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The ionothermal synthesis of metal organic frameworks, $Ln(C_9O_6H_3)((CH_3NH)_2CO)_2$, using deep eutectic solvents

Farida Himeur, Irene Stein, David S. Wragg, Alexandra M.Z. Slawin, Philip Lightfoot, Russell E. Morris*

EaStChem School of Chemistry, University of St. Andrews, Purdie Building, St. Andrews KY16 9ST, UK

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ABSTRACT

Three new isostructural materials $Ln(TMA)(DMU)_2$ ($Ln(C_9O_6H_3)((CH_3NH)_2CO)_2$; Ln: La **1**, Nd **2**, Eu **3**; TMA: trimesate, DMU: dimethylurea) have been synthesised ionothermally using a choline chloride/dimethylurea deep eutectic mixture as the solvent. Normally in ionothermal synthesis the urea portion of the deep eutectic solvent is unstable, breaking down to release ammonium cations that act as templates. In the case of **1**–**3**, however, the dimethylurea remains intact and is incorporated into the final structure.

1. Introduction

Because of their attractive features, ionic liquids [1] now rank as a major research topic in fields as diverse as organic synthesis, electrochemistry, nanotechnology and more recently in materials science. In particular, over the past five years or so, much effort has been directed towards the use of these ionic solvents as water or volatile organic compounds (VOCs) replacements and in many cases structure-directing agents in materials synthesis, especially in the synthesis of zeolites [2], and transition metal organic frameworks [3].

Lanthanide compounds are widely studied due to their significance in biological and material chemistry. As luminescence materials, they have potential commercial applications in electroluminescent displays, fluorescent lighting, X-ray imaging, scintillators, fiber-optic amplifiers and solid state lasers as well as fluorescence tags of biological molecules [4]. Among these compounds the lanthanide-organic frameworks are of special interest owing to their unique topological structures and fascinating chemical/physical properties [5]. Due to the high coordination number and more variable nature of their coordination sphere, as well as their interesting magnetic and luminescent properties, they have been applied in fields such of porosity, luminescence, magnetism and catalytic activity [5–10]. Therefore, many spectacular lanthanide-organic frameworks have been well documented recently. Although, they have been widely reported, there has not been – to the best of our knowledge – any preparation of such materials under ionothermal synthesis [11] where the ionic liquid acts as solvent and template. Indeed such technique presents many advantages over the traditional solvo/hydrothermal synthesis [11]. In addition, metal organic frameworks have many other uses, most famously in gas adsorption and storage applications [12].

In this paper we report the use of deep eutectic solvents (DESs) [13] as the reaction media for the synthesis of lanthanide-organic frameworks. DESs are a mixture of two compounds where there is a depression in the freezing point of the mixture compared with that of the separate compounds [13,14]. They can be formed between a variety of quaternary ammonium halide salts and a wide range of hydrogen bond donors such as amides, acids, amines and alcohols. In addition of having the exceptional features of ionic liquids, DESs exhibit some more significant advantages, such as relatively high polarity so they can dissolve many metal salts and metal oxides, their trivial preparation from easily available components and their relative unreactivity towards atmospheric moisture [14]. They can also be regarded as eco-friendly as they do not need any further purification, which is an important step in the preparation of most other types of ionic liquids. This step generally requires a large amount of organic solvents, raising the argument of how “green” these solvents really are.

Previous reports on the synthesis of zeolitic materials [15], organophosphate compounds [16] and transition metal organic

* Corresponding author. Tel.: +44 1334 463818; fax: +44 1334 463808.
E-mail address: rem1@st-andrews.ac.uk (R.E. Morris).

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frameworks [17] using choline chloride mixed with urea (and its derivatives) or carboxylic acids demonstrated that DESs can act as unusual reaction media, serving as template delivery agents in a controlled manner and can as well be used for the synthesis of materials that can not be prepared using other standard techniques. However, this invariably involves the breakdown of the urea or urea derivative in the DES under ionothermal conditions.

Herein we report the ionothermal synthesis of three novel materials Ln(TMA)(DMU)$_2$ (Ln: La **1**, Nd **2**, Eu **3**) (TMA-H$_3$ stands for trimesic acid, DMU for 1,3-dimethylurea) in a deep eutectic mixture of hydroxy-ethyltrimethylammonium (choline) chloride with 1,3-dimethylurea. The important feature of the work is that for the first time we show that the 1,3-dimethylurea can not only act as a template delivery agent through its breakdown, but also it can be occluded into the final material as it is, opening up even more potential for use of this type of DES.

2. Experimental

2.1. Materials and methods

All reagents were commercially available and used without further purification. The CHN analyses were performed on a Carlo Erba EA1110 CHNS Analyser. In addition, phase purity was confirmed by comparison of powder X-ray diffraction patterns simulated on the basis of the observed crystal structures to those measured experimentally on a Stoe STADI-P powder diffractometer, using X-rays Cu Kα radiation (1.5406 Å).

2.2. General synthesis

The preparation of **1**, **2** and **3** was conducted via ionothermal synthesis. The appropriate Ln(III) salt, TMA-H$_3$, choline chloride and DMU were placed into a 23 ml Teflon lined autoclave in the molar ratios of (1:1:5:10). Exact amounts and the particular lanthanide salts used are given in Table 1. The reaction vessel was then sealed and placed in 110 °C oven for six days for **1** and **2** and five days for **3**. For **2** the addition of 0.05 ml of HF (48% in water) increases the crystallinity of the product. Upon cooling to room temperature, the products were filtered, washed with methanol and dried in the air for 24 h to give colourless prism-like crystals for **1** and **3** and light pink prism-like crystals for **2**. Elemental analysis, together with comparison of the observed and simulated powder X-ray diffraction patterns, confirmed phase purity in each case (for **1**: Calcd. C, 34.48; H, 3.64; N, 10.72%. Found: C, 34.38; H, 3.28; N, 10.21%; for **2**: Calcd. C, 34.14; H, 3.60; N, 10.62%. Found: C, 33.76; H, 3.31; N, 10.12%; for **3**: Calcd. C, 33.64; H, 3.55; N, 10.70%. Found: C, 33.80; H, 3.43; N, 10.70%).

2.3. Crystallography

Compound **3** was the first material to be made with single crystals suitable for full X-ray structure determination. Compounds **1** and **2** were confirmed as isostructural with compound **3** using powder X-ray diffraction. Single crystal X-ray diffraction data for **3** were collected using Mo Kα (0.7107 Å) radiation utilising a Rigaku rotating anode single-crystal X-ray diffractometer at the University of St. Andrews. The structure was solved with standard direct methods using SHELXS and refined with least-squares minimisation techniques against F^2 using SHELXL under WinGX packages. All non-hydrogen atoms have been anisotropically refined. Hydrogen atoms for the methyl group and the N–H were fixed using, respectively, the SHELXL commands HFIX 137 and HFIX43.

Full details of the structure determination of compound **3** can be found in Supplementary data. Crystallographic data and structural refinements are summarized in Table 2.

Table 1
The lanthanide salts used and the exact amounts of other reagents added in the synthesis of compounds **1**, **2** and **3**.

	Ln(III) salt used	Ln(III) salt g (mol)	Trimesic acid g (mol)	Cholinechloride g (mol)
1	$La(NO_3)_3\cdot 6H_2O$	0.43 (1×10^{-3})	0.21 (1×10^{-3})	0.70 (5×10^{-3})
2	$NdCl_3\cdot 6H_2O$	0.36 (1×10^{-3})	0.21 (1×10^{-3})	0.70 (5×10^{-3})
3	$Eu(NO_3)_3\cdot 5H_2O$	0.43 (1×10^{-3})	0.21 (1×10^{-3})	0.70 (5×10^{-3})

2.4. Structure description

Single crystal and powder diffraction studies of the three materials reveal that compounds **1**–**3** are isomorphous and crystallise in the triclinic space group $P\overline{1}$ ($Z = 2$). Only the structure of compound **3** will be discussed in detail as an example.

The asymmetric unit of compound **3** is composed of one Eu(III) ion, one TMA and two DMU molecules. The coordination environment around each central atom can be regarded as a distorted square antiprism, made up from two carboxylate groups from two different bidentate chelating TMA, two carboxylate oxygen atoms from two different bridging TMA and two DMU oxygens totally describing an eight coordination as illustrated in Fig. 1. The Eu–O distances range from 2.284(8) to 2.526(8) Å.

In the structure, two of the COO$^-$ groups of TMA are acting as bidentate ligands to chelate two different europium ions, the remaining COO$^-$ group is acting as a bridging group between two further europium ions. Thus one TMA is connecting four different europium ions, the coordination behaviour of TMA is presented in Fig. 2. The structure consists of an infinite network spreading along the axis a, where the TMA acts as the linking agent between the neighbouring Eu atoms. Furthermore, one can observe that the basic constituting unit is the centrosymmetric dimer, consisting of two Eu atoms with two TMA acting as bridges between them (Fig. 3). The distance between two Eu atoms belonging to the same dimer is 5.295(2) Å. The infinite network is assembled by the coordination of the free carboxylate groups of the dimer to some next Eu atoms.

DMU contains both an efficient coordination site and two hydrogen-bonding functionalities. Interestingly, in **3** the DMU is directly coordinated to the europium through the oxygen atom and also provides a hydrogen bonding donor site where all the NH

Table 2
Unit cell and space group data for compounds **1**, **2** and **3**, together with final refinement details for compound **3**.

Compound	1	2	3
Formula	LaTMA(DMU)$_2$	NdTMA(DMU)$_2$	EuTMA(DMU)$_2$
FW	522.24	527.6	535.31
Space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
a/Å	9.4558(4)	9.729(3)	9.5970(40)
b/Å	10.8193(7)	11.0461(52)	10.3970(40)
c/Å	11.1193(6)	11.3065(90)	10.9840(40)
α/Å	74.432(16)	78.88(13)	74.017(3)
β/Å	65.817(14)	70.69(10)	65.569(3)
γ/Å	66.449(14)	64.705(91)	66.357(3)
V/Å^3	953.14(82)	1034.92(10)	906.18(18)
Z	2	2	2
Crystal size/mm			0.03 × 0.03 × 0.03
F(000)			527.9
Reflections collected			3307
R_{int}			0.0645
GOOF on F^2			1.131
$R1$, $wR2$ ($I > 2\sigma(I)$)			0.0657, 0.159
$R1$, $wR2$ (all data)			0.085, 0.173