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Two 3D noninterpenetrated chiral coordination polymers with uniform (10^3)-srs and ($4^2.6^3.8$)-**sra** nets

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ABSTRACT

Two new noninterpenetrated three-dimensional chiral coordination polymers $[Cu(L\text{-}cys)(H_2O)]_n$ (**1**) and $[Cd(L\text{-}cys)(H_2O)]_n$ (**2**) (where H_2cys = cysteic acid) have been synthesized and characterized using single-crystal X-ray diffraction, elemental analysis, infrared spectroscopy, and thermogravimetric analysis. In the two complexes, L-cys acts as a μ_3-bridge for **1** and a μ_4-bridge for **2**, respectively, to link metal centers in different modes, forming two different three-dimensional networks. The topological analysis of them shows that **1** can be simplified to a three-connected topology with the short symbol of 10^3 and the full vertex symbol of $10_5.10_5.10_5$ while **2** a four-connected topology with the short symbol of $4^2.6^3.8$ and the full vertex symbol of $4.6.4.6.6.8_2$, respectively.

1. Introduction

The observation and exploration of infinite high-dimensional chiral coordination polymers with various topological networks have been a growing interesting area because of their potential physical properties, for example, second harmonic generation (SHG), magneto-chiral dichroism (MChD), ferroelectricity, catalysis, etc., [1]. In addition to the useful properties and applications directly arising from those networks, another motivation stimulated by the activity has been focused on the investigation of intriguing, often complicated, architectures and topologies in chiral coordination polymers [2]. A useful and simplifying method to analyze the extended frameworks, especially for the complicated three-dimensional networks, is based on a valuable conceptual catalogue of nets [3] where Wells elucidated many topologies in his classic monographs on networks and described a particularly fundamental class of networks called uniform nets, represented using a general symbol. The reduction of networks to node-and-spacer representations that illustrate their connectivity has facilitated the analysis and understanding of seemingly complex topologies that have been generated *via* crystal engineering [4]. In particular, circuit symbols and Schläfli (vertex) notations can be used to describe topologies and facilitate comparison of networks of different composition and metrics. In order to identify uniquely nets and topologies and avoid/minimize errors, O'Keeffe et al. proposed a 3-letter code (as "dia", "ths", "pcu" etc.) as code-name for nets (similar to zeolites names) [5]. Adding the corresponding Schläfli Symbol before the three-letter symbol is possible to uniquely check and define the topology of a net [6].

Although some intriguing topological networks have been successfully generated [7], O'Keeffe et al. [8] discovered that there were only a handful of nets, particularly rare chiral nets, actually observed in the real crystal structures through analyzing the underlying topology of extended metal–organic frameworks reported in the Cambridge Structure Database. Therefore, the synthesis of chiral coordination polymers with different topological networks is still challenging.

For the synthesis of chiral coordination polymers, three general rational approaches have been taken: (1) use of a monochiral organic ligand as a spacer to link adjacent metal centers or secondary building units (SBUs) [9]; (2) use of a monochiral ligand as an auxiliary pendant which does not directly participate in the formation of a framework backbone, but forces the framework to adopt a specific chiral topology [10]; (3) a metal ion and a readily available homochiral organic ligand are used to form homochiral SBUs, which in turn, are linked together by rigid spacers to build a network structure [11]. In this context, we present the synthesis and crystal structures of two interesting chiral coordination polymers $[Cu(L\text{-}cys)(H_2O)]_n$ (**1**) and $[Cd(L\text{-}cys)(H_2O)]_n$ (**2**) (where H_2cys = cysteic acid) that provide a 3-connected (10^3)-**srs** net and a 4-connected ($4^2.6^3.8$)-**sra** net, respectively. Such two chiral complexes are achieved by eschewing interpenetration of nets using small chiral spacers.

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2. Experimental

The ligand L-cysteic acid was prepared according to the literature [12]. All reagents were used as received without further purification. IR spectra were taken on a Perkin–Elmer spectrum One FT-IR spectrometer in the 4000–400 cm^{-1} region with KBr pellets. Elemental analyses for C, H, N and S were carried out on a Model 2400 II, Perkin–Elmer elemental analyzer. Thermal analysis was performed on a TA Instruments PE Pyris Diamond thermal analyser with a heating rate of 10 °C min^{-1} in nitrogen.

2.1. Synthesis of the two complexes

*2.1.1. [Cu(L-cys)(H₂O)]ₙ (**1**)*

L-Cysteic acid (0.094 g, 0.5 mmol) and KOH (0.056 g, 1 mmol) dissolved in water (10 ml) were added to a methanol (10 ml) solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.121 g, 0.5 mmol) and the mixture was stirred for 3 h at room temperature and filtered. Blue block-shaped crystals of **1** were obtained from the filtrate after several days. Yield: 0.0671 g (54%). Elemental *Anal.* Calc. for $C_3H_7CuNO_6S$: C, 14.49; H, 2.84; N, 5.63; S, 12.89; Found: C, 14.71; H 2.47; N 5.49; S, 12.14%. IR (KBr pellet, cm^{-1}): 3339s, 3266s, 1632s, 1588s, 1562m, 1433m, 1226s, 1121s, 1047s, 1003w, 822w, 699w, 600m, 509w.

*2.1.2. [Cd(L-cys)(H₂O)]ₙ (**2**)*

The synthesis of complex **2** followed the similar process for complex **1** except using $Cd(OAc)_2 \cdot 2H_2O$ instead of $Cu(NO_3)_2 \cdot 3H_2O$. Yield: 0.051 g (34%). Elemental *Anal.* Calc. for $C_3H_7CdNO_6S$: C, 12.11; H, 2.37; N, 4.71; S, 10.78; Found: C, 12.34; H 2.13; N 5.09; S, 10.14%. IR (KBr pellet, cm^{-1}): 3484s, 3277s, 1600s, 1573s, 1423m, 1210s, 1080m, 1042s, 947w, 818w, 663w, 589m.

2.2. X-ray diffraction determination

All the data for complexes **1** and **2** were collected with a Bruker SMART CCD instrument by using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). The data were collected at 293(2) K. Absorption effects were corrected by semi-empirical methods. The structure was solved by direct methods with the program SHELXS-97 [13] and refined by full-matrix least-squares methods on all F^2 data with SHELXL-97 [14]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were located in a difference Fourier map and refined with distance restraints of O–H = 0.83 (2) Å and H···H = 1.39 (2) Å. Other hydrogen atoms were placed in calculated positions and refined by using a riding model. Crystallographic data for **1** and **2** are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

Table 1
Crystal data and structure refinement for complexes **1** and **2**

Complex	1	2
Empirical formula	$C_3H_7CuNO_6S$	$C_3H_7CdNO_6S$
Formula weight	248.72	297.56
Temperature (K)	293(2)	293 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.4854 (9)	7.0758 (4)
b (Å)	9.7820 (11)	9.7611 (5)
c (Å)	9.7762(17)	10.4967 (7)
V (Å³)	732.02 (14)	724.98 (7)
Z	4	4
D_{calc} (Mg/m³)	2.257	2.726
Absorption coefficient (mm^{-1})	3.26	3.29
F(000)	500	576
θ range for data collection	2.91–27.49	2.85–27.48
Reflections collected	6431	5106
Independent reflections	1679 $R_{(int)}$ = 0.0146]	1589 $R_{(int)}$ = 0.0171]
Data/restraints/parameters	1679/51/117	1589/3/117
Goodness-of-fit on F^2	1.131	1.176
Final *R* indices [$I > 2sigma(I)$]	0.024	0.0171
R indices (all data)	0.072	0.0210
Flack parameter	−0.006(15)	0.01(2)

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

	1		2
Cu1–O6	1.960 (2)	Cd1–O1	2.2514 (17)
Cu1–O1	1.963 (2)	Cd1–O1W	2.276 (2)
Cu1–N1	1.972 (2)	Cd1–N1A	2.290 (2)
Cu1–O2A	1.980 (2)	Cd1–O2A	2.3074 (18)
Cu1–O3B	2.310 (3)	Cd1–O4C	2.3744 (18)
		Cd1–O3B	2.4027 (17)
O6–Cu1–O1	91.42 (9)	O1–Cd1–O1W	83.75 (9)
O6–Cu1–N1	175.09 (10)	O1–Cd1–N1A	118.11 (6)
O1–Cu1–N1	83.67 (9)	O1W–Cd1–N1A	157.73 (9)
O6–Cu1–O2A	86.04 (9)	O1–Cd1–O2A	168.53 (7)
O1–Cu1–O2A	165.12 (10)	O1W–Cd1–O2A	86.10 (9)
N1–Cu1–O2A	98.65 (9)	N1A–Cd1–O2A	72.49 (6)
O6–Cu1–O3B	88.93 (12)	O1–Cd1–O4C	87.25 (6)
O1–Cu1–O3B	94.53 (11)	O1W–Cd1–O4C	82.68 (10)
N1–Cu1–O3B	91.66 (11)	N1A–Cd1–O4C	93.61 (8)
O2A–Cu1–O3B	100.07 (11)	O2A–Cd1–O4C	96.74 (7)
		O1–Cd1–O3B	89.11 (7)
		O1W–Cd1–O3B	84.08 (10)
		N1A–Cd1–O3B	99.49 (8)
		O2A–Cd1–O3B	84.54 (7)
		O4C–Cd1–O3B	166.58 (7)

Symmetry codes for complex **1**: (A) $-x+2, y-1/2, -z+1/2$; (B) $-x+5/2, -y, z+1/2$. Symmetry codes for complex **2**: (A) $-x+1, y-1/2, -z+3/2$; (B) $x-1/2, -y+3/2, -z+2$; (C) $x+1/2, -y+3/2, -z+2$.

2.3. Thermal analysis

Thermogravimetric analysis (TGA) shows, for the two complexes, the TG curves illustrate no weight loss occurred from 40 to 200 °C, and thermal decomposition begin at about 200 °C and complete at about 710 °C. In the temperature range, complexes **1** and **2** were thermally transformed to CuO (remaining weight: found 33.4%, calc. 32.1%) and CdO (remaining weight: found 41.7%, calc. 42.9%), respectively.

3. Results and discussion

*3.1. Structural description of [Cu(L-cys)(H₂O)]ₙ (**1**)*

The X-ray diffraction analysis of **1** reveals a three-dimensional framework linked by Cu–cysteic–Cu fragments as shown in Fig. 1. The copper atom is coordinated to three oxygen atoms (O1, O2A, O3B) belonging to three different cysteic ligands, one amino nitrogen atom (N1) and one water molecule. The geometry around the metal center is a distorted square pyramidal with sulfonate oxygen atom (O3B) lies in the axial position. All the metal–ligand bonds are consistent with other copper (II) systems, except for the Cu–O3A bond distance which is relatively longer, 2.310 Å. However, comparing to similar derivatives of Cu analogues having a sulfonate substituent [15], this bond in **1** is still reasonable.

The cysteic moiety acts as a multidentate ligand to coordinate with three different copper atoms. Conversely, each copper atom forms a total of five bonds of which four are to three different cysteic molecules. The terminal carboxylate group adjacent to the amino group shows a *syn–anti* bonding to two different copper(II) centers, whereas the other terminal sulfonate oxygen atom are bonded to a single copper(II) ion. The replication of this basic unit builds a chiral three-dimensional network of **1** as shown in Fig. 2.

The network topology can be simplified by considering just the copper atoms and the cysteic moieties are represented as