Asian Journal of Chemistry Vol. 20, No. 5 (2008), 3687-3701

Three-Dimensional Metal-Organic Hybrid Material Bearing an Open-Framework Self-Assembled by Mononuclear Cerium Benzene Tetracarboxylate Complex

MIAO-JUAN REN*, ZHONG ZHANG, PENG ZHAO and JUN ZHANG
School of Science, Jinan University, Jinan 250022, Shandong, P.R. China
Tel: (86)(531)86211620; E-mail: ss_renmj@ujn.edu.cn

A kind of novel metal-organic hybrid material formed by stacking and self-assembly of the mononuclear cerium benzene tetracarboxylate complex $[Ce(H_2btec)_{½}(btec)_{½}(H_2O)]_n$ (H_4btec = 1,2,4,5-benzene tetracarboxylic acid), simplified as MCBC, has been synthesized under solvothermal conditions (H_2O/acetic acid). MCBC obtained was characterized by differential thermal analysis/thermogravimetry, single crystal X-ray diffraction, elemental analysis and FT-IR analysis. Single-crystal X-ray diffraction analysis shows that MCBC crystallizes to mononuclear metal carboxylate complex with a 3D-supramolecular open-framework containing nine-coordinate cerium centers.

Key Words: Metal-organic hybrid material, Open framework, Cerium, Carboxylic complex.

INTRODUCTION

The study and design of multi-dimensional infinite frameworks of metal-organic supramolecular coordination polymers is of interest in inorganic, organic chemistry and in functional materials science and has attracted much attention. Metal-carboxylate coordination polymer is one of the typical examples, not only because of their promising potential properties, such as gas-occlusion properties[1], catalytic activities[2] as well as the photochemistry and electrochemistry properties[3], but also because of their intriguing architectures[4]. Therefore, the design and synthesis of the materials with novel structure is a continuing challenge.

It is well known that deprotonation of 1,2,4,5-benzene tetracarboxylic acid gives anion with 1-4 negative charges, which can act as multi-dentate ligands[5] and often used as a versatile building block for the architectures of polymeric structures ascribed to its variety of bridging abilities between metallic centers, generating various and sometimes surprising molecular architectures[6]. This kind of ligand can also be considered a multitude of interesting properties such as molecular magnetization[7], one-dimensional conductivity[8] and in applying gravimetric analysis[9]. In contrast to transition metal complexes, lanthanide coordination polymers have attracted considerable attention owing to large radii and high coordination numbers. As a result, a series of lanthanide-carboxylate complex examples have also been synthesized owing to their variable structures[10]. On the other hand, apart from their intrinsic aesthetic appeal, interest in these new families of interlinked coordination polymer has been heightened by the fact that their resulting overall architectures are more flexible than the usual coordination polymer based entirely on coordination bonds and hydrogen bonds[11]. Consequently, from the perspective of molecular architecture, the exploitation of such species not only increases the diversity of supramolecular coordination polymers based upon function material science, but also provides new insights into the relationships between the structure and function of these materials.

From the aspect of synthesis, compounds with coordination polymer structures have a tendency to form powders rather than single crystals because of their low solubility on formation. By altering the growing conditions it is possible to induce slower crystallization and then improve the quality and size of crystals for single crystal X-ray diffraction experiments. Therefore, hydrothermal and solvothermal synthesis have been developed quickly.

Herein, the solvothermal synthesis and structural characterization of a novel cerium carboxylate complex $[Ce(H_2btec)_{½}(btec)_{½}(H_2O)]_n$ assembled from 1,2,4,5-benzenetetracarboxylic acid (H_4btec) ligand and cerium ion are reported. At the same time, its thermal stability and FT-IR modes are also discussed.

EXPERIMENTAL

Mononuclear cerium benzene tetracarboxylate complex (MCBC) was prepared solvothermally from a mixture of $Ce(NO_3)_3{\cdot}6H_2O$, 1,2,4,5-benzene tetracarboxylic dianhydride, acetic acid (36 %) and H_2O in a molar ratio of 1:1:160:900, heated in a Teflon-lined stainless steel autoclave at 180 ºC for 7 d under static conditions and the filling volume is 75 %. After cooling the reaction mixture to room temperature, the yellow block-like crystals were separated and washed by distilled water and ethanol several times. Finally, the products were dried in air at room temperature. The average size of the crystals is about $1.0 \times 1.0 \times 1.0$ mm^3 and no other phase was found in the final product.

The elemental analysis (C and H) was carried out on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. Inductively coupled plasma (ICP) analysis (Ce) performed on a Perkin-Elmer Optima 3300DV spectrometer. Anal. (%) Found: C, 29.22; H, 1.21; Ce, 34.22. Calcd. (%) for $C_{10}H_5O_9Ce$:

C, 29.25; H, 1.23; Ce, 34.24. The composition analysis is in good agreement with calculated values based on the empirical formula of $C_{10}H_5O_9Ce$ given by single-crystal structure analysis.

X-Ray intensity data were measured at 298 ± 2 K on a Bruker SMART APEX CCD-based diffractometer (MoKα radiation, $\lambda = 0.71073$ Å). The raw frame data for the compound were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT[12]. Corrections for incident and diffracted beam absorption effects were applied using SADABS[12].

MCBC crystallized in the space group P-1, as determined by the systematic absences in the intensity data, intensity statistics and the successful solution and refinement of the structures. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full matrix least-squares technique. Crystal data, data collection parameters and refinement statistics for the MCBC are listed in Table-1. Selected bond distances and bond angles are given in Table-2. The atomic coordinates and thermal parameters of MCBC are also listed in Table-3.

TABLE-1
SUMMARY OF CRYSTALLOGRAPHIC DATA AND
STRUCTURE REFINEMENT FOR MCBC

Complex	MCBC
Empirical formula	$C_{10}H_5O_9Ce$
Formula weight	409.26
Crystal system	Triclinic
Space group	P-1
a (Å)	6.4164(11)
b (Å)	9.4080(16)
c (Å)	9.5927(16)
a (deg)	88.501(2)
b (deg)	74.574(2)
γ (deg)	76.704(2)
V ($Å^3$)	542.87(16)
Z	2
ρ_{cal} (g cm^{-3})	2.504
μ (mm^{-1})	4.241
Reflections collected	2863
Independent reflections	1876 [R(int) = 0.0199]
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0222, wR2 = 0.0560
R indices (all data)	R1 = 0.0241, wR2 = 0.0572

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (deg) FOR MCBC (SYMMETRY TRANSFORMATIONS USED TO GENERATE EQUIVALENT ATOMS: # 1 = -x + 3, -y + 1, -z + 1; #2 = -x + 3, -y + 1, -z + 2)

Ce(1)-O(6)#1	2.411(3)	Ce(1)-O(1)	2.538(3)	Ce(1)-O(2)	2.645(3)
Ce(1)-O(5)	2.458(3)	Ce(1)-O(7)	2.564(3)	O(2)-Ce(1)#2	2.536(3)
Ce(1)-O(9)	2.489(3)	Ce(1)-O(4)	2.577(3)	O(6)-Ce(1)#1	2.411(3)
Ce(1)-O(2)#2	2.536(3)	Ce(1)-O(3)	2.594(3)		
O(6)#1-Ce(1)-O(5)	77.50(10)	O(5)-Ce(1)-O(4)	142.54(9)	O(1)-Ce(1)-O(2)	50.10(8)
O(6)#1-Ce(1)-O(9)	140.10(11)	O(9)-Ce(1)-O(4)	130.63(10)	O(7)-Ce(1)-O(2)	143.24(9)
O(5)-Ce(1)-O(9)	66.38(10)	O(2)#2-Ce(1)-O(4)	73.32(9)	O(4)-Ce(1)-O(2)	114.23(9)
O(6)#1-Ce(1)-O(2)#2	144.84(10)	O(1)-Ce(1)-O(4)	122.57(9)	O(3)-Ce(1)-O(2)	74.47(9)
O(5)-Ce(1)-O(2)#2	136.59(10)	O(7)-Ce(1)-O(4)	70.30(9)	C(1)-O(1)-Ce(1)	96.8(2)
O(9)-Ce(1)-O(2)#2	70.50(11)	O(6)#1-Ce(1)-O(3)	73.27(10)	C(1)-O(2)-Ce(1)#2	151.4(2)
O(6)#1-Ce(1)-O(1)	81.71(9)	O(5)-Ce(1)-O(3)	137.69(9)	C(1)-O(2)-Ce(1)	91.3(2)
O(5)-Ce(1)-O(1)	72.46(9)	O(9)-Ce(1)-O(3)	146.31(10)	Ce(1)#2-O(2)-Ce(1)	116.25(9)
O(9)-Ce(1)-O(1)	102.10(11)	O(2)#2-Ce(1)-O(3)	80.40(9)	C(5)-O(3)-Ce(1)	93.5(2)
O(2)#2-Ce(1)-O(1)	112.94(8)	O(1)-Ce(1)-O(3)	73.60(9)	C(5)-O(4)-Ce(1)	93.8(2)
O(6)#1-Ce(1)-O(7)	88.90(10)	O(7)-Ce(1)-O(3)	120.69(9)	C(6)-O(5)-Ce(1)	138.9(3)
O(5)-Ce(1)-O(7)	88.15(9)	O(4)-Ce(1)-O(3)	50.42(8)	C(6)-O(6)-Ce(1)#1	170.5(3)
O(9)-Ce(1)-O(7)	74.04(11)	O(6)#1-Ce(1)-O(2)	127.74(9)	C(10)-O(7)-Ce(1)	141.2(3)
O(2)#2-Ce(1)-O(7)	84.83(9)	O(5)-Ce(1)-O(2)	101.46(9)	Ce(1)-O(9)-H(11)	103.1
O(1)-Ce(1)-O(7)	159.84(10)	O(9)-Ce(1)-O(2)	77.60(11)	Ce(1)-O(9)-H(12)	105.0
O(6)#1-Ce(1)-O(4)	72.00(10)	O(2)#2-Ce(1)-O(2)	63.75(9)		

TABLE-3
ATOMIC COORDINATES (× 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (Å^2×10^3) FOR THE COMPOUND MCBC

Atom	x	y	z	U(eq)
Ce(1)	3487(1)	4405(1)	2209(1)	11(1)
O(1)	471(4)	6599(3)	1964(3)	18(1)
O(2)	3430(4)	6283(3)	111(3)	18(1)
O(3)	1303(5)	3523(3)	615(3)	19(1)
O(4)	3528(5)	1785(3)	1464(3)	19(1)
O(5)	2671(4)	6051(3)	4331(3)	20(1)
O(6)	-361(5)	6309(3)	6161(3)	25(1)
O(7)	6079(5)	2559(3)	3367(3)	26(1)
O(8)	5891(5)	255(3)	3017(4)	27(1)
O(9)	6592(5)	5555(4)	2263(4)	40(1)
C(1)	1546(6)	7029(4)	810(4)	13(1)
C(2)	718(6)	8540(4)	334(4)	11(1)
C(3)	-957(6)	8920(4)	-386(4)	12(1)
C(4)	-1641(6)	10377(4)	-715(4)	14(1)
C(5)	1978(6)	2199(4)	843(4)	14(1)
C(6)	1022(6)	6805(4)	5225(4)	14(1)
C(7)	566(6)	8460(4)	5131(4)	14(1)
C(8)	8956(6)	-885(4)	4442(4)	15(1)
C(9)	8384(6)	628(4)	4307(4)	14(1)
C(10)	6670(6)	1236(4)	3521(4)	16(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ii} tensor.

RESULTS AND DISCUSSION

Structural description [Ce(H_2btec)$_{½}$(btec)$_{½}$(H_2O)]$_n$: Fig. 1 reveals that MCBC exhibits a framework consisting of nine-coordinate cerium centers. The local environment around the carboxylate ligands is depicted in Fig. 2(a) and 2(b). It is evident that there are two types of coordination modes for the carboxylate ligands. Firstly, each of two *para*-protonated carboxylic groups coordinates to one cerium through carbonyl oxygen atom, while each of the other two *para*-deprotonated carboxylic groups bridges two cerium atoms adopting bidentate coordinating mode [Fig. 2(a)]. Secondly, each of the two *para*-carboxylate groups adopts bidentate chelating mode to coordinate one cerium atom and each of the other two *para*-carboxylate groups adopts bidentate chelating-bridging mode to connect two cerium atoms [Fig. 2(b)]. As shown in Fig. 1, the central cerium ion is coordinated by nine oxygen atoms, in which, five oxygen atoms (O1, O2, O3, O4 and O2) originate from three btec^{4-} ligands, other three ones (O5, O6 and O7)

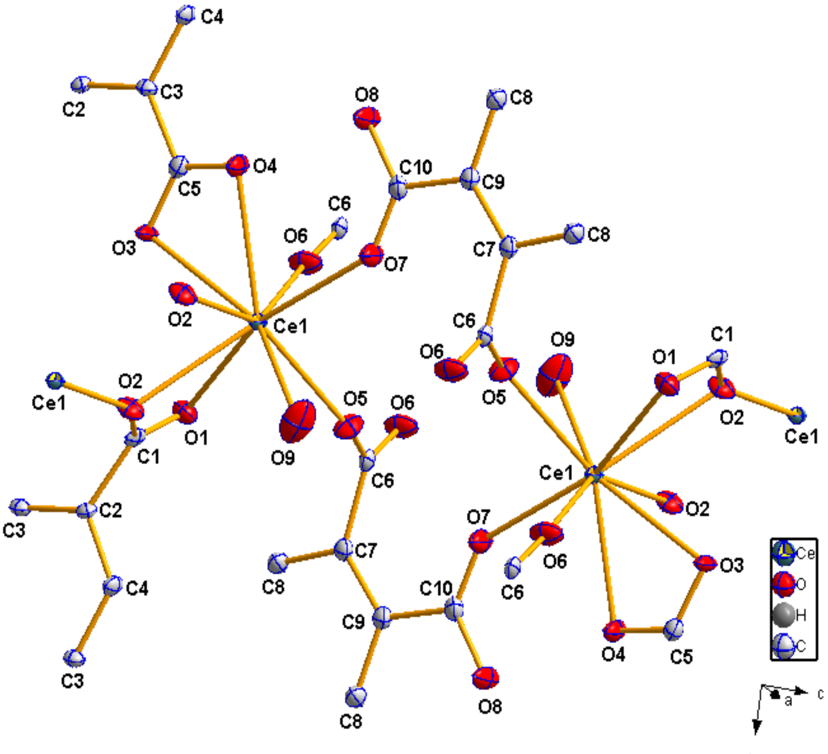
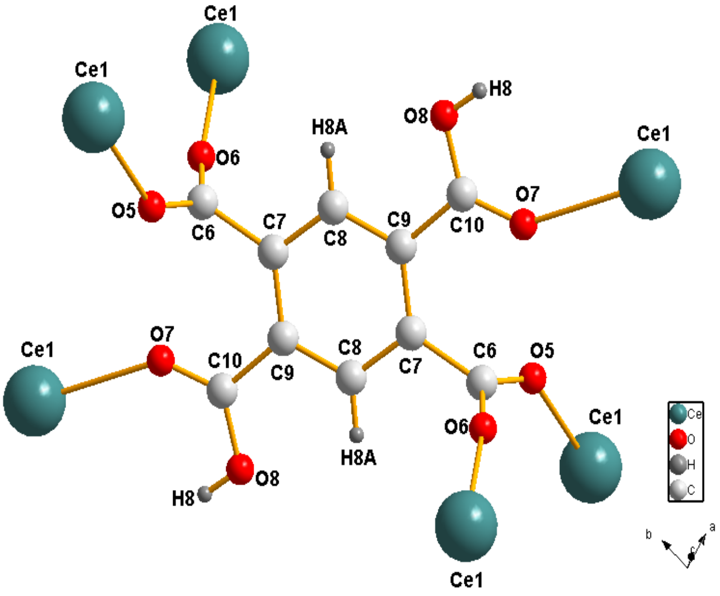
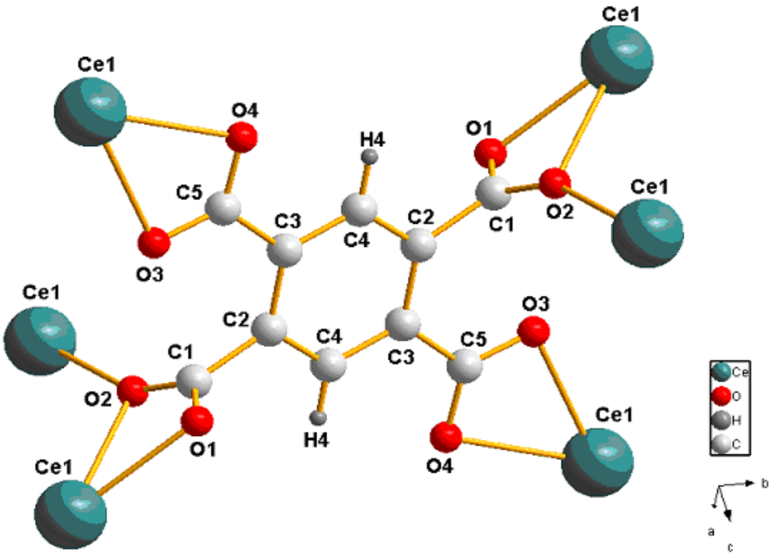


Fig. 1. ORTEP diagram showing the coordination environments for Ce ion in MCBC, thermal ellipsoids are drawn at the 50 % probability level



(a)



(b)

Fig. 2. (a) Ball-and-stick representation of the local environment around the H_2btec^{2-} ion; (b) Ball-and-stick representation of the local environment around the $btec^{4-}$ ion

from H_2btec^{2-} ligands, with the bond distances of Ce-O range from 2.411(3) Å (Ce1-O6) to 2.645(3) Å (Ce1-O2). While another coordination situation is occupied by an oxygen atom from coordinated water molecule with the Ce1-O9 bond distance being 2.489(3) Å. At the same time, the bond distances of C-O bond observed in the protonated carboxylic group, C10-O7 1.232(5) Å is shorter than C10-O8 1.304(5) Å, in agreement with the presence of the absorption peak at 1669cm-1 for -COOH in IR spectrum (Fig. 7). As a generally simple rule, the un-ionized and uncoordinated COO stretching band occurs at about 1750-1700 cm^{-1}. But Fig. 7 shows a red shift from 1700 cm^{-1} of H_4btec, which may be caused by strong hydrogen bonding[5(a)]. From Table-4 and Fig. 6, it can be seen that the typical example of the two kinds of hydrogen bonding for MCBC is presented as following:

TABLE-4
DONOR-H, DONOR-H DISTANCES, ACCEPTOR, INTERMOLECULAR HYDROGEN BOND DISTANCES, DONOR-ACCEPTOR DISTANCES (Å) AND ANGLES (deg) OF HYDROGEN BONDS FOR MCBC

D-H	d(D-H)	A	d(H···A)	d(D···A)	<DHA
O8-H8	0.820(4)	O4	1.782(3)	2.584(5)	165.186(2)
O9-H11	0.850(3)	O3 [x+1, y, z]	2.481(3)	3.201(4)	142.989(3)
O9-H11	0.850(3)	O6 [-x+1,-y+1, -z+1]	2.652(3)	3.326(5)	137.223(2)
O9-H12	0.850(4)	O3 [-x+1,-y+1, -z]	2.120 (3)	2.937(5)	161.130(3)

(a) hydrogen bonding between the coordinated water molecules and deprotonated carboxylate oxygen atoms with O9···O3 and O9 ··· O6 distance range from 2.937(5) to 3.326(5) Å; (b) hydrogen bonding between the protonated and deprotonated carboxylate oxygen atoms with an O8 ··· O4 distance of 2.584(5) Å.

As depicted above, the deprotonated carboxylic groups adopted bidentate chelating mode (-O3-C5-O4-) in $btec^{4-}$ and the protonated carboxylic groups adopted unidentate coordination (-O7-C10-O8-) in H_2btec^{2-} have a universal plane together with the benzene ring. Therefore, a 2D layer structure with the nearest cerium-cerium distance of 4.3998(7) Å was generated from the coordination of the cerium atoms and the carboxylic groups in the plane. And the coordinated water molecules situated above or under the plane (Fig. 3).

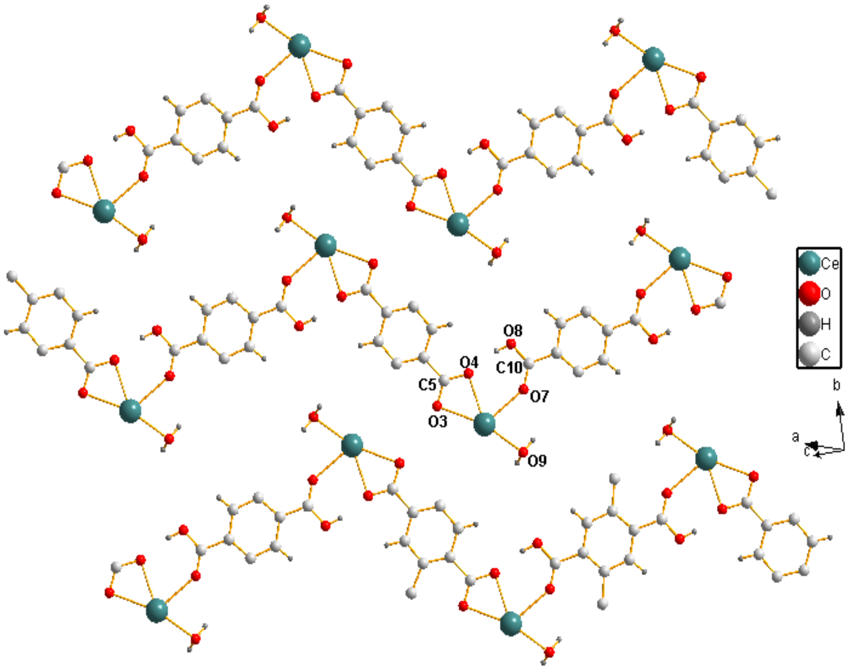


Fig. 3. Ball-and-stick representation of the 2D layer framework in MCBC (all the oxygen atoms adopted bidentate chelating-bridging and bidentate coordinating mode are omitted for clarity)

On the other hand, the deprotonated carboxylic groups adopted bidentate chelating-bridging mode (-O1-C1-O2-) in $btec^{4-}$ and the deprotonated carboxylic groups adopted bidentate coordinating (-O6-C6-O5-) in H_2btec^{2-} have a different plane compared to the benzene ring above, they are not in the plane of benzene ring. The dihedral angles between benzene ring and the carboxylic planes are 74.11(5) and 78.09(5)º, respectively. At the same time, the van der Waals interaction between the benzene rings of the ligands, the so-called "π-π stack", also might act as a driving force for the self-assembly of the 1D cerium(III) carboxylate to form 2D lattice structures. Fig. 4 represents the infinite 2D lattice with open frameworks in MCBC. It is obvious that infinite linear micropores are created by stacking the 2D lattices.

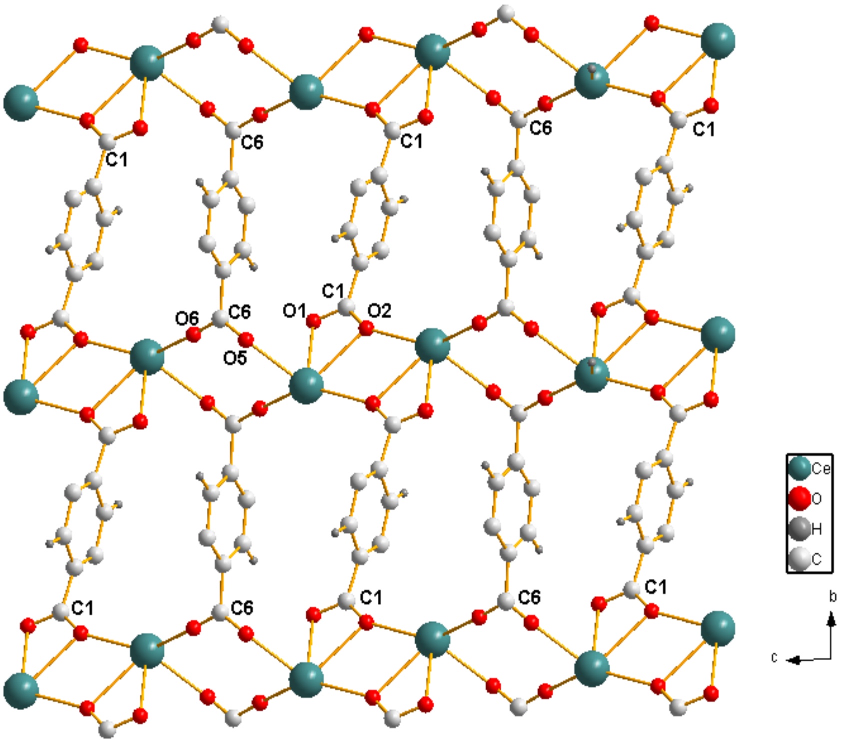


Fig. 4. Ball-and-stick representation of the infinite 2D lattice with open frameworks in MCBC (all the oxygen atoms adopted bidentate chelating and unidentate coordinating mode are omitted for clarity)

The two different kinds of planes originated from the coordination of the cerium atom and the different carboxylic groups cross-linked further and finally formed a 3D supramolecular open framework structure with many regular window-shape channels. The large channel size of MCBC is *ca.*11.6148 (2) × 8.1362 (6) $Å^2$ along the b-axis and it is occupied by the coordinated H_2O molecules (Fig. 5).

Similar with 1,2,4,5-benzene tetracarboxylic acid[6(d)], the 3D supramolecular framework of MCBC is also consolidated by hydrogen bonds since H-bonding increase the structural dimensionality, which is characterized

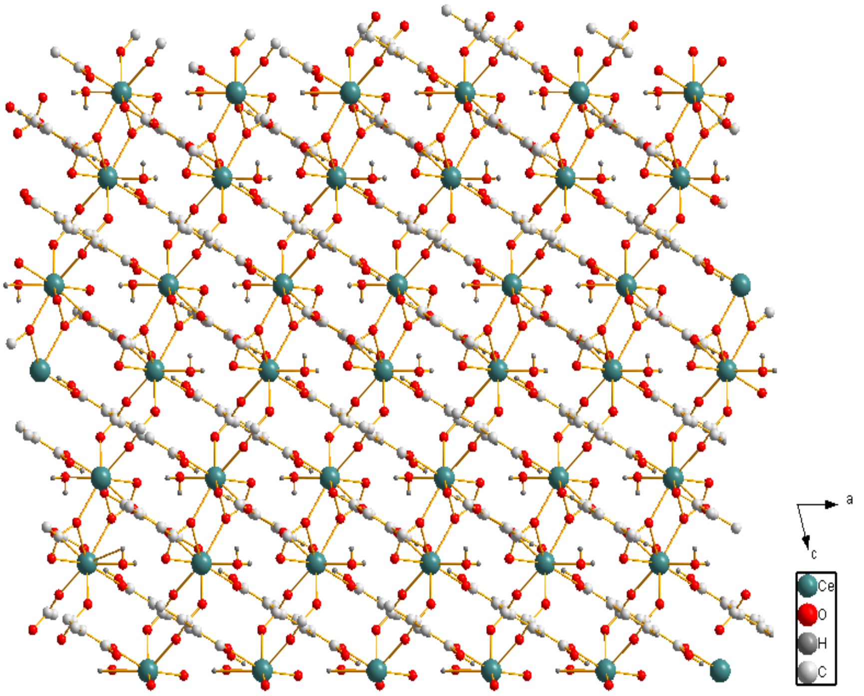


Fig. 5. Crystal packing of the 3-D supramolecular open framework structure along the b axis in MCBC, indicating many irregular channels occupied by the H_2O molecules

by X-ray crystallography clearly. Fig. 6 shows the presence of the intermolecular hydrogen bonds by dashed lines. It demonstrated that the hydrogen bonding is mainly formed through the O atoms of the carboxylate groups and the coordinated water molecules. Which makes it have a potential application in gas-occlusion[1(a)].

The FT-IR spectra were measured on Perkin-Elmer spectrum one FT-IR spectrometer in the 4000-200 cm^{-1} region with pressed CsI pellet.

The main FT-IR spectra of MCBC are given in Fig. 7. A band centered at *ca.* 3624 and 3488 cm^{-1}, which is due to the O-H stretching vibration of water molecules involved in extensive hydrogen bonding interactions[13]. At the same time, the coordinated water exhibits the frequencies 659 and 588 cm^{-1}, which assigned to ρ_r (H_2O) and ρ_w (H_2O)[14]. The stretching bands of O-Ce-O ascribed to 769 (ν_1), 758 (ν_3) and harmonic frequencies (ω_e) of Ce-O is characteristic[14] of 843 and 882 cm^{-1}. Frequency at 1669 cm^{-1} is characteristic of the protonated carboxylic group (-C(10)-O(7)-(O8)-) and coordinated carboxylic groups (-C(1)-O(1)-O(2)-, -C(5)-O(3)-O(4)- and -C(6)-O(5)-O(6)-) exhibit three frequencies 1501, 1557, 1598 and 1621 cm^{-1} according to the rule given by Busch and coworkers[15], which is consistent with the results of single crystal X-ray analysis above.

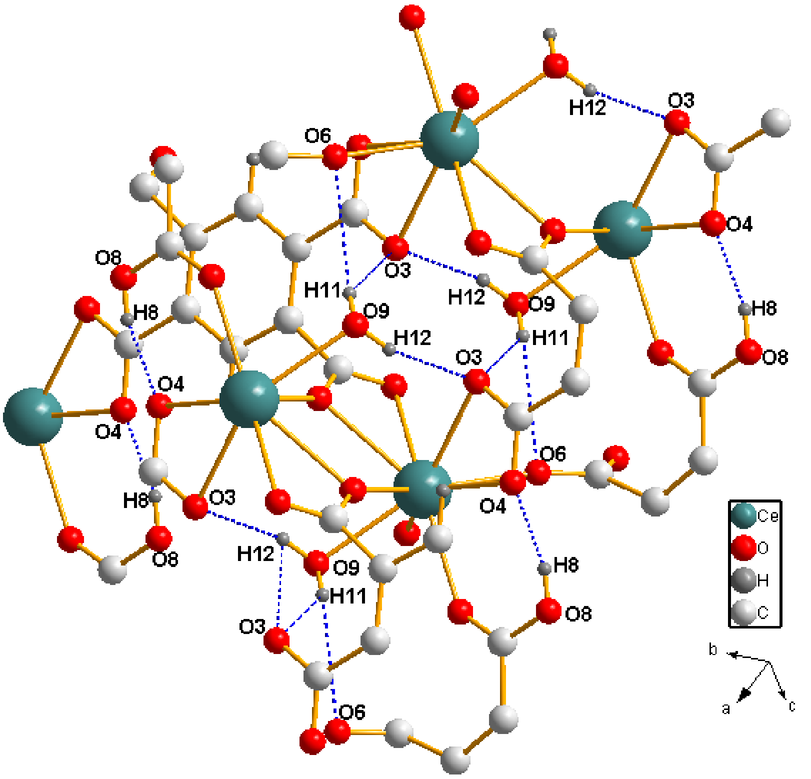


Fig. 6. Two kinds of intermolecular hydrogen bonds drawn by dashed lines for MCBC

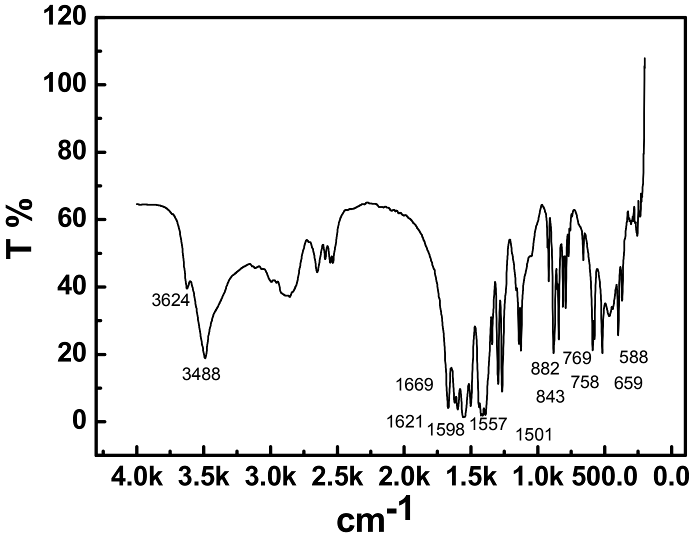


Fig. 7. FT-IR spectra for MCBC

The thermal stability of MCBC was examined by TGA-DTA experiments, which were carried out under a flow of the dry air and at a heating rate of 5 ºC min^{-1} from room temperature to 850 ºC with a Perkin-Elmer Diamond TG/DTA instrument. The TG curve (Fig. 8) indicates that the weight loss of MCBC can be completely divided into two distinct stages. The second stage took place in the temperature range of 430 up to 490 ºC and showed a weight loss of 49.603 % with a distinctly exothermic peak, which ascribed to MCBC decomposing to the metal oxides like CeO_2. While the first one is noticeable that there is only one weight loss of 10.789 % with no endothermal or exothermic peak below 430 ºC. The same result was obtained by adjusting the heating rate or increasing the sample weight in the TG-DTA measurement. In addition, we have observed the alike phenomenon with several transition metals, such as a sandwich crystal compound $Co(H_2O)_6(H_2btec)$, which has an ionic structure built of $[Co(H_2O)_6]^{2+}$ dications and dianions of doubly deprotonated H_4btec, which are linked to each other only through hydrogen bonds and ionic interactions (Fig. 9). In Supporting Information). In which, $Co(H_2O)_6(H_2btec)$ also showed this phenomenon in the temperature range of 180-320 ºC (Fig. 10). As a general rule it should be a thermal change in DTA curves together with a corresponding weight loss in TG curves. But, there is an exception in MCBC. The exact mechanism of the TG/DTA for MCBC needs to be studied further. According to the fact of experimental results that there is a moderate weight loss with no endothermal or exothermic peak, it may be probably originated

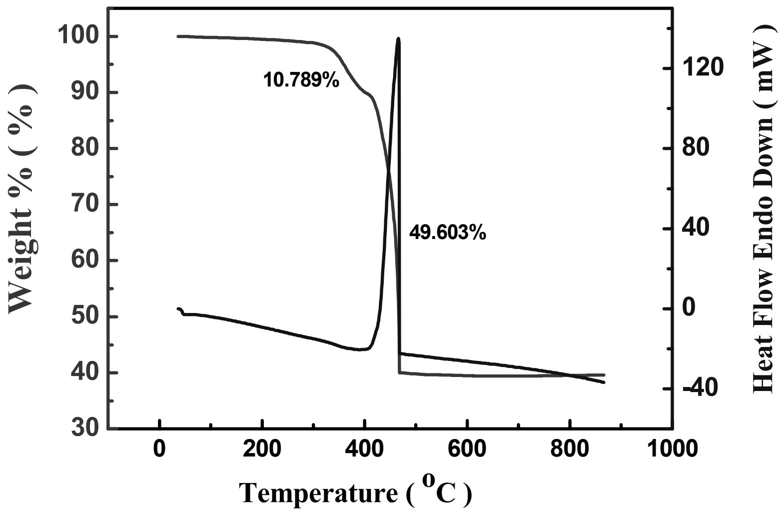


Fig. 8. TG-DTA curves for MCBC

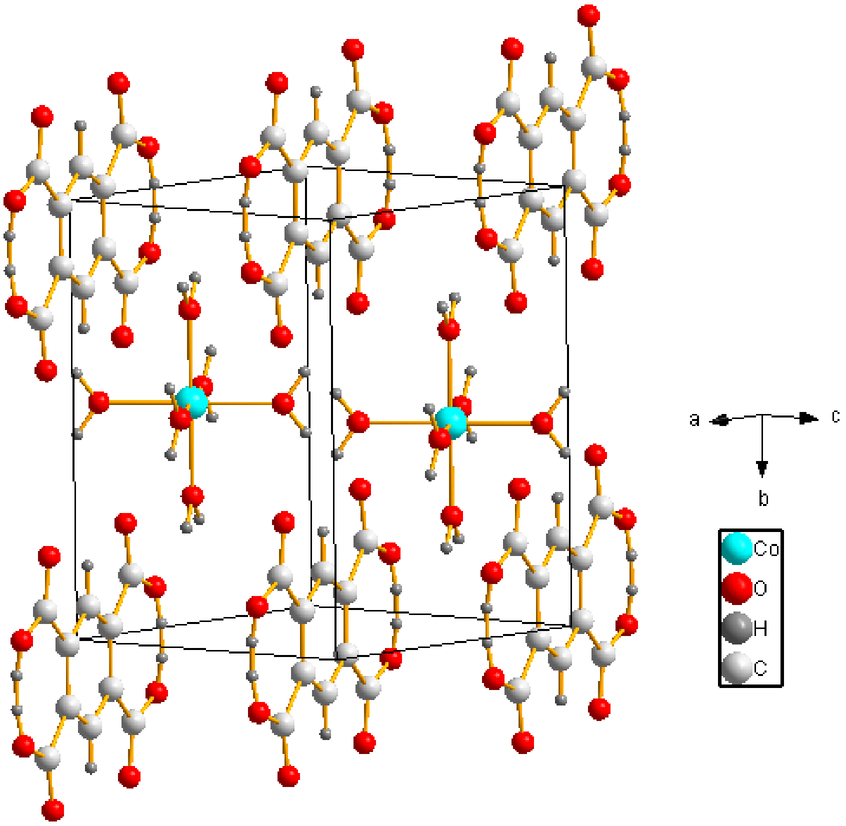


Fig. 9. Ball-and-stick representation of the 3D layer framework in $Co(H_2O)_6(H_2btec)$

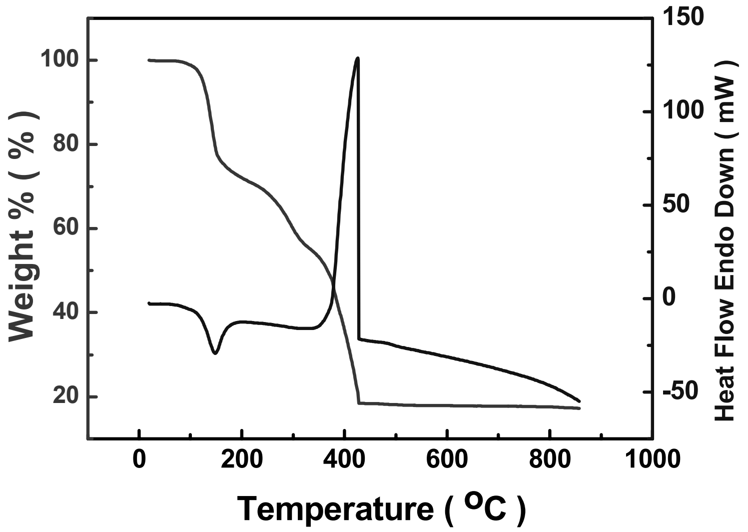


Fig. 10. TG-DTA curves of $Co(H_2O)_6(H_2btec)$

from that two reactions (the decomposing of the protonated carboxylic group and the removal of the coordinated water molecules) took place synchronously. In which, one reaction is endothermal, the other one is exothermic and the value of calorimetry of them is the same.

Conclusion

We have succeeded in synthesizing a novel metal-organic hybrid material self-assembled by mononuclear cerium benzene tetracarboxylate complex $[Ce(H_2btec)_{½}(btec)_{½}(H_2O)]_n$ bearing an open-framework under solvothermal conditions (H_2O/acetic acid) and characterized by single crystal XRD, elemental analysis, FT-IR and TG/DTA. Single crystal XRD results showed that the central cerium ion is coordinated by nine oxygen atoms from H_2btec^{2-}, $btec^{4-}$ and H_2O ligands with a triclinic symmetry as well as the space group P-1. In which, five oxygen atoms come from three $btec^{4-}$ ligands, other three ones from H_2btec^{2-} ligands and another coordination situation is occupied by a coordinated water molecule. In MCBC, each ligand (the deprotonated carboxylic groups adopting bidentate chelating mode in $btec^{4-}$ and the protonated carboxylic groups adopting unidentate coordination in H_2btec^{2-}) has two co-planar carboxylic groups in *para*-orientation, which link the cerium atoms into a layer. Other carboxylic groups (containing the deprotonated carboxylic groups adopted bidentate chelating-bridging mode in $btec^{4-}$ and the deprotonated carboxylic groups adopted bidentate coordinatingin H_2btec^{2-}) are not in the plane of benzene ring. These groups cross-link the layers to form a 3D supramolecular open-framework structure with many channels, which are occupied by the coordinated H_2O molecules.

FT-IR showed that the characteristic absorption at 1669 cm^{-1} is an evidence of the presence for -COOH. And the coordinated water absorption frequencies, stretching bands of O-Ce-O, harmonic frequencies of Ce-O, protonated carboxylic groups and coordinated carboxylic groups were also designated in FT-IR.

TG/DTA results showed, the framework of MCBC was completely damaged above 490 ºC.

Supporting information: Crystallographic data (excluding structure factors) for the structure of MCBC in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 606403. Copies of the data can be obtained, free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK ; fax: +44 1223 336033 ; or e-mail: deposit@ccdc.cam.ac.uk).

At the same time, supplementary information on the structure of the sandwich crystal compound $Co(H_2O)_6(H_2btec)$ and its TGA/DTA mentioned above is available from the authors.

ACKNOWLEDGEMENTS

The authors thank the Doctoral Foundation of Jinan University for financial support (B0404) and Science Study Plan Foundation of Educational Bureaue of Shandong Provience (J2005A02).

REFERENCES

1. (a) S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.*, **124**, 2568 (2002); (b) T. Ohmura, W. Mori, M. Hasegawa, T. Takei and A. Yoshizawa, *Chem. Lett.*, **32**, 34 (2003); (c) T. Ohmura, W. Mori, M. Hasegawa, T. Takei, T. Ikeda and E. Hasegawa, *Bull. Chem. Soc. (Japan)*, **76**, 1387 (2003).
2. T. Sato, W. Mori, C.N. Kato, T. Ohmura, T. Sato, K. Yokoyama, S. Takamizawa and S. Natio, *Chem. Lett.*, **32**, 854 (2003).
3. (a) Q.M. Wang and B. Yan, *J. Photochem. Photobiol. A: Chem.*, **177**, 1 (2006); (b) K. Mitra, D. Mishra, S. Biswas, C.R. Lucas and B. Adhikary, *Polyhedron.*, **25**, 1681 (2006); (c) D. Prodius, C. Turta, V. Mereacre, S. Shova and M. Gdaniec, *Polyhedron.*, **25**, 2175 (2006).
4. (a) H.F. Zhu, J. Fan, T. Okamura, Z.H. Zhang, G.X. Liu, K.B. Yu, W.Y. Sun and N. Ueyama, *Inorg. Chem.*, **45**, 3941 (2006); (b) Z.H. Zhang, T. Okamura, Y. Hasegawa, H. Kawaguchi, L.Y. Kong, W.Y. Sun and N. Ueyama, *Inorg. Chem.*, **44**, 6219 (2005); (c) A. Deluzet and O. Guillou, *Acta Crystallogr.*, **C59**, m277 (2003); (d) L.P. Wu, M. Munakata, K.S. Takayoshi, M. Maekawa and Y. Suenaga, *Inor. Chim. Acta.*, **249**, 183 (1996); (e) H. Endres and A. Knieszner, *Acta Cryst.*, **C40**, 770 (1984).
5. (a) K.A. Kapildev and V.R. Pedireddi, *J. Org. Chem.*, **68**, 9177 (2003); (b) K. Biradha and M.J. Zaworotko, *Crystal Eng.*, **1**, 67 (1998).
6. (a) O.M. Yaghi, H. Li and T.L.Z.K. Groy, *New. Crystal. Struct.*, **212**, 457 (1997); (b) T.R. Whitfield, X. Wang, L. Liu and A.J. Jacobson, *Solid State Sci.*, **7**, 1096 (2005); (c) C.R. Perez, P.L. Luis and M.H. Molina, *Eur. J. Inorg. Chem.*, **16**, 3873 (2004); (d) O. Fabelo, L.C. Delgado, F.S. Delgado, P.L. Luis, M.M. Laz, M. Julve and C.R. Pérez, *Crystal Growth & Design*, **5**, 1163 (2005); (e) L.C. Delgado, O. Fabelo and C.R. Pérez, *Crystal Growth & Design*, **6**, 87 (2006); (f) X. Shi, G. Zhu, X. Wang, G. Li, Q. Fang, G. Wu, G. Tian, M. Xue, X. Zhao, R. Wang and S. Qiu, *Crystal Growth & Design*, **5**, 207 (2005); (g) S.K. Ghosh and P.K. Bharadwaj, *Inorg. Chem.*, **43**, 5180 (2004); (h) M.D. Ye, H.P. Xiao, Y.Q. Cheng and M.L. Hu, *Acta Cryst.*, **E60**, m219 (2004); (i) Y.Q. Sun, J. Zhang and G.Y.Yan, *Acta Cryst.*, **E58**, m548 (2002).
7. H. Kumagai, C.J. Kepert and M. Kurmoo, *Inorg. Chem.*, **41**, 3410 (2002).
8. J.S. Milier and A.J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976).
9. A.K. Mukherji, *Anal. Chem.*, **36**, 1064 (1964).
10. (a) L.P, Wu, M. Munakata, T.K. Sowa and M. Maekawa, *J. Coord. Chem.*, **37**, 361 (1996); (b) J.Z. Zou, R. Liu, Z. Xu, X.Z. You and H.X.Y. Uang, *Polyhedron.*, **17**, 1863 (1998); (c) K.G. Sujit and K.B. Parimal, *Inorg. Chem.*, **42**, 8250 (2003).
11. L. Carlucci, G. Ciani, M. Moret and D.M. Proserpio, *Angew. Chem. Int. Ed.*, **39**, 1506 (2000).
12. Bruker Analytical X-Ray Systems, Inc., Madison, WI, p. 1 (1998).
13. E. Berti, F. Cecconi, C.A. Ghilardi and S. Midollini, *Inorg. Chem. Commum.*, **5**, 1041 (2002).
14. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, A Wiley-Interscience Publication, John Wiley & Sons, Inc., p. 1 (1986).
15. (a) D.H. Busch and J.C. Bailar, *J. Am. Chem. Soc.*, **75**, 4574 (1953); (b) D.H. Busch and J.C. Bailar, *J. Am. Chem. Soc.*, **78**, 716 (1956); (c) M.L. Morris and D.H. Busch, *J. Am. Chem. Soc.*, **78**, 5178 (1956).

(*Received*: 23 August 2007; *Accepted*: 6 February 2008) AJC-6303