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Design and construction of six coordination polymers with imidazole-4,5-dicarboxylate ligand

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ABSTRACT

Six new metal–organic frameworks based on a rigid multifunctional ligand imidazole 4,5-dicarboxylic acid (H_3idc), namely, $[Zn_3(\mu_3\text{-idc})(\mu_5\text{-idc})]_n$ (**1**), $\{[Zn_3(\mu_3\text{-idc})_2(H_2O)(\text{dpeten})]_n{\cdot}2H_2O\}_n$ (**2**), $[Zn(\mu\text{-Hidc})(\mu\text{-obix})_{0.5}]_n$ (**3**), $[Zn_4(\mu\text{-Hidc})_4(\mu\text{-mbix})_2]_n$ (**4**), $\{[Cd_5(\mu_5\text{-idc})_2(\mu_4\text{-Hidc})_2(H_2O)_2]{\cdot}2H_2O\}_n$ (**5**) and $[Cd_2(\mu_3\text{-Hidc})_2(\mu\text{-obix})]_n$ (**6**) (H_3idc = imidazole-4,5-dicarboxylic acid, obix = 1,2-bis(imidazol-1-yl-methyl)-benzene, mbix = 1,3-bis(imidazol-1-ylmethyl)-benzene and dpeten = 1,2-di(pyridin-4-yl)-ethene), have been constructed under hydro(solvo)thermal conditions and structurally characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, powder X-ray diffraction (PXRD) and thermal analyses (TG, DTA, DSC) techniques. In these compounds, the ligand, H_3idc, exhibits different coordination modes, constructing various architectures by bridging a variety of metal ions or polynuclear clusters. All of these coordination polymers exhibited intense fluorescent emissions in the solid state at room temperature. Furthermore, topological properties were studied.

1. Introduction

In the last decade, coordination polymers (CPs), also known as metal–organic frameworks have been attracted attention as inorganic–organic hybrid compounds that can extend into one, two or three dimensions via coordinated covalent bonds [1,2]. These compounds are built from inorganic connectors (metal ions or polynuclear clusters) and neutral or anionic organic ligands as linkers.

Coordination polymers are used in applications such as gas storage/separation [3–6], magnetism [7,8], molecular sensors [9–12] drug delivery platform [13] and catalyst or catalysis support material [14–16] because of their high surface areas. A wide variety of interesting structures are accessible, depending on a number of factors including the symmetry and electron density of ligand, charge of metal ions and nature of the coordinating sites. The coordination modes of ligands with certain symmetry are important factors to the high-dimensional structures and features of the final products. Symmetric heterocyclic compounds containing dicarboxylate group which are coordinated to metal ions as bridging ligand are used as anionic linkers in the syntheses of coordination polymers. We have been recently interested in the solid-state coordination chemistry of a *N*-heterocyclic dicarboxylate. Imidazole-4,5-dicarboxylic acid (H_3idc, as shown in Scheme 1a) which has six potential donor atoms (four oxygen atoms in the carboxylate group and two nitrogen atoms in the imidazole ring) is a rigid planar ligand and shows diverse coordination modes. It can be deprotonated at different pH values to generate different species ($H_n$idc: n = 0, 1, 2) and thereby may result in a large diversity of coordination polymers [17–26]. Also H_3idc can be used for the construction of two or three dimensional structures without colinker because of these different species [27]. On the other hand, semi-flexible bis(imidazole) ligands and rigid dipyridyl ligands (dpeten, Scheme 1b) which are widely employed for the binding of 2D layered structures, are also used as a colinker to arrange the structures of the CPs [28–30]. Semi-flexible bis(imidazole) ligands, for example, 1,2-bis(imidazol-1-ylmethyl)-benzene (obix, Scheme 1c) and 1,3-bis(imidazol-1-ylmethyl)-benzene (mbix, Scheme 1d) can restrain the interpenetration with rigid groups and can generate two or three dimensional structures due to freely rotation with flexible groups in the assembly process [31–34].

In this paper, we report the synthesis and structures of six metal–organic coordination polymers using imidazole-4,5-dicarboxylic acid as linkers and divalent transitional-metal ions (Zn(II) and Cd(II)) as connecters. These structures were characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The photoluminescence, thermal stability and topological properties were investigated in detail.

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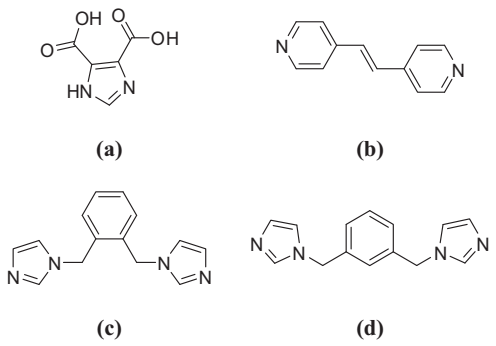

Scheme 1. The ligands used in synthesis of the CPs: (a) imidazole-4,5-dicarboxylic acid, (b) 1,2-di(pyridin-4-yl)ethene, (c) 1,2-bis(imidazol-1-ylmethyl)-benzene and (d) 1,3-bis(imidazol-1-ylmethyl)-benzene.

2. Materials and physical measurements

H_3idc was prepared from benzimidazole in 70% yield [20]. obix and mbix were synthesized by the literature method [35]. All the other chemicals used were of analytical grade and were purchased commercially. IR spectra were obtained with a Bruker Tensor 27 FT-IR spectrometer using KBr pellets in the 4000–400 cm^{-1} range. Elemental analyses for C, H, and N were carried out at the TÜBİTAK Marmara Research Centre. A Perkin Elmer Diamond TG/DTA Thermal Analyzer was used to record simultaneous TG, DTG and DTA curves in the static atmosphere (air) at a heating rate of 10 °C min^{-1} in the temperature range 30–700 °C using platinum crucibles. The decomposition enthalpies (ΔH, J/mol) of each stage were examined by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} in a Seiko DSC 6200 (Exstar 6000, Seiko Instruments Inc.). Powder X-ray diffraction patterns (PXRD) were acquired on a Rikagu Smartlab X-ray diffractometer operating at 40 kV and 30 mA with Cu Kα radiation (λ = 1.5406 nm). The photoluminescence spectra for the solid complex sample was determined with a Perkin–Elmer LS-55 fluorescence spectrometer.

2.1. X-ray diffraction analysis

Suitable crystals of **1**–**6** were selected for data collection which was performed on a Stoe IPDS diffractometer equipped with a graphite-monochromatic Mo Kα radiation at 296 K. The structures were solved by direct methods using SHELXS-97 [36] and refined by full-matrix least-squares methods on F^2 using SHELXL-97 [36] from within the WINGX [37] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. Water H atoms were located in a difference map and refined subject to a DFIX restraint of O–H = 0.83(2) Å. All other H atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93–0.96 Å and O–H distances of 0.82 Å. In **1**, the C3 atom in the imidazole ring is located on a center of symmetry and is caused by the symmetrical disorder. Molecular diagrams were created using MERCURY [38]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [39]. Topological analyses were performed using TOPOS40 software [40]. Details of data collection and crystal structure determinations are given in Table 1. Selected bond lengths, angles and hydrogen-bond parameters are listed in Tables S1–S3. The crystallographic information files are deposited with the CCDC 918345–918350.

2.2. Preparation of the complexes

2.2.1. $[Zn_3(\mu_3\text{-idc})(\mu_5\text{-idc})]_n$ (**1**)

The complex was synthesized by hydrothermal method. A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.47 g; 1.6 mmol), H_3idc (0.25 g, 1.6 mmol) and water (30 mL) was sealed in a 45 mL Parr brand teflon-lined acid digestion bomb and heated at 180 °C for 5 days, and then cooled to room temperature at a rate of 5 °C/h. Pale yellow crystals of **1** were obtained (yield: 0.195 g, 73% based on $Zn(NO_3)_2{\cdot}6H_2O$). *Anal.* Calc. for $C_{10}H_2N_4O_8Zn_3$: C, 23.91; H, 0.40; N, 11.15. Found: C, 23.90; H, 0.52; N, 10.90%. IR data (KBr, cm^{-1}): 3531m, 3359m, 3120m, 1589s, 1544s, 1474s, 1477s, 1384s, 1296m, 1253s, 1205m, 1107s, 1020w, 871m, 835m, 792m, 661m, 540w.

2.2.2. $\{[Zn_3(\mu_3\text{-idc})_2(H_2O)(dpeten)]_n{\cdot}2H_2O\}_n$ (**2**)

The complex was synthesized by hydrothermal method. A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.47 g; 1.6 mmol), H_3idc (0.25 g, 1.6 mmol), dpeten (0.29 g; 1.6 mmol) and water (30 mL) was stirred at 90 °C for half an hour. Then the mixture was sealed in a 45 mL Parr brand teflon-lined acid digestion bomb and heated at 160 °C for 5 days, and then cooled to room temperature at a rate of 5 °C/h. Pale orange crystals of **2** were obtained (yield: 0.214 g, 54% based on $Zn(NO_3)_2{\cdot}6H_2O$). *Anal.* Calc. for $C_{22}H_{18}N_6O_{11}Zn_3$: C, 35.77; H, 2.46; N, 11.38. Found: C, 35.38; H, 2.13; N, 11.63%. IR data (KBr, cm^{-1}):

Table 1
Crystal data and structure refinement parameters for complexes **1**–**6**.

Crystal data	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{14}H_2N_4O_{10}Zn_3$	$C_{22}H_{18}N_6O_{11}Zn_3$	$C_{12}H_9N_4O_4Zn$	$C_{48}H_{36}N_{16}O_{16}Zn_4$	$C_{20}H_{14}Cd_5N_8O_{20}$	$C_{24}H_{18}Cd_2N_8O_8$
Formula weight	582.31	738.53	338.60	1354.41	1248.39	771.26
Crystal system	orthorhombic	orthorhombic	monoclinic	triclinic	monoclinic	triclinic
Space group	$Pmn2_1$	$Pccn$	$C2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	14.0867(4)	10.3008(14)	19.6269(11)	11.5512(4)	10.6186(4)	10.4173(7)
b (Å)	8.5719(2)	13.3246(12)	11.3602(4)	11.6312(5)	15.7795(7)	10.6423(7)
c (Å)	6.0706(1)	20.462(3)	11.5903(7)	19.8074(8)	14.1620(6)	13.2837(8)
α (°)	90.00	90.00	90.00	87.989(3)	90.00	89.346(5)
β (°)	90.00	90.00	109.470(4)	89.165(2)	130.430(2)	83.442(6)
γ (°)	90.00	90.00	90.00	87.051(3)	90.00	69.158(5)
V (Å^3)	733.02(3)	2808.5(6)	2436.5(2)	2655.83(18)	1806.27(13)	1366.64(15)
Z	2	4	8	2	2	2
D_{calc} (g cm^{-3})	2.638	1.747	1.846	1.694	2.295	1.874
μ (mm^{-1})	4.95	2.61	2.04	1.87	2.98	1.62
θ range (°)	3.4–30.4	3.2–26.3	1.9–28.1	1.8–28.1	1.9–28.0	2.1–28.1
Measured refls.	2042	6465	17840	31660	20810	13653
Independent refls. (R_{int})	1228 (0.016)	2464 (0.148)	2528 (0.091)	12188 (0.052)	3346 (0.081)	5662 (0.108)
S	1.07	1.03	1.11	1.03	1.19	1.03
R_1/wR_2	0.073/0.202	0.108/0.333	0.038/0.080	0.055/0.150	0.054/0.140	0.034/0.065
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.81/−1.69	1.89/−0.71	0.42/−0.31	1.22/−0.74	1.64/−1.17	1.05/−1.78