



## A Novel Cerium Metal-Organic Framework Constructed from Tri-ligand: Hydrothermal Synthesis and Crystal Structure

CHONG-CHEN WANG\* and PENG WANG

Key Laboratory of Urban Stormwater System and Water Environment (Beijing University of Civil Engineering and Architecture), Ministry of Education, No. 1, Zhanlanguan Road, Xicheng District, Beijing 100044, P.R. China

\*Corresponding author: E-mail: chongchenwang@126.com

(Received: 31 January 2011;

Accepted: 26 September 2011)

AJC-10450

The cerium based metal-organic framework,  $\text{Ce}(\text{phen})(\text{DA})(\text{OX})_{0.5}(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}$  (**1**) (DA = diphenic acid, OX = oxalic acid), was obtained by hydrothermal reaction of the mixture of  $\text{CeCl}_3\cdot 7\text{H}_2\text{O}$ , diphenic acid (DA) and oxalic acid (OX) and 1,10-phenanthroline (phen) in 1:1:1: molar ratio at 140 °C for 96 h. The crystal of  $\text{Ce}(\text{phen})(\text{DA})(\text{OX})_{0.5}(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}$  crystallizes in triclinic, space group  $\pi$  with cell parameters  $a = 8.602(14)$  Å,  $b = 12.62(2)$  Å,  $c = 13.54(2)$  Å,  $V = 1282(3)$  Å<sup>3</sup> and  $Z = 1$ . X-ray diffraction reveals that in complex **1**, Ce1 is a nine-coordinated tricapped trigonal prism made up of two nitrogen from phen ligand, two oxygen atoms from the same carboxylate group attached on a diphenic acid ligand, two oxygen atoms from two carboxylate groups attached on another ligand, two oxygen atoms from an oxalic acid ligand and one oxygen atoms from a water molecule. The centers  $\text{Ce}^{3+}$  ions are linked by diphenic acid and oxalic acid ligands into one-dimensional infinite and neutral chains.

**Key Words:** Hydrothermal synthesis, Cerium, Diphenic acid, Oxalic acid, Metal-organic framework.

### INTRODUCTION

The metal-organic frameworks are built up by lanthanide metal centers and poly-functional organic ligands through coordination bonds to form 1-D chain, 2-D sheet or 3-D network<sup>1-5</sup>. The interest toward metal-organic frameworks is not only at getting intriguing structures but also probing its possible usages in hydrogen storage<sup>6</sup>, catalysis<sup>7</sup> and fluorescence<sup>8</sup>. Diphenic acid and oxalic acid have been employed as exo-multidentate ligands for the design and construction of novel coordination polymers owing to their thermal stability and symmetry<sup>9-18</sup>.

With this communication, we employed cerium ions, with large radii and high coordination numbers, exo-multidentate ligands like diphenic acid and oxalic acid and 1,10-phenanthroline as the third ligand to hydrothermally synthesize metal-organic framework compounds with interesting topologic 1-D chain structures.

### EXPERIMENTAL

**Synthesis of  $\text{Ce}(\text{phen})(\text{DA})(\text{OX})_{0.5}(\text{H}_2\text{O})\cdot 2\text{H}_2\text{O}$ :** All commercially available chemicals were of reagent grade and used as received without further purification.

A mixture of  $\text{CeCl}_3\cdot 7\text{H}_2\text{O}$  (0.05 mmol, 0.019 g), diphenic acid ( $\text{H}_2\text{DA}$ ) (0.05 mmol, 0.012 g), oxalic acid ( $\text{H}_2\text{OX}$ ) (0.05

mmol, 0.005 g) and Phen (0.05 mmol, 0.036 g) in 1:1:1: molar ratio was sealed in a 25 mL Teflon-lined stainless steel Parr bomb containing deionized  $\text{H}_2\text{O}$  (14 mL), heated at 140 °C for 96 h and then cooled down to room temperature. Colourless block-like crystals were isolated and washed with deionized water and ethanol.

**Crystal structure determination:** A suitable crystal with dimensions of 0.48 mm × 0.41 mm × 0.40 mm for  $\text{Ce}(\text{phen})(\text{DA})(\text{OX})_{0.5}\cdot 3\text{H}_2\text{O}$  was selected for X-ray diffraction. Diffraction intensities for the present complex were recorded with a Bruker CCD area detector diffractometer with a graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å) using  $\phi$ - $\omega$  mode at 298(2) K. A total of 6610 reflections for the present compound were collected in the range of  $1.70^\circ < \theta < 25.0^\circ$ , of which 4401 were unique ( $R_{\text{int}} = 0.124$ ). Semi-empirical absorption correction was applied using the SADABS program<sup>19</sup>. The structure were solved by direct methods<sup>20</sup> and refined by full-matrix least-squares on  $F^2$  using SHELXS 97 and SHELXL 97 programs respectively<sup>20,21</sup>. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of organic ligands were added according to theoretical models. The final full-matrix least-squares refinement gave  $R1 = 0.046$ ,  $wR2 = 0.095$ . The highest and lowest residual peaks in the final difference Fourier map are 5.44 and  $-2.07 e/\text{Å}^3$ , respectively. The crystal belongs to triclinic crystal system, space

TABLE-1  
BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE COMPOUND

Bond	Length/Å	Angle	Angle/(°)	Bond	Angle/(°)	Bond	Angle/(°)
Ce1—O4 <sup>i</sup>	2.38 (2)	O5—Ce1—O2	107.5 (6)	O4 <sup>i</sup> —Ce1—O2 <sup>i</sup>	82.4 (7)	O2 <sup>i</sup> —Ce1—O1	115.6 (6)
Ce1—O2 <sup>i</sup>	2.512 (18)	O6 <sup>ii</sup> —Ce1—O2	64.7 (6)	O4 <sup>i</sup> —Ce1—O5	79.0 (7)	O5—Ce1—O1	69.2 (6)
Ce1—O5	2.546 (18)	O1—Ce1—O2	48.9 (5)	O2 <sup>i</sup> —Ce1—O5	143.5 (6)	O6 <sup>ii</sup> —Ce1—O1	72.4 (7)
Ce1—O6 <sup>ii</sup>	2.575 (19)	O7—Ce1—O2	66.6 (6)	O4 <sup>i</sup> —Ce1—O6 <sup>ii</sup>	81.7 (7)	O4 <sup>i</sup> —Ce1—O7	135.9 (7)
Ce1—O1	2.575 (18)	N2—Ce1—O2	136.3 (7)	O2 <sup>i</sup> —Ce1—O6 <sup>ii</sup>	82.7 (6)	O2 <sup>i</sup> —Ce1—O7	75.5 (6)
Ce1—O7	2.607 (19)	N1—Ce1—O2	112.7 (6)	O5—Ce1—O6 <sup>ii</sup>	63.8 (5)	O5—Ce1—O7	137.5 (6)
Ce1—N2	2.70 (2)	O6 <sup>ii</sup> —Ce1—N1	133.5 (6)	O4 <sup>i</sup> —Ce1—O1	145.4 (7)	O6 <sup>ii</sup> —Ce1—O7	131.2 (6)
Ce1—N1	2.712 (15)	O1—Ce1—N1	74.2 (6)	O1—Ce1—O7	78.7 (6)	O7—Ce1—N2	71.1 (7)
Ce1—O2	2.890 (18)	O7—Ce1—N1	70.4 (7)	O4 <sup>i</sup> —Ce1—N2	72.2 (7)	O4 <sup>i</sup> —Ce1—N1	110.8 (7)
		N2—Ce1—N1	60.6 (5)	O2 <sup>i</sup> —Ce1—N2	92.5 (6)	O2 <sup>i</sup> —Ce1—N1	141.8 (6)
		O4 <sup>i</sup> —Ce1—O2	136.2 (6)	O5—Ce1—N2	111.0 (6)	O5—Ce1—N1	74.6 (6)
		O2 <sup>i</sup> —Ce1—O2	66.8 (6)	O6 <sup>ii</sup> —Ce1—N2	153.9 (7)	O1—Ce1—N2	131.6 (6)

Symmetry codes: (i)  $-x, -y+2, -z+2$ ; (ii)  $-x+1, -y+2, -z+2$

group  $\pi$  with cell parameters  $a = 8.602$  (14) Å,  $b = 12.62$  (2) Å,  $c = 13.54$  (2) Å,  $V = 1282$  (3) Å<sup>3</sup> and  $Z = 1$ . The selected bond distances and bond angles for the present compound are listed in Table-1.

## RESULTS AND DISCUSSION

The coordination environments around cerium ions and the numbering scheme of the title complex are illustrated in Fig. 1. The local geometry around Ce1 is a nine-coordinated tricapped trigonal prism made up of two nitrogen (N1 and N2) from phen ligand, two oxygen atoms (O1 and O2) from the same carboxylate group attached on a diphenic acid ligand, two oxygen atoms (O2<sup>i</sup> and O4<sup>i</sup>) from two carboxylate groups attached on another ligand, two oxygen atoms (O6<sup>i</sup> and O5) from an oxalic acid ligand and one oxygen atoms (O7) from a water molecule. The selected bond lengths and bond angles of the title complex are listed in Table-1.

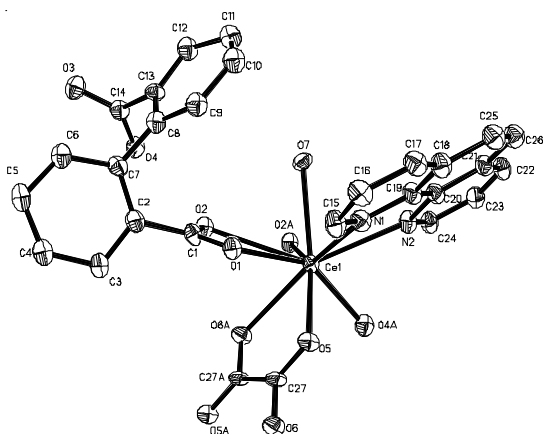


Fig. 1. Ortep view of the title compound (the water molecules are omitted for clarity)

In the  $\text{Ce}(\text{phen})(\text{DA})(\text{OX})_{0.5}(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ , the phen acts as typical chelating ligand to coordinate the cerium ions *via* two nitrogen atoms. The oxalic acid ligands chelate two different cerium ions. The diphenic acid ligands acts as tetradentate linker to join two different cerium ions, in which two oxygen atoms (O1 and O2) from a carboxylate group link one  $\text{Ce}^{3+}$  in chelating mode, also the O2 and O4 also link the other  $\text{Ce}^{3+}$  ions, while the O3 is the terminal oxygen atom. As illustrated in Fig. 2, the  $\text{Ce}^{3+}$  ions are linked by oxalic acid ligands into

double metal centers and further joined into 1-D infinite chain by diphenic acid ligands, while the phen ligands can be looked as to modify the neutral chain.

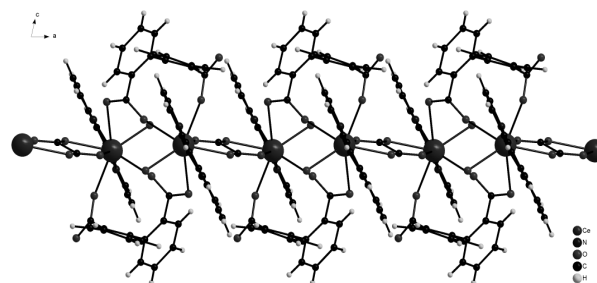


Fig. 2. One dimensional chain of the title complex viewed along b-axis

The adjacent double chains are stacked in a staggered fashion through  $\pi$ - $\pi$  interactions between phenyl rings of phen ligands of the neighboring chains. Thus, a two-dimensional layered supramolecular networks parallel to the  $c$ -axis is constructed with chains pulled together by  $\pi$ - $\pi$  interactions, as shown in Fig. 3. The two-dimensional sheets are further strengthened by hydrogen bonds between coordinated carboxyl oxygen atoms and water molecules.

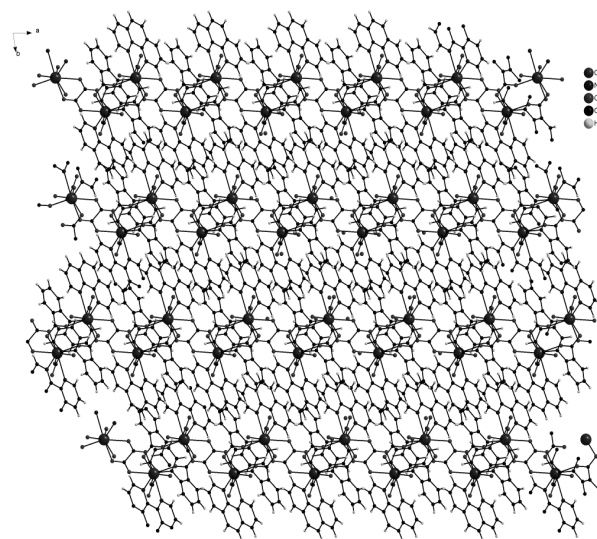


Fig. 3. 2-Dimensional sheet of complex 1 formed by 1-D neutral chains *via*  $\pi$ - $\pi$  interactions

### ACKNOWLEDGEMENTS

This work is financially supported by Funding Project for Academic Human Resources Development in Institutions of Higher Learning Under the Jurisdiction of Beijing Municipality (Grant No. PHR201008372 & PHR201106124) and the Research Fund of Beijing University of Civil Engineering and Architecture (Grant No. 100902602).

### REFERENCES

1. N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O.M. Yaghi, *Acc. Chem. Res.*, **38**, 176 (2005).
2. G.S. Guo, C.C. Wang and Y.C. Liu, *Chin. J. Inorg. Chem.*, **26**, 1583 (2010).
3. C.C. Wang, Z.H. Wang and G.S. Guo, *J. Mol. Struct.*, **979**, 92 (2010).
4. C.C. Wang, *Asian J. Chem.*, **21**, 4711 (2009).
5. C.C. Wang, *Z. Kristallogr. NCS*, **223**, 475 (2008).
6. N.L. Rosi, M. Eddaoudi, D.T. Vodak, J. Eckert, M. O'Keeffe and O.M. Yaghi, *Science*, **300**, 1127 (2003).
7. O. Ohmori and M. Fujita, *Chem. Commun.*, **4**, 1586 (2004).
8. M. Yang, L. Wang, G. Li, L. Yang, Z. Shi and S. Feng, *J. Alloys Compd.*, **440**, 57 (2007).
9. I.L. Malaestean, M. Speldrich and S.G. Baca, *Eur. J. Inorg. Chem.*, 1011 (2009).
10. L. Gou, B. Zhang and H.M. Hu, *J. Mol. Struct.*, **889**, 244 (2008).
11. R. Wang, F. Jiang and L. Han, *J. Mol. Struct.*, **699**, 79 (2004).
12. R. Wang, Y. Zhou and Y. Sun, *Cryst. Growth Design.*, **5**, 251 (2005).
13. X. L. Wang, C. Qin, E.B. Wang and L. Xu, *Eur. J. Inorg. Chem.*, 3418 (2005).
14. C.C. Wang and Z. Kristallogr, *NCS*, **222**, 351 (2007).
15. S.S. Ge, X.M. Wu, Q.X. Liu, Z.Y. Zheng, Y. Zang, S.W. Liu and J.C. Feng, *Chin. J. Struct. Chem.*, **27**, 1538 (2008).
16. L.C. Li, C.L. Dong, D.Z. Liao, Z.H. Jiang and S.P. Yan, *Chin. J. Struct. Chem.*, **23**, 296 (2004).
17. Z.H. Zhang, Y.M. Lu, H.L. Yang and Y. Tang, *Chin. J. Inorg. Chem.*, **21**, 477 (2005).
18. J. Kim, U. Lee and B.K. Koo, *Bull. Korean Chem. Soc.* **31**, 487 (2010).
19. G.M. Sheldrick. SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany (1997).
20. G.M. Sheldrick. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany (1997).
21. G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).