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Mendeleev Commun., 2015, **25**, 65–66
Mendeleev Communications

Chiral four-fold interpenetrating 2D cadmium networks based on two achiral ligands

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DOI: 10.1016/j.mencom.2015.01.024

The new coordination polymer $\{[Cd(DPPA)(ecdbc)](H_2O)_2\}_n$ was prepared and characterized by X-ray diffraction analysis revealing chiral four-fold interpenetrating 2D networks, within which two kinds of helical chains can be distinguished.

Chiral coordination polymers are of interest due to their special properties, such as ferroelectricity, circular dichroism and second-order nonlinear optics.[1–4] Their architectures and properties can provide potential applications in telecommunication, optical storage, information processing and chiral catalysis.[5–7] Previously, chiral coordination polymers were synthesized by the coordination of chiral ligands and metal ions, while chiral coordination polymers based on achiral ligands were barely reported,[3,4] which restrained the development of theoretical studies and practical applications of such polymers.

We designed and synthesized the new achiral V-shaped ligand 4,4′-(9-ethylcarbazole-3,6-diyl)dibenzoic acid (H_2ecdbc),[†] which may be regarded as a semi-rigid ligand. We used tri(4-pyridylphenyl)amine (TPPA)[8] as an achiral co-ligand to react with H_2ecdbc and bivalent metal salts. Then, a new coordination polymer $\{[Cd(DPPA)(ecdbc)](H_2O)_2\}_n$ **1** with an intriguing chiral structure was obtained under solvothermal conditions.[†] The yield of complex **1** is very low and irreproducible; therefore, we report here only the crystal structure of **1**.

The crystal structure analysis[9,10] showed that complex **1** crystallizes in chiral monoclinic crystal system $P2_1$.[‡] The asymmetric unit of **1** contains one Cd^{2+} ion, one TPPA molecule, one $ecdbc^{2-}$ anion and two lattice water molecules. Figure 1 shows

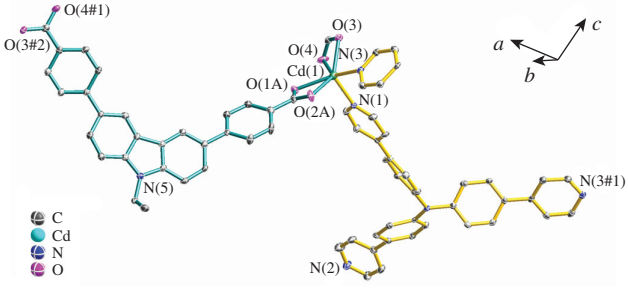

Figure 1 Coordination environments of complex **1** (30% ellipsoid probability). The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = = –*x*, –0.5 + *y*, 2 – *z*; #2 = 4 – *x*, 0.5 + *y*, 2 – *z*. Selected bond lengths (Å): Cd(1)–O(3) 2.269(5), Cd(1)–O(1A) 2.263(19), Cd(1)–N(1) 2.287(6), Cd(1)–N(3) 2.296(6), Cd(1)–O(2A) 2.394(12), Cd(1)–O(4) 2.438(6); selected bond angles (°): O(1A)–Cd(1)–O(3) 115.1(6), O(1A)–Cd(1)–N(1) 98.5(5), O(3)–Cd(1)–N(1) 121.3(2), O(1A)–Cd(1)–N(3) 137.9(4), O(3)–Cd(1)–N(3) 88.8(2), N(1)–Cd(1)–N(3) 97.0(2), O(1A)–Cd(1)–O(2A) 56.1(5), O(3)–Cd(1)–O(2A) 135.5(5), N(1)–Cd(1)–O(2A) 103.1(5), N(3)–Cd(1)–O(2A) 82.4(3), O(1A)–Cd(1)–O(4) 79.0(5), O(3)–Cd(1)–O(4) 55.30(19), O(1B)–Cd(1)–O(4) 89.7(17), N(1)–Cd(1)–O(4) 89.3(2), N(3)–Cd(1)–O(4) 140.1(2), O(2A)–Cd(1)–O(4) 134.5(3).

that Cd(1) has an octahedral coordination environment with two N atoms from two TPPA molecules and four O atoms from two $ecdbc^{2-}$ anions. The Cd–N bond lengths are 2.287(6) and 2.296(6) Å, and the Cd–O lengths are 2.263(19)–2.438(6) Å,

† Commercial reagents and solvents were used as received.

Synthesis of H_2ecdbc. A mixture of 3,6-dibromo-9-ethylcarbazole (3.53 g, 10 mmol), $Pd(PPh_3)_4$ (0.580 g, 0.5 mmol), 4-carboxyphenylboronic acid (3.98 g, 24 mmol), 1 mM K_2CO_3 (25 ml, 25 mmol) and 1,4-dioxane (100 ml) was refluxed under N_2 for 24 h. Then, the pH value was modified to 6, and the solvents were evaporated *in vacuo*. The residue was washed with water and purified by silica gel column chromatography to give the target compound as a yellow solid (3.09 g, 71%). ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 12.93 (s, 2H), 8.79 (s, 2H), 8.06 (d, 4H, *J* 8.5 Hz), 7.97 (d, 4H, *J* 8.5 Hz), 7.91 (d, 2H, *J* 8.5 Hz), 7.76 (d, 2H, *J* 8.5 Hz), 4.53 (q, 2H, *J* 7.0 Hz), 1.38 (t, 3H, *J* 7.0 Hz). ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 167.77, 145.65, 140.59, 132.00, 130.45, 129.08, 126.96, 125.59, 123.65, 119.86, 110.38, 37.78, 14.27. MS (ESI-MS), *m*/*z*: 434.18 $[M-H]^-$ (calc. for $C_{28}H_{21}NO_4$, *m*/*z*: 435.15).

Synthesis of complex **1**. A mixture of $Cd(NO_3)_2{\cdot}6H_2O$ (30.1 mg, 0.1 mmol), TPPA (47.6 mg, 0.1 mmol) and H_2ecdbc (43.5 mg, 0.1 mmol) was dissolved in 15 ml of DMF–H_2O (1:1). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25 ml) under autogenous pressure and heated at 120 °C for three days. Yellow crystals of **1** were collected in 18% yield (based on TPPA ligand). IR (KBr, ν/cm^{-1}): 3424 (s), 1553 (s), 1450 (w), 1406 (s), 1359 (w), 1282 (m), 1232 (m), 1212 (w), 1110 (s), 1087 (s), 1029 (w), 939 (w), 807 (w), 748 (s), 692 (w), 656 (m), 475 (w).

‡ *Crystallographic data for* **1**. Crystals of $C_{61}H_{47}CdN_5O_6$ (M = 1058.44) are monoclinic, space group $P2_1$, at 296 K: a = 6.993(2), b = 23.785(7) and c = 15.898(5) Å, β = 101.535(5)°, V = 2591.0(13) Å^3, Z = 2, d_{calc} = = 1.357 g cm^{-3}, μ(MoKα) = 0.479 mm^{-1}, F(000) = 1088. 13418 reflections were measured and 8538 independent reflections (R_{int} = 0.0412) were used in further refinement. The refinement converged to wR_2 = 0.1365 and GOF = 1.076 for all independent reflections [R_1 = 0.0424 was calculated against F for 7979 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[9] The disordered O atoms in **1** (O1, O2) were refined using O atoms split over two sites with site occupancies of 0.64 : 0.36. Hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms.

CCDC 988390 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

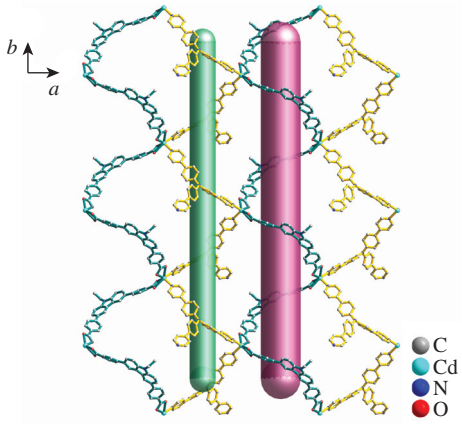

Figure 2 Neighbouring cadmium ions linked TPPA or ecbdc^{2-} into infinitely helical chains, the helical directions of (TPPA–Cd–TPPA)$_n$ or (ecbdc–Cd–ecbdc)$_n$ chains are all left-hand.

which are similar to those in other Cd complexes.[11] The dihedral angles between pyridyl and adjacent phenyl rings in the TPPA molecule are 17.877(3)°, 49.520(3)° and 21.944(3)°. The dihedral angles between the carbazole unit and adjacent phenyl rings in the ecdbc^{2-} anion are 26.366(3)° and 40.242(3)°.

The neighbouring Cd(1) ions link V-shaped ecdbc^{2-} anions into one kind of helical chains, in which the adjacent Cd(1)···Cd(1) distance is 18.605(8) Å. The angle of adjacent Cd(1)–N(5)–Cd(1) is 95.305(5)°. TPPA ligands also link Cd(1) ions to form another kind of helical chains, in which the adjacent distance of Cd(1)···Cd(1) is 18.173(1) Å. The angle of adjacent Cd(1)–N(4)–Cd(1) is 114.628(5)°. Complex **1** forms a 2D network, in which two kinds of helical chains can be distinguished (Figure 2).

The network in **1** is composed of irregular windows; each window includes four Cd^{2+} ions, two TPPA molecules and two ecdbc^{2-} anions. The helical directions of (TPPA–Cd–TPPA)$_n$ or (ecbdc–Cd–ecbdc)$_n$ chains are all left-hand; therefore, the 2D network is chiral (Figure 2). The windows in each network are large enough to accommodate three other equivalent networks (Figure 3), giving rise to four-fold interpenetrating networks.

Better insight into this intricate network can be accessed by a topological method.[12] The Cd(1) atoms can be regarded as four-connected nodes. TPPA ligands and ecdbc^{2-} anions can be regarded as linkers, thus forming four-fold interpenetrating networks (Figure 4). The Schläfli symbol for this uninodal net is $\{4^4.6^2\}$, and the topology type of this net is sql in terms of

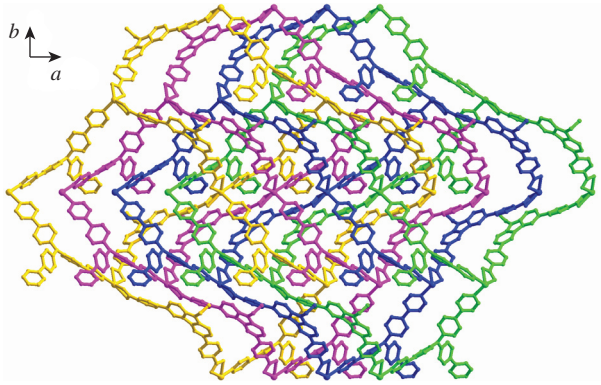

Figure 3 Four-fold interpenetrating 2D network of **1**.

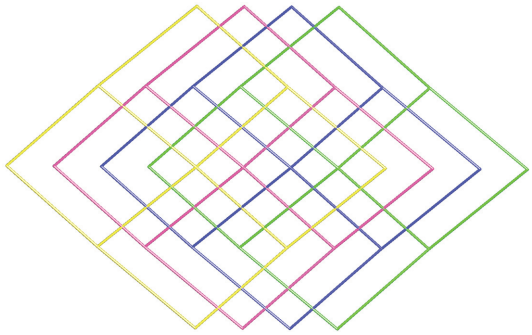

Figure 4 Perspective view of the four-fold interpenetrating 2D network of **1** (TPPA ligand and ecbdc^{2-} anions were simplified into linkers).

RCSR symbols,[13] which is the most widespread among 2D networks.[14]

In conclusion, new chiral four-fold interpenetrating 2D coordination polymer $\{[Cd(DPPA)(ecdbc)](H_2O)_2\}_n$ was prepared under hydrothermal conditions based on two achiral ligands, tri(4-pyridylphenyl)amine (TPPA) and 4,4′-(9-ethylcarbazole-3,6-diyl)dibenzoic acid (H_2ecdbc).

This work was supported by grants from the Natural Science Foundation of China (nos. 21401107, 21272118), the Natural Science Foundation of Jiangsu, China (nos. BK20140986, BK20130986), and Natural Science Foundation of the Jiangsu Higher Education Institutions of China (no. 14KJB150013) as well as by Startup Foundation of Nanjing University of Information Science & Technology, a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Jiangsu Joint Laboratory of Atmospheric Pollution Control, and Jiangsu Engineering Technology Research Center of Environmental Cleaning Materials.

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Received: 25th February 2014; Com. 14/4315