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Structural diversity in two dimensional chiral coordination polymers involving 4,4′-bipyridine and L-cysteate as bridging ligands with Zn and Cd metal centres: Synthesis, characterization and X-ray crystallographic studies

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ABSTRACT

Two chiral coordination polymers involving amino acid backbone L-cysteic acid (H_2L-cys) and N-donor ligand 4,4′-bipyridine (4,4′-bpy) $[\{Cd(\text{L-cys})(4,4'\text{-bpy})(H_2O)\}3.5H_2O]_n$ **1**, $[\{Zn_2(\text{L-cys})_2(4,4'\text{-bpy})_2(H_2O)_4\}\cdot(H_2O)\cdot(4,4'\text{-bpy})]_n$ **2** with rectangular grids have been synthesized. Both compounds are insoluble in common polar/non-polar solvents and well characterized by various physico-chemical techniques such as CHN, IR, TGA, NMR, solid state CD and single crystal X-ray diffraction methods. Complexes **1** and **2** comprise L-cysteate dianions self assembled into chiral coordination polymers by bridging the adjacent metal centres through the carboxylate oxygen generating one-dimensional helical chains. The helical chains are pillared by 4,4′-bpy generating two dimensional network. Complex **1** generates two dimensional (4,4) rectangular grid network with dimension 4.77 Å × 11.74 Å (based on $d_{Cd\cdots Cd}$) involving with the edge sharing L-cys and 4,4′-bpy ligands, respectively. Complex **2** possesses a brick-wall type (6,3) network topology with edge lengths of the grids 11.42 Å × 10.11 Å based on $d_{Zn\cdots Zn}$. Lattice water molecules are encapsulated between the adjacent rectangular grids via hydrogen bonding interactions. One 4,4′-bpy moiety is stacked between the adjacent layers of brick-wall network via weak $\pi\cdots\pi$ interaction with the edge sharing N-donor ligand. Even though both the complexes are rigid and stable, N_2 adsorption studies by these complexes revealed not much promising results. The terminal protruding sulphonate groups, angular orientation of the grids within the two-dimensional network and interpenetration of the adjacent offset sheets concomitantly prevent the formation of through tubular channels. Flexible coordination geometry around the metal centre and the versatile coordination mode of the amino carboxylate group from the L-cys moiety are accountable for the variation of the appealing network topology in these complexes. Chiral nature is established by solid state CD spectrum which shows a positive cotton effect for both complexes.

1. Introduction

Metal–organic frameworks (MOFs) also known as coordination polymers are inorganic–organic hybrid solids with infinite network structures built from organic ligands such as linkers and metal ions as connecting points [1]. Metal organic frameworks can be constructed via two kinds of interactions *viz.*, coordinate covalent bond and weaker intermolecular forces such as hydrogen bonding and $\pi\cdots\pi$ stacking interactions. By the judicious choice of the ligand moiety and inorganic nodal points of transition metals possessing versatile coordination geometry, multidimensional MOFs can be constructed. In recent years, research in the area of MOFs has grown rapidly because these materials can be constructed from designer building blocks with unique properties, for a wide range of potential applications in gas storage [2], separation [3], heterogeneous catalysis, non-linear optics [4], enantioselective separations and heterogeneous asymmetric catalysis [5,6]. The importance of chirality in biological processes and the increasing demand of materials for enantioselective separation and catalysis have encouraged extensive research in the area of chiral coordination polymers. Optically pure amino acids have been successfully used to craft chiral helical coordination polymers [7,8]. Achiral ligands such as multi-carboxylates can also introduce chirality by coordinating with the metal centre in the formation of helical chains [9]. The use of organic enantiopure chiral building blocks for the construction of extended frameworks has been shown to be a useful method for the synthesis of homochiral materials with aesthetic multi-dimensional network topology [10]. Synthesis of molecular chiral metal complexes is of current interest, and increasing research in this area can be noted in coordination and supramolecular chemistry not only for their extended multi-dimensional structures but also for various application in gas adsorption properties and catalysis [6a,10b–e].

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L-amino acids are easily accessible, and upon deprotonation they can chelate/bridge with metal atoms through their amino nitrogen and versatile carboxylate oxygen atoms in the formation of extended helical networks. Additional vacant coordination sites of the metal centre can be utilized to link the adjacent helical chains by exo-bidentate N-donor ligands (such as 4,4′-bpy) which can act as pillars in generating two dimensional grid type architecture. Helical complexes are the subject of much scientific interest not only because of their aesthetic beauty but also increasingly for self-organization in supramolecular chemistry reminiscent of DNA molecules.

Recently we have reported coordination assemblies incorporating amino acids such as cysteic acid, histidine, tryptophan and phenylalanine as bridging ligands with various coligands and transition metal centres [8]. In an endeavour to assemble two dimensional networks by incorporating neutral and dianionic ligands, herein we report the synthesis of two chiral metal–organic coordination polymers $[\{Cd(L\text{-}cys)(4,4'\text{-}bpy)(H_2O)\}3.5H_2O]_n$ **1** and $[\{Zn_2(L\text{-}cys)_2(4,4'\text{-}bpy)_2(H_2O)_4\}(H_2O)\cdot(4,4'\text{-}bpy)]_n$ **2** with (4,4) and (6,3) rectangular grid type networks, respectively, and their characterization by various physico-chemical methods including X-ray crystallography. Optically pure L-cysteic acid precursor has been preferred to introduce chirality in the MOF backbone and by virtue of the versatile coordination mode via aminocarboxylate end and possibly through the terminal sulphonate moiety in generating the extended homochiral network. Zn/Cd metal centres are chosen due to their adaptable coordination geometry. Exo-bidentate N-donor ligand 4,4′-bpy can act as a pillar in linking the one dimensional metal–amino acid cluster in generating two dimensional motifs. Coordination polymers with Cd(II) and Zn(II) centres are well documented in the literature [11], and amongst them, reports of hepta coordinated cadmium coordination polymers could be found scarcely [12]. The present investigation highlights synthesis, characterization (various physico-chemical methods in solid state including CD and NMR) and detailed structural aspects of two grid type chiral coordination networks including weak supramolecular interactions of these two-dimensional nets with the included lattice moieties, i.e., water molecules in **1** and both water and N-donor ligand in **2**.

2. Experimental

2.1. Materials

L-cysteic acid, $Cd(NO_3)_2\cdot4H_2O$ and $Zn(NO_3)_2\cdot6H_2O$ were obtained from Sigma–Aldrich and NaOH was purchased from Rankem. Double distilled water and ethanol were used as solvents for the synthesis of complexes.

2.2. X-ray crystallography

Summary of crystallographic data and details of data collection for both the compounds are given in Table 1. Crystal of suitable size was selected from the mother liquor and immersed in paratone oil, then mounted on the tip of a glass fiber and cemented using epoxy resin. Intensity data for both the crystals were collected using Mo K_α ($\lambda = 0.71073$ Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 100 K. The data integration and reduction were processed with SAINT [13] software. An empirical absorption correction was applied to the collected reflections with SADABS [14]. The structures were solved by direct methods using SHELXTL [15] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-97 [16] program package. All non-hydrogen atoms were refined anisotropically till convergence is reached. Hydrogen atoms attached to the ligand moieties are stereo chemically fixed in both the complexes. Hydrogen atoms attached to the coordinated and lattice water molecules in **2** are located from the difference Fourier map and kept fixed, while in the case of **1** hydrogen atoms could not be located from the difference Fourier map for both coordinated and lattice water molecules.

Table 1
Crystal data and refinement parameters for complexes **1** and **2**.

Identification code	Compound **1**	Compound **2**
Chemical formula	$C_{13}H_{13}N_3O_{9.50}S_1Cd_1$	$C_{26}H_{36}N_6O_{15}S_2Zn_2$
Formula weight	507.72	867.47
Crystal colour	white	white
Crystal size (mm)	0.20 × 0.14 × 0.06	0.38 × 0.34 × 0.29
T (K)	100(2)	100(2)
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	P1
a (Å)	8.628(9)	7.5389(12)
b (Å)	11.743(12)	10.1054(16)
c (Å)	19.817(18)	13.185(2)
α (°)	90	69.441(2)
β (°)	90	81.181(3)
γ (°)	90	69.029(2)
Z	4	1
V (Å^3)	2008(3)	877.8(2)
D_{calc} (Mg/m^3)	1.680	1.641
Absorption coefficient (mm^{-1})	1.243	1.562
F(0 0 0)	1008	446
Reflections collected	8905	5074
Independent reflections	3516	4381
$R_{(int)}$	0.1350	0.0160
Number of parameters	253	462
S (Goodness-of-fit (GOF)) on F^2	0.909	1.035
Final R_1 , wR_2 ($I > 2\sigma(I)$)	0.0611/0.1082	0.0289/0.0748
Weighted R_1, wR_2 (all data)	0.1066/0.1250	0.02970/0.0765
Flack parameter	0.18(7)	0.019(10)

2.3. Physical measurements

Elemental analyses (C, H and N) were performed with a model 2400 Perkin–Elmer elemental analyzer. IR spectra were recorded using KBr pellets on a Perkin–Elmer Spectrum GX FTIR spectrometer. Thermo gravimetric analyses were carried out on a METTLER TOLEDO STAR SW 7.01 thermal analyzer in a heating rate of 10 °C min^{-1} between room temperature and 650 °C using a sample size of 5–6 mg per run. X-ray powder diffraction data were collected using Philips X-Pert MPD system with Cu Kα radiation. Single crystal structures were determined using BRUKER SMART APEX (CCD) diffractometer. Surface area, pore size and nitrogen adsorption–desorption measurements, at 77.4 K, were carried out on a static volumetric adsorption system Micromeritics ASAP 2010. The CP/MAS ^{13}C NMR measurements were performed at 295 K with a Bruker Avance 500 MHz spectrometer equipped with solid state 4 mm ^{1}H/BB probe. The operating frequencies of proton and carbon are 500.13 and 125.758 MHz, respectively. Conventional CP/MAS method was used for solid state ^{13}C measurements. The 4 mm rotors which contain samples were spun at 8 KHz using 90° pulse and contact time, as 4 μs and 2 ms, respectively. The ^{13}C chemical shifts were calibrated through the carbonyl carbon resonance of glycine as an external reference at 176.03 ppm. CD spectra were recorded using JASCO J-851-150L CD spectrometer and the UV–Vis spectra were recorded using Shimadzu UV-3101PC spectrophotometer.

2.4. Synthesis of the chiral coordination polymers 1 and 2

An ethanolic solution (10 mL) of 4,4′-bpy (0.312 g, 2 mmol) was added drop-wise to a stirring aqueous solution (10 mL) of