28)–H(28)⋯O(6) 148.4(7), D-H 0.930(2), H⋯A 2.480(4), D⋯A 3.309(1); C(21)–H(21)⋯O(1) 163.2(5), D-H 0.930(4), H⋯A 2.598(1), D⋯A 3.498(2). Equivalent positions: (a) −x + 2, −y, −z; (b) −x + 2, −y, −z + 1.
2.826 Å, \( \angle \text{O(5)}-\text{H116} \cdots \text{O(116)} \) 134.7°] as shown in figure 3. As a result, all the secondary interactions along with \( \pi-\pi \) aromatic stacking interactions lead to a 2-D supramolecular assembly in the solid state as shown in figure 3.

### 3.3. Fluorescence property of 1

Compound 1 shows two types of electronic excited state transitions, ligand-to-ligand charge transfer and ligand-to-metal charge transfer. The two bands are assigned to intraligand \( \pi-\pi^* \) transition between \( \pi \) bonding HOMO and \( \pi^* \) antibonding LUMO [23]. The luminescent emission of 1 is dual emission, at 325 nm and 402 nm for excitation at 285 nm in methanol at room temperature (figure 4). Molecules that display dual emission are unusual and the twin peaks in the emission spectra may originate from the mixed-ligand system of (2-cpida and 2,2'-bpy) and supramolecular interactions, such as \( \pi-\pi \) stacking and hydrogen bond interactions. It can be compared with respective free ligands, the emissions occurred at 320 nm (2-H\(_3\) cpida) and 318 nm (2,2'-bpy). The fluorescence emission spectrum of tetrameric 1 exhibits a significant red shift at the emission maximum, which may be ascribed to cooperative effects of intraligand emission [24, 25]. The result is consistent with the existence of two emissive states and an assignment of the orbitals may be involved in the \( \pi^* \) of 2-H\(_3\)cpida and 2,2'-bpy phenyl orbitals [15, 26]. The red shift is perturbed at least in the following factors: (i) the introduction of metal ions enhances the mobility of the electron transfer in the backbone and decreases the electron transition energy of intra-ligand charge transfer due to backcoupling \( \pi \)-bond between the metal and the ligand; (ii) chelating of ligand to metal ion; (iii) the lack of coplanarity of 2,2'-bpy rings, shifting the emission energy to longer wavelength; (iv) the influence of \( \pi-\pi \) stacking interaction on 2,2'-bpy. The broad overlap emission band implies more complicated relationship between structure and fluorescent behavior. Furthermore, time-resolved fluorescence studies provide invaluable information about a system when more than one emitting species contributes to steady-state fluorescence intensities. In the present study, we have carried out fluorescence lifetime studies to confirm involvement of the two emission species present in the molecule. The intensity decay is best fit by a bi-exponential decay with a mean decay time near 2.58 ns when monitored at an emission wavelength at 325 nm (inset figure 4). The second emission is attributed with tri-exponential decay with mean decay time near 1 ns when the emission wavelength is 402 nm [27].

![Figure 4. Absorption and emission spectrum of 1 (inset: time resolved lifetime spectrum).](image-url)
3.4. Thermal analysis of 1

The thermal stability of 1 has been investigated by thermogravimetric (TG) analysis. TG curve for 30 °C at 10.0 (K/min) to 1000 °C under N₂ is illustrated in figure 5. The TG curve of 1 shows a weight loss of 9.36% from 86 to 206 °C, ascribed primarily to removal of lattice water and lattice 2,2’-bpy. The second stage mass loss occurred at 211–266 °C (4.75%) and corresponded to the removal of the perchlorate [13]. The third maximum rate of mass loss (68.11%) from 271 to 661 °C corresponded to coordinating ligand. Total mass loss of 1 was observed at 968 °C (11.25%), with CdO as a residue.

4. Conclusion

We synthesized and structurally characterized the tetrameric cadmium carboxylate 1 based on a multicarboxylate ligand. The carboxylate group showed monodentate and bidentate bridging modes, which led to formation of a tetrameric cage-type cluster. The lattice water molecules form a water trimer due to hydrogen bonding interactions and stabilization by the tetrameric cadmium cluster. Secondary interactions, including π–π aromatic stacking interactions, lead to a 2-D supramolecular assembly in the solid state. Luminescence investigations show that 1 has enhanced twin emissions as compared with the free ligands in the liquid state. The observations provide valuable information to develop multinuclear Cd(II) based optical materials.

Supplementary material

CCDC 908147 contains the supplementary crystallographic data for 1. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif or E-mail: data_request@ccdc.cam.ac.uk.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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