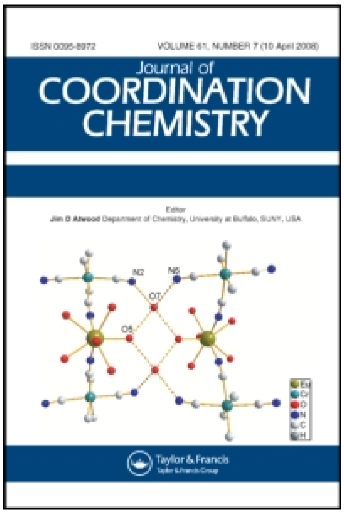

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Two different 2,2'-bipyridine cadmium(II) perchlorate complexes, $[Cd(2,2'\text{-}bipy)_2(H_2O)(ClO_4)]ClO_4$ and $[Cd(2,2'\text{-}bipy)_3](ClO_4)_2 \cdot 0.5$ 2,2'-bipy, syntheses, characterization, thermal and structural studies

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Two different 2,2′-bipyridine cadmium(II) perchlorate complexes, $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5\ 2,2'\text{-bipy}$, syntheses, characterization, thermal and structural studies

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Reactions of 2,2′-bipyridine (2,2′-bipy) with cadmium perchlorate in a ratio of M : L 1 : 2 and 1 : 3 give complexes with stoichiometry $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**) and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5\ 2,2'\text{-bipy}$ (**2**), respectively. The new complexes were characterized by elemental analyses and IR-, ^{1}H-, ^{13}C-NMR spectroscopy. The crystal structures of the $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**) and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5\ 2,2'\text{-bipy}$ (**2**) were determined by X-ray crystallography and the their thermal behavior studied by TG and DTA. Complexes **1** and **2** are built up of monomeric $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5\ 2,2'\text{-bipy}$ with Cd^{2+} coordination, $CdN_4O_{water}O_{perchlorate}$ and CdN_6, respectively. There are classical $O\text{–}H \cdots O_{perchlorate}$ hydrogen bonds in complex **1** and non-classical $C\text{–}H \cdots O_{perchlorate}$ approaches in complex **2**. The monomeric units of **1** and **2** grow into dimeric and one-dimensional units by packing *via* hydrogen bonding.

Keywords: Cd(II); 2,2′-Bipyridine; Crystal structure; Thermal behavior

1. Introduction

Cadmium is an extremely toxic element that is naturally present in the environment and also as a result of human activities. Its toxicity arises from the fact that it is rapidly localized intracellularly, mainly in the liver, and then bound to metallothionein forming a complex that is slowly transferred to the bloodstream to be deposited in the kidneys. The chemistry of cadmium constitutes an area of increasing interest, especially in relation to its bioinorganic chemistry and toxicology [1–4]. The ligand 2,2′-bipyridine (2,2′-bipy) has been widely used in metal complexes [5–8]. Structures of Cd(II) perchlorate complexes with conjugated *N*,*N*′ chelate ligands such as "2,2′-bipy" are not thoroughly investigated.

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We report here the preparation, crystal structures and thermal behavior of two compounds of Cd(II) with different stoichiometry of "2,2′-bipy" ligands, water and perchlorate anions, $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**) and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5$ 2,2′-bipy (**2**). Some Cd(II) complexes of 2,2′-bipyridine have been reported [9–12].

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN–O– rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. The thermal behavior was measured with a PL-STA 1500 apparatus.

Caution Although no problems were encountered in the preparation of the perchlorate salts care should be taken during handling such potentially hazardous compounds.

2.2. *Preparation of $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (1)*

Cadmium(II) acetate dihydrate (0.230 g, 1 mmol) and sodium perchlorate monohydrate (0.281 g, 2 mmol) were dissolved in distilled water (20 mL) and a methanolic solution of 2,2′-bipy (0.312 g, 2 mmol) was added to it. The resulting solution was stirred for 2 h. and then allowed to stand for 2–3 days at room temperature. Colorless crystals of the desired product precipitated, which were filtered off, washed with acetone and ether and air dried (m.p. 252°C). Yield: 0.256 g, 40%. (Found: C, 37.80; H, 2.50; N, 8.50%; calculated for $C_{20}H_{18}CdCl_2N_4O_9$: C, 37.40; H, 2.80; N, 8.72%). IR (cm^{-1}) selected bands: 762(s), 1009(s), 1100(vs), 1300(s), 1361(s), 1426(s), 1466(s), 1589(m), 3085(w) and 3329(br). ^{1}H-NMR (DMSO, δ): 7.57(s, 1H), 8.06(s, 1H), 8.48(s, 1H), and 8.68(d, 1H) ppm. ^{13}C-NMR (DMSO, δ): 121.3, 130.5, 143.5, 149.6, and 150.1 ppm

2.3. *Preparation of $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5$ 2,2′-bipy (2)*

Complex **2** has been prepared by following the method adopted for complex **1** except that the molar ratio of cadmium acetate to 2,2′-bipy was 1 : 3 instead of 1 : 2 (m.p. >320°C). Yield: 0.386 g, 44%. Found: C, 49.20; H, 3.50; N, 11.50%; calculated for $C_{35}H_{28}CdCl_2N_7O_8$: C, 48.95; H, 3.26; N, 11.42%). IR (cm^{-1}) selected bands: 755(m), 1004(m), 1081(vs), 1414(m), 1590(m), and 3045(w). ^{1}H-NMR (DMSO, δ): 7.50(s, 1H), 8.10(s, 1H), 8.50(s, 1H), 8.70(d, 1H) ppm. ^{13}C-{^{1}H} NMR (DMSO, δ): 121.2, 130.6, 143.3, 149.4, and 150.2 ppm.

2.4. *Crystallography*

X-ray measurements were made at 295(2) and 293(2) K using a Siemens R3m V^{-1} diffractometer for compounds **1** and **2**, respectively. Accurate unit cell parameters and the orientation matrix for data collection were obtained from least-squares refinement. The structures have been solved by direct methods and refined by full-matrix least-squares on F^2. The positions of hydrogen atoms were calculated at idealized geometrical positions and included in the structure-factor calculation as fixed-atom contributions.

Crystal data and structure refinement are given in table 1. Selected bond lengths and angles are given in tables 2 and 3. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and perspective views of the packing in the unit cells are shown in figures 3–6.

Table 1. Crystal data and structure refinement for $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**) and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5$ 2,2′-bipy (**2**).

Identification code	**1**	**2**
Empirical formula	$C_{20}H_{18}CdCl_2N_4O_9$	$C_{35}H_{28}CdCl_2N_7O_8$
Formula weight	641.68	857.94
Temperature (K)	295(2)	293(2)
Wavelength	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P21/n$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	9.0746(8)	9.5289(9)
b	13.6676(12)	13.3296(13)
c	19.5255(16)	14.7463(14)
α	90	96.182(2)
β	100.8390(10)	106.378(2)
γ	90	91.001(2)
Volume (Å^3)	2378.5(4)	1784.3(3)
Z	4	2
Density (calculated) (Mg m^{-3})	1.792	1.597
Absorption coefficient (mm^{-1})	1.792	0.824
$F(000)$	1280	866
Crystal size (mm^3)	0.22 × 0.25 × 0.40	0.20 × 0.10 × 0.10
θ range for data collection (°)	2.33–25.50	1.54–28.00
Index ranges	$-10 \le h \le 10$, $-16 \le k \le 16$, $-23 \le l \le 23$	$-12 \le h \le 12$, $-17 \le k \le 17$, $-19 \le l \le 19$
Reflections collected	17209	18412
Independent reflections	4398 [$R(\text{int}) = 0.0213$]	8597 [$R(\text{int}) = 0.0277$]
Completeness to θ (%)	99.7	99.8
Refinement method	Full-matrix least squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5482/0/315	8597/0/478
Goodness-of-fit on F^2	0.894	1.000
Final R [$I > 2\sigma(I)$]	Indices for 3435 ref1.	Indices for 5646 ref1.
R indices (all data)	$R_1 = 0.0735$, $wR_2 = 0.2173$	$R_1 = 0.0417$, $wR_2 = 0.1040$
	$R_1 = 0.0591$, $wR_2 = 0.1944$	$R_1 = 0.0642$, $wR_2 = 0.1128$
Largest diff. peak, hole (e Å^{-3})	0.787 and −1.233	0.755, −0.456

Table 2. Bond lengths (Å) and angles (°) for $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**).

Cd1–O1W	2.277(5)	N4–Cd1–N3	70.72(19)
Cd1–N1	2.316(5)	O1W–Cd1–N2	101.55(19)
Cd1–N4	2.322(5)	N1–Cd1–N2	71.2(2)
Cd1–N3	2.338(5)	N4–Cd1–N2	93.9(2)
Cd1–N2	2.359(6)	N3–Cd1–N2	102.19(18)
Cd1–O1	2.424(5)	O1W–Cd1–O1	82.6(2)
O1W–Cd1–N1	95.39(17)	N1–Cd1–O1	84.57(19)
O1W–Cd1–N4	92.0(2)	N4–Cd1–O1	110.05(19)
N1–Cd1–N4	164.4(2)	N3–Cd1–O1	82.4(2)
O1W–Cd1–N3	151.37(18)	N2–Cd1–O1	155.65(18)
N1–Cd1–N3	107.25(18)		

Table 3. Bond lengths (Å) and angles (°) for $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 2,2'\text{-bipy}$ (**2**).

Cd1–N6	2.326(2)	N6–Cd1–N1	97.72(9)
Cd1–N3	2.327(2)	N3–Cd1–N1	97.86(9)
Cd1–N1	2.329(2)	N6–Cd1–N2	98.97(9)
Cd1–N2	2.332(3)	N3–Cd1–N2	99.46(9)
Cd1–N4	2.333(3)	N1–Cd1–N2	71.26(9)
Cd1–N5	2.385(2)	N6–Cd1–N4	97.14(9)
N6–Cd1–N3	158.90(9)	N3–Cd1–N4	70.94(9)
N1–Cd1–N4	161.44(9)	N3–Cd1–N5	92.68(9)
N2–Cd1–N4	95.47(9)	N1–Cd1–N5	100.74(9)
N6–Cd1–N5	70.46(9)	N2–Cd1–N5	166.21(9)
N4–Cd1–N5	94.67(9)		

Table 4. Hydrogen bonds for $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**) (Å, °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O1W–H1A···O7$[-1/2+x,\ 3/2-y,\ 1/2+z]$	0.85	1.91	2.755(8)	172
O1W–H1B···O2$[1-x,\ 2-y,\ 1-z]$	0.85	2.00	2.826(8)	164

3. Results and discussion

Reaction between 2,2′-bipyridine and mixtures of cadmium(II) acetate with sodium perchlorate with ratio of 2 : 1 and 3 : 1 provided crystalline materials analyzed as $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**) and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5\ 2,2'\text{-bipy}$ (**2**). The IR spectra of these compounds show absorption bands resulting from the skeletal vibrations of aromatic rings in the range 1400–1523 cm^{-1}. The relatively weak bands at around 3085 and 3045 cm^{-1} are assigned to the ν(CH) mode of the "2,2′-bipy" rings in **1** and **2**, respectively. Very strong band 1100 and 1081 cm^{-1} characterizes the ν(Cl–O) vibrations in **1** and **2**, respectively. The broad absorption band for ν(H–O) in **1** appears at ca 3329 attributable to ν(O–H···X) hydrogen bands. The structures of compounds **1** and **2** were confirmed by X-ray crystallography. ^{1}H-NMR spectra of the DMSO solution of compounds **1** and **2** displays four signals assigned to protons of aromatic rings of 2,2′-bipy. The ^{13}C-NMR spectra of DMSO solutions of **1** and **2** have five distinct resonance signals assigned to the aromatic carbons of aromatic rings of 2,2′-bipy.

The thermal decomposition behavior of [Cd(2,2′-bipy)$_2$(H$_2$O)(ClO$_4$)]ClO$_4$ (**1**) and [Cd(2,2′-bipy)$_3$](ClO$_4$)$_2$ · 0.5 2,2′-bipy (**2**) was investigated in static air from ambient to 700°C (figures 1 and 2). Compound **1** does not melt and is stable to 132°C at which temperature it begins to decompose. Removal of one water molecule takes place at

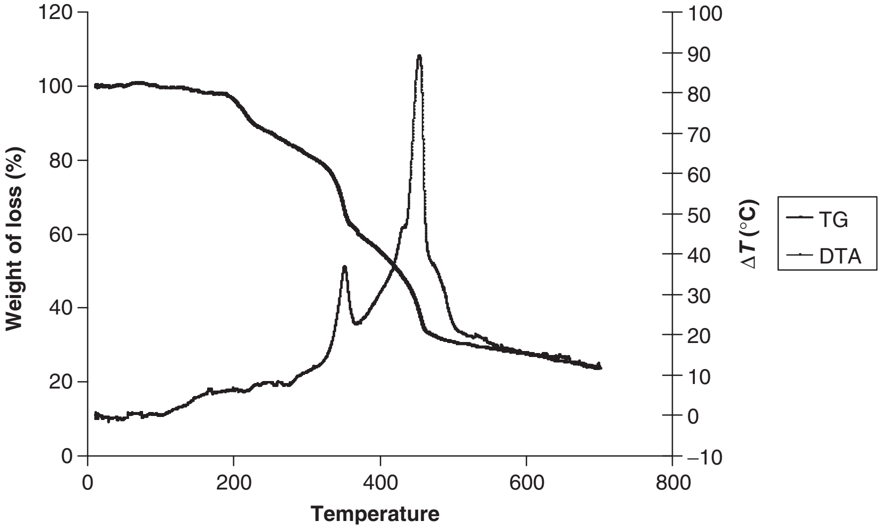

Figure 1. Thermal behavior of [Cd(2,2′-bipy)$_2$(H$_2$O)(ClO$_4$)]ClO$_4$ (**1**).

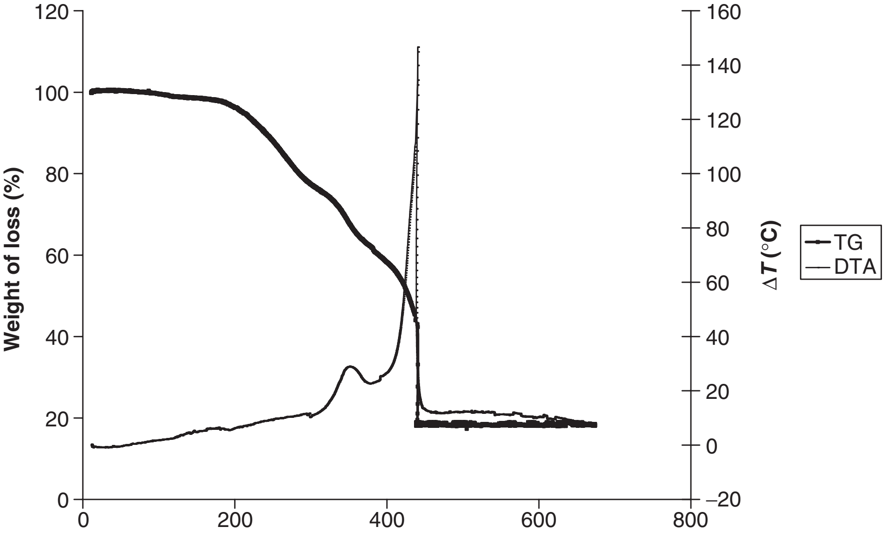

Figure 2. Thermal behavior of [Cd(2,2′-bipy)$_3$](ClO$_4$)$_2$ · 0.5 2,2′-bipy (**2**).

132°C with an exothermic effect at 169°C. The experimental mass loss of 3% is consistent with the calculated value 3% for the elimination of 1 mole water. Removal of two 2,2′-bipy molecules takes place at 197°C with an exothermic effect at 352°C. The experimental mass loss of 49% is consistent with the calculated value 49% for the elimination of 2 moles of 2,2′-bipy molecules. Decomposition of the perchlorate anions takes place at 425–524°C and the experimental mass loss of 19% consistent with the calculated value of 19% for the elimination of seven oxygen and two chlorine atoms from two pechlorate anions. The solid residue formed at around 475°C is suggested to be CdO (remaining weight 20, Calcd: 20%). Compound **2** begins to decompose at 195°C. Removal of 0.5 mole of uncoordinated "2,2′-bipy" and 3 moles of coordinated "2,2′-bipy" takes place in 195–430°C and the experimental mass loss of 66% is consistent with the calculated value 67% for the elimination of 2.5 moles of "2,2′-bipy". The weight loss of 56% from 340 to 430°C is equivalent to the loss of three moles of "2,2′-bipy" [Calcd: 55%] with two exothermic effects at 350 and 420°C. Decomposition of the perchlorate anions takes place at 425°C with one exothermic effect at 429°C and the experimental mass loss of 19% is consistent with the calculated value 21% for the elimination of seven oxygen and two chlorine atoms from two perchlorate anions. The solid residue formed at around 475°C is suggested to be CdO (remaining weight 16, Calcd: 15%).

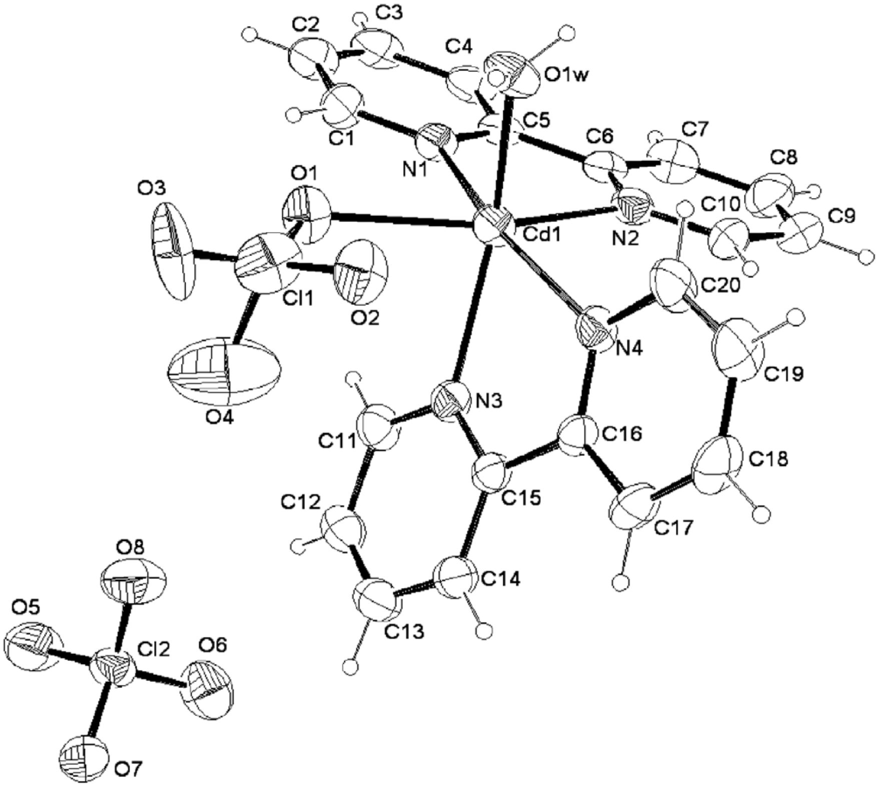

Figure 3. ORTEP diagram of [Cd(2,2′-bipy)$_2$(H$_2$O)(ClO$_4$)]ClO$_4$ (**1**).

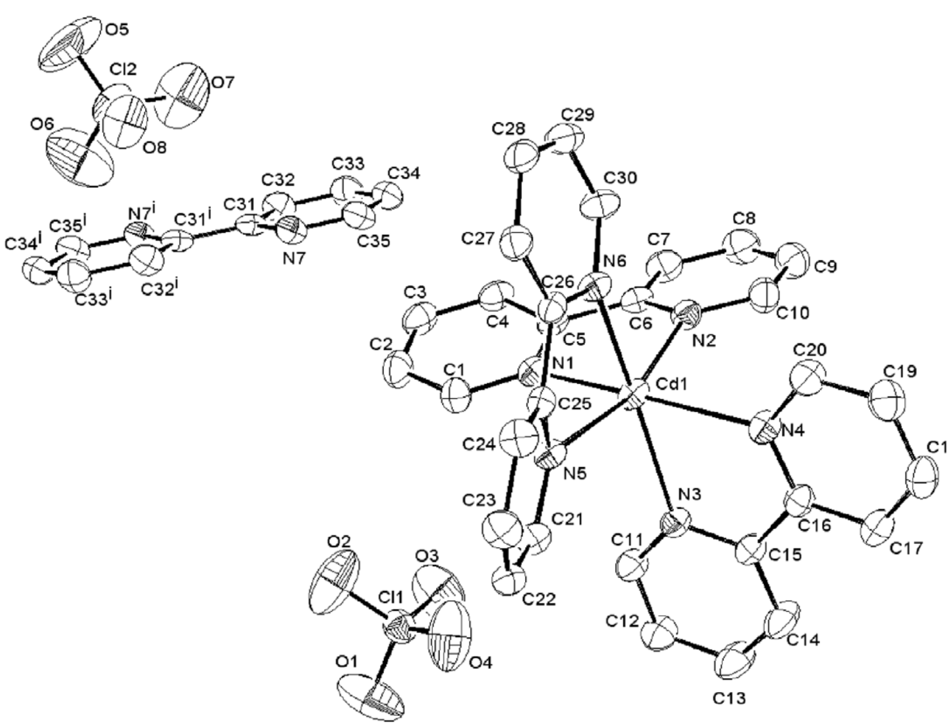

Figure 4. ORTEP diagram of $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5$ 2,2′-bipy (**2**); i: $-x$, $-y$, $-z$.

Single X-ray crystal analysis reveals that $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]ClO_4$ (**1**) and $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5$ 2.2′-bipy (**2**) crystallize in monoclinic and triclinic space groups of $P21/n$ and $P\bar{1}$, respectively. The structures of **1** and **2** consist of discrete $[Cd(2,2'\text{-bipy})_2(H_2O)(ClO_4)]^+$ and $[Cd(2,2'\text{-bipy})_3]^{2+}$ cations and ClO_4^- anions. The coordination number of these complexes is six and the Cd atoms are coordinated by six donors: four 'N' atoms of two "2,2′-bipy" ligands, one 'O' atom of one water molecule and one oxygen atom of perchlorate anion in **1** and six 'N' atoms of three "2,2′-bipy" ligands in **2** with $CdN_4O_{water}O_{perchlorate}$ and CdN_6 chromophores, respectively, and the resulting geometry around the Cd atoms being distorted octahedral. In **1** the oxygen atom from perchlorate anion and oxygen atom of water are *cis* [the angles O1–Cd1–O1w is 82.6(2)°] and two "2,2′-bipy" ligands are *cis*. In **2** the Cd atoms are coordinated by three "2,2′-bipy" ligands in a D_3 symmetry. The crystal space group **2** is $P\bar{1}$, therefore the crystal must contain a racemic mixture of the Λ and Δ isomers. There is a half "2,2′-bipy" molecule not coordinated to the cadmium atom in complex **2** and the two pyridine rings of "2,2′-bipy" have a dihedral angle of only $-0.74°$ and are coplanar because they are related by the inversion center (figure 3) whereas the dihedral angles in the three coordinated "2,2′-bipy" ligands are -13.74, -6.04 and $-19.85°$ and these "2,2′-bipy" ligands are not coplanar. The dihedral angles in the two coordinated "2,2′-bipy" ligands in complex **1** are 5.78 and 5.11° and are also not coplanar.

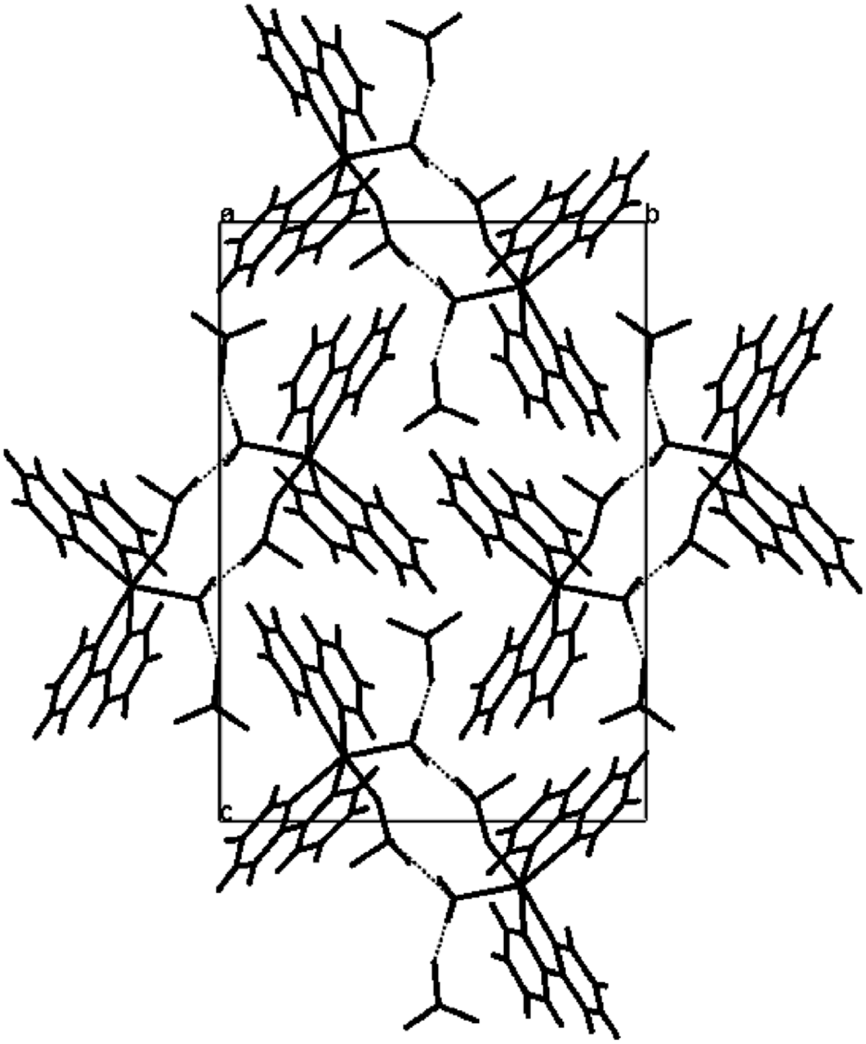

Figure 5. The unit cell of [Cd(2,2′-bipy)$_2$(H$_2$O)(ClO$_4$)]ClO$_4$ (**1**), Showing the hydrogen bonding and dimeric units.

Classical O–H ⋯ O hydrogen bonds exist between the hydrogen atoms of the water molecules and oxygen atoms of perchlorate anions **1**. The hydrogens of coordinated water act as hydrogen-bond donors with O atoms from perchlorate anions. Consequently, as O–H ⋯ O hydrogen bonding grows, the monomeric structure is converted into a dimeric unit (figure 3).

A search was made for non-classical CH ⋯ N and CH ⋯ O approaches in complex **2**. There are CH ⋯ N and CH ⋯ O interactions between the N(py) atoms of uncoordinated "2,2′-bipy" molecules with the distance of N ⋯ H = 2.681 Å and O ⋯ H = 2.56–2.70 Å as shown in figure 4. The weak CH ⋯ N and CH ⋯ O hydrogen bonds grow the monomeric structure into a one-dimensional polymeric unit (figure 6).

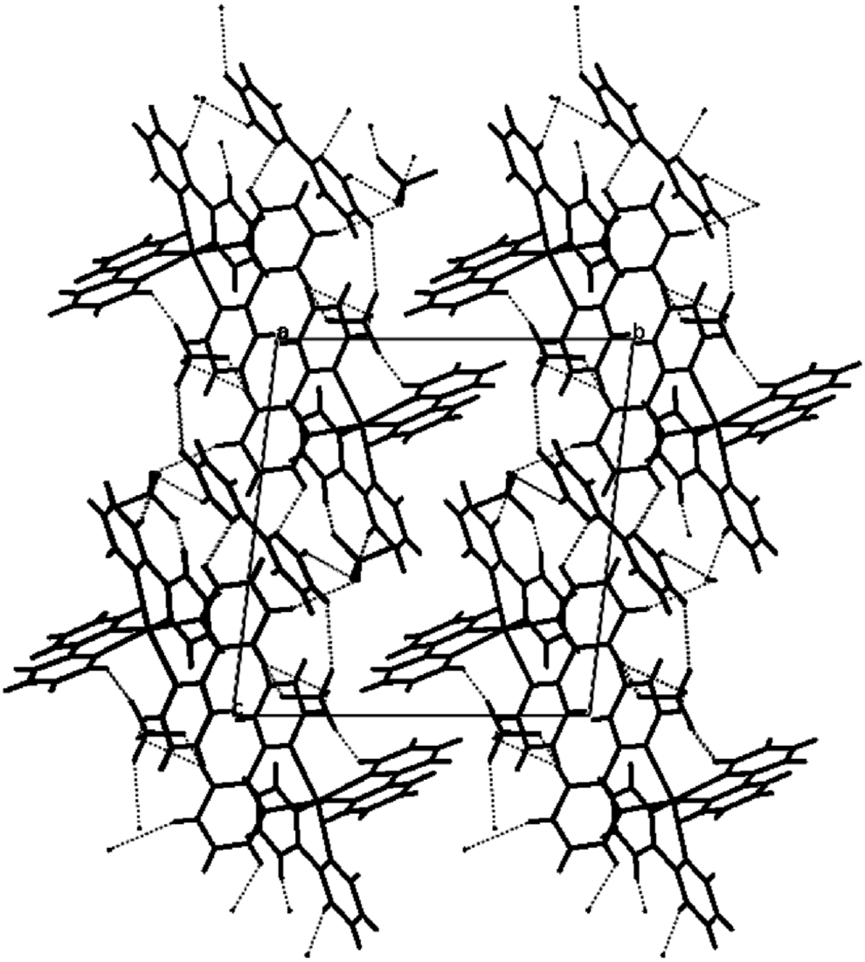

Figure 6. The unit cell of $[Cd(2,2'\text{-bipy})_3](ClO_4)_2 \cdot 0.5\ 2,2'\text{-bipy}$ (**2**), Showing C–H ··· O and C–H ··· O weak hydrogen bonding.

Supplementary material

Crystallographic data for the structures reported in this article has been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-289459 for **1** and 297345 for **2**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336033; Email: deposit@ccdc.cam.ac.uk).

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