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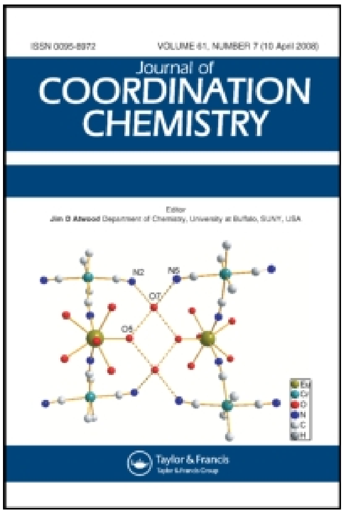

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New nano-particle La(III) supramolecular compound as a precursor for preparation of lanthanum oxybromide-, hydroxide-, and oxide-nanostructures

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New nano-particle La(III) supramolecular compound as a precursor for preparation of lanthanum oxybromide-, hydroxide-, and oxide-nanostructures

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Nano-particles of a new La(III) supramolecular compound $[La(4,4'\text{-bipy})(H_2O)_2(NO_3)_{3.75}Br_{0.25}]\cdot(4,4'\text{-Hbipy})$ (**1**), have been synthesized from reaction of 4,4′-bipy with $La(NO_3)_3$ and NaBr by the sonochemical method. For the first time LaOBr, $La(OH)_3$ and La_2O_3 nano-structures were prepared from $[La(4,4'\text{-bipy})(H_2O)_2(NO_3)_{3.75}Br_{0.25}]\cdot(4,4'\text{-Hbipy})$ (**1**) by calcination at 400, 500, and 700°C, respectively. The structure of **1** was determined by X-ray crystallography and the nano-structures were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Thermal stabilities of nano and crystal samples of **1** were studied and compared with each other.

Keywords: Supramolecular; Lanthanum oxybromide; Lanthanum hydroxide; Lanthanum oxide; Nanoparticle

1. Introduction

Chemical and physical properties of solid materials strongly depend on both the size and shape of the microscopic particles from which they are made. This is especially true for materials with morphological features smaller than a micron in at least one dimension, commonly called nano-scale materials, or simply nanomaterials. If exact control of size and shape of a compound is possible, their chemical and physical properties can be altered as desired [1, 2]. The need for development of synthetic methods in which the size and morphologies of nanostructured materials can be controlled becomes obvious – both from the viewpoint of basic sciences as well as applied technology [3–7]. The construction of supramolecular complexes developed rapidly, owing to their interesting molecular topologies and crystal packing motifs along with potential applications as functional materials [8–21]. The coordination chemistry of lanthanide complexes is rich in diversity because of the high coordination numbers (normally 6–10), the lanthanide contraction and the unusual structures and properties [22–25]. However, research about crystal engineering of lanthanide complexes is limited compared with transition metal ions [26–28]. In contrast to

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inorganic materials, specific syntheses of nano-structured supramolecular complexes is surprisingly sparse. Nano-structured supramolecular complexes as precursors for the preparation of inorganic nanomaterials has not yet been investigated thoroughly. This article focuses on the simple synthetic preparation of nano-powders of a new La(III) supramolecular complex, $[La(4,4'\text{-bipy})(H_2O)_2(NO_3)_{3.75}Br_{0.25}]\cdot(4,4'\text{-Hbipy})$ (**1**), and conversion into nanostructured LaOBr, $La(OH)_3$ and La_2O_3 by calcination at moderately elevated temperatures. Lanthanum oxide (La_2O_3) ultrafine powders have attractive properties for industrial and technological applications [29–40].

2. Experimental

All reagents for synthesis and analysis were commercially available and used as received. A multiwave ultrasonic generator (Sonicator_3000; Misonix, Inc., Farmingdale, NY, USA) equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation. Microanalyses were carried out using a Heraeus CHN–O– Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. The thermal behavior was measured with a PL-STA 1500 apparatus. Crystallographic measurements were made using a Bruker APEX area-detector diffractometer. Intensity data were collected using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. The intensity data were collected within the range $2.05^\circ \le \theta \le 28.28^\circ$ for a crystal of dimension $0.26 \times 0.20 \times 0.20\,mm^3$. Crystal data: formula, $C_{20}H_{21}Br_{0.25}LaN_{7.75}O_{13.25}$; $M_r = 740.83\,g\,M^{-1}$; orthorhombic system, space group $P2_12_12_1$; $a = 7.2357(6)$, $b = 18.4006(14)$, $c = 19.9058(16)\,Å$, $V = 2650.3(4)\,Å^3$; $D_c = 1.857\,Mg\,m^{-3}$ ($Z = 4$); $F(000) = 1468$; $R(wR) = 0.0288(0.0468)$ for 6575 reflections, with $I > 2\sigma(I)$; $R(wR) = 0.0346\ (0.0488)$ for all data. Structure solution and refinement was accomplished using SHELXL-97 program packages [41]. Two of the nitrates show disorder with bromide with 19.5 (2) and 6.9 (2)% of bromide, respectively. The overlapping Br and N atoms were set to have identical ADPs. The molecular structure plot and simulated XRD powder pattern based on single crystal data were prepared using Mercury software [42]. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer of X'pert Company with monochromated Cu-Kα radiation. The crystallite sizes of selected samples were estimated using the Sherrer method. The samples were characterized with a scanning electron microscope with gold coating.

To prepare nanoparticles of $[La(4,4'\text{-bipy})(H_2O)_2(NO_3)_{3.75}Br_{0.25}]\cdot(4,4'\text{-Hbipy})$ (**1**), a proper amount of the solution of $La(NO_3)_3$ (10 mL, 0.1 M) and NaBr (10 mL, 0.1 M) in EtOH was positioned in a high-density ultrasonic probe, operating at 20 kHz with a maximum power output of 600 W then into this solution, a proper volume of 4,4'-bipy solution (10 mL, 0.1 M) was added in drops. The obtained precipitates were filtered, washed with EtOH and then dried (Found C(%): 32.40, H: 2.70, N: 14.30: Calcd for $C_{20}H_{21}Br_{0.25}LaN_{7.75}O_{13.25}$(%): C: 32.39, H: 2.83, N: 14.64). IR (cm^{-1}) bands: 3520 (br), 3085 (w), 1626 (w), 1593 (m), 1435 (vs), 1382 (vs), 1212 (w), 1031 (vw), 1022 (m), 810 (s), 722 (w), 691 (w), 614 (w), 556 (w).

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To isolate the single crystals of [La(4,4′-bipy)(H_2O)$_2$(NO_3)$_{3.75}$Br$_{0.25}$] · (4,4′-Hbipy) (**1**), 4,4′-bipy (1 mM, 0.1 56g), NaBr (1 mM, 0.103 g) and La(NO_3)$_3$ · 3H_2O (0.5 mM, 0.159 g) were placed in the main arm of a branched tube. Methanol was carefully added to fill the arms, the tube was sealed and the ligand-containing arm was immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After 2–3 days, yellow crystals (d.p $> 300°$C) deposited in the cooler arm were isolated, filtered off, washed with acetone and ether and air dried (0.37 g, yield 50%) (Found C(%): 32.50, H: 2.60,N: 14.50: Calcd for $C_{20}H_{21}Br_{0.25}LaN_{7.75}O_{13.25}$(%): C: 32.39, H: 2.83, N: 14.64%). IR (cm^{-1}) bands: 3503 (br), 1626 (w), 1589 (m), 1435 (vs), 1382 (vs), 1204 (w), 1031 (m), 1022 (m), 808 (s), 726 (w), 691 (w), 614 (m), 560 (w).

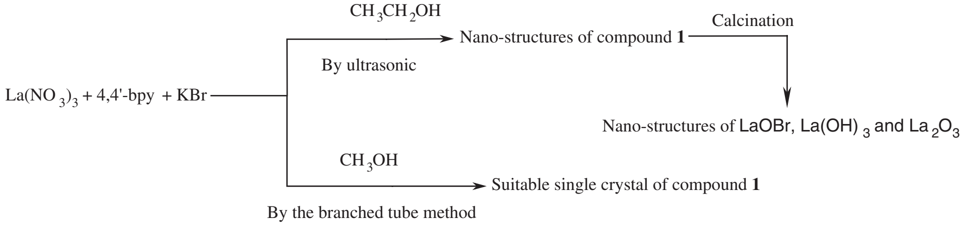
3. Results and discussion

Scheme 1 shows the reaction between La(NO_3)$_3$, 4,4′-bipy and KBr by two different methods.

The compound **1** is air-stable and high-melting solid soluble in DMSO. The IR spectra of **1** shows characteristic absorption bands for the 4,4′-bipy ligands and nitrate. The absorption bands with variable intensity in the frequency range 1400–1580 cm^{-1} correspond to ring vibrations of the py of 4,4′-bipy; $\nu(NO_3)$ is at *ca* 1382 cm^{-1}.

XRD patterns of typical samples of **1** prepared by the branched tube and sonochemical process show acceptable matches to the XRD pattern simulated from the single crystal X-ray data, indicating the presence of only one crystalline phase in the samples prepared using the branched tube and sonochemical process (Supplementary material). Estimated from the Sherrer formula for calculation of particle sizes from the broadening of the XRD peaks ($D = 0.891\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively [43]), the average size of the particles was found to be around 80 nm, in agreement with the value obtained from the SEM images (figure 1). We used other solvents such as water and acetonitrile by the sonochemical process, but particle sizes were not in nano scales.

Single crystal X-ray analysis reveals that [La(4,4′-bipy)(H_2O)$_2$(NO_3)$_{3.75}$Br$_{0.25}$] · (4,4′-Hbipy) (**1**) crystallizes in an orthorhombic setting with space group of $P2_12_12_1$. Determination of the structure of **1** by X-ray crystallography showed the complex (figure 2) consists of monomeric units. The lanthanums are linked by 1 nitrogen atom of 4,4′-bipy ligand and 10 oxygens of nitrate and water and can be considered to be



Scheme 1. Materials produced and synthetic methods.

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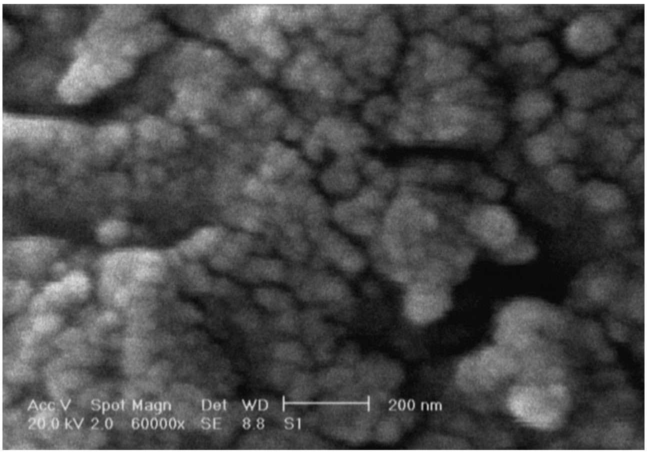

Figure 1. SEM images of compound **1** nanopowders.

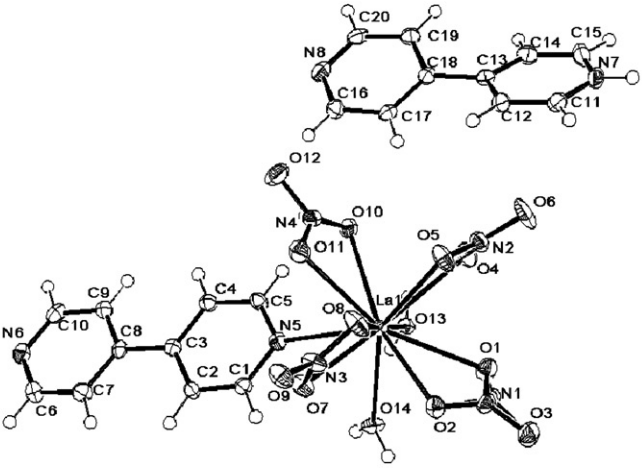

Figure 2. X-ray crystal structure of Compound **1** (30% thermal displacement ellipsoids).
Selected bond lengths (Å): La1–O1 2.639, La1–O2 2.664, La1–O4 2.735, La1–O5 2.571, La1–O7 2.627, La1–O8 2.711, La1–O10 2.604, La1–O11 2.654, La1–O13 2.574, La1–O14 2.472, La1–N5 2.816.
Selected bond angles (°): O8–La1–O4 109.30, O14–La1–N5 69.83, O5–La1–N5 145.94, O13–La1–N5 74.60, O10–La1–N5 72.15, O7–La1–N5 71.40, O1–La1–N5 139.56, O11–La1–N5 69.83, O2–La1–N5 128.62, O8–La1–N5 109.90, O4–La1–N5 126.97, O14–La1–O5 144.11, O14–La1–O13 70.57, O5–La1–O13 113.53, O14–La1–O10 133.38, O5–La1–O10 78.41, O13–La1–O10 74.15, O14–La1–O7 74.29, O(5)–La1–O7 108.91, O13–La1–O7 137.52, O10–La1–O7 117.17, O14–La1–O1 74.05, O5–La1–O1 72.60, O13–La1–O1 76.79, O10–La1–O1 125.61, O7–La1–O1 115.43, O14–La1–O11 133.24, O5–La1–O11 78.02, O(13)–La1–O11 119.02, O10–La1–O11 48.70, O7–La(1)–O(11) 71.26, O1–La1–O11 150.45, O14 –La1–O2 69.36, O5–La1–O2 78.57, O13–La1–O2 118.04, O10–La1–O2 156.84, O7–La1–O2 68.56, O1–La1–O2 47.92, O11–La1–O2 122.92, O14–La1–O8 113.09, O5–La1–O8 61.32, O13–La1–O8 1724.8, O10–La1–O8 104.48, O7–La1–O8 47.60, O1–La1–O8 100.45, O11–La1–O8 61.54, O2–La1–O8 61.49, O14–La1–O4 122.78, O5–La1–O4 47.97, O13–La1–O4 65.56, O10–La1–O4 64.50, O7–La1–O4 156.87, O1–La1–O4 61.80, O11–La1–O4 100.21, O2–La1–O4 101.17.

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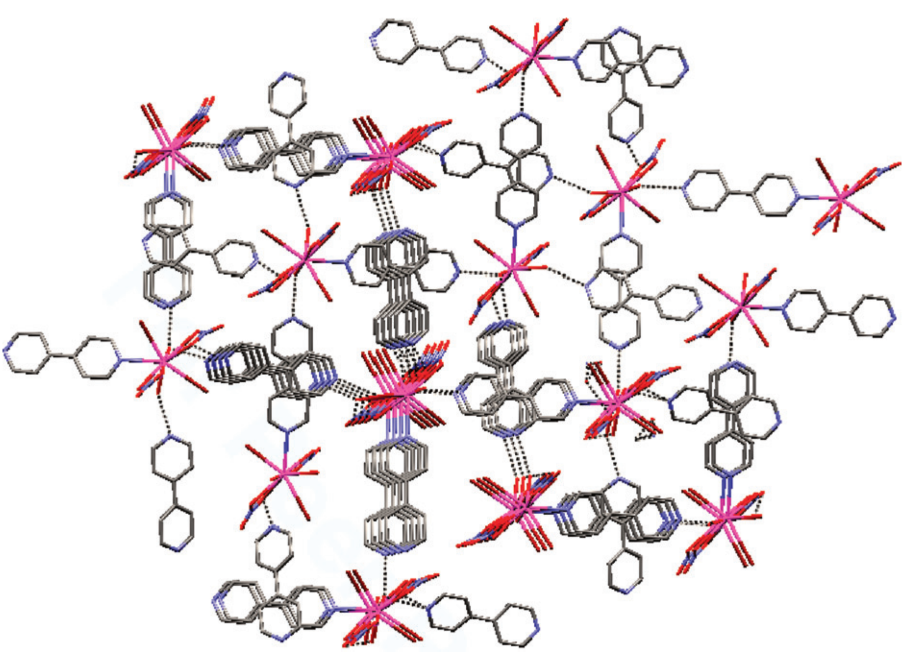

Figure 3. A fragment of the 3-D network formed by hydrogen bonds in Compound **1**.

11-coordinate with NO_{10} donor array. One nitrogen of 4,4′-bipy is not coordinated to La (figure 2) and is a less common unidentate ligand. There is one other protonated 4,4′-bipy that was not coordinated to La. The nitrogens from both the coordinated and uncoordinated 4,4′-bipy ligands and oxygen of water are involved in hydrogen bonding and consequently, the two perpendicular anionic and cationic components form a 3-D network (figure 3). π–π stacking [44, 45] interactions between aromatic rings of 4,4′-bipy belonging to dimeric units in **1** exist. The py groups of 4,4′-bipy are almost parallel and this parallel array of the planes of the aromatic moieties indicates face-to-face π-stacking [46]. The centroid–centroid distance of py groups is 3.94 Å and the angle between the ring normal and the centroid vectors is 100.56°.

Thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 34 and 610°C in a static atmosphere of N_2 to examine the thermal stability of the new compound at crystal and nano forms (Supplementary material). For the crystal, the first weight loss at 170°C corresponds to release of aqua ligands (observed: 4.73%; calculated: 4.86%). The second step about 220–340°C corresponds to removal of bipy and H-bipy (observed: 47.2%; calculated: 48.96%). Further heating to 610°C gives a slow weight loss. The final residual weight is 25.13% (calculated: 25.15%) corresponding to La_2O_3. The DTA curve displays two endothermic peaks at 156 and 275°C and a distinct exothermic peak at 337°C.

For the nano sample, the first weight loss in the range 150°C are loss of aqua ligands (observed: 5.73%; calculated: 4.86%). The next step (about 210–270°C) corresponds to the removal of two organic ligands (observed: 47.2%; calculated 47%). The remaining weight loss occurs in the 270–340°C region, corresponding to decomposition to $La(NO_3)_3$ (observed: 53.4%; calculated: 53.9%). Further heating to 600°C, the final

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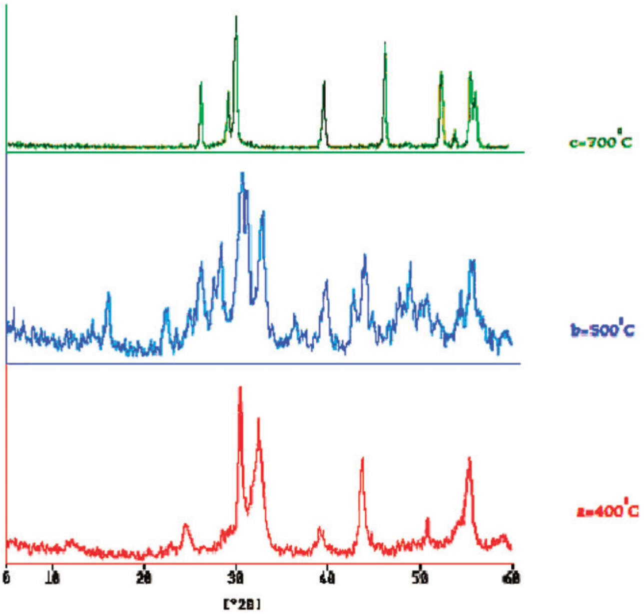

Figure 4. XRD patterns of calcinated **1** at (a) 400°C, (b) 500°C, and (c) 700°C.

residual weight is 27.3% (calculated: 25.15%) corresponding to the La_2O_3. The DTA curve displays three endothermic peaks at 147, 225, and 246°C and an exothermic peak at 360°C. Decomposition of **1** at nano size starts about 20 degrees earlier than its single crystals, probably due to more heat needed to decompose the bulk samples.

Nano-structures of LaOBr, $La(OH)_3$, and La_2O_3 have been generated by thermal decomposition of nano-structured **1** at 400, 500, and 700°C, respectively (figure 4). Powder X-ray diffraction of the residue at 400, 500, and 700°C indicates the formation of LaOBr (figure 4a) and JCPDS Card No. 47-1676), $La(OH)_3$ (figure 4b) and JCPDS Card No. 36-1481) and La_2O_3 (figure 4c) and JCPDS Card No. 05-0602). SEM images of nanostructures La_2O_3 obtained from calcination of nano-structured **1** under air at 700°C are provided in Supplementary material.

4. Conclusions

Nano-particles of a new La^{III} supramolecular compound $[La(4,4'\text{-bipy})(H_2O)_2(NO_3)_{3.75}Br_{0.25}]\cdot(4,4'\text{-Hbipy})$ (**1**) were synthesized by sonochemical method and characterized by IR, XRD and SEM. The structure of **1** was determined by X-ray crystallography. Reduction of the particle size of the supramolecular compound to a few dozen nanometers results in a lower thermal stability when compared to single crystalline samples. Calcinations of **1** under three different temperatures (400, 500, and 700°C) produces LaOBr, $La(OH)_3$ and La_2O_3, respectively. This study demonstrates that supramolecular compounds may be suitable precursors for the preparation of nanoscale materials with interesting morphologies and different products. To the best of our knowledge, this is the first report on the synthesis of nano-structured LaOBr,

$La(OH)_3$ and La_2O_3 from a supramolecular precursor. From this perspective, further systematic studies of other supramolecular compounds with La(III) and different metal ions are ongoing in our laboratory, which may offer new insight into metal-organic supramolecular assembly and nanochemistry.

Supplementary material

The crystallographic data (excluding structure factors) for **1** has been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-687684. Copies of the data can be obtained, free of charge, by application to *CCDC*, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: data_request@ccdc.cam.ac.uk), or *via* the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

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