Zn(II) and Cd(II) Coordination Dimers Based on Mixed Benzodioxole-Carboxylate and N-Donor Ligands: Synthesis, Characterization, Crystal Structures and Photoluminescence Properties

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ABSTRACT:

Four new compounds, formulated as [Zn(m-Pip)2(3-Phpy)]2 (1), [Zn(m-Pip)2(4-Phpy)]2 (2), [Cd(m-Pip)(Pip)(3-Phpy)2]2 (3) and [Cd (m-Pip)(Pip)(4-Phpy)2]2 (4) (HPip=1,3-benzodioxole-5-carboxylic acid; Phpy= phenylpyridine), have been successfully assembled based on rigid carboxylate/pyridine ligands. These four compounds have been fully characterized by analytical and spectroscopic methods. The aim of the present study is to investigate the structural effect and the influence of the size of metal on the class, geometry and type of coordination of the carboxylate ligands (syn-syn, syn-anti) in the final 3D-arrangements of the structures. Finally, luminescence properties of these new four coordination dimers have been investigated.

INTRODUCTION

During the last years, the synthesis of metal-organic coordination compounds has attracted enormous interest not only for their intriguing structural diversity but also their potential application in catalysis, drug delivery, magnetism and so on.[1] Studies in this field permit relationships between the structure of the compounds and their properties. Generally, the three dimensional structure of complexes depends on the coordination preferences of the metal center and the functionality/ versatility of the ligands. Furthermore, additional factors as hydrogen bonding or p-p stacking interactions, solvent molecules of media, counterions or the metal salt:organic ligand ratio also influence the final disposition of the architectures of the compounds.[2]

Carboxylate ligands have been used as multifunctional tectons, not only for their ability in the formation of covalent bonds with metal ions, but also for supramolecular interactions.[3] Heterocyclic nitrogen donors, such as pyridine, pyrazole, and related molecules, are also fascinating ligands. As a result, during the last years a great number of coordination complexes with diverse frameworks: one dimensional (1D) chains, twodimensional (2D) layers or three dimensional (3D) cavities have been described in the literature.[4]

Zn(II) and Cd(II) ions with d10 electron configuration are particularly suitable for the construction of polynuclear compounds. These exhibit a variety of coordination numbers and arrangements varying from tetrahedral to octahedral. The Zn(II) and Cd(II) compounds can readily form mononuclear and binuclear compounds and all kinds of architectures such as 1D, 2D and 3D structures. These metals are particularly promising due to their interesting luminescent properties[5] and broad applications in the biological area.[6] In particular, mononuclear and binuclear zinc carboxylates complexes are of great importance to study them as biological model compounds.[7] The versatility in many biological systems is ascribed to the variety and flexibility of the different coordination modes of the carboxylate ligands. Interestingly, the paddle-wheel type of structure from Zn-carboxylate and Cd-carboxylate is already reported in the literature; however, it is not very clear on what conditions such complexes are formed.[8]

Cu(II) compounds with 1,3-benzodioxole-5-carboxylic acid (HPip)[9] and N-derived pyrazole ligands[10], were recently designed in our group. As a continuation of this study we chose Zn(II) and Cd(II) as metals to construct different frameworks with 3-phenylpyridine (3-Phpy) and 4-phenylpyridine (4- Phpy), and reported two Zn(II), [Zn(m-Pip)2(3-Phpy)]2 (1) and [Zn (m-Pip)2(4-Phpy)]2 (2) and two Cd(II), [Cd(m-Pip)(Pip)(3-Phpy)2]2 (3) and [Cd(m-Pip)(Pip)(4-Phpy)2]2 (4) coordination dimers in which the metal has an important role on their structures and properties.

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RESULTS AND DISCUSSION

Synthesis and general characterization

Complexes 1–4 were prepared in MeOH at room temperature via combination of the M(MeCO2)2·2H2O (M=Zn or Cd) salt reagents, 3-phenylpyridine (3-Phpy) or 4-phenylpyridine (4-Phpy), and 1,3-benzodioxole-5-carboxylic acid (Pyperonylic acid, HPip) ligands (Scheme 1). In these reactions the acetate anions were displaced by carboxylate groups. The corresponding crystals suitable for X-ray crystallographic analysis were grown via slow evaporation of their solution.

The new four complexes were characterized via elemental analysis, infrared (IR), Raman, nuclear magnetic resonance (NMR) spectroscopy and single-crystal X-ray diffraction. The elemental analysis for compounds 1–4 are in agreement with their formula. The IR spectra of 1–4 display the characteristic carboxylate bands in the range of 1641–1539 cm 1 for nas(CO2) and at 1489–1384 cm 1 for ns(CO2) and were fully consistent with their formulations (SI Figure S1-S4). For 1–4, the differences between nas(CO2) and ns(CO2) are 162, 160, 167, and 171 cm 1, respectively, indicating a bidentate bridging coordination mode for the carboxylates.[11] Moreover, for compounds 3 and 4, other D values of nas(CO2) and ns(CO2) were observed (115 and 118 cm 1, respectively), indicating the presence of bidentate chelate carboxylate groups in both complexes.[11] Absence of a band at 1720–1690 cm 1 in the four spectra indicates that the carboxylic acids are deprotonated in the corresponding compounds. The bands attributable to the aromatics groups n(C=C)ar, n(C=N)ar, d(C H)ip and d(C H)oop are also observed. The IR spectral data thus clearly lend support to the structures determined by the X-ray diffraction method.

Raman spectroscopy experiments were also performed to further characterize the compounds. The most relevant bands of the spectra of the four compounds and their assignations are shown in Supporting Information (SI, Figure S5-S8).[12]

Compounds 1–4 have similar Raman spectra, showing comparable bands at approximately the same wavelength. On the high wavelength part of the spectra only two signals can be observed, at 3082–3071 cm 1, assigned to the =(C H) vibration of aromatic carbons and a less prominent band at 2906–2894 cm 1 assigned to the C H vibration of the dioxole group of the Pip ligands. Two strong signals at 1632–1626 cm 1 and 1613–1585 cm 1, respectively, are assigned to the C=N vibration of the 3-phpy and 4-phpy ligands and to the C=O vibrations of the carboxylates of the Pip ligands. A band between 1300–1297 cm 1 is assigned to the C N vibration of the 3-phpy and 4-phpy, and at 810–807 cm 1 the C O-C vibration of the dioxole group of the Pip ligands can be observed. On the low wavelength part of the spectra, strong and broad bands appear for the four compounds, corresponding to the lattice vibrations of the crystals.

Crystal structure of Zn(II) complexes 1and 2

The reaction of Zn(MeCO2)2·2H2O, 1,3-benzodioxole-5-carboxylic acid (HPip) and 3-phenylpyridine (3-Phpy) (1) or 4-phenylpyridine (4-Phpy) (2), in methanol at room temperature with a ratio of 1:2:4, leads to [Zn(m-Pip)2(3-Phpy)]2 (1) and [Zn(m-Pip)2 (4-Phpy)]2 (2). The structural determination revealed that Zn(II), Pip and 3-Phpy or 4-Phpy are present in 1:2:1 ratio in both complexes. A perspective view of 1 and 2 is shown in Figure 1 (left and right, respectively). Selected bond distances and angles are provided in Table 1.

The crystal structure of 1 and 2 consists of two independent centrosymmetric tetracarboxylate in a syn-syn configuration bridged dimers. The Zn atoms adopt a [ZnO4N] coordination mode with four oxygen atoms from four different 1,3- benzodioxole-5-carboxylate units and one nitrogen atom of the 3-Phpy or 4-Phpy ligands. The carboxylates display a paddlewheel-like arrangement about the Zn···Zn axis. The tetracarboxylate bridging framework can accommodate a metal-metal separation up to 3.452 Å .[13] The Zn···Zn separation in compounds 1 and 2 are 2.9253(9) and 2.9692(2) Å , respectively. Each Zn(II) ion adopts a slightly distorted square-pyramidal environment (t=0.0035 (1) and 0.042, 0.045 (2))[14], coordinated equatorially to four carboxylate oxygen atoms [Zn–O: 2.018- 2.077 Å (1); 2.0092-2.0614 Å (2)] and apically to the 3-Phpy or 4- Phpy [Zn–N: 2.045 Å (1); 2.0396 and 2.0465 Å (2)]. The values are comparable with the reported values in [Zn(L1)2(ql)]2 (L1= p-chlorophenoxyacetic acid; ql=quinoline)[15], [Zn(m-4-OBz)2 (py)]2,[16] [Zn(m-4-OBz)2(py)]2·0.5CH3OH (4-OBz=p-chlorobenzoic acid; py=pyridine)[17] and [Zn(L2)2(L1)]2 (L2=1,1':3',1''-terphenyl- 4,4',4'',6'-tetracarboxylic acid; L1=4-amino-3,5-diphenyl-1Hpyrazole).[18]

Crystal structure of Cd(II) complexes 3and 4

Compounds 3 and 4 were prepared by reaction of Cd (MeCO2)2·2H2O, 1,3-benzodioxole-5-carboxylic acid (HPip) and 3-phenylpyridine (3-Phpy) (3) or 4-phenylpyridine (4-Phpy) (4), in MeOH solvent at room temperature with a ratio of 1:2:4, yielding [Cd(m-Pip)(Pip)(3-Phpy)2]2 (3) and [Cd(m-Pip)(Pip)(4-Phpy)2]2 (4). Interestingly, the structural determination revealed that Cd(II), Pip and 3-Phpy or 4-Phpy are present in ratio 1:2:2 in both complexes while in 1 and 2 (Zn(II) complexes) the ratio was 1:2:1. A perspective view of 3 and 4 is shown in Figure 2 (left and right, respectively). Selected bond distances and angles are provided in Table 1.

The crystal structure of 3 and 4 consists of two independent centrosymmetric dicarboxylate bridged dimers. An asymmetric unit of [Cd(m-Pip)(Pip)(dpy)2]2 (dpy=3-Phpy, 4-Phpy) contains two six-coordinated Cd(II) ions, two Pip bridges, two Pip bidentate chelate ligands, and two lattice dpy molecules. Both Cd atoms adopt a [CuO4N2] coordination mode with four oxygen atoms from four different Pip units and two nitrogen atoms of the dpy ligands coordinated in trans disposition. In compound 4, the phenyl of 4-Phpy molecule is disordered. The bridging carboxylate ligands show an asymmetric syn-anti coordination mode, with Cd–O distances (Cd–O5 2.2967(9) Å , Cd–O6 2.3095(10) Å (3); Cd–O1 2.2802(11) Å , Cd–O2 2.3401(11) Å (4)). The Cd–O bond lengths of the Pip chelate ligand are longer than the corresponding Pip bridging mode (Cd-O(1) 2.4267 Å, Cd-O(2) 2.3659 (9) Å (3) and Cd-O(5) 2.4257 Å, Cd-O(6) 2.3490 Å (4)). The angles around the Cd atom are 55.13(3)-173.77(4)8 (3) and 55.34(3)-178.06(5)8 (4).

Interestingly, Zn(II) compounds (1 and 2) present the same dimer paddle-wheel structure with 3-Phpy and 4-Phpy, while Cd(II) atoms have the same octahedral dimer coordination (3 and 4). This clearly indicates that the metal atom influences the coordination of the ligands, while the difference on the phenilpyridine ligands does not present significant influence on the core of the compounds.

Extended Structures of 1-4complexes

Molecular solids, which consist of coordination complexes assembled in the solid state as a consequence of non-covalent bonding, are a developing field of research due to their potential applications in diverse areas.[19] Among non-covalent interactions, hydrogen bonding interaction is one of the major cohesive forces in supramolecular aggregation and plays the most important role in material science.[20] In all the new four compounds, the binuclear units are linked together via hydrogen bond interactions involving the Pip ligands forming a compact 3D supramolecular network.

In compound 1, an oxygen from the carboxylate group forms two different hydrogen bonds: C24-H24B···O1 (2.486 Å), interacting with a hydrogen from the dioxole group of an adjacent Pip ligand, and C26-H26···O1 (2.486 Å), interacting with a hydrogen from the aromatic ring of another adjacent Pip ligand. These interactions are responsible for the expansion in the crystallographic in directions a and b. Another hydrogen bond, C7-H7···O4 (2.521 Å), between an oxygen of the dioxole ring of a Pip ligand and a hydrogen from the aromatic ring of the 3-Phpy, is responsible for the final expansion in direction c (Figure 3, Table 2).

In compound 2, the hydrogen bonds C12-H12···O9 (2.488 Å), involving an oxygen from the carboxylate group and a hydrogen from an adjacent Pip unit, and C50-H50···O11 (2.524 Å), connecting the dioxole ring of the Pip ligand and a hydrogen from the aromatic ring of a 4-Phpy, and a p···H interaction, C44-H44···Cg1 (3.029 Å, Cg1=C2-C8), are responsible for the expansion in the crystallographic a and b directions. Final expansion in the c direction is caused by another hydrogen bond, C29-H29···O4 (2.544 Å), between the dioxole rings of adjacent Ppi units (Figure 4, Table 3).

In compound 3, an oxygen from the carboxylate group of the chelate Pip unit forms a hydrogen bond with a hydrogen from of pyridine ring of 3-Phpy (C3-H3···O2, 2.356 Å). This bond is responsible for the expansion in the crystallographic a direction. The other oxygen of the carboxylate group of the same chelate bonding Pip forms another hydrogen bond by linking with a hydrogen of the dioxole group of the chelate Pip of a different binuclear unit (C28-H28B···O1, 2.468 Å). This bond expands the structure in the direction that makes an angle of ca. 308 with the bc plane. A short contact between the carbon atom of the dioxole group of the chelate Pip with a hydrogen of the aromatic ring of a binding piperolinate (C34-H34···C28, In compound 4, an oxygen from the carboxylate group of a chelate Pip unit forms two hydrogen bonds, one with a hydrogen from the phenyl ring of a 4-Phpy ligand (C18- H18···O6, 2.547 Å), and another with a hydrogen from the pyridine ring of the same 4-Phpy ligand (C15-H15···O6, 2.509 Å). The same hydrogen from the pyridine ring forms another hydrogen bond with an oxygen from the carboxylate group of a bridging Pip unit (C15-H15···O2, 2.491 Å). The dioxole oxygens from a chelate Pip ligand form one hydrogen bond each, one with a hydrogen of the phenyl ring of a 4-Phpy ligand of an adjacent binuclear unit (C19-H19···O7, 2.455 Å) and the other with a hydrogen from the pyridine ring of a 4-Phpy ligand of a different adjacent binuclear unit (C4-H4···O8, 2.549 Å). These interactions expand the structure in the a and c directions, forming layers on the ac plane. A hydrogen-hydrogen contact (C16-H16···H16'-C16', 2.093 Å) further supports the expansion in the a direction, while a second hydrogen-hydrogen contact (C13-H13···H22-C22, 2.270 Å) is responsible for the final expansion of the structure in the b direction. (Figure 6, Table 3).

NMR experiments

1HNMR spectra of the complexes 1–4 were recorded in DMSOd6 (Figure 7) and clearly show the signals of two kind of ligands: 1,3-benzodioxole-5-carboxylate (Pip) and 3-phenylpyridine (3- Phpy) (1, 3) or 4-phenylpyridine (4-Phpy) (2, 4). The Pip ligand is coordinated through the carboxylate group, while the derivatives amine ligands are coordinated to the metallic center by the nitrogen atom. HMQC spectra were used to assign the signals (SI, Figure S9-S12).

The 1HNMR spectra present three signals between 6.84 and 7.52 ppm, assigned to the protons of the dioxole group. Other signals are attributable to the protons of the pyridyl group (3- Phpy or 4-Phpy). The chemical shifts of ortho-H pyridyl protons are consistent with the presence of N-coordinated of thepyridyl groups. The rest of the signals correspond to phenyl groups (Pip and 3-Phpy or 4-Phpy). 13C{1H} NMR spectra could not be recorded for either complex owing to the very low solubility in common solvents. NMR data are reported in experimental section.

Photoluminescence properties

Emissive coordination compounds are of great interested currently due to their various applications in the areas of chemical sensors and photochemistry.[21]

In order to clarify the structural modification effects of the Pip ligand on the complexes, we have performed luminescence spectroscopy. Figure 8 shows the emission spectra of the Pip ligands in a concentration of 10 6 M and its complexes 1–4 in a concentration of 10 7 M in methanol at 298 K. The fluorescence emission spectra of the complexes were carried out with an excitation wavelength of 289 nm. The fluorescence intensity of these complexes is larger than that of the free ligand. This could be explained by the rigidity enhancement of the coordinated ligand in these complexes.[22] For the four complexes, the quantum yields are quite similar, and exhibit the same fluorescence spectra, in this case, the fluorescence intensity is enhanced by a factor between ~60 and ~90, in comparison with the ligand.

The free HPip ligand displays a weak luminescence at ca. 345 nm and the derivatives amines (3-Phpy and 4-Phpy) do not present luminescence properties. It is important to take into account that the fluorescent bands of the four complexes are slightly bathochromically shifted (352 nm), indicating the lengthening of the conjugate p-electronic system in complexes 1–4. The fluorescence intensity of the obtained complexes does not change for a long time (more the 72 h); this is very promising for the use of the corresponding ligand for the sensitive luminescence determination for heavy metals.[23]

CONCLUSIONS

Four new 3D compounds [Zn(m-Pip)2(3-Phpy)]2 (1), [Zn(m-Pip)2 (4-Phpy)]2 (2), [Cd(m-Pip)(Pip)(3-Phpy)2]2 (3) and [Cd(m-Pip)(- Pip)(4-Phpy)2]2 (4) (HPip=1,3-benzodioxole-5-carboxylic acid; Phpy=phenylpyridine), with diverse structures were successfully obtained when combining carboxylate and pyridine ligands. The four compounds have been fully characterized by elemental analysis, infrared (IR), Raman, nuclear magnetic resonance (NMR) spectroscopy and single-crystal X-ray diffraction. It has been demonstrated that the size of the metal (Zn(II) vs. Cd(II)) clearly influences the coordination of the Pip ligand, while the difference on the phenilpyridine ligands does not present significant influence on the core of the compounds. The complexes are assembled to form three dimensional supramolecular frameworks by hydrogen-bonding interactions. The supramolecular structures of the four compounds are quite different, indicating that the different phenilpyridine ligands are able to tune the intermolecular contacts. In all cases, the dioxole group of the Pip ligands was responsible of most of the intermolecular interactions. Finally, a great enhancement of the fluorescence intensity was observed for the Cd(II) compounds, indicating that they may be potential candidates for lumines- cent materials. In short, this study provides new approach to construct new functional materials.

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Keywords: Cd(II) dimer · Piperonylic acid · Supramolecular networks · Zinc(II) paddle-wheel

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Legends to figures

Scheme 1. Schematic outline of the synthesis of complexes 1–4.

Figure. 1 ORTEP drawing of [Zn(m-Pip)2(3-Phpy)]2 (1) and [Zn(m-Pip)2(4-Phpy)]2 (2) (left: compound 1 right: compound 2), showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Figure. 2 ORTEP drawing of [Cd (m-Pip)(Pip)(3-Phpy)2]2 (3) and [Cd (m-Pip)(Pip)(4-Phpy)2]2 (4) (left: compound 1 right: compound 2), showing all non-hydrogen atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.

Figure. 3 3D supramolecular layer stabilized by hydrogen bond interactions in compound 1, projection on the ab plane. Hydrogen atoms not participant in intermolecular interactions omitted for clarity.

Figure. 4 3D supramolecular interactions of compound 2 showing contacts expanding on the a and c directions. Hydrogen atoms not participant in intermolecular interactions omitted for clarity.

Figure. 5 3D supramolecular interactions of compound 3 showing contacts expanding on the a, b and c directions. Hydrogen atoms not participant in intermolecular interactions omitted for clarity.

Figure. 6 3D supramolecular interactions of compound 4 stabilized by hydrogen bonds, projection on the plane bc plane. Hydrogen atoms not participant in intermolecular interactions omitted for clarity.

Figure. 7 1HNMR spectra of compounds [Zn(m-Pip)2(3-Phpy)]2 (1), [Zn(m -Pip)2(4-Phpy)]2 (2), [Cd(m-Pip)(Pip)(3-Phpy)2]2 (3) and [Cd(m-Pip)(Pip)(4-Phpy)2]2 (4).

Figure. 8 Emission spectra of [Zn(m-Pip)2(3-Phpy)]2 (1), [Zn(m -Pip)2(4-Phpy)]2 (2), [Cd(m-Pip)(Pip)(3-Phpy)2]2 (3) and [Cd(m-Pip)(Pip)(4-Phpy)2]2 (4) as well as the free ligand (HPip) in the solution of MeOH (10 6 M for the HPip and 10 7 M for 1–4 complexes) at room temperature.

SCHEME 1

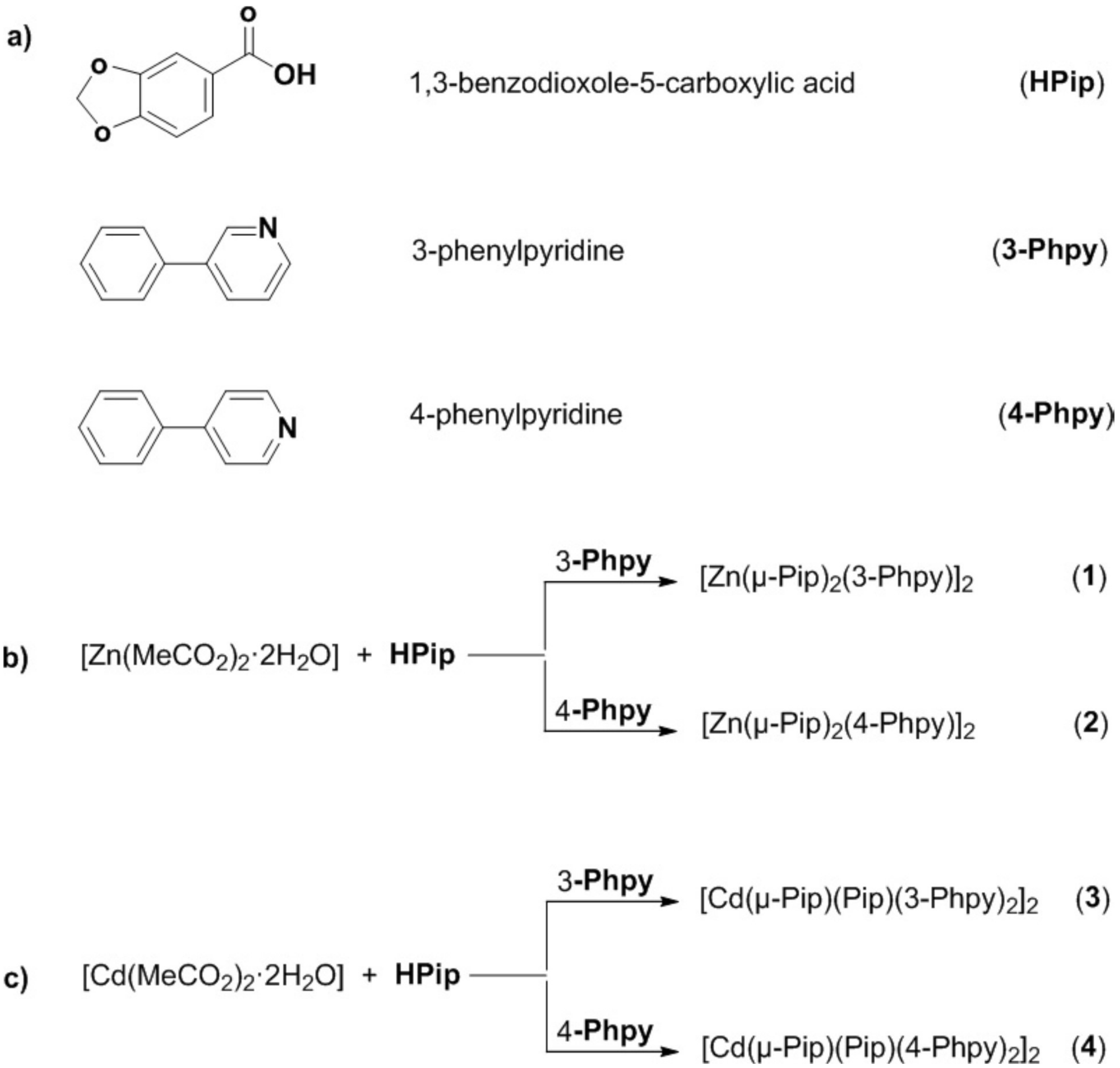
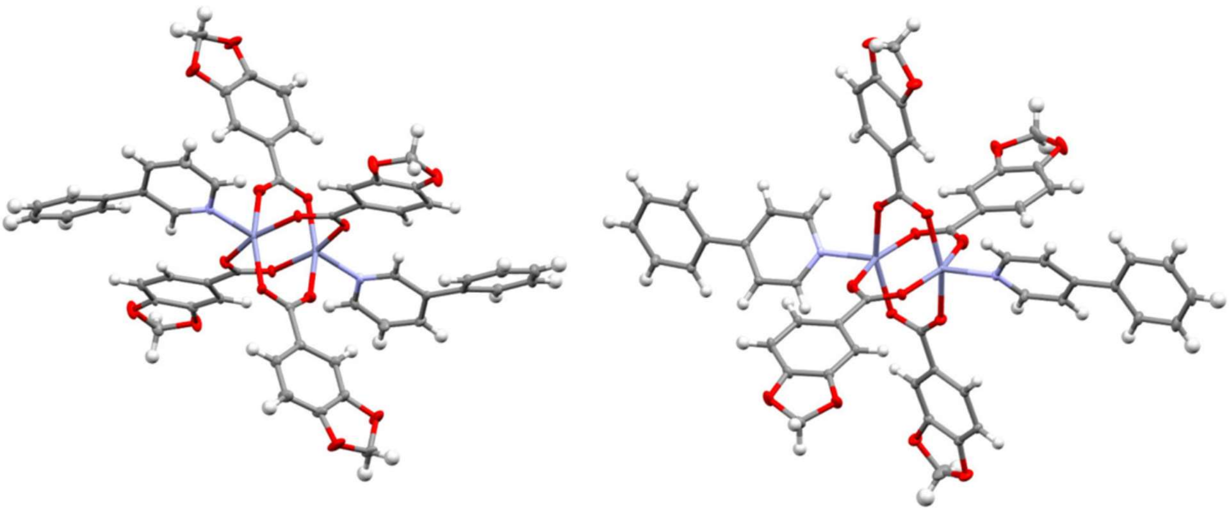

a)
O
OH
O
O
1,3-benzodioxole-5-carboxylic acid
(HPip)
N
3-phenylpyridine
(3-Phpy)
N
4-phenylpyridine
(4-Phpy)
b)
$[Zn(MeCO_2)_2 \cdot 2H_2O]$ + HPip
3-Phpy
$[Zn(\mu\text{-}Pip)_2(3\text{-}Phpy)]_2$
(1)
4-Phpy
$[Zn(\mu\text{-}Pip)_2(4\text{-}Phpy)]_2$
(2)
c)
$[Cd(MeCO_2)_2 \cdot 2H_2O]$ + HPip
3-Phpy
$[Cd(\mu\text{-}Pip)(Pip)(3\text{-}Phpy)_2]_2$
(3)
4-Phpy
$[Cd(\mu\text{-}Pip)(Pip)(4\text{-}Phpy)_2]_2$
(4)

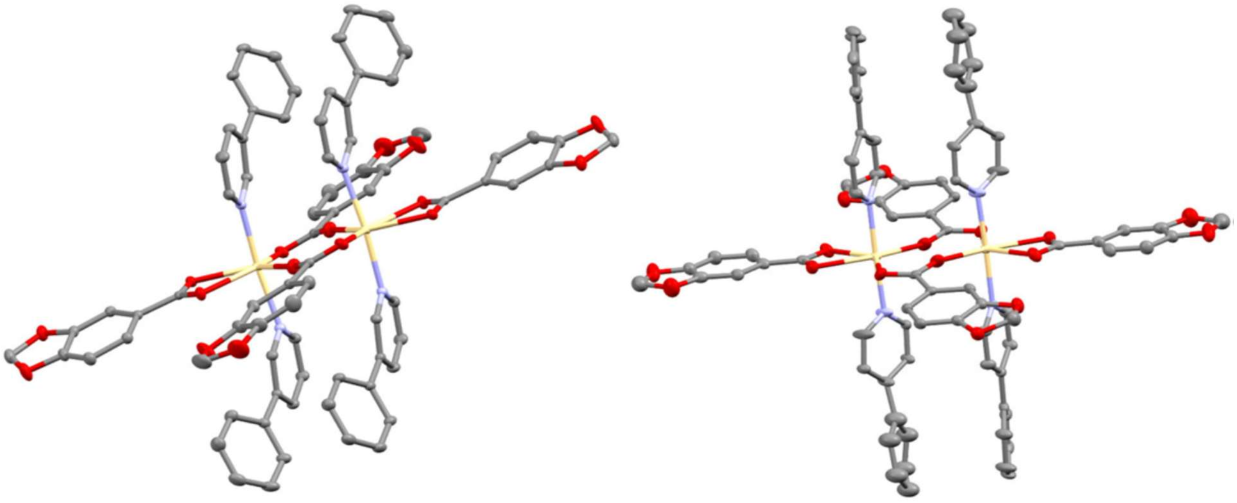
FIGURE 1



(**1**) $[Zn(\mu\text{-}Pip)_2(3\text{-}Phpy)]_2$

(**2**) $[Zn(\mu\text{-}Pip)_2(4\text{-}Phpy)]_2$

FIGURE 2



(**3**) [Cd(μ-Pip)(Pip)(3-Phpy)$_2$]$_2$

(**4**) [Cd(μ-Pip)(Pip)(4-Phpy)$_2$]$_2$

FIGURE 3

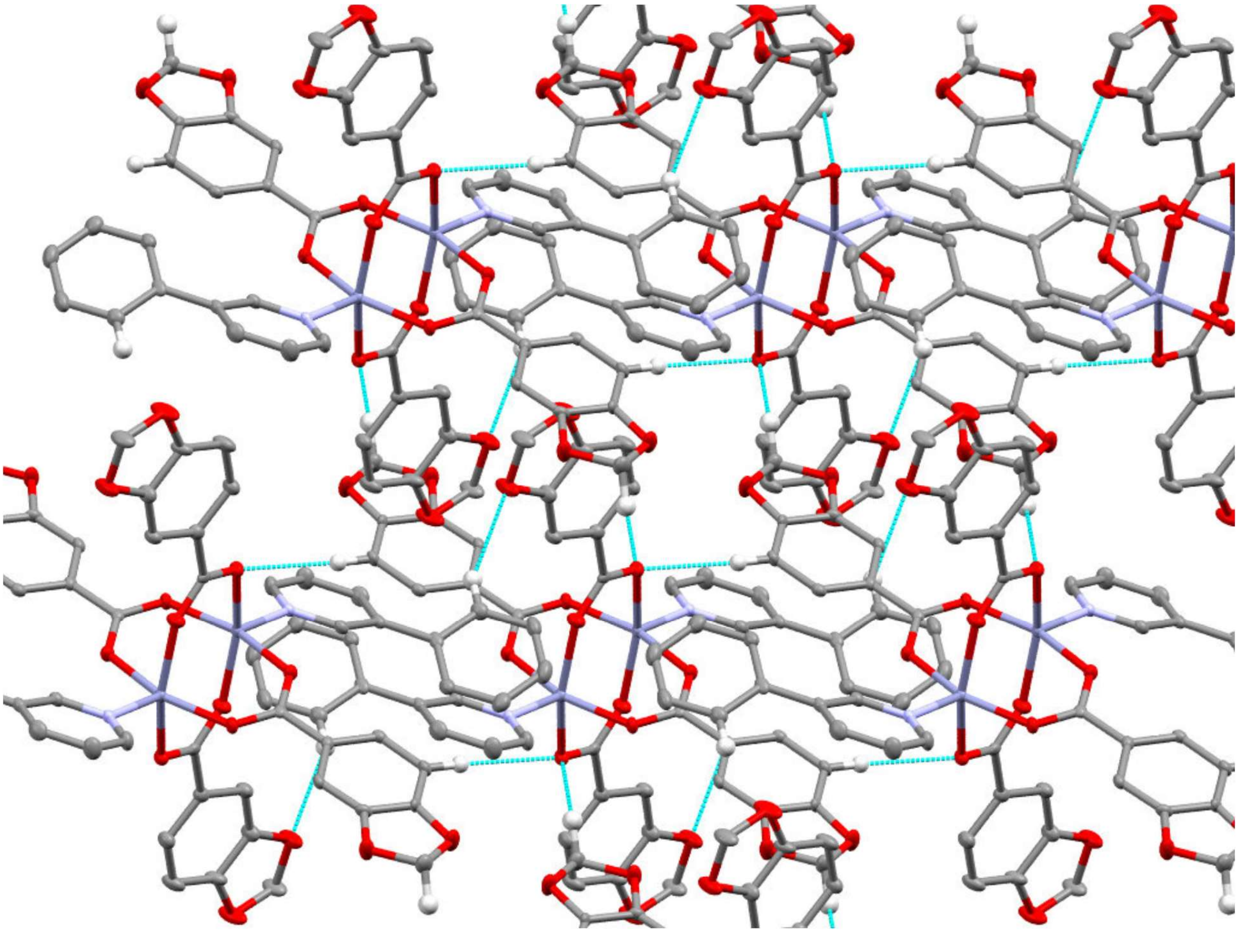


FIGURE 4

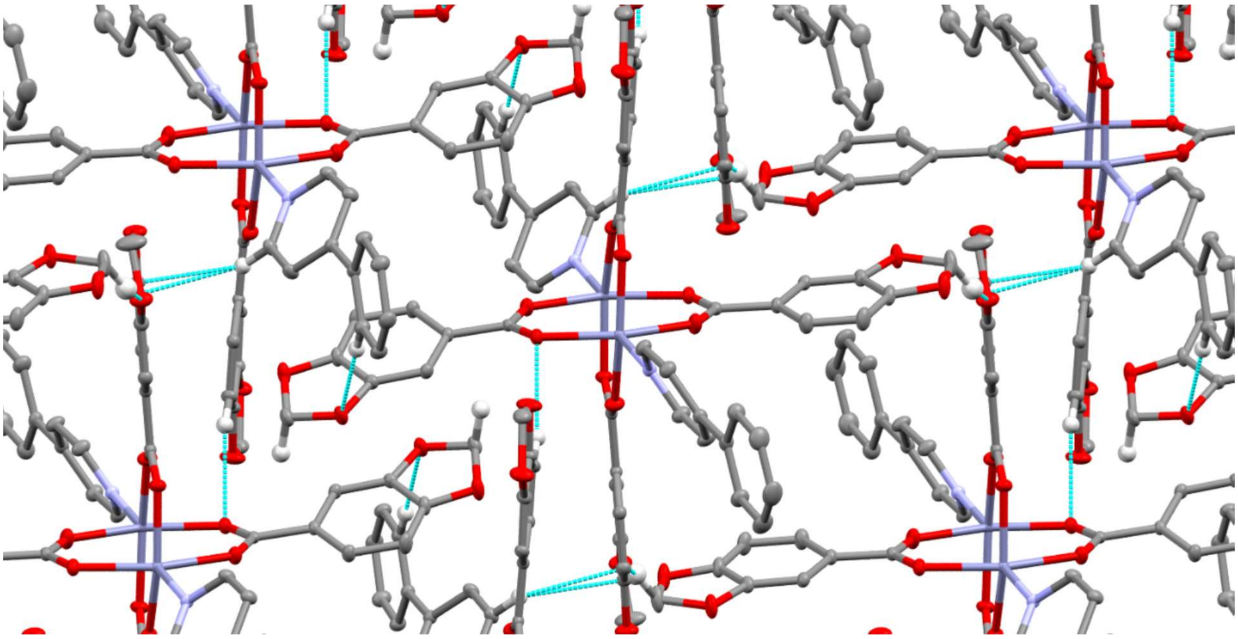


FIGURE 5

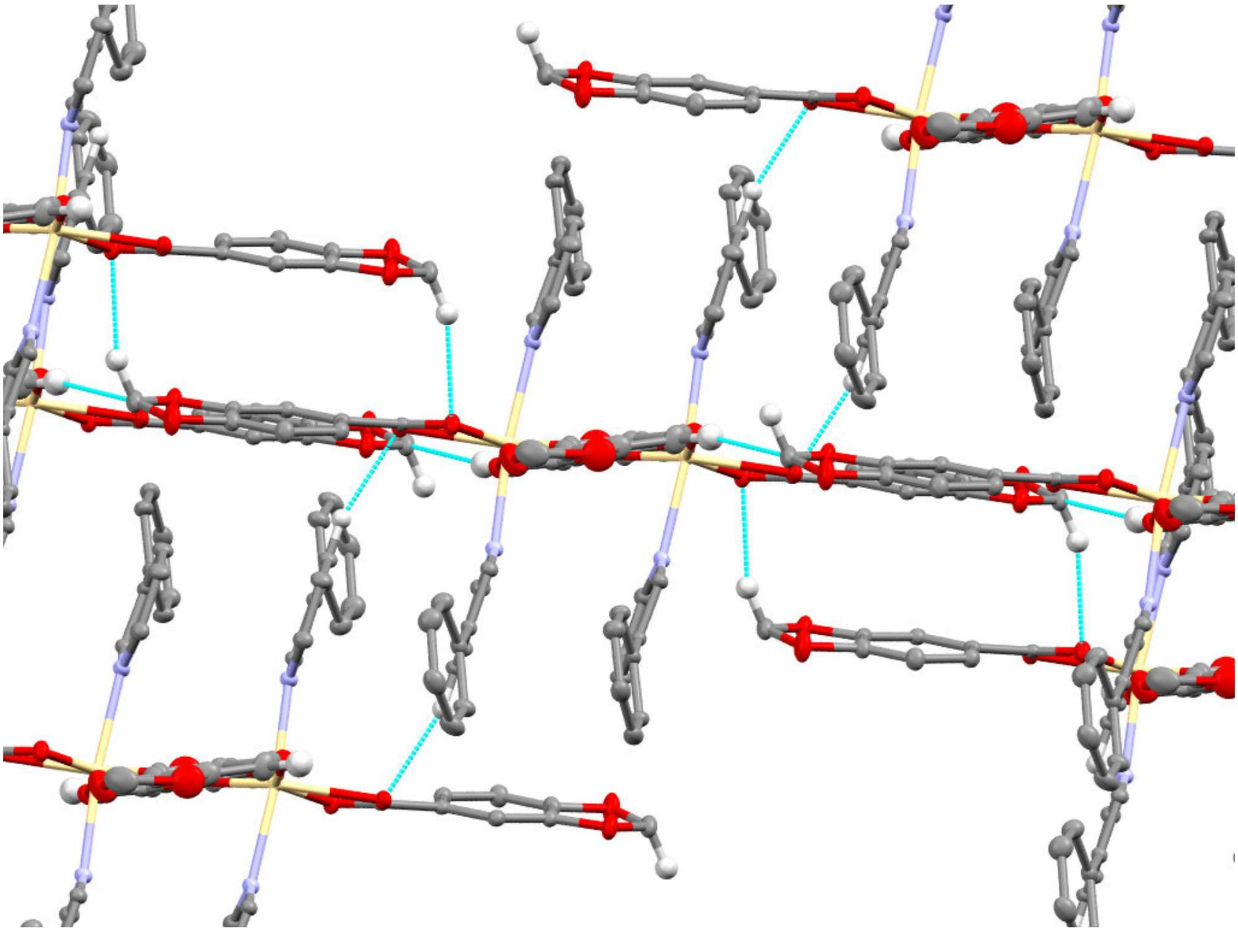


FIGURE 6

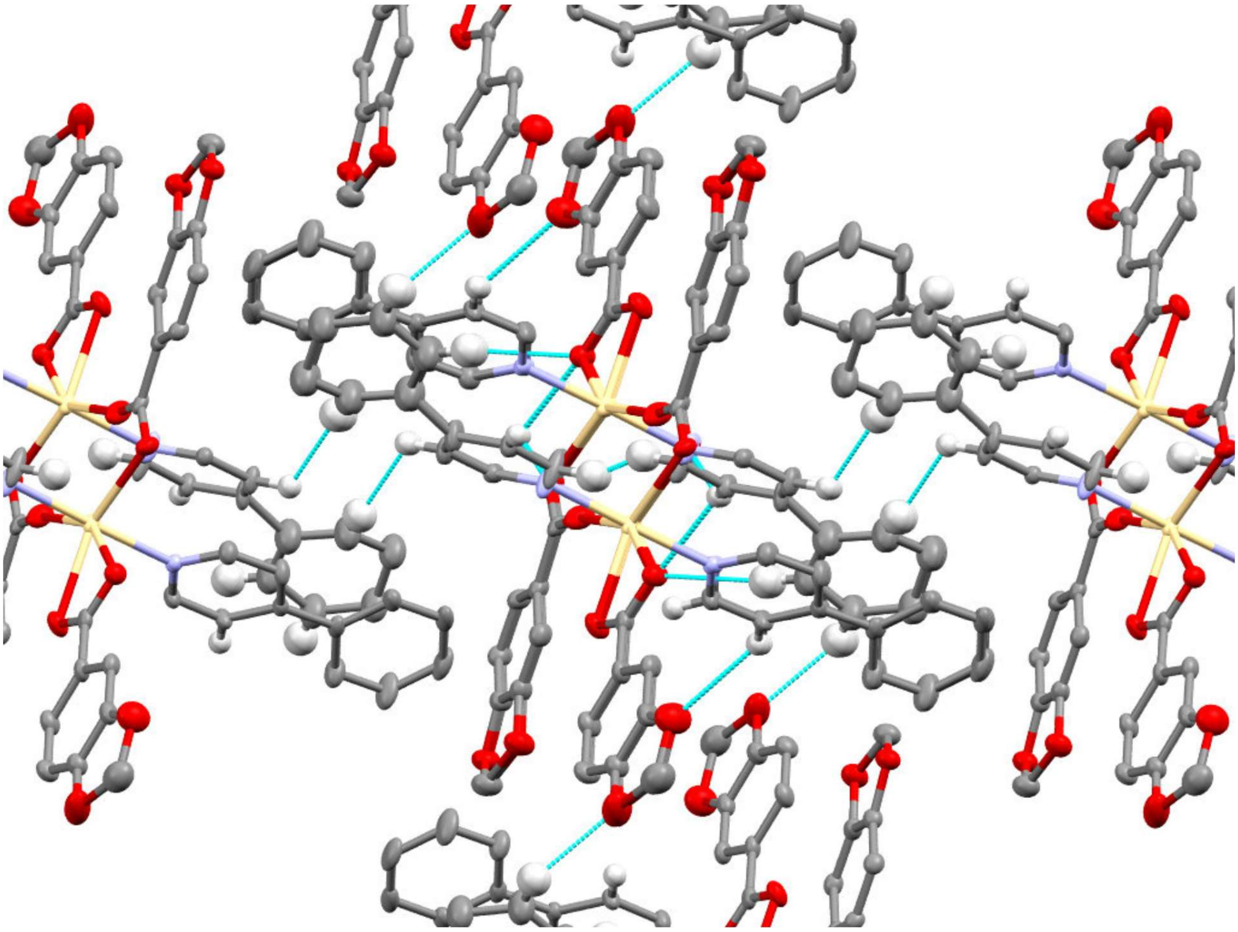
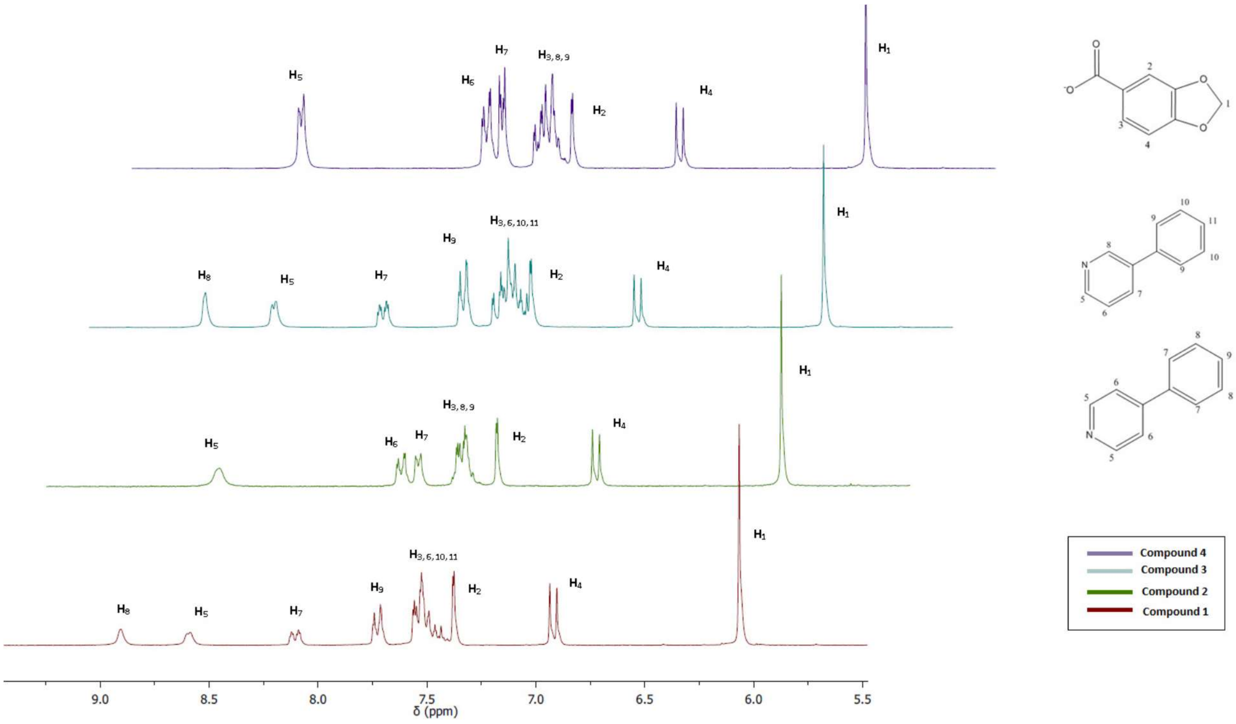


FIGURE 7



H5
H6
H7
H3, 8, 9
H2
H4
H1
H8
H5
H7
H9
H3, 6, 10, 11
H2
H4
H1
H5
H6
H7
H3, 8, 9
H2
H4
H1
H8
H5
H7
H9
H3, 6, 10, 11
H2
H4
H1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
δ (ppm)
O
⁻O
2
1
3
4
N
8
5
6
7
9
10
11
10
9
N
5
6
6
5
7
8
9
8
7
Compound 4
Compound 3
Compound 2
Compound 1

FIGURE 8

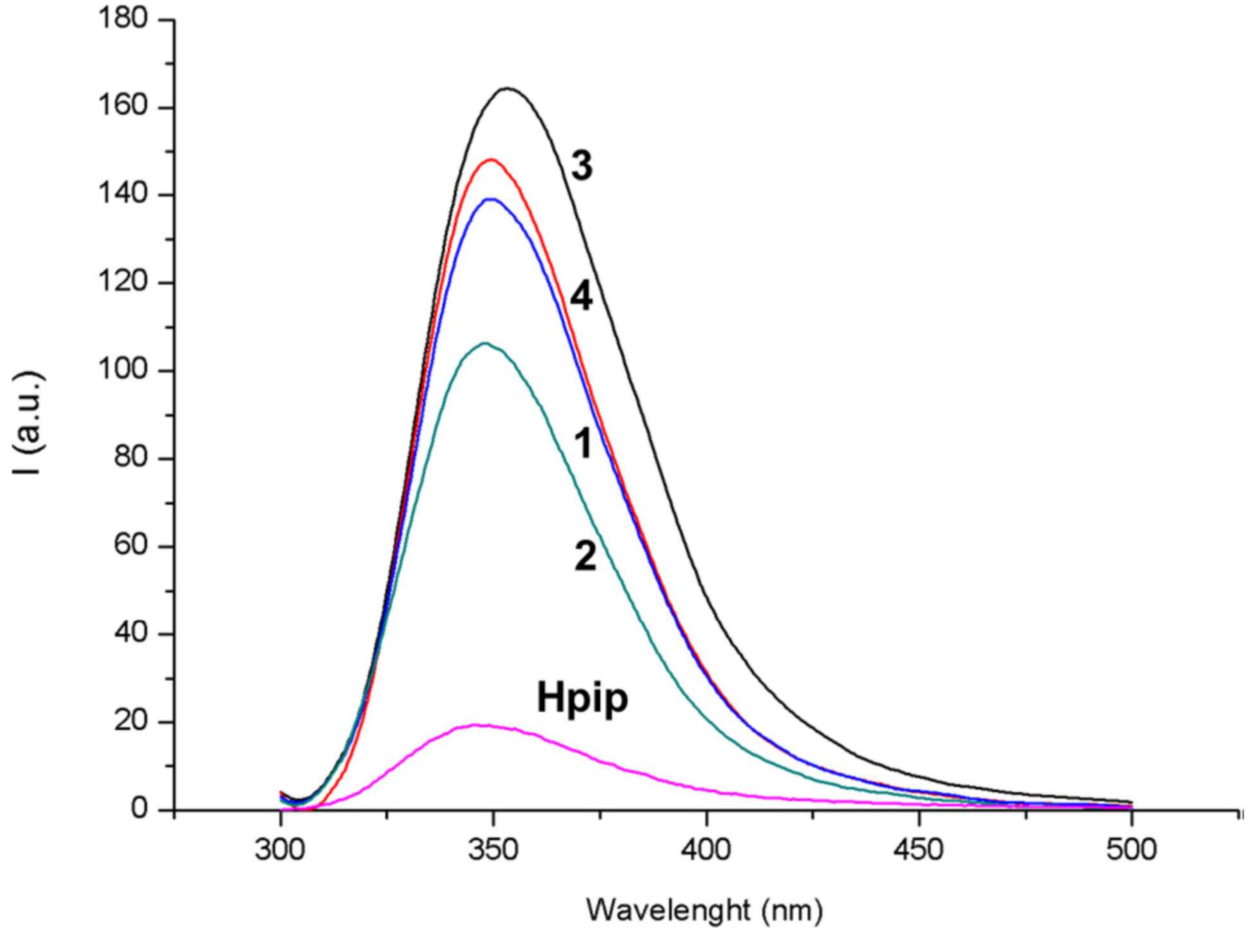
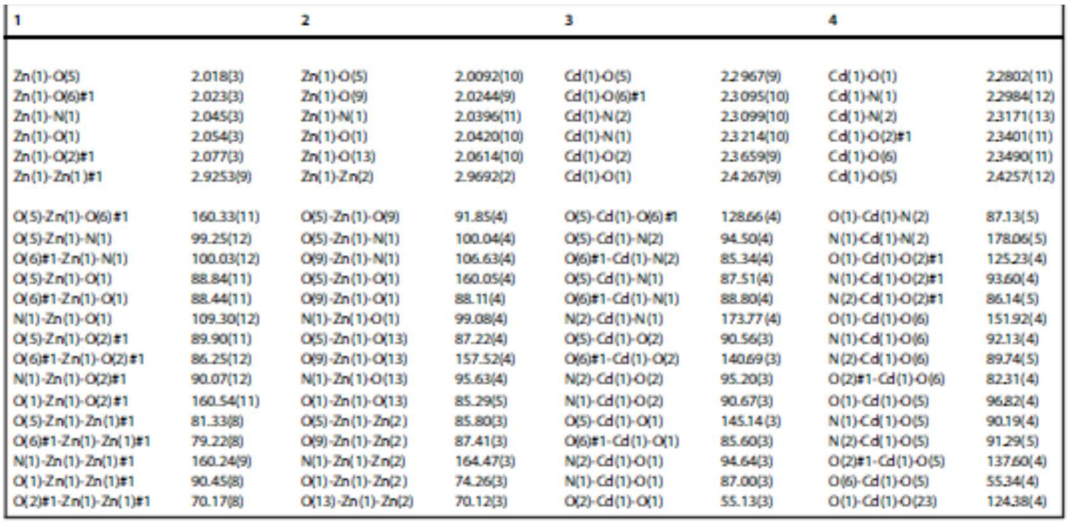
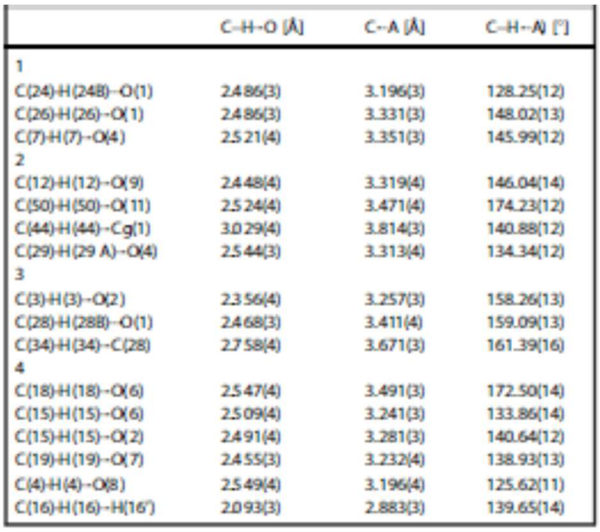

I (a.u.)
180
160
140
120
100
80
60
40
20
0
300
350
400
450
500
Wavelenght (nm)
3
4
1
2
Hpip

Table 1 Selected bond lengths ( ) and bond angles (8) for complexes 1–4



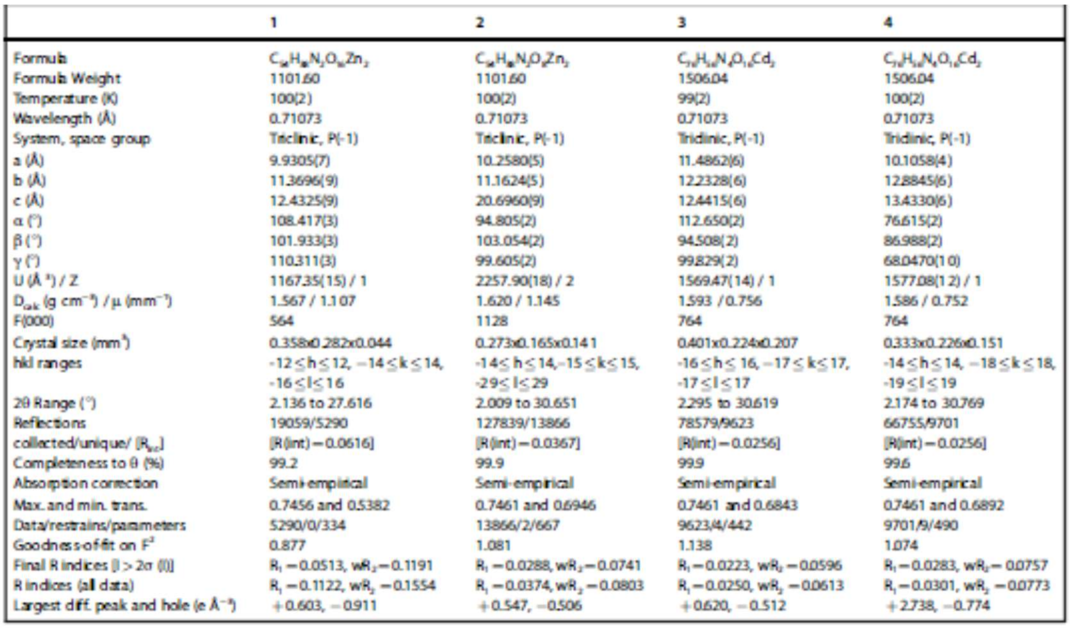
1		2		3		4	
Zn(1)-O(5)	2.018(3)	Zn(1)-O(5)	2.0092(10)	Cd(1)-O(5)	2.2967(9)	Cd(1)-O(1)	2.2802(11)
Zn(1)-O(6)#1	2.023(3)	Zn(1)-O(9)	2.0244(9)	Cd(1)-O(6)#1	2.3095(10)	Cd(1)-N(1)	2.2984(12)
Zn(1)-N(1)	2.045(3)	Zn(1)-N(1)	2.0396(11)	Cd(1)-N(2)	2.3099(10)	Cd(1)-N(2)	2.3171(13)
Zn(1)-O(1)	2.054(3)	Zn(1)-O(1)	2.0420(10)	Cd(1)-N(1)	2.3214(10)	Cd(1)-O(2)#1	2.3401(11)
Zn(1)-O(2)#1	2.077(3)	Zn(1)-O(13)	2.0614(10)	Cd(1)-O(2)	2.3659(9)	Cd(1)-O(6)	2.3490(11)
Zn(1)-Zn(1)#1	2.9253(9)	Zn(1)-Zn(2)	2.9692(2)	Cd(1)-O(1)	2.4267(9)	Cd(1)-O(5)	2.4257(12)
O(5)-Zn(1)-O(6)#1	160.33(11)	O(5)-Zn(1)-O(9)	91.85(4)	O(5)-Cd(1)-O(6)#1	128.66(4)	O(1)-Cd(1)-N(2)	87.13(5)
O(5)-Zn(1)-N(1)	99.25(12)	O(5)-Zn(1)-N(1)	100.04(4)	O(5)-Cd(1)-N(2)	94.50(4)	N(1)-Cd(1)-N(2)	178.06(5)
O(6)#1-Zn(1)-N(1)	100.03(12)	O(9)-Zn(1)-N(1)	106.63(4)	O(6)#1-Cd(1)-N(2)	85.34(4)	O(1)-Cd(1)-O(2)#1	125.23(4)
O(5)-Zn(1)-O(1)	88.84(11)	O(5)-Zn(1)-O(1)	160.05(4)	O(5)-Cd(1)-N(1)	87.51(4)	N(1)-Cd(1)-O(2)#1	93.60(4)
O(6)#1-Zn(1)-O(1)	88.44(11)	O(9)-Zn(1)-O(1)	88.11(4)	O(6)#1-Cd(1)-N(1)	88.80(4)	N(2)-Cd(1)-O(2)#1	86.14(5)
N(1)-Zn(1)-O(1)	109.30(12)	N(1)-Zn(1)-O(1)	99.08(4)	N(2)-Cd(1)-N(1)	173.77(4)	O(1)-Cd(1)-O(6)	151.92(4)
O(5)-Zn(1)-O(2)#1	89.90(11)	O(5)-Zn(1)-O(13)	87.22(4)	O(5)-Cd(1)-O(2)	90.56(3)	N(1)-Cd(1)-O(6)	92.13(4)
O(6)#1-Zn(1)-O(2)#1	86.25(12)	O(9)-Zn(1)-O(13)	157.52(4)	O(6)#1-Cd(1)-O(2)	140.69(3)	N(2)-Cd(1)-O(6)	89.74(5)
N(1)-Zn(1)-O(2)#1	90.07(12)	N(1)-Zn(1)-O(13)	95.63(4)	N(2)-Cd(1)-O(2)	95.20(3)	O(2)#1-Cd(1)-O(6)	82.31(4)
O(1)-Zn(1)-O(2)#1	160.54(11)	O(1)-Zn(1)-O(13)	85.29(5)	N(1)-Cd(1)-O(2)	90.67(3)	O(1)-Cd(1)-O(5)	96.82(4)
O(5)-Zn(1)-Zn(1)#1	81.33(8)	O(5)-Zn(1)-Zn(2)	85.80(3)	O(5)-Cd(1)-O(1)	145.14(3)	N(1)-Cd(1)-O(5)	90.19(4)
O(6)#1-Zn(1)-Zn(1)#1	79.22(8)	O(9)-Zn(1)-Zn(2)	87.41(3)	O(6)#1-Cd(1)-O(1)	85.60(3)	N(2)-Cd(1)-O(5)	91.29(5)
N(1)-Zn(1)-Zn(1)#1	160.24(9)	N(1)-Zn(1)-Zn(2)	164.47(3)	N(2)-Cd(1)-O(1)	94.64(3)	O(2)#1-Cd(1)-O(5)	137.60(4)
O(1)-Zn(1)-Zn(1)#1	90.45(8)	O(1)-Zn(1)-Zn(2)	74.26(3)	N(1)-Cd(1)-O(1)	87.00(3)	O(6)-Cd(1)-O(5)	55.34(4)
O(2)#1-Zn(1)-Zn(1)#1	70.17(8)	O(13)-Zn(1)-Zn(2)	70.12(3)	O(2)-Cd(1)-O(1)	55.13(3)	O(1)-Cd(1)-O(23)	124.38(4)

Table 2 Supramolecular interactions (C H···A) for complexes 1–4



	C–H···O [Å]	C···A [Å]	C–H···A) [°]
1			
C(24)-H(24B)···O(1)	2.486(3)	3.196(3)	128.25(12)
C(26)-H(26)···O(1)	2.486(3)	3.331(3)	148.02(13)
C(7)-H(7)···O(4)	2.521(4)	3.351(3)	145.99(12)
2			
C(12)-H(12)···O(9)	2.448(4)	3.319(4)	146.04(14)
C(50)-H(50)···O(11)	2.524(4)	3.471(4)	174.23(12)
C(44)-H(44)···Cg(1)	3.029(4)	3.814(3)	140.88(12)
C(29)-H(29 A)···O(4)	2.544(3)	3.313(4)	134.34(12)
3			
C(3)-H(3)···O(2)	2.356(4)	3.257(3)	158.26(13)
C(28)-H(28B)···O(1)	2.468(3)	3.411(4)	159.09(13)
C(34)-H(34)···C(28)	2.758(4)	3.671(3)	161.39(16)
4			
C(18)-H(18)···O(6)	2.547(4)	3.491(3)	172.50(14)
C(15)-H(15)···O(6)	2.509(4)	3.241(3)	133.86(14)
C(15)-H(15)···O(2)	2.491(4)	3.281(3)	140.64(12)
C(19)-H(19)···O(7)	2.455(3)	3.232(4)	138.93(13)
C(4)-H(4)···O(8)	2.549(4)	3.196(4)	125.62(11)
C(16)-H(16)···H(16′)	2.093(3)	2.883(3)	139.65(14)

Table 3. Crystallographic data for complexes 1–4



	1	**2**	**3**	**4**
Formula	$C_{54}H_{38}N_2O_{16}Zn_2$	$C_{54}H_{38}N_2O_{16}Zn_2$	$C_{76}H_{56}N_4O_{16}Cd_2$	$C_{76}H_{56}N_4O_{16}Cd_2$
Formula Weight	1101.60	1101.60	1506.04	1506.04
Temperature (K)	100(2)	100(2)	99(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
System, space group	Triclinic, P(-1)	Triclinic, P(-1)	Triclinic, P(-1)	Triclinic, P(-1)
a (Å)	9.9305(7)	10.2580(5)	11.4862(6)	10.1058(4)
b (Å)	11.3696(9)	11.1624(5)	12.2328(6)	12.8845(6)
c (Å)	12.4325(9)	20.6960(9)	12.4415(6)	13.4330(6)
α (°)	108.417(3)	94.805(2)	112.650(2)	76.615(2)
β (°)	101.933(3)	103.054(2)	94.508(2)	86.988(2)
γ (°)	110.311(3)	99.605(2)	99.829(2)	68.0470(10)
U (Å^3) / Z	1167.35(15) / 1	2257.90(18) / 2	1569.47(14) / 1	1577.08(12) / 1
D_{calc} (g cm^{-3}) / μ (mm^{-1})	1.567 / 1.107	1.620 / 1.145	1.593 / 0.756	1.586 / 0.752
F(000)	564	1128	764	764
Crystal size (mm^3)	0.358x0.282x0.044	0.273x0.165x0.141	0.401x0.224x0.207	0.333x0.226x0.151
hkl ranges	$-12 \le h \le 12$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-29 \le l \le 29$	$-16 \le h \le 16$, $-17 \le k \le 17$, $-17 \le l \le 17$	$-14 \le h \le 14$, $-18 \le k \le 18$, $-19 \le l \le 19$
2θ Range (°)	2.136 to 27.616	2.009 to 30.651	2.295 to 30.619	2.174 to 30.769
Reflections collected/unique/ [R_{int}]	19059/5290 [R(int) − 0.0616]	127839/13866 [R(int) − 0.0367]	78579/9623 [R(int) − 0.0256]	66755/9701 [R(int) − 0.0256]
Completeness to θ (%)	99.2	99.9	99.9	99.6
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical
Max. and min. trans.	0.7456 and 0.5382	0.7461 and 0.6946	0.7461 and 0.6843	0.7461 and 0.6892
Data/restrains/parameters	5290/0/334	13866/2/667	9623/4/442	9701/9/490
Goodness-of-fit on F^2	0.877	1.081	1.138	1.074
Final R indices [$I > 2\sigma(I)$]	$R_1 - 0.0513$, $wR_2 - 0.1191$	$R_1 - 0.0288$, $wR_2 - 0.0741$	$R_1 - 0.0223$, $wR_2 - 0.0596$	$R_1 - 0.0283$, $wR_2 - 0.0757$
R indices (all data)	$R_1 - 0.1122$, $wR_2 - 0.1554$	$R_1 - 0.0374$, $wR_2 - 0.0803$	$R_1 - 0.0250$, $wR_2 - 0.0613$	$R_1 - 0.0301$, $wR_2 - 0.0773$
Largest diff. peak and hole (e Å^{-3})	+0.603, −0.911	+0.547, −0.506	+0.620, −0.512	+2.738, −0.774