

# Ytterbium Coordination Polymer with Four Different Coordination Numbers: The First Structural Characterization of Lanthanide Phthalate Complex

WAN, Yong-Hong(万永红) JIN, Lin-Pei\*(金林培) WANG, Ke-Zhi(王科志)

Department of Chemistry, Beijing Normal University, Beijing 100875, China

The novel ytterbium coordination polymer is a two-dimensional framework in which the central metal ions have four different coordination numbers and form four kinds of coordination polyhedra. The four kinds of coordination polyhedra connect into infinite chains by sharing oxygen atoms

**Keywords** ytterbium phthalate complex, coordination polymer, coordination number

Recently, much attention has been paid to the assembly of metal-organic infinite frameworks by use of multi-functional organic ligands.<sup>1</sup> Polycarboxylic acids, such as diacid, triacid, have been widely used in the synthesis of these fascinating structures,<sup>2</sup> in which the carboxylate groups coordinate in different ways to the central metal ions, namely, bridging, chelating and bridging-chelating and connect multiple metal ions into high-dimensional structures. Lanthanide-organic polymers have recently raised considerable interest,<sup>3</sup> due to their applications in the fields of fluorescent probe, phase separation and adsorption/desorption processes. The structures of lanthanide-polyacid polymers have been reported recently.<sup>3a,3b</sup> As expected, the lanthanide(III) ions (Er,<sup>3a,3b</sup> Tb,<sup>3c</sup> Ce<sup>3b</sup>, Eu<sup>3b</sup>, etc.) were connected by carboxylate groups into high-dimensional structures.

The lanthanide ions are well-known for the variable coordination number, in the range of 3 to 12. Due to their large ionic radii and the ionic nature of the metal-ligand bonding, trivalent lanthanide ions commonly form complexes of higher coordination numbers of typically 8 and 9. Al-

though the same lanthanide ions having two different coordination numbers have been reported to exist in one complex,<sup>3b,4</sup> to the best of our knowledge, the crystal structures with three or more different coordination numbers for the same lanthanide ions in one complex have not been reported. Herein, we report the first crystal structure of ytterbium phthalate complex  $[\text{Yb}_4(1,2\text{-BDC})_6(\text{H}_2\text{O})_2]_n$  (1, 2-BDC = 1,2-benzenedicarboxylate), in which the Yb(III) ions have four different coordination numbers.

The crystals of  $[\text{Yb}_4(1,2\text{-BDC})_6(\text{H}_2\text{O})_2]_n$  were obtained by hydrothermal synthesis.  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ , 1,2-benzenedicarboxylic acid, and 1,10-phenanthroline in the mole ratio of 1:1.5:1 were dissolved in 10 mL of distilled water, and the pH value was adjusted to 3.8 with NaOH solution. The mixture was heated at 150 °C for 3 days and then cooled in programmed control to the room temperature for 6 days. The colorless sheet-like crystals were collected and the suitable crystal was subjected to X-ray analysis.<sup>5</sup>

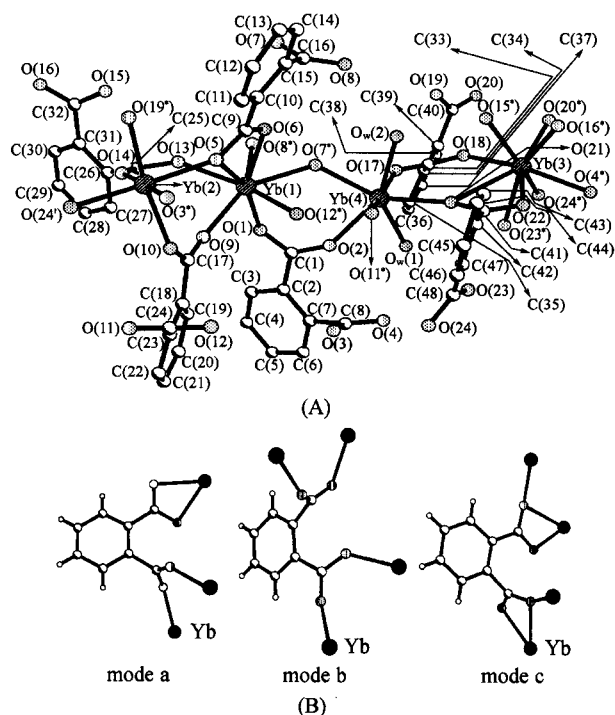
As expected, Yb ions are connected by 1,2-BDC, extending to a two-dimensional framework. The structure is made up of layers, the mean plane of which is parallel to the *ac* plane, stacked along *b*-axis. The asymmetric unit and the labeling of atoms are shown in Fig. 1A.<sup>6</sup> It is interesting to note that the Yb ions in this complex have four different coordination environments, and the four Yb ions are surrounded by six, seven, eight and nine oxygen atoms, respectively. Yb(1) ion is bound to eight oxygen atoms from six 1,2-BDC, four of which O(5), O(6) and

\* E-mail: lpjin@bnu.edu.cn

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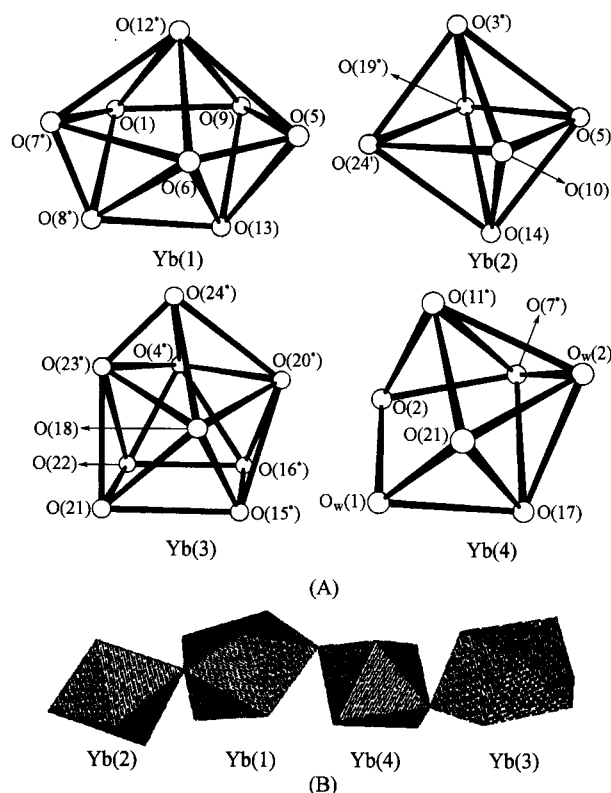
O(7<sup>\*</sup>), O(8<sup>\*</sup>) belong to two bridging-chelating carboxylate groups of two 1,2-BDC; Yb(2) ion coordinates to six oxygen atoms from six 1,2-BDC; Yb(3) ion is surrounded by nine oxygen atoms from six 1,2-BDC [including six oxygen atoms: O(21), O(22); O(15<sup>\*</sup>), O(16<sup>\*</sup>) and O(23<sup>\*</sup>), O(24<sup>\*</sup>) from three bridging-chelating carboxylate groups of three 1,2-BDC]; Yb(4) ion connects seven oxygen atoms from five 1,2-BDC and two water molecules. In this complex, each 1,2-BDC coordinates to three or four Yb ions extending to 2-D layer structure by adopting three coordination modes of the carboxylate group (Fig. 1B). Coordination modes a and b are the common ones adopted by BDC coordinating to the metal ions,<sup>3a,3c,7</sup> but mode c has not been reported before.



**Fig. 1** Structure of  $[\text{Yb}_4(1,2\text{-BDC})_6(\text{H}_2\text{O})_2]_n$  [(A) Structure of one asymmetric unit with labeling of atoms, (B) Coordination modes of 1,2-BDC].

Four kinds of coordination polyhedra exist in this complex due to the four coordination environments (Fig. 2A). The coordination geometry around the Yb(1) can be described as a distorted bicapped trigonal prism. As noted previously,<sup>8</sup> the capped atoms are O(5) and O(7<sup>\*</sup>) with the longer Yb(1)···O distance [Yb(1)···O(5) 0.2814(6) nm, Yb(1)···O(7<sup>\*</sup>) 0.2544(5) nm, respectively]. The coordination polyhedron of Yb(2) can be seen as a slightly distorted octahedron, the six oxygen atoms are well-dis-

tributed around the Yb(2) ion. The nine oxygen atoms binding Yb(3) form a distorted capped square antiprism. O(21), O(22), O(15<sup>\*</sup>) and O(16<sup>\*</sup>) form a plane having the mean deviation of *ca.* 0.0011 nm, while O(18), O(4<sup>\*</sup>), O(20<sup>\*</sup>) and O(23<sup>\*</sup>) form another one with larger mean deviation of *ca.* 0.0257 nm. The coordination geometry around the Yb(4) can be described as a capped trigonal prism. O<sub>w</sub>(2) with the longest Yb(4)···O distance [Yb(4)···O<sub>w</sub>(2) 0.2340(6) nm] occupies the capped position. The four kinds of coordination polyhedra connect into infinite chains by sharing oxygen atoms (Fig. 2B).



**Fig. 2** (A) Four kinds of coordination polyhedra of the Yb ions in  $[\text{Yb}_4(1,2\text{-BDC})_6(\text{H}_2\text{O})_2]_n$ , (B) Chain of coordination polyhedra by connecting vertices.

The varied range of Yb···O distance is enlarged with increasing coordination numbers (CN): Yb(2) with coordination number, CN = 6, less than 0.005 nm [0.2205(5) to 0.2247(6) nm]; Yb(4), CN = 7, nearly 0.014 nm [0.2198(5) to 0.2340(6) nm]; Yb(1), CN = 8, about 0.061 nm [0.2206(5) to 0.2814(6) nm]; Yb(3), CN = 9, more than 0.070 nm [0.2183(6) to 0.2889(5) nm]. This is due to the steric effect of the co-

ordinated oxygen atoms. The results show that the more the numbers of oxygen atoms surrounding the Yb ions are, the more crowded it would be around the central metal ions and the larger the difference of Yb...O distances becomes.

It is believed that four coordination environments of the Yb ions arise from the steric effect of the ligand coordinating to the Yb ions and there exists "adjusting effect" of steric hindrance caused by coordination modes of the carboxylates and the coordinated water molecules. Though the numbers of ligands surrounding Yb(1), Yb(2) and Yb(3) are identical (surrounded by six 1,2-BDC groups), the three kinds of Yb ions have different steric environments because of different coordination modes adopted by 1,2-BDC (modes a, b and c). However, Yb(4) ion binds five 1,2-BDC and two water molecules. It is obvious that 1,2-BDC is much larger than water molecule, and the Yb(4) ion is the least crowded. This effect also results in the difference in the Yb...Yb distances: Yb(1)...Yb(4) 0.4218, Yb(1)...Yb(2) 0.4296, Yb(3)...Yb(4) 0.4633 nm. In addition, the Yb ions are not strictly coplanar in the layer structure (Fig. 3).

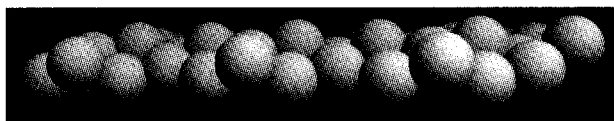


Fig. 3 Arrangement diagram of the Yb ions in  $[Yb_4(1,2-BDC)_6(H_2O)_2]_n$  viewed along  $a$ -axis, other atoms (C, H, O) are omitted for clarity.

In this complex, 1,10-phenanthroline does not take part in coordination with the ytterbium(III) ions. Under the reaction conditions, the N atoms of 1,10-phenanthroline were protonated,<sup>9</sup> which weakens the complexing ability of the N atoms. In addition, Yb(III) ions are surrounded by oxygen atoms coming from the carboxylate groups and the water molecules, and the O atom has stronger coordination ability to lanthanide ions than the N atom. Results show that 1,10-phenanthroline may have buffered effect in the formation of crystals because we could not obtain the same result when 1,10-phenanthroline was not added to the reaction mixture under the same reaction conditions.

In conclusion, a new lanthanide coordination polymer  $[Yb_4(1,2-BDC)_6(H_2O)_2]_n$  was described. In this complex, the Yb(III) ions have four different coordination environments and form four kinds of coordination polyhedra and the first crystal structure of lanthanide *o*-phthalate

complex so far reported and believed that this structure will contribute to construction of fascinating infinite metal-organic frameworks.

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- Crystal data for  $[Yb_4(1,2-BDC)_6(H_2O)_2]_n$ :  $C_{48}H_{28}O_{26}Yb_4$ ,  $M = 1712.86$ , Triclinic, space group  $P\bar{1}$  with cell dimensions of  $a = 1.2570(4)$ ,  $b = 1.3780(4)$ ,  $c = 1.5869(5)$  nm,  $\alpha = 75.363(4)^\circ$ ,  $\beta = 69.196(5)^\circ$ ,  $\gamma = 65.697(4)^\circ$ ,  $V = 2.3233(12)$  nm<sup>3</sup>,  $T = 293(2)$  K,  $Z = 2$ ,  $\mu(\text{Mo K}\alpha) = 8.076$  mm<sup>-1</sup>,  $D_c = 2.448$  g/cm<sup>3</sup>,  $F(000) = 1608$ . Convergence to the final  $R$  values of  $R_1 = 0.0423$ ,  $wR_2 = 0.1110$  [ $I > 2\sigma(I)$ ], and  $R_1 = 0.0477$ ,  $wR_2 = 0.1158$  (all data). Anal. calcd C 33.66, H 1.65; found C 33.87, H 1.38.
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