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Conformation change of the cyclohexanedicarboxylate ligand toward 2D and 3D La(III)-organic coordination networks

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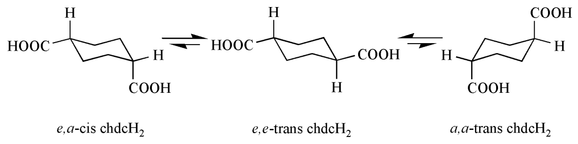
2D and 3D structures of La-1,4-cyclohexanedicarboxylates (chdc) coordination networks, have been constructed using flexible chdc ligands which can have *cis* and *trans* conformations of two dicarboxylate groups, controlled by the solution pH in hydrothermal reaction conditions.

Rational design by incorporating appropriate structure-directing ligands and coordination geometries of metal ions into the extended structure offers possible production of novel metal–organic materials of current interest with various crystal structures and properties.[1] Rigid spacer ligands such as benzene di-,[2] and tri-carboxylates[3] successfully produce various extended structures with metal ions. A guiding principle of our work is the attempt to control the conformations of flexible spacer ligands in the architecture of the products. For instance, we previously reported the novel 3D coordination networks of transition metal alkyldicarboxylates with specific ligand conformations.[4] We and other groups have used succinate ligands as structure-templating ligands with *anti*/*gauche* conformations in various open frameworks.[5] We consider two basic aspects of the structure-directing ligands with the expected conformations, *viz.* selectivity and limited flexibility of ligand conformations. In this context, we chose 1,4-cyclohexanedicarboxylic acid ($chdcH_2$) as a spacer ligand which possesses three possible conformations of two carboxylate groups, *a,a-trans*-, *e,e-trans*-, and *e,a-cis*-$chdcH_2$. The *e,e-trans*-form is thermodynamically more stable than the *e,a-cis*-form due to two equatorial substituents and the *a,a-trans*-form is the least stable because of 1,3-diaxial hindrance.[6] (Scheme 1)

Under hydrothermal condition using aqueous KOH solution at 180 °C, we expect the α-protons located on the 1,4 carbons of cyclohexane to be easily deprotonated to accelerate the equilibrium state among different conformations of chdc ligands. The two carboxylic protons of $chdcH_2$ have different acidity values (pK_{a1} and pK_{a2} are 4.18 and 5.42, respectively, for *e,e-trans*-form), and the conformational equilibrium involves the first deprotonated state of $chdcH^-$,[7] and is the key to '*in-situ*' conformational modification of chdc ligands in this study. The methodology allows us to create different structural topologies, and here we report on the formation and properties of three compounds representing the 1D, 2D and 3D networks.

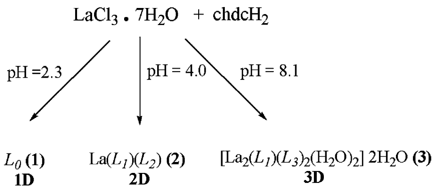
Three different chdc containing frameworks were prepared using the hydrothermal method. 0.37 g (1.0 mmol) of $LaCl_3{\cdot}7H_2O$, 0.085 g (0.5 mmol) of 1,4-cyclohexanedicarboxylic acid ($chdcH_2$, mixture of *cis* and *trans*), 5.0 mL of distilled water and KOH solution were heated in a 23 mL capacity Teflon-lined reaction vessel at 180 °C for 3 days and then cooled to room temperature. 1.0 mL (0.5 mmol) of 0.5 M KOH solution for La(*trans*-$chdc^{2-}$) (*cis*-$chdcH^-$) (**2**) and 2 mL (2 mmol) of 1 M KOH solution for [La_2(*trans*-$chdc^{2-}$)(*cis*-$chdc^{2-}$)$_2$(H_2O)$_2$]$\cdot 2H_2O$ (**3**) were used, respectively. The hydrothermal reaction without KOH addition produces *e,e-trans*-$chdcH_2$ (**1**)[8] and lanthanum ions remain in solution as the salt forms. These compounds were formulated and characterized by elemental microanalysis[†] and single crystal X-ray diffraction.[‡] for crystallographic files in .cif or other format.



Scheme 1

The crystal structure of **1** reveals each *trans*-$chdcH_2$ to be hydrogen-bonded to two other molecules, one at each end, to give 1D chains. In contrast, **2** involves 2D and **3** involves 3D networks. The synthetic pathway for the prepared compounds and the conformational isomers found in the prepared compounds, is summarized in Scheme 2. We observed four coordination modes of chdc produced from two different conformations, *viz.*, *e,e-trans*-$chdcH_2$ (L_0, protonated), *e,e-trans*-$chdc^{2-}$ (L_1, deprotonated), *e,a-cis*-$chdcH^-$ (L_2, partially deprotonated), and *e,a-cis*-$chdc^{2-}$ (L_3, deprotonated). The structure of **2** consists of infinite edge-sharing LaO_9 polyhedral chains, interleaved by L_1 and connected by L_2 ligand (Fig. 1).

The coordination sphere of La(III) in **2** consists of L_1 and L_2, alternately (L_1 : L_2 = 1 : 1). Two carboxylate groups of L_2 in **2**, coordinate to three La ions, one is bidentate and the other is chelating. A partially deprotonated carboxylate group (L_2) is confirmed by FT-IR analysis and by distinguishable carbon–oxygen bond lengths (1.293 and 1.214 Å). The crystal structure of **3** is a 3D network built up by L_1 and L_3 with the ratio of L_1 : L_3 = 1 : 2 (Fig. 2). The ligand environments of L_1 and edge-sharing $LaO_8(H_2O)$ polyhedra chains in **3** present the same structural moieties as those found in **2** except for hydrate coordination. **3** contains two types of water molecule, one is coordinated to La



Scheme 2

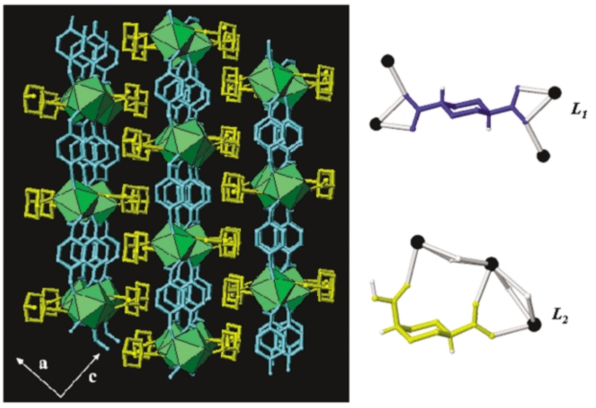


Fig. 1

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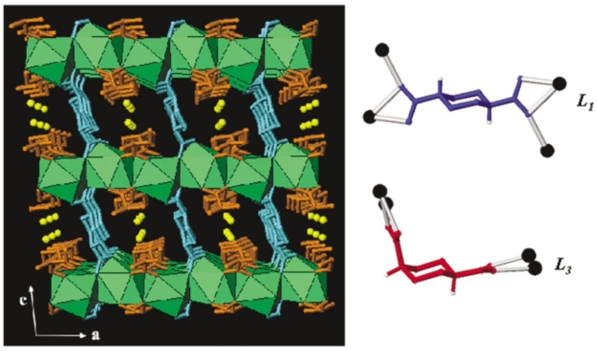

Fig. 2

and the other physically adsorbed in the pore. All the water molecules are interconnected by an extended hydrogen bonding network, lending structural stability to compound **3**. The water molecules are reversibly desorbed and re-adsorbed in **3**. The TGA data of **2** show the first weight loss at *ca.* 400–420 °C (19.7%) corresponding to removal of one chdc ligand per unit (20.9%) and the second one at above 450 °C. The data for **3** present 7.3% (Calc: 8.3%) loss from 100–180 °C (dehydration of both coordinate and non-coordinate H_2O) and 55.9% (Calc: 53.9%) loss over 450 °C (decomposition of chdc ligand).

We believe that the construction of various dimensionalities was possible thanks to the variable concentration of chdc conformational isomers, controlled by the pH and temperature applied. All three compounds basically contain the thermodynamically most stable *trans*-forms (L_1 or L_0), which probably have higher concentrations and a greater preference to bind La ions due to the higher acidity. As pH increases, the *cis*-form becomes deprotonated in the equatorial rather than the axial position due to the higher acidity of equatorial one, which results in the 2D network of **2**. At higher pH (>7), all the carboxylate groups of chdc (L_3) are deprotonated and interlock the 2D La L_1 sheets into the 3D structure of **3**.

The present work demonstrates that 1D, 2D and 3D coordination networks were achieved by using chdc ligand with flexible *cis*/*trans* conformations, which involve protonated, partially and/or fully deprotonated carboxylates, depending on the pH of the applied solution media. It is noteworthy that the prepared compounds are the first examples of coordination polymers constructed using both *cis*-chdc and *trans*-chdc in different molar ratios. The sequential change of ligand conformations depending on the reaction conditions implies a fundamental aspect of the crystallization mechanism of coordination networks.

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Notes and references

† **2**: 31% yield based on lanthanum used; elemental analysis calcd (%) for $LaC_{16}H_{21}O_8$: C, 39.98; H, 4.42. found: C, 39.62; H, 4.37. **3**: 48% yield, Calcd (%) for $La_2C_{24}H_{38}O_{16}$: C, 33.47; H, 4.46. Found: C, 32.56; H, 4.34.

‡ *Crystallographic data*: **2**: M = 480.24, monoclinic, space group $P2_1/n$, a = 10.699(2), b = 8.335(2), c = 18.8774(13) Å, β = 96.774(9)°, V = 1671.8(4) Å³, Z = 4, μ = 2.598 mm^{-1}, D_c = 1.908 Mg m^{-3}, Mo-Kα radiation (λ = 0.71073 Å), 3093 reflections collected, 2925 independent (R_{int} = 0.0231) Final $R1(I > 2\sigma(I))$ = 0.0412, $wR2$ (all data) = 0.1154.

3: M = 860.37, triclinic, space group $P\bar{1}$, a = 8.085(2), b = 9.0746(8), c = 10.606(3) Å, α = 71.981(13), β = 83.635(14), γ = 83.845(12)°, V = 733.2(2) Å³, Z = 1, μ = 2.948 mm^{-1}, D_c = 1.939 Mg m^{-3}, Mo-Kα radiation (λ = 0.71073 Å), 2729 reflections collected, 2530 independent (R_{int} = 0.0202) Final $R1(I > 2\sigma(I))$ = 0.0368, $wR2$(all data) = 0.0967. The data collection was perfomed on a Siemens P4 automated four-circle diffractometer. Data were corrected for absorption. The structures of **2** and **3** were solved by direct methods (SHELX-86) and standard difference Fourier techniques (SHELX-97).[9] All hydrogen atoms attached to carbon positions were program generated and included in the refinements as a riding model except those on water molecules which were refined separately according to electron density difference. All non-hydrogen atoms were treated anisotropically.

CCDC reference numbers 175051 and 175052. See http://www.rsc.org/suppdata/cc/b2/b200658h/

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