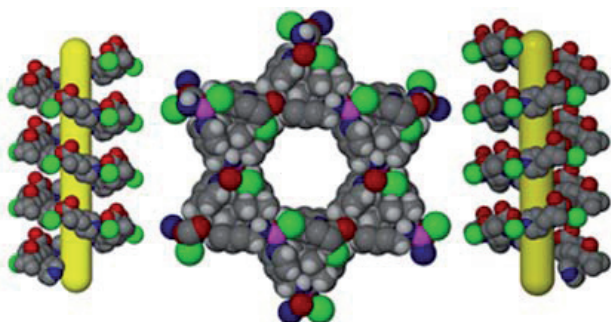


## MS87.P11

*Acta Cryst.* (2011) A67, C752**Homochiral metal organic framework with *unh*-Topology**

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Four new homochiral metal organic frameworks using amino acid derived links as a pure chiral precursor named,  $[Zn(l/d\text{-Val-Py})(X)](H_2O)$  (**1-4**),  $[X = Cl^-$  (**1,3**),  $Br^-$  (**2,4**)] have been synthesized from aqueous media via solvothermal route and characterized by single-crystal X-ray diffraction. Structural analysis reveals that a 3D MOF with a 1D channel in the direction of c-axis were formed having a pore aperture of  $\sim 13\text{\AA}$ . All the structures form a rare zeolitic topology i.e. *unh* type, which is not reported so far in the literature. The guest water molecule sits inside the 1D channel in a helical fashion and can be removed without affecting the crystal structure as revealed from TGA analysis. The anions used in these reaction systems (either from metal or ligand source) play a crucial role in formation of 3D structure. The structures with desired topology forms only when the ligand source is either pure *l* or *d* but in from the racemic. Applications of these chiral MOFs towards catalytic or chiral separations under process in our lab. Owing to the importance of chiral MOFs for various applications as shown by Web lin et.al and others<sup>1-3</sup>, we believe that the successful synthesis of these four chiral MOFs form a easy chiral source like amino acids, will open up new vistas in the search for useful applications.



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**Keywords:** porous, homochiral, zeolitic

## MS87.P12

*Acta Cryst.* (2011) A67, C752**1D and 2D Zn(II) and Cd(II) sulfates with bipyridine and dioxime ligands**

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Nowadays extensive researches contribute to elaborating low-dimensional coordination compounds with the wheel-and-axle (WAA) geometry which similar to 3D metal-organic frameworks (MOFs) are capable to accommodate small molecules [1-3]. Being in line with these investigations we report herein the products of interaction of Zn(II) or

Cd(II) sulfate with 4,4'-bipyridine (bpy) or 4,4'-bipyridinethane(bpe) in the presence of 1,2-cyclohexanedionedioxime (NioxH<sub>2</sub>) which represent four novel polymeric compounds with the compositions  $\{[Zn(H_2O)_6][Zn(SO_4)_2(H_2O)_2(bpy)][Zn(SO_4)(H_2O)_3(bpy)]\}_n$  (**1**),  $\{[Zn(SO_4)(NioxH_2)(bpy)] \cdot 0.5H_2O \cdot DMF\}_n$  (**2**),  $[Zn(SO_4)(NioxH_2)(bpe)]_n$  (**3**), and  $[Cd(SO_4)(NioxH_2)(bpe)]_n$  (**4**) [4]. All compounds are characterized by spectroscopic techniques and single crystal X-ray method. Compound **1** crystallizes in the triclinic non-centrosymmetric *P1* (No.1) space group. The bpy molecules as bridging ligands generate two types of linear chains, differing by the number of sulfate anions and water molecules coordinated to the metal center. The adjacent chains are arranged in a cross-like fashion at the midpoints of the bpy ligands and form the rhombic channels along the *a*-axis. The  $[Zn(H_2O)_6]^{2+}$  cations are located within the structure channels and serve as structure-directing templates. The hydrogen bonds between the coordinated water molecules and sulfate anions contribute to the crystal stability. The chiral layer coordination polymer built up from the helices of the same handedness is the robust structural motif in **2-4**. The NioxH<sub>2</sub> bulky ligand and the tetrahedral sulfate anion impose the asymmetry around the metal center that provides an access to the chiral structural motifs in the form of porous layers. Although compounds **3** and **4** were isolated in the same crystallization conditions, the layers of opposite chirality constitute the achiral (**3**, sp. gr. *P2<sub>1</sub>/n*), and the layers of the same chirality result in chiral (**4**, sp. gr. *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*) architectures. The mode of sulfate-anion coordination to the metal center makes main impact on the dimensionality of the final coordination compounds, while the differences in the metal radii for Zn(II) and Cd(II) atoms and in the conformation of the bidentate bipyridine ligands prove to be not decisive for the final architecture resulting in the formation of supramolecular isomers differing by the packing of the similar layers. The low packing efficacy of **2-4** with the WAA structure topology provides the possibility of small molecules inclusion in the interlayer space. All compounds reveal blue luminescent properties.

**Acknowledgements:** This work was supported by the 10.819.05.03F project

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**Keywords:** cadmium(II), zinc(II), chirality

## MS87.P13

*Acta Cryst.* (2011) A67, C752-C753**Synthesis and crystal structure of a new cadmium coordination polymer with 2-(pyrazol-1-yl)-2-thiazoline (PyTn)**

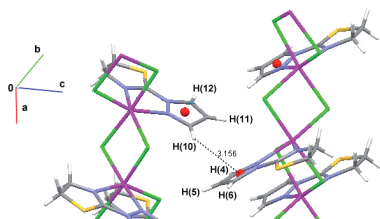
R. Pedrero-Marín, F. Luna-Giles, A. Bernalte-García, F. J. Barros-García, E. Viñuelas-Zahinos, P. Torres-García, *Organic and Inorganic Chemistry Department, Universidad de Extremadura, Badajoz (Spain)*. E-mail: rospema@unex.es

We report here the synthesis and crystal structure of the coordination polymer  $[Cd(\mu\text{-Cl})_2(\text{PyTn})]_n$ . For the synthesis of this compound, ethanol-water solutions of  $CdCl_2 \cdot 2.5H_2O$  and PyTn [1] (1:1 ratio) were mixed, precipitating a white solid that was recrystallized from water. Colourless, plate crystals were obtained by slow evaporation of the solvent.

Unit cells are orthorhombic [ $a = 7.315(1)\text{\AA}$ ,  $b = 9.083(1)\text{\AA}$ ,  $c = 29.698(1)\text{\AA}$ ,  $V = 1973(3)\text{\AA}^3$ , space group *Pca2<sub>1</sub>*,  $Z = 8$ ], each one

containing two crystallographically independent monomeric units that are enantiomers. A refinement of the Flack parameter led to a direct estimation of the enantiomeric composition. Moreover, these structural units show a disorder affecting to heterocycles, probably due to the presence of two enantiomers in the crystal lattice.

The coordination polymer framework consists of chains made up of  $[\text{Cd}(\mu\text{-Cl})_2(\text{PtTn})]$  structural units, each one bound to other two units through chloro bridging ligands. Chains are held together by van der Waals forces and aromatic interactions, forming parallel sheets in such a way that sheets belonging to each enantiomer alternate.



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**Keywords:** coordination polymer, racemic twinning

## MS87.P14

*Acta Cryst.* (2011) **A67**, C753

### Synthesis and structural study of a circular trimetallic Cu(I) helicate

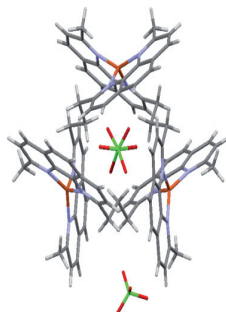
Luis Lemus,<sup>a</sup> Juan Guerrero,<sup>a</sup> Juan Costamagna,<sup>a</sup> Danilo Jara,<sup>a</sup> José Zagal,<sup>a</sup> Allen Oliver,<sup>b</sup> Guillermo Ferraudi,<sup>b</sup> Graham Lappin,<sup>b</sup> <sup>a</sup>*Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago, (Chile)*. <sup>b</sup>*Department of Chemistry and Biochemistry, University of Notre Dame, IN, (USA)*. E-mail: luis.lemus@usach.cl

Bridged polypyridines ligands have been widely used for the building of multimetallic supramolecular structures upon coordination to copper (I). Adequate choice of ligand design allows the formation of a variety of linear and circular helicates. [1], [2]

This work presents the synthesis and X-ray structure of the circular trimetallic helicate  $[\text{Cu}(\text{mphenpr})]_3(\text{ClO}_4)_3$ , (see figure) where *mphenpr* = 1,3-bis(9-methyl-1,10-phenanthrolin-2-yl)propane. The complex crystallizes as a racemic mixture in the trigonal  $P3_1c$  space group, with  $a = b = 16.9700(5)$  Å,  $c = 17.6573(6)$  Å,  $V = 4403.7(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $R(F^2 > 2\sigma(F^2)) = 0.065$  and  $wR(F^2) = 0.230$  for 3028 independent reflections (2063 with  $I > 2\sigma(I)$ ), and 190 parameters. The perchlorate counterions were found to be disordered.

The trimetallic helicate is produced from suspensions of its related bimetallic helicate [3] in coordinating solvents, such as acetonitrile. The coordination geometry around each copper atom is pseudo-tetrahedral with angles of 72.18° between the phenanthroline planes.

1D and 2D NMR studies show that the complex remains in its structural nature in concentrated solutions of non-coordinating solvents, while the decrease of the concentration and the use of coordinating solvents drive to the unfolding of the trimer, followed by the formation of an equilibrium between the bimetallic and monometallic related species.



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**Keywords:** circular helicates, copper (I) complexes, supramolecular

## MS87.P15

*Acta Cryst.* (2011) **A67**, C753-C754

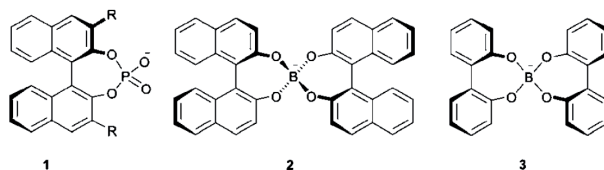
### Chiral selection in the formation of borates from racemic binaphthols and related diols

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Chiral counterions have received increasing attention from the asymmetric catalysis community over the past few years [1]. BINOL is the foremost example of axial chirality. The chiral backbone of BINOL is stereochemically stable (*atropos*) and the enantiomers can be readily resolved [2]; it has been one of the most extensively used motifs in the creation of chiral anions. Some spectacular applications of BINOL-based chiral phosphates in asymmetric catalysis have recently been demonstrated [3], [4]. The bis-BINOL borate **2**, initially introduced by Periasamy for the purpose of resolving amino alcohol derivatives [4], has been studied less extensively in the asymmetric catalysis context [5].

The synthesis of bis-BINOL borates from racemic BINOL can yield the homochiral (R,R)<sub>ax</sub> and (S,S)<sub>ax</sub> or the heterochiral (R,S)<sub>ax</sub> diastereomers. Recent studies of bis-BINOL **2** or biphenol **3** borates by Wuest and co-workers have demonstrated that both form homochiral anions upon crystallisation from a racemic solution in the presence of various amines as well as other counterions [6]. The bis-biphenol borate anion (**3**) framework is stereochemically labile (*tropos*) and the stereoselection is therefore limited to the solid state.

As part of a project designed to study chiral ion pairs of relevance to asymmetric catalysis [7], homochiral racemates of various substituted bis-BINOL borates with sodium as counterion were required. A series of racemic or stereochemically labile chiral borate anions based on the 2,20-biphenol motif was investigated [8]. All borates were homochiral in the solid state, although in some cases the heterochiral diastereomers were computed to be thermodynamically preferred (DFT). The crystallographic preference for the homochiral diastereomer was attributed to its lower bulk, higher molecular symmetry, and the therewith associated better packing ability. We report the results of our systematic investigation.



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