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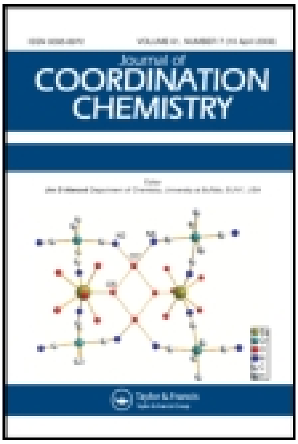

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Syntheses, characterization, and crystal structures of two zinc(II) carboxylates containing pyridine

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Syntheses, characterization, and crystal structures of two zinc(II) carboxylates containing pyridine

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Two organic–inorganic hybrid compounds $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]\cdot0.5CH_3OH$ (**1**) and $[Zn(2\text{-}Cl\text{-}OBz)_2(py)_2]$ (**2**) (OBz = benzoate; 2-Cl-OBz = 2-chlorobenzoate; py = pyridine) have been synthesized from aqueous methanol at room temperature and characterized by analytical, spectroscopic, and single-crystal X-ray diffraction. Compound **1** crystallizes in space group $P2_1/c$ and exhibits a dinuclear paddle-wheel-like structure with Zn—Zn separation of 2.9602(7) Å. Zn–O distances in **1** range from 2.0272(18) to 2.057(2) Å and Zn–N distances are 2.043(5) and 2.004(9) Å. Each Zn has a square-pyramidal geometry bridged by four carboxylates in the basal plane with the pyridine at the apex. The dinuclear unit also contains 0.5 methanol. Compound **2** crystallizes in space group $P\bar{1}$ and consists of discrete molecules having a distorted tetrahedral environment around zinc; 2-chlorobenzoate and pyridine are monodentate. The observed Zn–O distances in **2** are 2.0255(19) and 2.0377(18) Å and Zn–N distances are 1.9535(14) and 1.9587(16) Å. Weak C–H—O and π–π stacking interactions between 2-chlorobenzoate and pyridine are operative in the crystal lattice of **2**. Complex **2** on excitation at 340 nm exhibits luminescence at room temperature arising probably due to intraligand π–π^* transition.

Keywords: Synthesis; Characterization; Crystal structure; Organic-inorganic hybrid

1. Introduction

Interest has been generated in coordination chemistry of zinc with nitrogen and oxygen donors because such compounds are biological models for various enzymes [1, 2], and they have important roles in catalytic processes [3, 4] and in rational design and synthesis of metal–organic frameworks (MOFs) [5, 6]. Carboxylic acids are important substrates in many biochemical processes [7]. Mono as well as dinuclear zinc carboxylates are important as biological models [2, 8]. Apart from the bioactive role of zinc carboxylate complexes, design and synthesis of MOFs with carboxylic acids

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continue to be interesting due to their potential applications in catalysis, guest–host chemistry, optics, magnetism, and also because of their intriguing architectures [9, 10]. Benzene-core carboxylic acids have rich coordination modes, such as terminal monodentate, chelating, and various modes of bridging coordination of two, three, or even more metal centers [11], and also function as hydrogen-bond acceptors and donors in assembling supramolecular complexes [12]. Heterocyclic nitrogen donors, such as pyridine and related molecules, are good ligands. Use of such ligands lead to the formation of compounds with a wide range of physical, chemical, and biological properties, spanning a broad spectrum of reactivity and stability [13]. With an effort to synthesize coordination compounds of zinc and to investigate their characteristics, we have prepared zinc complexes involving aromatic carboxylic acids incorporating pyridine. The present work deals with a direct method of synthesis, characterization, and structure determination of dinuclear zinc benzoate complexe with pyridine. We also present the synthesis, spectral characterization, luminescence, and crystal structure of a new mononuclear compound based on zinc, 2-chlorobenzoic acid, and pyridine.

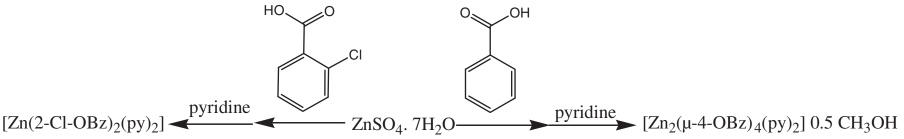
2. Experimental

2.1. *Materials and measurements*

Chemicals were all reagent grade products. Infrared (IR) spectra were recorded as KBr disks using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. ^{1}H NMR spectra were obtained with Bruker Avance II 200 and 400 MHz spectrometers at ambient temperature using DMSO-d$_6$ and $CDCl_3$ as solvents. Electronic spectra of **1** and **2** were recorded using a Perkin-Elmer Model Lamda 25 spectrometer. Fluorescence behavior of the complexes was studied using a Shimadzu Spectrofluorophotometer RF-500 at room temperature. C, H, N contents of the compounds were determined by microanalytical methods from SAIF, NEHU, Shillong, India. Zinc was estimated volumetrically by complexometric titration with EDTA using Erio-T as the indicator [14].

2.2. *Synthesis*

2.2.1. Synthesis of tetrakis[μ-4-benzoato-*O*:*O′*]bis[(pyridine-N)zinc(II)] · 0.5-methanol, $[Zn_2(\mu\text{-4-OBz})_4(py)_2]\cdot 0.5CH_3OH$ (1) (OBz = benzoate). To a methanolic solution (20 mL) of benzoic acid (0.244 g, 2.0 mmol) was added 0.5 mL (0.49 g, 6.2 mmol) of pyridine slowly with stirring. To the resultant solution an aqueous solution (20 mL) of zinc sulfate heptahydrate (0.287 g, 1.0 mmol) was added dropwise giving a homogeneous solution. The reaction mixture was stirred at room temperature for ~3 h, filtered to remove any undissolved residue, and kept in a freezer for 2–3 days when colorless crystals were formed. Yield >50%, based on zinc. Anal. Calcd for $C_{38.5}H_{32}Zn_2N_2O_{8.5}$ (**1**) (%): Zn, 16.56; C, 58.57; H, 4.08; N, 3.54. Found (%): Zn, 16.76; C, 58.62; H, 4.03; N, 3.62. IR (KBr, cm^{-1}) 3502$_w$ (νOH), 3066$_w$ (νCH), 1638$_s$ ($\nu_{as}COO^-$), 1607$_s$ [ν(C=C), py], 1450$_s$ (ν_sCOO^-), 1400–1028$_m$ (pyridine ring vibrations), 642$_m$, 422$_m$ cm^{-1} (out of



Reaction scheme

plane and in plane def. of py). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 8.62 (s, 4H), 7.86–7.95 (m, 10H), 7.38–7.50 (m, 16H). UV λ_{max} 236 and 283 nm.

2.2.2. Synthesis of bis(2-chlorobenzoato-*O*)bis(pyridine-N)zinc(II), [Zn(2-Cl-OBz)$_2$(py)$_2$] (2) (2-Cl-OBz = 2-chlorobenzoate, py = pyridine).

To a methanolic solution (20 mL) of 2-chlorobenzoic acid (0.312 g, 2.0 mmol) was added 0.5 mL (0.49 g, 6.2 mmol) of pyridine slowly with stirring. To the resultant solution was added 20 mL of an aqueous solution of zinc sulfate heptahydrate (0.574 g, 2.0 mmol) dropwise. The resultant homogeneous mixture was stirred for a period of ~3 h, filtered to remove any undissolved impurities, and left undisturbed in a freezer for 4–5 days when colorless single crystals suitable for X-ray diffraction were deposited. Yield >40%, based on zinc. Anal. Calcd for $C_{24}H_{18}ZnN_2O_4Cl_2$ (**2**) (%): Zn, 12.23; C, 53.91; H, 3.39; N, 5.23. Found (%): Zn, 12.32; C, 53.81; H, 3.41; N, 5.28. IR (KBr, cm^{-1}) 3069$_w$ (νCH), 1635$_s$ (ν_{as}COO$^-$), 1609$_s$ [ν(C=C), py], 1394$_s$ (ν_sCOO$^-$), 1355–1016$_m$ (pyridine ring vibrations), 642$_m$, 422$_m$ cm^{-1} (out of plane and in plane def. of py). ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.00–8.05 (m, 4H), 7.49–7.51 (m, 7H), 7.48 (m, 5H), 7.26–7.27 (d, 2H). UV λ_{max} 274 nm.

2.3. *X-ray crystallography*

X-ray diffraction data for **1** were collected by using an Oxford Diffraction Xcalibur Eos Gemini diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Data were analyzed with "CrysAlis PRO" software [15] and the collected data was reduced by using the "CrysAlis PRO" program. An empirical absorption correction using spherical harmonics was implemented in "SCALE3 ABSPACK" scaling algorithm. The crystal structure of the compound was solved by direct methods using SHELXS-97 [16] and the refinement was carried out against F^2 using SHELXL-97 [17]. All non-hydrogen atoms were refined anisotropically. Hydrogens on carbon were added from calculation. The hydroxyl hydrogen was fixed as a riding model and refined with a distance restraint of 0.82 Å.

The X-ray measurements for **2** were carried out on a BRUKER SMART APEX CCD area diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω mode at 293 K. Absorption effects in the compound were corrected using SADABS [18]. The crystal structure of the compound was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL-97 [19]. The summary of crystallographic data and details of the structure refinement parameters for **1** and **2** are given in table 1. Selected bond distances and angles for **1** and **2** are presented in tables 2 and 3, respectively.

Table 1. Crystallographic details of **1** and **2**.

	$[Zn_2(C_7O_5O_2)_4(C_5H_5N)_2] \cdot 0.5CH_3OH$	$[Zn(C_7H_4O_2Cl)_2(C_5H_5N)_2]$
Empirical formula	$C_{38.5}H_{32}N_2O_{8.5}Zn_2$	$C_{24}H_{18}Cl_2N_2O_4Zn$
Formula weight	789.40	534.67
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.2347(14)	7.8745(16)
b	10.5637(12)	12.318(3)
c	18.485(4)	13.110(3)
α	90.00	104.837(3)
β	113.323(15)	102.956(3)
γ	90.00	102.262(3)
Volume (Å^3), Z	1835.2(5), 2	1147.8(4), 2
Calculated density ($g\,m^{-3}$)	1.429	1.547
Absorption coefficient (mm^{-1})	1.362	1.337
$F(000)$	810	544
Crystal size (mm^3)	$0.42 \times 0.32 \times 0.24$	$0.30 \times 0.16 \times 0.10$
θ range for data collection	3.08 to 26.37	1.68 to 26.06
Limiting indices	$-12 \le h \le 7$, $-13 \le k \le 8$, $-22 \le l \le 23$	$-9 \le h \le 9$, $-15 \le k \le 15$, $-16 \le l \le 16$
Reflection collected	7130	10,511
Independent reflections	3745 [R(int) = 0.0312]	4408 [R(int) = 0.0241]
Data/restraints/parameters	3745/229/300	4408/0/298
Goodness-of-fit on F^2	0.912	1.844
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0375$, $wR_2 = 0.0803$	$R_1 = 0.0394$, $wR_2 = 0.0677$
R indices (all data)	$R_1 = 0.0614$, $wR_2 = 0.0845$	$R_1 = 0.0459$, $wR_2 = 0.0687$
Largest difference peak and hole (e Å^{-3})	0.334 and −0.633	0.597 and −0.456

Table 2. Selected bond distances (Å) and angles (°) of $[Zn_2(C_7O_5O_2)_4(C_5H_5N)_2] \cdot 0.5CH_3OH$ (**1**).

Zn(1)–O(1)	2.029(2)	Zn(1)–O(4)	2.0272(18)
Zn(1)–O(2)	2.057(2)	Zn(1)–N(1)	2.043(5)
Zn(1)–O(3)	2.044(19)	Zn(1)–N(1′)	2.004(9)
N(1)–Zn(1)–O(1)	104.8(3)	N(1′)–Zn(1)–O(1)	99.5(5)
N(1)–Zn(1)–O(2)	95.9(3)	N(1′)–Zn(1)–O(2)	101.1(5)
N(1)–Zn(1)–O(3)	98.9(2)	N(1′)–Zn(1)–O(3)	93.8(4)
N(1)–Zn(1)–O(4)	101.8(2)	N(1′)–Zn(1)–O(4)	107.1(4)
N(1)–Zn(1)–N(1′)	7.3(5)	O(1)–Zn(1)–O(2)	159.28(8)
O(1)–Zn(1)–O(3)	88.07(9)	O(1)–Zn(1)–O(4)	89.17(8)
O(2)–Zn(1)–O(3)	88.29(9)	O(2)–Zn(1)–O(4)	87.09(8)
O(3)–Zn(1)–O(4)	159.13(8)	–	–

Table 3. Selected bond distances (Å) angles (°) of $[Zn(C_7H_4O_2Cl)_2(C_5H_5N)_2]$ (**2**)

Zn(1)–O(1)	1.9535(14)	Zn(1)–N(2)	2.0377(18)
Zn(1)–O(3)	1.9587(16)	Cl(1)–C(3)	1.736(2)
Zn(1)–N(1)	2.0255(19)	Cl(2)–C(10)	1.724(3)
O(1)–Zn(1)–O(3)	96.61(7)	N(1)–Zn(1)–O(3)	118.42(7)
O(1)–Zn(1)–N(1)	118.81(7)	N(1)–Zn(1)–N(2)	104.29(7)
O(1)–Zn(1)–N(2)	107.54(7)	N(2)–Zn(1)–O(3)	110.86(7)

3. Results and discussion

3.1. *Synthesis*

The literature reported method [20] for the synthesis of dinuclear zinc benzoate complex, $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]$, involves a solid-state reaction of anhydrous zinc chloride with potassium hydroxide at *ca* 100°C, followed by the addition of pyridine. The synthetic strategy adopted in the present case employs a direct and simpler method of reaction involving zinc sulfate heptahydrate, benzoic acid, and pyridine in aqueous methanolic solution at room temperature, which led to the synthesis of a dinuclear zinc benzoate complex with ancillary pyridine containing 0.5 methanol, $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]\cdot 0.5CH_3OH$ (compound **1**). Diffraction quality single crystals of **1** were obtained on storing the reaction solution in a freezer for 2–3 days. While $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]$ [20] and **1** are very similar, the solid-state structures are not identical, as discussed in section 3.2.1. Following a similar synthetic strategy and by carrying out reaction with zinc sulfate heptahydrate, 2-chlorobenzoic acid, and pyridine in aqueous methanol at room temperature afforded mononuclear $[Zn(2\text{-}Cl\text{-}OBz)_2(py)_2]$ (**2**) in reasonable yield. The synthesized complexes were characterized on the basis of elemental analyses, molar conductance measurements, FT-IR, ^1H NMR, UV-Vis spectral studies, and also by X-ray crystallography. The compounds are air stable and soluble in common organic solvents. Molar conductance measurements of **1** and **2** in methanolic solution exhibit values of $2\text{–}5\,\Omega^{-1}\,cm^{-1}\,mol^{-1}$, indicating non-electrolytes. The analytical data of **1** and **2** are in good agreement with the composition of the complexes.

3.2. *Crystallographic studies*

3.2.1. Structural elucidation of $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]\cdot 0.5CH_3OH$ (1). Single crystal X-ray diffraction reveals that **1** consists of $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]\cdot 0.5CH_3OH$ and crystallizes in the monoclinic space group $P2_1/c$. An ORTEP representation of **1** is shown in figure 1 with the atom numbering scheme. A view of the packing pattern in **1** is shown in figure 2. Selected bond distances and angles of **1** are given in table 2. The structure of **1** consists of centrosymmetric dinuclear zinc units and is typical of dinuclear $[M_2(carboxylate)_4L_2]$ complexes [21], with the benzoate ligands providing four metal-bridging bidentate carboxylate residues. The benzoate ligands display a paddle-wheel-like arrangement about the Zn—Zn axis. Each Zn(II) cation has a distorted square-pyramidal coordination geometry, with the apex provided by axial coordination of the pyridine. Analysis of the shape determining bond angles using the geometrical parameter τ ($\tau = |\alpha - \beta|/60$) [22], where α and β are the largest angles around the central atom), gives a value of 0.0025 and also suggest that the zinc is a distorted square pyramid, $[ZnO_4N]$. The tetra carboxylate bridging framework can accommodate metal–metal separation up to 3.452 Å [23], the Zn—Zn separation in the present case is 2.9602(7) Å. Zinc is displaced from the plane of the four oxygens toward pyridine by 0.368 Å. The Zn–O distances range from 2.027 to 2.057 Å and Zn(1)–N(1) and Zn(1)–N(1′) were 2.043(5) and 2.004(9) Å, respectively. The pyridine rings [N(1), C(15)–C(19)/N(1′), C(15′)–C(19′)] are disordered over two positions with an observed percentage occupancy of 66 : 34. For each dinuclear unit of **1**, the structure contains half a molecule

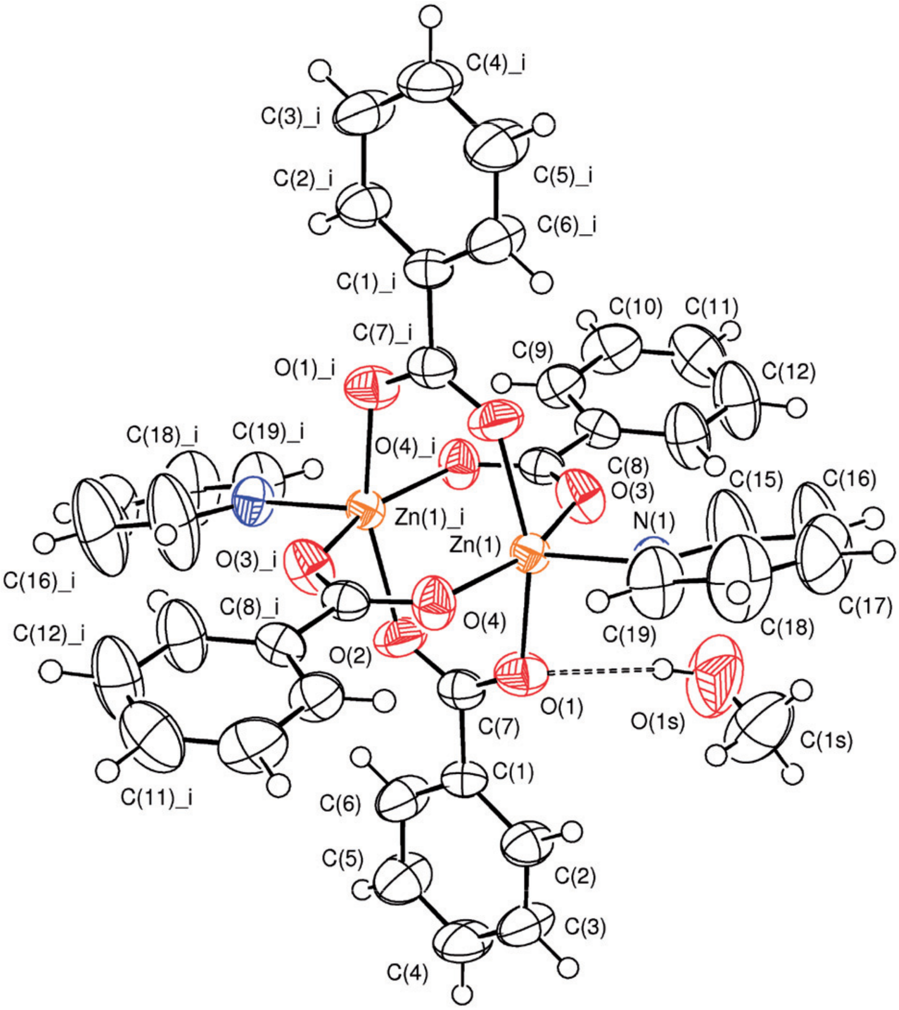


Figure 1. ORTEP view of $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2] \cdot 0.5CH_3OH$ (**1**) at the 50% probability level. The pyridine ring [N(1), C(15)–C(19)/N(1′), C(15′)–C(19′)] is disordered over two sites at a percentage occupancy ratio of 66 : 34, with only the major site shown for clarity. Methanol O(1S), C(1S) is present at 50% occupancy and disordered over two sites about an inversion center. Only one site is shown for clarity.

of methanol disordered about an inversion center over two positions. Hydrogen bonding between the hydroxyl (O1S–H1S4) of methanol and O(1) of benzoate, with an O—O separation of 3.14(2) Å and an O–H—O separation of 2.34 Å, is also observed (figure 2a). The crystal packing is shown in figure 2(b). The geometries of $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]$ [20] and **1** are very similar, although there is no disorder reported in the structure described [20]. The two solid-state structures differ in the presence of solvent methanol in **1** and in the unit cell values (**1**: $a = 10.235(1)$ Å, $b = 10.564(1)$ Å, $c = 18.485(4)$ Å, $\alpha = 90^\circ$, $\beta = 113.32(2)^\circ$, $\gamma = 90^\circ$ compared with $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]$ in [20]: $a = 10.0517(1)$ Å, $b = 10.5364(1)$ Å, $c = 17.3429(2)$ Å, $\alpha = 90^\circ$, $\beta = 99.266(1)^\circ$, $\gamma = 90^\circ$).

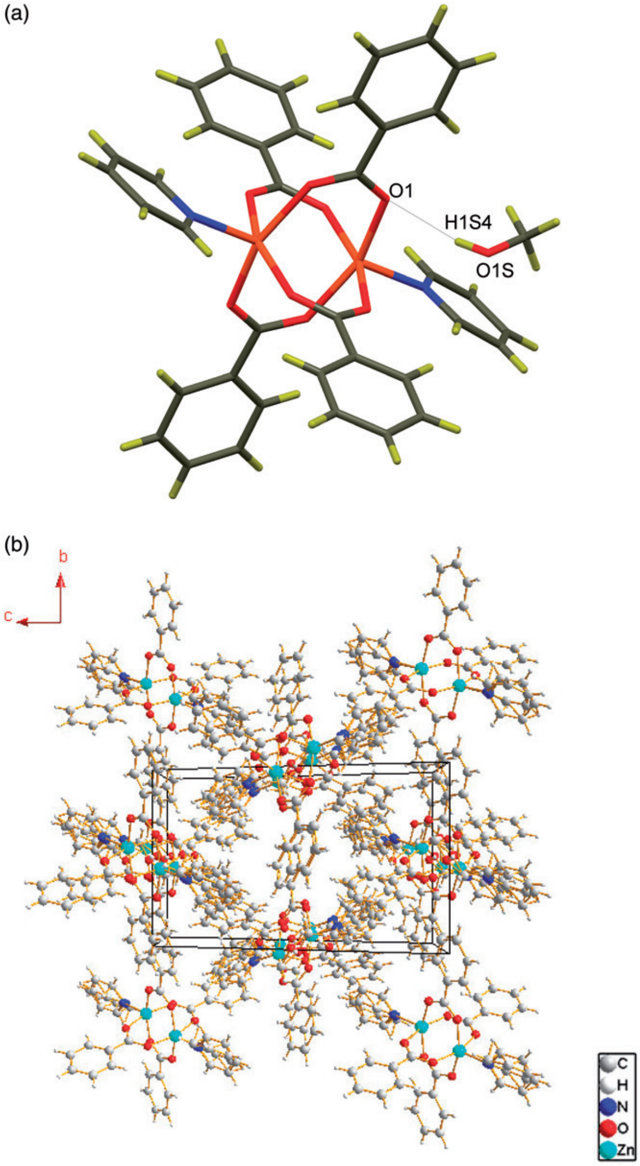


Figure 2. (a) Hydrogen bonding (shown as a black dotted line) between methanol and a benzoate in **1** with only one component of disordered moieties shown for clarity. (b) The crystal packing of $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]\cdot 0.5CH_3OH$ (**1**) viewed along the "*a*" direction. Methanol solvates are omitted for clarity.

3.2.2. Structural elucidation of $[Zn(2\text{-}Cl\text{-}OBz)_2(py)_2]$ (2). $[Zn(2\text{-}Cl\text{-}OBz)_2(py)_2]$ (**2**) exists as a mononuclear complex and crystallizes in space group $P\bar{1}$. A perspective view of **2** is shown in figure 3 together with the atom labeling scheme used. Selected bond lengths and angles are given in table 3 and the crystallographic data of the compound are presented in table 1. The crystal structure consists of discrete molecular species in which zinc is a distorted tetrahedron, $[ZnO_2N_2]$, ligated by N(1) and N(2) of two

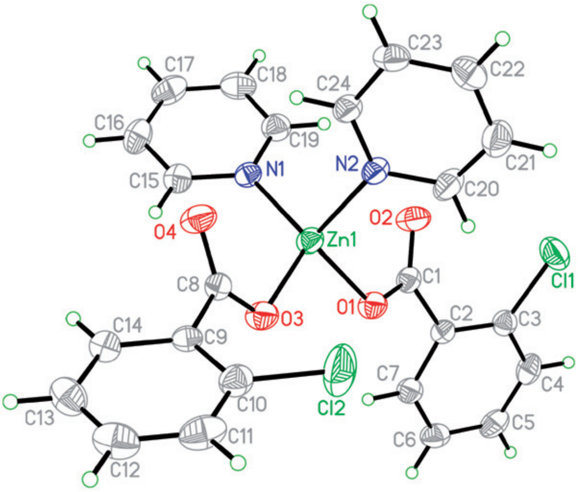


Figure 3. The crystal structure of **2** with atom labeling.

pyridines and O(1) and O(3) from two 2-chlorobenzoate groups. Deviation from regular tetrahedral geometry is apparent from the observed bond angles, N(1)–Zn(1)–O(1) = 118.81(7)°, O(3)–Zn(1)–N(1) = 118.42(7)°, and O(1)–Zn(1)–O(3) = 96.61(7)°, respectively, which are significantly different from the ideal value of 109°. However, the bond angles for O(1)–Zn(1)–N(2) = 107.54(7)° and O(3)–Zn(1)–N(2) = 110.86(7)° are not much deviated from the ideal value. The observed bond distances for Zn–N and Zn–O are 2.0255(19) Å [Zn(1)–N(1)], 2.0377(18) Å [Zn(1)–N(2)], 1.9535(14) Å [Zn(1)–O(1)], and 1.9587(16) Å [Zn(1)–O(3)], similar to the values reported for zinc complexes having similar distorted tetrahedral geometry [24]. In the crystal packing of **2**, π–π stacking interactions exist between pyridine and 2-chlorobenzoate (figure 4). The partially overlapped arrangement of pyridine ring and benzene core of 2-chlorobenzoate with centroid–centroid separation of 3.74 Å is observed. Weak C–H—O interactions between O(2)—H(6), O(3)—H(23), and O(4)—H(24) are operative in the crystal lattice (figure 4).

3.3. *IR spectra*

The IR spectra of **1** and **2** (Supplementary material) display characteristic absorptions due to coordinated carboxylate and pyridine. Solid-state IR spectra of **1** show strong absorption at 1638 $\mathrm{cm^{-1}}$ due to asymmetric carboxylate stretch ($\nu_{as}\mathrm{COO^-}$) and the corresponding symmetric stretch ($\nu_s\mathrm{COO^-}$) is observed at 1450 $\mathrm{cm^{-1}}$. The separation of 188 $\mathrm{cm^{-1}}$ between these two bands [$\nu_{as}(\mathrm{COO^-})$–$\nu_s(\mathrm{COO^-})$] is indicative of bridging bidentate carboxylate [25]. For **2**, IR spectrum exhibits strong bands at 1635 and 1394 $\mathrm{cm^{-1}}$ due to asymmetric ($\nu_{as}\mathrm{COO^-}$) and symmetric ($\nu_s\mathrm{COO^-}$) stretches of carboxylate [26]. The difference between antisymmetric and symmetric stretching modes [$\nu_{as}(\mathrm{COO^-})$–$\nu_s(\mathrm{COO^-})$], $\Delta\nu \sim 241\ \mathrm{cm^{-1}}$ ($>200\ \mathrm{cm^{-1}}$), is typical of monodentate carboxylate [27]. In addition, IR spectra of **1** and **2** show a band at 1607–1609 $\mathrm{cm^{-1}}$ assignable to the stretching vibration of pyridine, ν(C=C). Characteristic out-of-plane

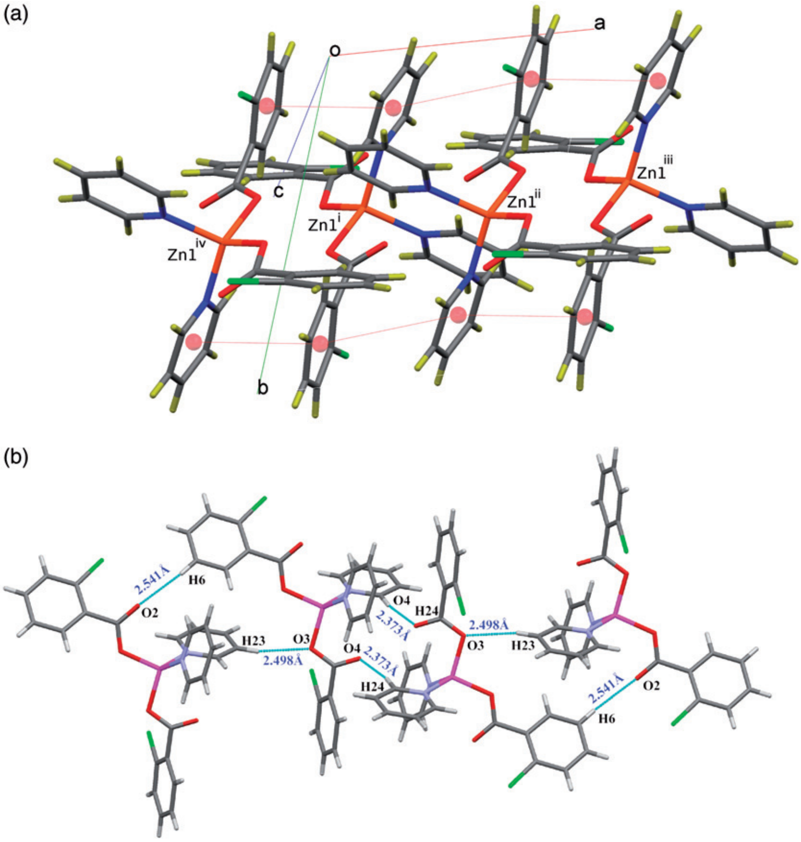


Figure 4. Depiction of (a) π–π stacking (symmetry transformations used to generate equivalent atoms: $^{(i)}x$, y, z; $^{(ii)}1-x$, $1-y$, $-z$; $^{(iii)}1+x$, y, z; $^{(iv)}-x$, $1-y$, $-z$); (b) weak C–H—O interaction in **2**.

and in-plane deformation bands for pyridine are observed at 642 and 422 cm^{-1}, shifted to higher frequency in comparison to values observed for free ligand (604 and 405 cm^{-1}), suggesting coordination of pyridine nitrogen. Medium intensity bands between 1016 and 1400 cm^{-1} are assignable to ring vibrations of pyridine. A band near 3500 cm^{-1} for **1** is assigned as ν(OH), arising from methanol in the crystal lattice. Absence of a band at 1690–1720 cm^{-1} in both compounds indicates that the carboxylic acids are deprotonated in the compounds. IR spectral data thus clearly lend support to the structures determined by X-ray diffraction method.

3.4. *^{1}H NMR*

^{1}H NMR spectra of **1** and **2** were recorded in DMSO-d_6 and $CDCl_3$, respectively. The room temperature ^{1}H NMR spectra of **1** and **2** do not show a signal due to carboxylic acid (–COOH) proton. The ^{1}H NMR spectra of $[Zn_2(\mu\text{-}4\text{-}OBz)_4(py)_2]\cdot 0.5CH_3OH$ (**1**) and $[Zn(2\text{-}Cl\text{-}OBz)_2(py)_2]$ (**2**) show signals assignable to aromatic hydrogens of carboxylate as well as pyridine. These signals undergo small shift with respect to the free ligands and provide evidence for coordination of ligands to metal through oxygen and nitrogen.

3.5. *Electronic spectra*

The UV-Vis spectrum (10^{-3} mol L^{-1} solution) of **1** was recorded in DMSO and that of **2** was recorded in methanol solution. The electronic absorption spectra of both benzoic and 2-chlorobenzoic acid consist of bands in the range 230–236 and 272–282 nm, respectively, whereas pyridine shows absorption bands at 251–264 nm. The observed absorption bands of carboxylate and pyridine are attributable to π–π^* transitions [28]. For **1**, strong absorptions were observed at 236 and 283 nm, whereas **2** exhibits a strong absorption at 274 nm. By comparing with the position of absorptions due to free ligands, the observed bands for **1** and **2** may originate from intraligand π–π^* transitions. In **2**, the higher energy absorption of 2-chlorobenzoate probably undergoes a red shift due to C–H—O interactions and may be concealed under the envelope of the observed lower energy absorption.

3.6. *Fluorescent properties*

Photoluminescence of **2** was studied at room temperature in methanol. Compound **2** displays a broad emission band at 656 nm upon excitation at 340 nm. No such fluorescence emission was observed for **1**. Benzoic acid is non-fluorescent and 2-chlorobenzoic acid and pyridine do not fluoresce to a measurable degree [29]. For Zn(II) complexes emission originating from metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) are not expected due to redox insensitive Zn^{+2} (d^{10}) configuration [30]. Thus the observed emission at room temperature of **2** may be ascribed to intraligand π–π^* transition and Zn^{+2} provides stability to the ligand system. We are unable to discern any obvious reason for lack of fluorescence emission in **1**. The difference in the fluorescence property of the complexes might be due to the difference in their structures as luminescence behavior is closely associated with the local environments around metal ions [31].

4. Conclusion

Syntheses of two new organic–inorganic hybrid compounds containing benzene-core carboxylic acids and pyridine have been demonstrated. Although a number of zinc complexes containing carboxylic acids and nitrogen donors with intriguing architectures and interesting properties have been reported [5, 6, 32, 33], a rational strategy to synthesize the desired compounds is still a great challenge. The reported hybrid compounds are generally prepared by hydro/solvo/iono thermal methods [34]. In the present report, the syntheses of new hybrid compounds are achieved by direct and simpler method of reaction in aqueous methanolic solution at room temperature. The single-crystal X-ray diffraction studies of the synthesized compounds show that **1** and **2** have different topologies, which may be attributed to the organic carboxylates affecting formation and architectures of the resulting Zn(II) complexes. The satisfactory analytical data and the spectral studies agree with the composition and structure of the complexes. Compound **2** exhibits a fluorescence emission at room temperature and may find use as a fluorescent material.

Supplementary material

Crystallographic details of the compounds in the form of CIF files are available and have the CCDC numbers 793828 and 773772. These data can be obtained free of charge from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033 or E-mail: deposit@ccdc.cam.ac.uk.

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