

# A mixed Ni(II) ionic complex containing V-shaped water trimer: Synthesis, spectral, structural and thermal properties of $\{[\text{Ni}(2,2'\text{-bpy})_3][\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]\}(\text{ClO}_4)\cdot 3\text{H}_2\text{O}$

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**Abstract.** A mixed Ni(II) ionic complex of  $\{[\text{Ni}(2,2'\text{-bpy})_3][\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]\}(\text{ClO}_4)\cdot 3\text{H}_2\text{O}$  (**1**) (2-H<sub>3</sub>cpida = N-(2-carboxyphenyl)iminodiacetic acid, 2,2'-bpy = 2,2'-bipyridyl) has been synthesized and characterized by infrared, ultraviolet and fluorescence spectroscopy, elemental and thermogravimetric analysis. The molecular structure of compound **1**, as determined by single-crystal X-ray diffraction studies, showed all the three carboxylate groups are in monodentate mode. Compound **1** consists of a discrete mononuclear  $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$  cation, a  $[\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]^-$  anion, a  $\text{ClO}_4^-$  anion and three lattice water molecules. The H-bonding interaction between three lattice water molecule forms a V-shaped trimer  $(\text{H}_2\text{O})_3$  which gives rise to a 1-D polymeric structure in the solid state.

**Keywords.** Ionic complex; hydrogen bonding; water trimer; thermal studies.

## 1. Introduction

“Inorganic–organic hybrid compounds with extended structures are of interest due to their intriguing structural motifs, biochemistries, and interesting electroconductive, optical, and magnetic properties. Among these, metal carboxylates have been extensively studied because the carboxylate group can bind to metal ions in various modes, such as monodentate, bidentate and bridging.”<sup>1–7</sup> Recent studies have focused on complexes with multidentate ligands such as with N-(carboxyphenyl)iminodiacetic acid (H<sub>3</sub>cpida) series, which has two important features: (a) the iminodiacetate group is more flexible than other groups, such as, benzene-tricarboxylate, and can adopt different coordination modes; (b) the introduced aromatic rings can offer additional  $\pi-\pi$  interactions that may stabilize the framework. With two or more coordinated groups, polytopic ligands can be utilized for the construction of molecular architectures with specific magnetic or optical properties due to various types of interactions with the metal ion.<sup>8–12</sup> The introduction of ancillary ligand like 2,2'-bipyridine (2,2'-bpy) has been widely used to impede

the aggregation of metal centres, owing to the excellent chelating mode of this ligand as well as its ability to provide potential supramolecular contact ( $\pi-\pi$  stacking interactions).<sup>13</sup> Lattice water and coordinated water exist extensively in supramolecular networks and often exhibit strong hydrogen bonding interactions. Recently, considerable attention has been paid to the crystal structures incorporating lattice water clusters. A series of water clusters such as  $(\text{H}_2\text{O})_n$  ( $n = 3-6, 8, 10-12, 14-18, 45$ ), 1D chain, 2D layer and 3D structures have been found in supramolecular networks,<sup>14–21</sup> and they are known to play important roles during the assembly of supramolecular systems. Here, we report the synthesis, structure and thermal properties of  $\{[\text{Ni}(2,2'\text{-bpy})_3][\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]\}(\text{ClO}_4)\cdot 3\text{H}_2\text{O}$  (**1**) (2-cpida = N-(2-carboxyphenyl)iminodiacetic acid, 2,2'-bpy = 2,2'-bipyridyl), a novel mixed ionic complex.

## 2. Experimental

### 2.1 Instruments and methods

All starting materials and products were found to be stable towards moisture and air, and hence no specific precautions were taken to rigorously exclude air during

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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 diluted KBr discs. UV–Visible spectra were recorded using JASCO UV–Vis–NIR in methanol as solvent. Thermal analysis was carried out on a Perkin Elmer thermal analysis system. Commercial grade solvents were purified using conventional procedures and were distilled prior to use.<sup>22</sup> Commercially available starting materials, nickel(II) 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-H<sub>3</sub>cpida) was synthesized as described previously in the literature.<sup>23</sup> *Caution! perchlorate salts of metal complexes with organic ligands should be handled with care as they can cause explosion.*

### 2.2 Synthesis of {[Ni(2,2'-bpy)<sub>3</sub>][Ni(2-cpida)(2,2'-bpy)]} (ClO<sub>4</sub>).3H<sub>2</sub>O (**1**)

A solution of 2,2'-bipyridine (0.156 g, 1.0 mmol) in methanol (5 mL) was added to a methanol solution (10 mL) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (0.124 g, 0.5 mmol). The solution was stirred at 40°C for 2 h, and 2-H<sub>3</sub>cpida (0.083 g, 0.33 mmol) in methanol (5 mL) was added dropwise. To this solution saturated aqueous solution of NaClO<sub>4</sub> (1 mL) was added. The purple clear solution so obtained was filtered and kept for crystallization at room temperature. Crystals formed after 2 weeks and were removed by filtration, washed with ethanol, and dried in vacuo. Yield: 68.2%. M.p.: ~271°C (dec). Anal. Calcd for C<sub>51</sub>H<sub>46</sub>ClN<sub>9</sub>Ni<sub>2</sub>O<sub>14</sub>: C 51.83; H 3.26; N 10.67 Found: C 52.17; H 3.75; N 10.74. IR (KBr, cm<sup>-1</sup>): 3415(s), 3089(w), 1600(vs), 1475(s), 1442(s), 1405(s), 1362(m), 1313(s), 1240(m), 1096(vs), 1020(m), 904(w), 775(s), 736(m). UV-Vis (CH<sub>3</sub>OH, nm): 208, 247, 296, 520. Fluorescence: (λ<sub>ex</sub> = 296 nm, MeOH): 340 nm. Φ = 0.021.

### 2.3 Crystal structure determination

Compound **1** was obtained as a dark purple crystal by the slow evaporation method by 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 (0.71073 Å). The crystal, with approximate size 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

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

	<b>1</b>
empirical formula	C <sub>51</sub> H <sub>46</sub> ClN <sub>9</sub> Ni <sub>2</sub> O <sub>14</sub>
Fw	1161.84
temp, K	293(2)
wavelength, Å	0.71073
crystal system	Monoclinic
space group	P2(1)/c
a, Å	16.6491(10)
b, Å	12.9446(7)
c, Å	24.2031(16)
α, °	90
β, °	98.974(2)
γ, °	90
V, Å <sup>3</sup>	5152.3(5)
Z	4.00
D(calcd), Mg/m <sup>3</sup>	1.498
abs coeff, mm <sup>-1</sup>	0.859
F(000)	2400
cryst size, mm <sup>3</sup>	0.40 × 0.35 × 0.30
θ range, °	1.24 to 28.31
Data/restraints/params	12584/9 /728
goodness-of-fit on F <sup>2</sup>	0.999
R <sub>1</sub> [I > 2σ(I)]	0.0572
R <sub>2</sub> [I > 2σ(I)]	0.1488

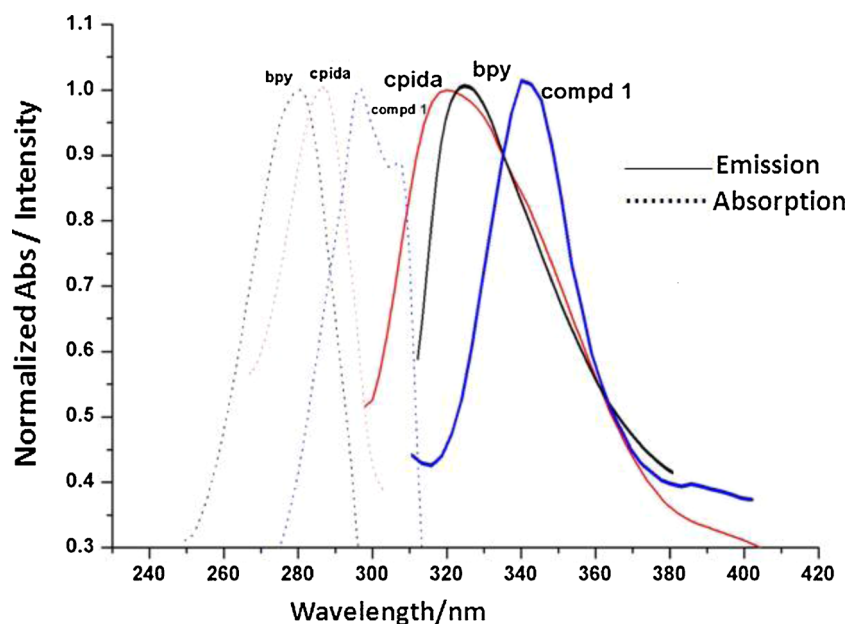
were performed using the Crystal Structure Crystallographic software package X shell. The structure solution was achieved by direct methods as implemented in SHELXS-97.<sup>24</sup> Final refinement of the structures was carried out using full least-squares methods on F<sup>2</sup> using SHELXS-97.<sup>25</sup> The crystal and refinement data are collected in table 1.

## 3. Results and Discussion

### 3.1 Synthesis and spectral characterization

Purple crystals of compound **1** was produced by combining N-(2-carboxyphenyl)iminodiacetic acid and 2,2'-bipyridine with nickel(II) acetate tetrahydrate in methanol as solvent. Compound **1** was obtained in an analytically pure state and characterized by FT–IR, UV–Vis absorption, emission spectroscopy, thermal and single crystal X-ray diffraction analysis.

In the IR spectrum of compound **1**, the Ni–O bond appeared at 482 cm<sup>-1</sup>, asymmetric and symmetric stretching vibration bands of COO<sup>-</sup> groups appeared at 1656, 1446, and 1397 cm<sup>-1</sup> respectively. The strong absorption band at 1112 cm<sup>-1</sup> indicates the presence of a perchlorate ion in the complex. The spectrum of the nickel



**Figure 1.** Absorption and Fluorescence spectra of compound **1** and other molecules.

complex shows one symmetrical band at  $3400\text{ cm}^{-1}$ , which was assigned to stretching vibrations of the  $-\text{OH}$  groups of water in the molecule (figure S1).<sup>26</sup>

The UV–Vis absorption spectrum of compound **1** showed three major peaks in the UV region, indicating the presence of  $\pi-\pi^*$  and  $n-\pi^*$  transitions. These peaks were at 208, 247, 296 nm attributed to the 2,2'-bpy and 2-cpida of ligand to metal charge transfer transition (LMCT). The band at 520 nm corresponded to a  $d-d$  transition ( ${}^3A_{2g}-{}^1E_g$ ) of a distorted octahedral Ni(II) complex (figure S2 in Supplementary Information).<sup>27</sup>

The emission spectrum of compound **1** at room temperature is shown in figure 1. Compound **1** displayed a fluorescence emission maximum at 340 nm upon excitation at 296 nm.

The emission peak of 2-cpida is at 323 nm for excitation at 284 nm.<sup>23</sup> The emission of **1** occurs at a longer wavelength than that of 2-cpida and 2,2'-bpy ligands. The bathochromic shift can be explained by ligand-to-metal charge transfer (LMCT) between 2-cpida, 2,2'-bpy ligands and Ni(II) metal ion.<sup>28</sup>

### 3.2 Molecular structure of $\{[\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})][\text{Ni}(2,2'\text{-bpy})_3]\}(\text{ClO}_4)_3\cdot 3\text{H}_2\text{O}$ (**1**)

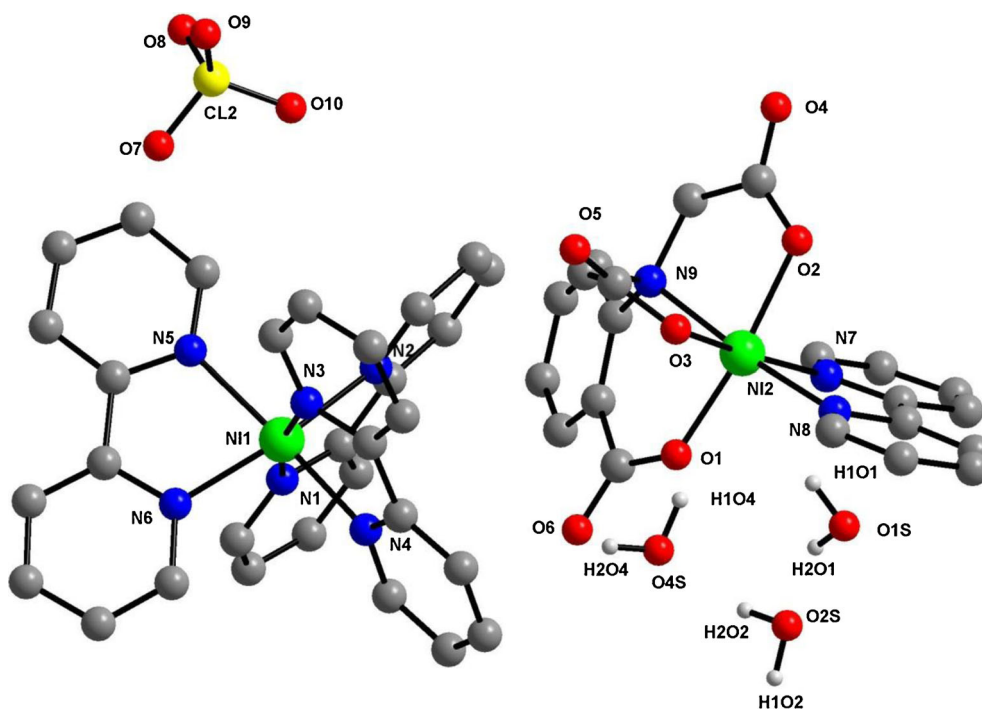
Compound **1** crystallizes in monoclinic  $P2(1)/c$  space group. Selected bond lengths and angles are listed in table 2. Single crystal X-ray analysis revealed that the asymmetric unit of compound **1** consists of one cation  $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$ , one anion of  $[\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]^-$ , one perchlorate  $(\text{ClO}_4)^-$  and three lattice water mole-

cules (figure 2). The structure of  $[\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]^-$  differed from those of  $[\text{Ni}(\text{PtcH})_2][\text{Ni}(2,2'\text{-bpy})(\text{H}_2\text{O})_4]\cdot 6\text{H}_2\text{O}$  (**A**),<sup>15</sup> ( $\text{PtcH}$  = Pyridine-2,4,6-tricarboxylic acid) and  $[\text{Ni}(\text{Phen})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{PtcH})_2]\cdot 11\text{H}_2\text{O}$  (**B**).<sup>18</sup> In **A** and **B**, the anionic complex is formed by two carboxylic acid ligands where as compound **1** it is constructed from 2-cpida and 2,2'-bpy ligands. The anionic unit of nickel(II) atom is coordinated by three oxygen atoms ( $\text{Ni}(2)-\text{O}(1) = 2.000(3)\text{ \AA}$ ,  $\text{Ni}(2)-\text{O}(2) = 2.061(3)\text{ \AA}$ ,  $\text{Ni}(2)-\text{O}(3) = 2.061(3)\text{ \AA}$ ) from carboxyl groups of 2-cpida ligand in monodentate co-ordination mode, one nitrogen atom ( $\text{Ni}-\text{N}(9) = 2.197(8)\text{ \AA}$ ) from 2-cpida and two nitrogen atom from 2,2'-bpy ligand. *Trans*  $\text{N}-\text{Ni}-\text{N}$ ,  $\text{O}-\text{Ni}-\text{N}$  and  $\text{N}-\text{Ni}-\text{N}$  bond angles were all close to  $175^\circ$ , whereas the *cis*  $\text{N}-\text{Ni}-\text{N}$ ,  $\text{O}-\text{Ni}-\text{N}$  and  $\text{N}-\text{Ni}-\text{N}$  bond angles were  $\sim 90^\circ$ , indicating a distorted octahedral structure. In the cationic part, the metal centre is coordinated to three 2,2'-bpy in a distorted octahedral fashion. Other bond lengths and angles lie in the normal of octahedral Ni(II) complexes.<sup>15,18</sup>

It is worthy to point out that the lattice water molecules form V-shaped water trimer<sup>20</sup> by intermolecular hydrogen bonds as shown in figure 3. The hydrogen bonding parameters are presented in table 3. The average  $\text{O}\cdots\text{O}$  distance in trimeric water is  $2.836\text{ \AA}$ , which is slightly longer than the corresponding values in ice *Ih* ( $2.759\text{ \AA}$ ) and very close to water ( $2.854\text{ \AA}$ ). The  $\text{O}\cdots\text{O}\cdots\text{O}$  angle is  $111.6^\circ$  which is very close to the value of  $109.3^\circ$  in hexagonal ice.<sup>19</sup> This is caused by no further hydrogen bonding interactions to a neighbouring molecule apart from

**Table 2.** Selected bond lengths (Å) and angles (°) for compound **1**.

Ni(1)–N(1)	2.087(3)	Ni(1)–N(5)	2.106(3)
Ni(1)–N(2)	2.086(3)	Ni(1)–N(6)	2.078(3)
Ni(1)–N(3)	2.066(3)	Ni(2)–N(7)	2.047(3)
Ni(1)–N(4)	2.095(3)	Ni(2)–N(8)	2.098(3)
Ni(2)–N(9)	2.117(3)	Ni(2)–O(1)	2.000(3)
Ni(2)–O(2)	2.061(3)	Ni(2)–O(3)	2.051(3)
Ni(2)–O(5)	4.014(3)	O(1)S–H(1)O(1)	0.873(5)
O(2)S–(1)O(2)	0.874(5)	O(4)S–H(1)O(4)	0.863(7)
N(2)–Ni(1)–N(1)	78.77(12)	O(1)–Ni(2)–O(2)	172.84(11)
N(3)–Ni(1)–N(4)	78.37(12)	O(1)–Ni(2)–N(7)	95.67(12)
N(6)–Ni(1)–N(5)	78.35(12)	O(1)–Ni(2)–N(9)	89.93(11)
N(7)–Ni(2)–N(8)	78.80(12)	H(1)O(1)–O(1)S–H(2)O(1)	100.5(11)
O(2)–Ni(2)–N(8)	89.25(11)	H(1)O(2)–O(2)S–H(2)O(2)	99.8(12)
O(1)–Ni(2)–N(9)	89.93(11)	H(1)O(4)–O(4)S–H(2)O(4)	104.7(11)

**Figure 2.** Molecular structure of  $\{[\text{Ni}(2,2'\text{-bpy})_3][\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]\}(\text{ClO}_4)\cdot 3\text{H}_2\text{O}$  (**1**) (hydrogen atoms are omitted for clarity).

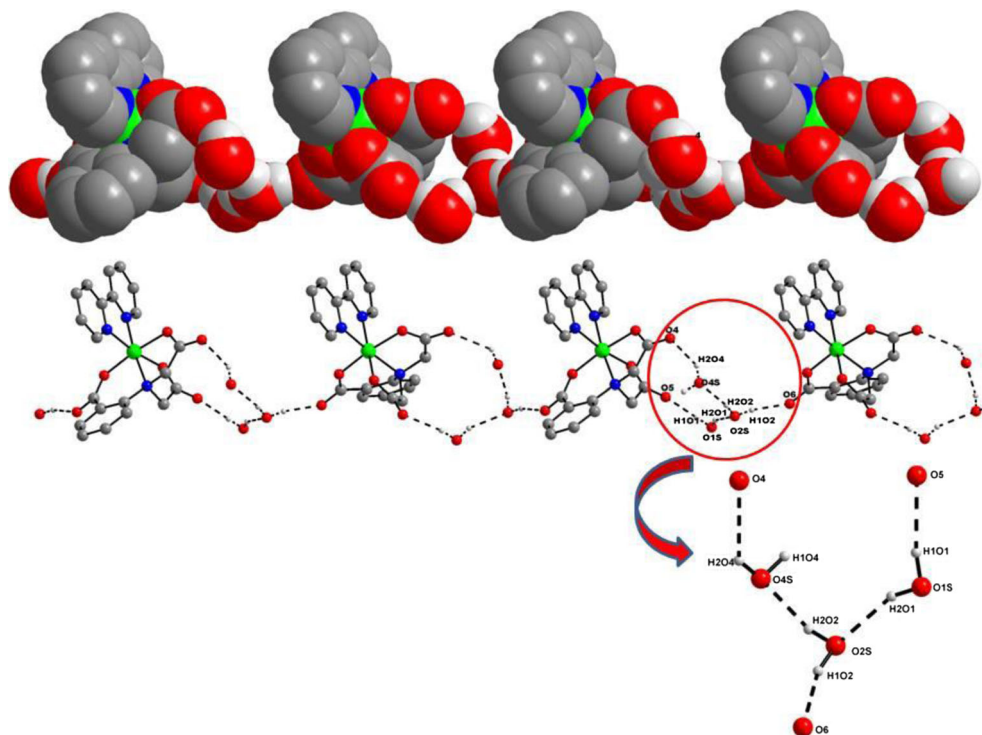
water trimer, which makes water molecules more linear than in hexagonal ice. The molecule is further stabilized by intermolecular hydrogen bonding between –OH group of water molecule and oxygen atom of carboxyl group from 2-cpida to form 1-D polymeric chain (figure 3).

### 3.3 Thermal analysis

Thermal analysis of compound **1** was carried out under a stream of dinitrogen. It was especially useful to

establish presence of water molecules in the complexes. The TG curve of compound **1** was depicted in figure 4. It suggests that mass loss of compound **1** starts at  $\sim 50^\circ\text{C}$ , with constant weight loss up to  $296^\circ\text{C}$ . The corresponding weight loss was  $\sim 5.34\%$ , which was due to the removal of lattice water molecules. The maximum rate of weight loss occurred at  $306\text{--}331^\circ\text{C}$  and  $336\text{--}341^\circ\text{C}$  (mass loss of  $8.46\%$  to  $64.54\%$ ) which is due to the removal of perchlorate anion and organic moieties. After the mass loss in decomposition stage of compound **1**, NiO is left as a residue appearing at



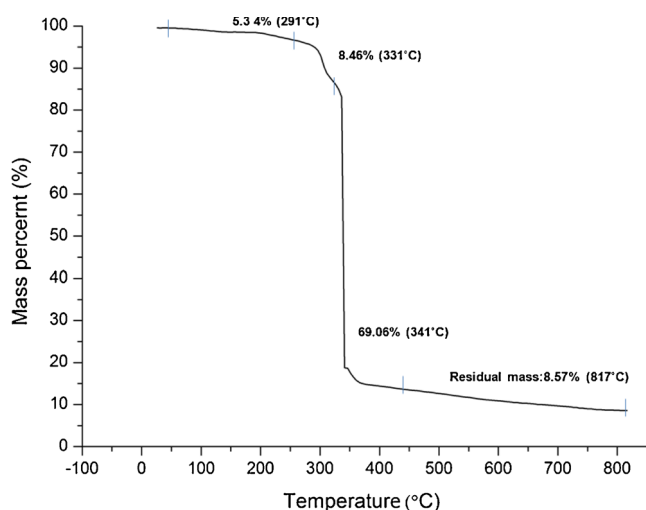


**Figure 3.** Detailed representation of the hydrogen bonding interactions and V-shaped water trimer in **1**.

**Table 3.** Geometrical parameters of hydrogen-bonds (Å, °) for the water trimer in **1**.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O(1)S–H(2)...O(2)S <sup>a</sup>	0.861(2)	2.068(3)	2.886(4)	158.44(5)
O(2)S–H(2)...O(4)S <sup>a</sup>	0.868(3)	1.933(1)	2.782(7)	165.82(6)
O(1)S–H(1)...O(5) <sup>b</sup>	0.873(3)	2.022(3)	2.874(6)	164.89(4)
O(4)S–H(2)...O(4) <sup>b</sup>	0.856(4)	2.303(1)	2.978(2)	135.99(5)
O(2)S–H(1)...O(6) <sup>c</sup>	0.875(3)	1.865(1)	2.708(7)	161.36(6)

Equivalent positions: (a)  $x, y, z$ , (b)  $-x+1, +y+1/2+1, -z+1/2$ , (c)  $-x+1, -y+1, -z+1$



**Figure 4.** Thermal analysis of compound **1**.

~820°C (8.57%). Total mass change of compound **1** is 91.46%.

## 4. Conclusions

We describe the synthesis of a mixed ionic Ni(II) complex **1**. Compound **1** was characterized by analytical and spectroscopic techniques. The X-ray diffraction studies revealed that the unit cell contains two crystallographically and chemically different molecules [Ni(1) and Ni(2)], a cation of  $[\text{Ni}(2,2'\text{-bpy})_3]^{2+}$  and an anion of  $[\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})]^-$ . The coordination mode of carboxylate anion is monodentate. The lattice water molecules form V-shaped water trimer ( $\text{H}_2\text{O}$ )<sub>3</sub> by intermolecular hydrogen bonds. Compound **1** is stabilized by intermolecular hydrogen bonding between water trimer and carboxyl oxygen atom to form a 1-D polymeric chain.

## Supplementary Information

CCDC 998663 contains the supplementary crystallographic data for  $\{[\text{Ni}(2\text{-cpida})(2,2'\text{-bpy})][\text{Ni}(2,2'\text{-bpy})_3]\}$

(ClO<sub>4</sub>).3H<sub>2</sub>O (**1**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). e-mail: [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk). Figures S1 and S2 show the FT-IR and Absorption spectrum of mixed ionic complex **1**, available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci).

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