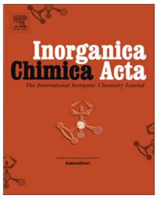
Inorganica Chimica Acta 414 (2014) 226–233

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Ionothermal syntheses, crystal structures and luminescence of three three-dimensional lanthanide-1,4-benzenedicarboxylate frameworks

Hai-Yan Cao [a], Qing-Yan Liu [a,b,*], Ming-Jun Gao [a], Yu-Ling Wang [a,b,*], Li-Li Chen [a], Ying Liu [a]

[a] College of Chemistry and Chemical Engineering and Key Laboratory of Small Functional Organic Molecule of Ministry of Education, Jiangxi Normal University, Nanchang, Jiangxi 330022, PR China
[b] Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China

ARTICLE INFO

Article history:
Received 9 January 2014
Received in revised form 8 February 2014
Accepted 11 February 2014
Available online 18 February 2014

Keywords:
Ionothermal syntheses
Lanthanide-1,4-benzenedicarboxylate frameworks
Lanthanide luminescence
Crystal structures

ABSTRACT

Ionothermal reactions of $LnCl_3$ (Ln = Sm(**1**), Eu(**2**) and Tb(**3**)) with 1,4-benzenedicarboxylic acid (H_2BDC) in 1-ethyl-3-methylimidazolium bromide (EMIM-Br) ionic liquid (IL) afforded three compounds, namely, $\{(EMIM)_2[Sm_2(BDC)_3(H_2\text{-}BDC)Cl_2]\}_n$ (**1**) and $\{(EMIM)[Ln_2(\mu_2\text{-}Cl)(BDC)_3]\}_n$ (Ln = Eu(**2**) and Tb(**3**)). These compounds consist of anionic three-dimensional frameworks and extraframework charge-balancing species of imidazolium $[EMIM]^+$ cations. Compound **1** has a 8-connected ($3^6{\cdot}4^{18}{\cdot}5^3{\cdot}6$) topology based on the dinuclear samarium(III) secondary building units. Compounds Eu(**2**) and Tb(**3**) are isomorphous and are constructed from the one-dimensional rod-shaped lanthanide-carboxylate secondary building units. Each lanthanide-carboxylate rod connects to six neighboring rods through the benzene rings of BDC^{2-} ligands to form a parallel packing of *hex* type topology. It is noted that the chloride ion deriving from lanthanide salt as the co-ligand is incorporated into the structures under the ionothermal reactions. Detailed photoluminescence studies showed all compounds exhibit typical lanthanide luminescent emissions and the Eu(III) and Tb(III) luminescence was efficiently sensitized by the organic ligand. Additionally, the use of an IL solvent for preparation of the lanthanide compounds can effectively prevent the coordination of water and organic solvent molecules from lanthanide centers. Thus the luminescence quenching resulting from the coordinated solvent molecules is avoided.

1. Introduction

Lanthanide coordination compounds are widely studied for their unique intrinsic optical and magnetic properties arising from 4f electrons of the lanthanide centers. The lanthanide compounds have potential applications in areas of science as diverse as electroluminescent devices, biological imaging probes and sensors [1–3]. The nature of the weak absorption of the forbidden f–f transitions leads to an inefficient direct excitation of lanthanide center [4]. The lanthanide emission is usually sensitized by organic antenna chromophores which strongly absorb the UV–Vis light and whose energy subsequently transfers to the lanthanide centers [5–8]. Owing to the fact that lanthanide ions possess strong affinity for hard donors such as oxygen or nitrogen atoms and high coordination numbers, almost all of the lanthanide coordination compounds obtained from hydro(solvo)thermal reactions contain the coordinated water or organic solvent molecules. The existence of the coordinated water or organic solvent molecules leads to luminescence quenching through non-radiative decay *via* vibronic coupling to vibrational states of O–H and N–H bond of the solvent molecules [9–11]. Thus it is necessary to develop a new approach to the synthesis of solvent-free lanthanide coordination compounds.

Ionic liquids (ILs) comprising only completely dissociated molecular cations and anions are a class of organic solvents [12,13]. ILs possess many intriguing characteristic physicochemical properties such as chemical and thermal stability, nonflammability and negligible vapor pressure [14], which are much different from those of the traditional organic molecular solvents. It is well-known ILs are extensively studied in separations, electrochemistry, lubrications, life sciences, and catalytically active solvents for synthetic chemistry [15–19]. Recently there is a growing interest in using ILs as solvents for preparation of crystalline materials, which is a new synthetic methodology developed—ionothermal synthesis [20–23]. The IL solvent with unique physical and chemical properties offers many advantages over traditional hydro(solvo)thermal

---

[*] Corresponding authors at: College of Chemistry and Chemical Engineering and Key Laboratory of Small Functional Organic Molecule of Ministry of Education, Jiangxi Normal University, Nanchang, Jiangxi 330022, PR China. Tel./fax: +86 791 88336372.

E-mail addresses: qyliuchem@hotmail.com (Q.-Y. Liu), ylwang@jxnu.edu.cn (Y.-L. Wang).

http://dx.doi.org/10.1016/j.ica.2014.02.014
0020-1693/© 2014 Elsevier B.V. All rights reserved.

materials synthesis methods [24–27]. In the present work the use of a IL solvent for preparation of the lanthanide compounds can effectively prevent the coordination of water and organic solvent molecules such as ethanol from Ln(III) ions. Thus the quenching effect from the coordinated solvent molecules is avoided. Herein three lanthanide compounds incorporating the 1,4-benzenedicarboxylate ligand, $\{(EMIM)_2[Sm_2(BDC)_3(H_2\text{-}BDC)Cl_2]\}_n$ (**1**) and $\{(EMIM)[Ln_2(\mu_2\text{-}Cl)(BDC)_3]\}_n$ (Ln = Eu(**2**) and Tb(**3**)) are reported. It should be noted the chloride ion derived from the starting materials of lanthanide salts incorporates into these compounds. Very recently many lanthanide compounds based on the other carboxylate ligands incorporating halide ion as co-ligand are documented [28,29,27]. All these compounds are synthesized from ionothermal reactions, which indicates that the ionothermal condition maybe in favor of the coordination of the halide ion to the lanthanide ion. Additionally, it should be noted that the chloride ion derived from lanthanide salt and the bromide ion of the IL are presented in the reaction medium simultaneously. However only the chloride ion is incorporate into the final structures, indicating the coordination ability of the chloride ion are stronger than that of bromide ion to the lanthanide ions in the present reactions.

2. Experimental

2.1. General remarks

All chemicals were purchased commercially and used without further purification. Elemental analyses were carried out on an Elemental Vario EL III analyzer and IR spectra (KBr pellets) were recorded on PerkinElmer Spectrum One. Fluorescent spectra were measured at room temperature with a single-grating Edinburgh EI920 fluorescence spectrometer.

2.2. Syntheses of compounds

2.2.1. Synthesis of $\{(EMIM)_2[Sm_2(BDC)_3(H_2\text{-}BDC)Cl_2]\}_n$ (**1**)

A mixture of $SmCl_3{\cdot}6H_2O$ (0.0912 g, 0.25 mmol), 1,4-benzenedicarboxylic acid (0.0830 g, 0.5 mmol) and 0.6 g 1-ethyl-3-methylimidazolium bromide was introduced into a Parr Teflon-lined stainless steel vessel (20 mL). The vessel was sealed and heated to 170 °C. This temperature was kept for 4 days and then the mixture was cooled naturally to form pale yellow crystals. Crystalline product was washed with ethanol, filtered, and dried at ambient temperature (yield: 0.0502 g, 33% based on $SmCl_3{\cdot}6H_2O$). *Anal.* Calc. for $C_{44}H_{40}N_4O_{16}Cl_2Sm_2$ (1252.40): C, 42.20; H, 3.22; N, 4.47. Found: C, 42.04; H, 3.14; N, 4.45%. IR spectrum (cm^{-1}, KBr pellet): 3419 (m), 3163 (w), 3066 (w), 2743 (w), 2616 (w), 2481 (w), 1686 (s), 1611 (s) 1588 (m), 1550 (m), 1503 (m), 1415 (s), 1394 (s), 1247 (w), 1174 (w), 1136 (m), 1013 (w), 940 (m), 889 (w), 867 (w), 836 (w), 827 (w), 753 (m), 622 (w), 519 (w).

2.2.2. Synthesis of $\{(EMIM)[Eu_2(\mu_2\text{-}Cl)(BDC)_3]\}_n$ (**2**)

A mixture of $EuCl_3{\cdot}6H_2O$ (0.0921 g, 0.25 mmol), 1,4-benzenedicarboxylic acid (0.0829 g, 0.5 mmol) and 0.6 g 1-ethyl-3-methylimidazolium bromide was introduced into a Parr Teflon-lined stainless steel vessel (20 mL). The vessel was sealed and heated to 170 °C. This temperature was kept for 4 days and then the mixture was cooled naturally to form pale brown crystals. Crystalline product was washed with ethanol, filtered, and dried at ambient temperature (yield: 0.0483 g, 41% based on $EuCl_3{\cdot}6H_2O$). *Anal.* Calc. for $C_{30}H_{23}N_2O_{12}ClEu_2$ (942.87): C, 38.14; H, 2.46; N, 2.97. Found: C, 38.06; H, 2.41; N, 2.93%. IR spectrum (cm^{-1}, KBr pellet): 3457 (m), 3147 (w), 3061 (w), 1688 (s), 1631 (s), 1586 (m), 1542 (m), 1507 (m), 1402 (s), 1311 (s), 1166 (m), 1137 (w), 1137 (m), 1112 (w), 1020 (m), 942 (s), 827 (m), 761 (m), 752 (m), 578 (w), 529 (w).

2.2.3. Synthesis of $\{(EMIM)[Tb_2(\mu_2\text{-}Cl)(BDC)_3]\}_n$ (**3**)

A mixture of $TbCl_3{\cdot}6H_2O$ (0.0933 g, 0.25 mmol), 1,4-benzenedicarboxylic acid (0.0831 g, 0.5 mmol) and 0.6 g 1-ethyl-3-methylimidazolium bromide was introduced into a Parr Teflon-lined stainless steel vessel (20 mL). The vessel was sealed and heated to 170 °C. This temperature was kept for 4 days and then the mixture was cooled naturally to form pale yellow crystals. Crystalline product was washed with ethanol, filtered, and dried at ambient temperature (yield: 0.0483 g, 41% based on $TbCl_3{\cdot}6H_2O$). *Anal.* Calc. for $C_{30}H_{23}N_2O_{12}ClTb_2$ (956.79): C, 37.66; H, 2.42; N, 2.93. Found: C, 37.58; H, 2.46; N, 2.98%. IR spectrum (cm^{-1}, KBr pellet): 3421 (m), 3103 (w), 3064 (w), 1681 (s), 1573 (m), 1545 (m), 1509 (m), 1422 (s), 1406 (s), 1285 (s), 1136 (m), 1167 (m), 1113 (w), 1137 (m), 1112 (w), 1018 (m), 940 (s), 881 (m), 780 (m), 757 (m), 732 (m), 563 (w), 527 (w).

2.3. X-ray crystallographic study

Single-crystal X-ray diffraction data of compounds **1**–**3** was collected on a Bruker Apex II CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. Adsorption corrections were applied using the SADABS routine [30]. The structures were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F^2 (SHELXTL Version 5.1) [31]. All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms were assigned to calculated positions. The two terminal methyl carbon atoms (C1 and C22) of the $[EMIM]^+$ cation in **1** have large thermal displacement parameters resulted from their freedom of libration. The C22 atom in **1** was refined isotropically in order to prevent it being "non-positive-definite". The extraframework $[EMIM]^+$ cation in **2** and **3** were highly disordered, and attempts to locate and refine the $[EMIM]^+$ cationic peaks were unsuccessful. The diffused electron densities resulting from these residual cations were removed from the data using the SQUEEZE routine of PLATON [32] and refined further using the data generated. The final Fourier map had a maximum and a minimum electron density of 3.381/−0.929 e $Å^{-3}$, 2.639/−3.301 e $Å^{-3}$, and 2.806/−3.270 e $Å^{-3}$ for compounds **1**, **2** and **3**, respectively. These residual peaks are within 1 Å of the lanthanide ion, which resulted from the smear effect of the lanthanide ion. The θ_{max} of compound **3** is a little bit low but the other parameters are all in typical range and reasonable. The R_1 values are defined as $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ and $wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$. The details of the crystal parameters, data collection, and refinement are summarized in Table 1, and the selected bond lengths are listed in Table 2.

3. Results and discussion

3.1. Crystal structures

3.1.1. Crystal structure of $\{(EMIM)_2[Sm_2(BDC)_3(H_2\text{-}BDC)Cl_2]\}_n$ (**1**)

Compound **1** has an anionic three-dimensional (3D) framework with $(3^6{\cdot}4^{18}{\cdot}5^3{\cdot}6)$ topology based on the 8-connected dinuclear samarium(III) secondary building units. The extraframework imidazolium cation $[EMIM]^+$ deriving from the IL acts as charge-balancing species for the anionic 3D framework. In the asymmetric unit of **1**, the half-occupied carboxylate ligand with monodentate carboxylate groups should be protonated for charge-balancing. As depicted in Fig. 1, the asymmetric unit of **1** contains one Sm(III) ion, one and a half dianionic BDC^{2-} ligands, one half neutral H_2-BDC ligand, one chloride ion, and one $[EMIM]^+$ cation. Each Sm(III) ion is nine-coordinated to two chelating carboxylate groups