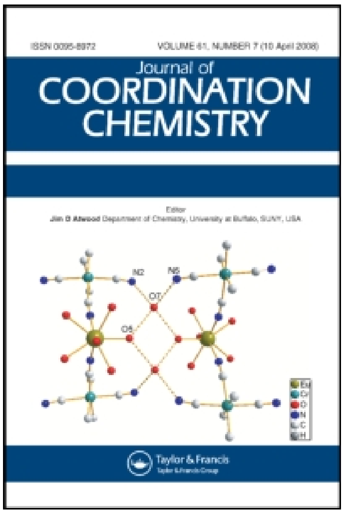

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Two metal-organic La(III) compounds as precursors for preparation of nano-sized LaO(OH) and $La(OH)_3$

Somayeh Khanjani[a]; Ali Morsali[a]
[a] Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, Tehran, Islamic Republic of Iran

To cite this Article Khanjani, Somayeh and Morsali, Ali(2009) 'Two metal-organic La(III) compounds as precursors for preparation of nano-sized LaO(OH) and $La(OH)_3$', Journal of Coordination Chemistry, 62: 22, 3642 — 3650, First published on: 10 December 2009 (iFirst)

To link to this Article: DOI: 10.1080/00958970903134290

URL: http://dx.doi.org/10.1080/00958970903134290

Journal of Coordination Chemistry
Vol. 62, No. 22, 20 November 2009, 3642–3650

Two metal-organic La(III) compounds as precursors for preparation of nano-sized LaO(OH) and La$(OH)_3$

SOMAYEH KHANJANI and ALI MORSALI*

Department of Chemistry, Faculty of Sciences, Tarbiat Modares University,
PO Box 14155-4838, Tehran, Islamic Republic of Iran

(*Received 18 February 2009; in final form 28 April 2009*)

Two La(III) complexes with 1,2-di(4-pyridyl)ethene (bpe), $[La(NO_3)_4(H_2O)_2] \cdot (Hbpe) \cdot 0.5(bpe)$ (**1**) and $\{[La(NO_3)_2(NCS)_3(H_2O)_2][La(NO_3)_3(NCS)_2(H_2O)_2] \cdot 2(Hbpe)\}$ (**2**) have been synthesized, characterized by IR spectroscopy, and structurally analyzed by single-crystal X-ray diffraction. Thermal stabilities of these compounds were studied by thermal gravimetric and differential thermal analyses. The bpe in **1** and **2** is not coordinated to La(III) and the uncoordinated pyridyl interacts via N–H $\cdots$ O, O–H $\cdots$ O and N–H $\cdots$ N hydrogen bonds with adjacent molecules in **1** and **2**. Finally they are all packed into 3-D frameworks through complicated hydrogen bonding and π–π stacking interactions. Nano-sized LaO(OH) and $La(OH)_3$ were obtained by calcination of **1** and **2** at 700°C under air.

Keywords: Lanthanum(III); 1,2-Di(4-pyridyl)ethene; Nanoparticle; Thermal study

1. Introduction

Crystal engineering and molecular recognition are current challenges in developing materials science [1–8]. Supramolecular architectures (1-D chain, 2-D sheet, or 3-D network) can be achieved by controlling noncovalent interactions between the ligands [9–21]. Hydrogen bonding, metal–ligand coordination, and π–π stacking have been employed as synthetic paradigms. The coordination chemistry of lanthanide complexes is rich in diversity because of the high coordination numbers (normally 6–10), the lanthanide contraction, and unusual structures and properties [22–29]. Lanthanide ions are good choices to build multi-dimensional compounds due to their tendency to adopt high coordination numbers, which can be employed for construction of high-dimensional and high-connected frameworks. The use of supramolecular complexes as precursors for the preparation of inorganic nanomaterials has not been thoroughly investigated. This article focuses on the preparation and description of two new La^{III} complexes with 1,2-di(4-pyridyl)ethene (bpe): $[La(NO_3)_4(H_2O)_2] \cdot (Hbpe) \cdot 0.5(bpe)$ (**1**) and $\{[La(NO_3)_2(NCS)_3(H_2O)_2][La(NO_3)_3(NCS)_2(H_2O)_2] \cdot 2(Hbpe)\}$ (**2**) and on their

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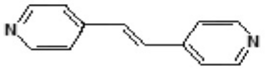
*Corresponding author. Email: morsali_a@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970903134290

conversion into nanostructured LaO(OH) and $La(OH)_3$ by calcination at moderately elevated temperatures. Compound **2** is very interesting and has two different complexes in one system.



1,2-di(4-pyridyl)ethene (bpe)

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Microanalyses were carried out using a Heraeus CHN–O–Rapid analyzer. The thermal behavior was measured with a PL-STA 1500 apparatus. Crystallographic measurements were made using a Bruker Smart APEX area-detector diffractometer. The intensity data were collected using graphite monochromated MoKα radiation. Accurate unit cell parameters and orientation matrices were obtained from least-squares refinement using SMART [30] and SAINT [31], and the data were integrated using SAINT [31]. The structures have been solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELXTL [32]. Molecular structure plots were prepared using ORTEPIII and Mercury [33].

One of the protonated 1,2-di(4-pyridyl)ethene molecules in **2** is disordered over two positions. The two moieties were restrained to have similar geometries and equivalent atoms were constrained to have identical ADPs. Also, two thiocyanate ligands in **2** are each disordered over two positions with occupancy ratios of 0.781(2) to 0.219(2) and 0.63(4) to 0.37(4), respectively. N–C and C–S distances were restrained to be similar for all thiocyanate units and atoms. C25 and C25b (which overlap significantly) were constrained to have identical ADPs and restrained to be approximately isotropic.

2.2. *Preparation of $[La(NO_3)_4(H_2O)_2]\cdot(Hbpe)\cdot 0.5(bpe)$ (1)*

1,2-Di(4-pyridyl)ethene (bpe) (0.182 g, 1 mmol) and lanthanum(III) nitrate (0.433 g, 1 mmol) were placed in the main arm of the branched tube. Acetonitrile 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 5 days, orange crystals deposited in the cooler arm were filtered off, washed with acetone and ether and air dried (0.65 g, yield 47%), d.p. >300°C. (Found C: 30.90, H: 2.80, N: 14.20; calculated for $C_{36}H_{40}La_2N_{14}O_{28}$: C: 30.97, H: 2.86, N: 14.05%). IR (KBr) (ν_{max}, cm^{-1}): 3420(m), 3035(w), 2835(br), 1592(m), 1481(s), 1310(vs), 1276(w), 1023(w), 973(w), 815(m), 729(w).

2.3. *Preparation of {[La(NO$_3$)$_2$(NCS)$_3$(H$_2$O)$_2$][La(NO$_3$)$_3$(NCS)$_2$(H$_2$O)2]·2(Hbpe)} (2)*

Complex **2** was prepared *via* the same method used for **1**.

Product (2): Reactant materials: bpe, lanthanum(III) nitrate and ammonium thiocyanate (1 : 1 : 1), pink crystals, d.p. > 300°C (0.92 g, yield 55%). (Found C: 37.70, H: 3.10, N: 14.90; calculated for $C_{53}H_{52}La_2N_{18}O_{19}S_5$: C: 37.79, H: 3.089, N: 14.97%).

IR (KBr) (ν_{max}, cm^{-1}): 3455(w), 3055(w), 2890(w), 1994(vs), 1620(m), 1593(m), 1496(w), 1407(m), 1334(m), 1310(m), 1193(w), 1055(w), 1024(w), 813(m), 729(w), 643(w), 537(m), 507(w).

3. Results and discussion

1,2-Di(4-pyridyl)ethene (bpe) and lanthanum(III) nitrate or a mixture of lanthanum(III) nitrate and ammonium thiocyanate were reacted in acetonitrile. Diffusion along a thermal gradient (the branched tube method) produced two new lanthanum(III) complexes, $[La(NO_3)_4(H_2O)_2]_2 \cdot (Hbpe)_2 \cdot (bpe)$ (**1**) and $\{[La(NO_3)_2(NCS)_3(H_2O)_2][La(NO_3)_3(NCS)_2(H_2O)_2] \cdot 2(Hbpe)\}$ (**2**) as orange and pink crystals, respectively. Both compounds are air-stable and high-melting solids soluble in DMSO. The IR spectra of **1** and **2** show the abortion bands in the region 3500–3100 cm^{-1} corresponding to coordinated water [34]. Relatively weak absorption bands around 3025–3055 cm^{-1} in IR spectra are due to C–H of aromatic ring hydrogens. Vibration of NO_3^- in **1** and **2** are strong peaks at 1481–1310 cm^{-1} [35]. In **2** the strong sharp band at 1994 cm^{-1} is due to $\nu(SCN^-)$.

Single-crystal X-ray diffraction (table 1 contains structure solution parameters and table 2 selected bond distances and angles) revealed that **1** is a dimer containing a La–O–La bond in which the asymmetric unit consists of two lanthanums coordinated by three oxygen from nitrate and one bridging oxygen from nitrate and two aqua ligands. There are two uncoordinated, monoprotonated bpe molecules (figure 1a). The 3-D supramolecular network in **1** is formed by face-to-face π–π stacking between bpe with distances of 3.682(1) Å and hydrogen bonding interactions (figure 1b). The lengths and angles of hydrogen bond parameters are shown in table S1.

Complex **2** exhibits, figure 2(a), two different complexes with unique La centers and different coordination environments, La(1) and La(2). La(1) is coordinated by three nitrates, two aquas, and two nitrogens of thiocyanate. La(2) is coordinated by two nitrates, two aquas, and three nitrogens of thiocyanate ligands. There are two monoprotonated bpe not coordinated to lanthanum. In **2** hydrogen bonds extended the structure into a 3D supramolecular network (figure 2b and table S1).

There are classical $N_{bpe} \cdots H\text{–}O_{water}$, $O_{nitrate} \cdots H\text{–}O_{water}$ and $O_{nitrate} \cdots H\text{–}N_{Hbpe}$ hydrogen bonds in **1** as well as classical $N_{bpe} \cdots H\text{–}O_{water}$, $N_{Hbpe} \cdots H\text{–}N_{Hbpe}$ and $O_{nitrate} \cdots H\text{–}O_{water}$ hydrogen bonds in **2** between hydrogens of $Hbpe^+$ and water ligands with oxygen and nitrogens of nitrate and bpe (table S1). The hydrogens of coordinated $Hbpe^+$ and water ligands are involved in hydrogen bonding, with N from uncoordinated bpe molecules and with O atoms from nitrate. The reported $N\text{–}H \cdots O$,

Table 1. Crystal data and structure refinement for $[La(NO_3)_4(H_2O)_2]\cdot(Hbpe)\cdot0.5(bpe)$ (**1**) and $\{[La(NO_3)_2(NCS)_3(H_2O)_2][La(NO_3)_3(NCS)_2(H_2O)_2]\cdot2(Hbpe)\}$ (**2**).

Identification code	**1**	**2**
Empirical formula	$C_{36}H_{40}La_2N_{14}O_{28}$	$C_{53}H_{52}La_2N_{18}O_{19}S_5$
Formula weight	1394.64	1682.85
Temperature (°C)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	*Pba2*
Unit cell dimensions (Å, °)		
a	10.0264(5)	17.4688(13)
b	10.5965(6)	17.6088 (13)
c	12.8379(7)	10.8003451(8)
α	104.9600(10)	90
β	105.7600(10)	90
γ	94.4370(10)	90
Volume (Å^3), *Z*	1252.14(12), 1	3322.22(4), 2
Calculated density ($g\,cm^{-3}$)	1.850	1.682
Absorption coefficient (mm^{-1})	1.791	1.509
Crystal size (mm^3)	$0.33\times0.21\times0.14$	$0.44\times0.38\times0.21$
θ range for data collection (°)	1.72–28.28	1.64–31.65
Limiting Indices	$-13\le h\le13$; $-14\le k\le14$; $-17\le l\le17$	$-25\le h\le25$; $-25\le k\le24$; $-15\le l\le15$
Reflections collected	6710	10479
Independent reflection	5937	9964
Absorption correction	ω scan	ω scan
Max. and min. transmission	0.6215 and 0.7462	0.6528 and 0.7462
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6710/4/373	10479/57/516
Goodness-of-fit on F^2	1.043	1.056
Final *R* indices $[I>2\sigma(I)]$	$R_1=0.0194$, $wR_2=0.0469$	$R_1=0.0232$, $wR_2=0.0613$
R indices (all data)	$R_1=0.0204$, $wR_2=0.0475$	$R_1=0.0248$, $wR_2=0.0622$
Largest difference peak and hole (e Å^{-3})	0.867 and −0.483	1.421 and −1.339

Table 2. Bond lengths (Å) and angles (°) for **1** and **2**.

1		**2**	
La1–O1	2.6842(13)	La1–N8	2.547(2)
La1–O2	2.5963(12)	La1–O1	2.683(15)
La1–O4	2.5780(12)	La1–O3	2.497(14)
La1–O6	2.6656(13)	La1–O4	2.645(16)
La1–O7	2.6296(13)	La1–O5	2.763(15)
La1–O8	2.6640(12)	La1–O6	2.589(14)
La1–O10	2.7293(12)	La1–O8	2.615(18)
La1–O13	2.5072(13)	La1–O10	2.595(17)
La1–O14	2.4753(13)	La2–N5	2.522(4)
O14–La1–O13	68.04(4)	La2–N6	2.616(2)
O14–La1–O4	121.66(4)	N8–La1–O6	80.83(6)
O13–La1–O4	69.73(4)	N8–La1–O10	70.07(6)
O14–La1–O2	72.99(4)	N8–La1–O8	134.54(6)
O14–La1–O7	116.24(4)	N8–La1–O5	115.23(6)
O13–La1–O7	142.19(4)	O6–La1–O10	73.86(5)
O4–La1–O7	78.23(4)	O6–La1–O8	131.00(5)
O2–La1–O7	144.84(4)	O6–La1–O5	136.25(5)
O14–La1–O8	68.27(4)	O10–La1–O5	70.37(5)
O13–La1–O8	123.85(4)	O3–La2–N5	141.65(5)
O4–La1–O8	106.88(4)	N6–La2–O4	67.97(8)
O2–La1–O8	123.85(4)	N5–La2–O4	75.64(4)

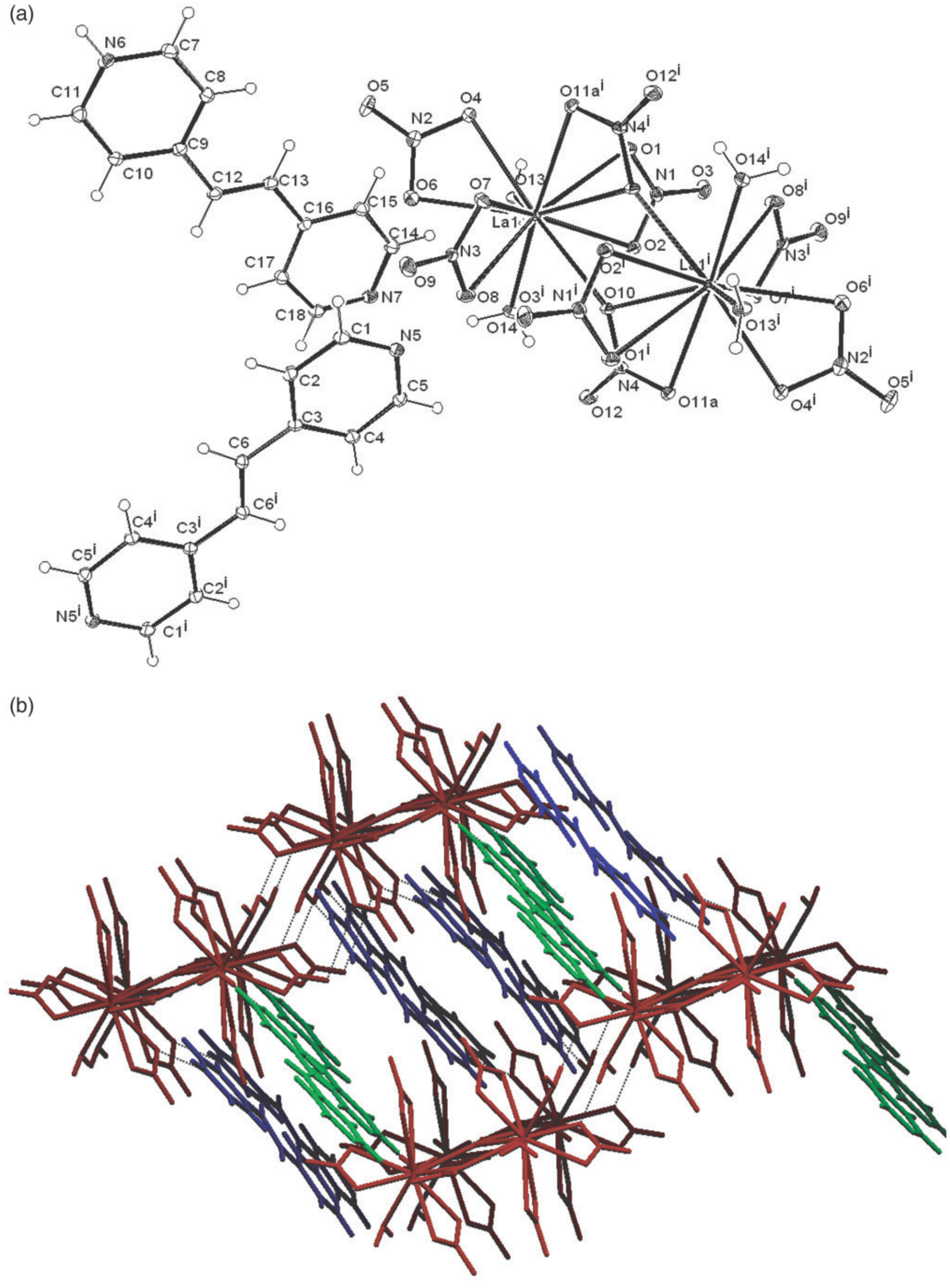


Figure 1. (a) ORTEP view and (b) 3D supramolecular architecture of **1**. i: $-x$, $-y$, $-z$.

O–H$\cdots$O and N–H$\cdots$N separations range in other La(III) supramolecular compounds is 3.20–4.00 Å [22–29].

In order to examine the thermal stability of **1** and **2**, thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out between 40°C and 610°C under

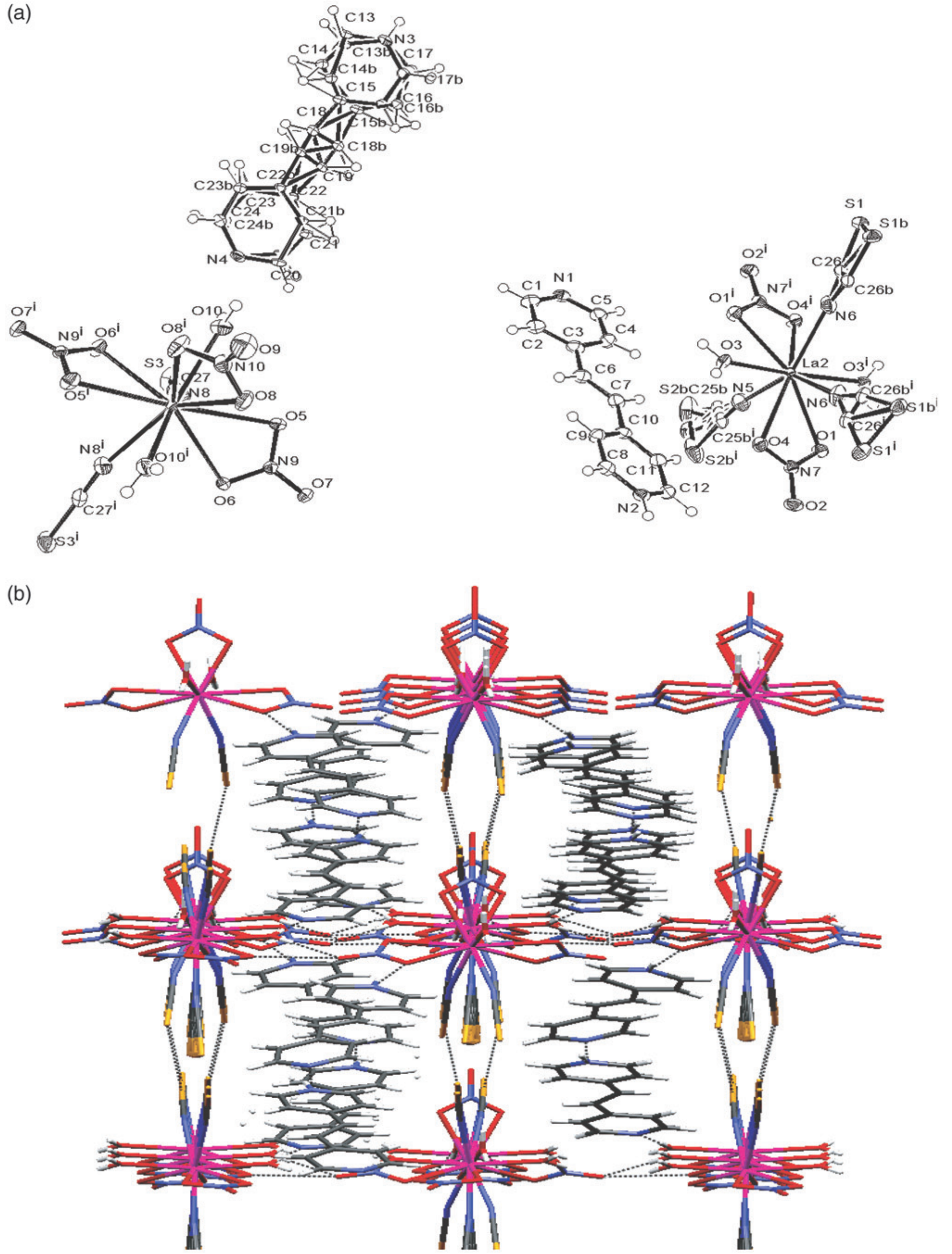


Figure 2. (a) ORTEP view and (b) showing the 3D network via π–π stacking and hydrogen bonding interactions in **2**. i: $-x$, $-y$, z.

nitrogen atmosphere (Supplemental material). Compound **1** is stable to 130°C at which temperature H_2O molecules are removed. The solid residue formed at around 175°C is suggested to be the H_2O-free compound (observed 2.7, Calcd 2.5%). At higher temperatures, further decomposition occurs to ultimately give a solid that appears to be

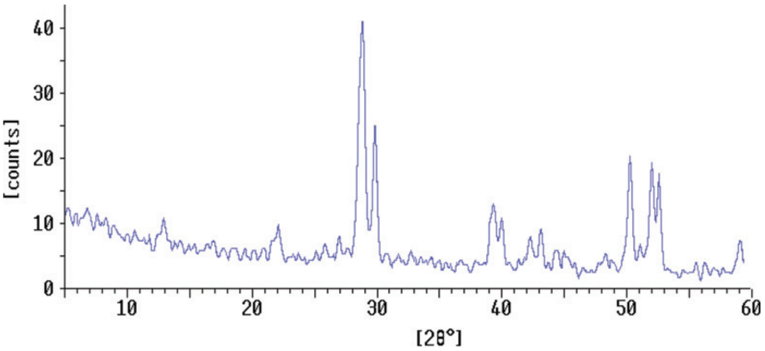


Figure 3. XRD patterns LaO(OH) prepared by calcination of **1** under air atmosphere.

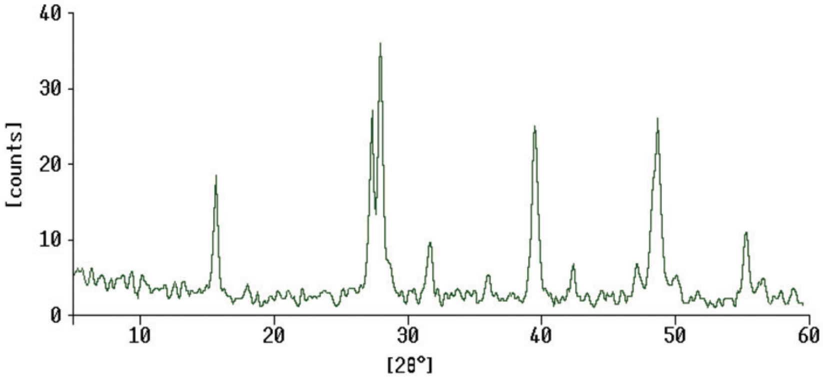


Figure 4. XRD patterns $La(OH)_3$ prepared by calcination of **2** under air atmosphere.

LaO(OH) (observed 26%, Calcd 25%). The DTA curve of **1** indicates that decomposition takes place with one endothermic effect at 146°C and three exothermic effects at 313°C, 430°C and 490°C. For **2** the first weight loss at 196°C corresponds to release of aqua ligands (observed 3%, Calcd 2.5%). Decomposition of water-free compound takes place at 290°C and the final residual weight is 21.35% (Calcd 22.00%) corresponding to $La(OH)_3$. The DTA curve displays one endothermic peak at 204°C and five exothermic peaks at 243°C, 302°C, 423°C, 503°C and 595°C.

Nano-sized LaO(OH) and $La(OH)_3$ have been generated by thermal decomposition of **1** and **2** at 700°C, respectively. Powder X-ray diffraction of the residue at 700°C indicates formation of LaO(OH) (figure 3 and JCPDS Card No. 13-0436) and $La(OH)_3$ (figure 4 and JCPDS Card No. 36-1481). Figure 5 shows the SEM image of nanostructures $La(OH)_3$ obtained from calcination of **1** under air at 700°C.

4. Conclusion

Two new La(III) complexes with 1,2-di(4-pyridyl)ethene (bpe), $[La(NO_3)_4(H_2O)_2] \cdot (Hbpe) \cdot 0.5(bpe)$ (**1**) and $\{[La(NO_3)_2(NCS)_3(H_2O)_2][La(NO_3)_3(NCS)_2(H_2O)_2] \cdot 2(Hbpe)\}$ (**2**) have

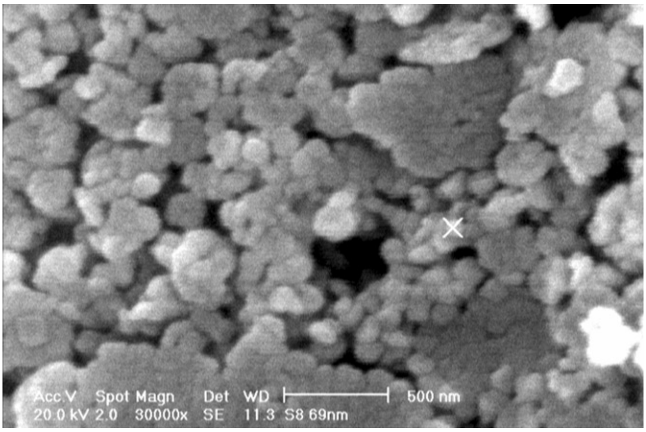


Figure 5. SEM photograph of LaO(OH) nanoparticles (produced by calcination of **1** under air atmosphere).

been characterized by CHN elemental analysis. The thermal stabilities of these compounds were studied by TG and DTA. The potentially bidentate bpe is not coordinated in the complexes, but are protonated. In **1** and **2** extensive hydrogen bondings, $N_{bpe}\cdots H\text{–}O_{water}$, $O_{nitrate}\cdots H\text{–}O_{water}$, $N_{Hbpe}\cdots H\text{–}N_{Hbpe}$ and $O_{nitrate}\cdots H\text{–}N_{Hbpe}$, extended the structures into a 3D supramolecular network. Calcinations of **1** and **2** at 700°C produce nano-sized LaO(OH) and $La(OH)_3$, respectively, showing that supramolecular compounds may be precursors for the preparation of nanoscale materials.

Supplementary material

The crystallographic data (excluding structure factors) for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-726586 and 726587 for **2** and **1**, respectively. 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; Email: data_request@ccdc.cam.ac.uk), or via the internet (http://www.ccdc.cam.ac.uk/products/csd/request).

Acknowledgment

This work was supported by the Iran National Science Foundation (INSF).

References

[1] S.S. Kuduva, D.C. Craig, A. Nangia, G.R. Desiraju. *J. Am. Chem. Soc.*, **121**, 1936 (1999).

[2] A. Anthony, G.R. Desiraju, R.K.R. Jetti, S.S. Kuduva, N.N.L. Madhavi, A. Nangia, R. Thaimattam, V.R. Thalladi. *Cryst. Eng.*, **1**, 1 (1998).

[3] C. Janiak. *Angew. Chem. Int. Ed. Engl.*, **36**, 1431 (1997).

[4] J.-Q. Liu, Y.-Y. Wang, L.-F. Ma, W.-H. Zhang, X.-R. Zeng, F. Zhong, Q.-Z. Shi, S.-M. Peng. *Inorg. Chim. Acta*, **361**, 173 (2008).

[5] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa. *Angew. Chem. Int. Ed. Engl.*, **36**, 1725 (1997).

[6] J.L. Manson, A.M. Arif, C.D. Incarvito, L.M. Liable-Sands, A.L. Rheingold, J.S. Miller. *J. Solid State Chem.*, **145**, 369 (1999).

[7] C. Chen, K.S. Suslick. *Coord. Chem. Rev.*, **128**, 293 (1993).

[8] K. Maruoka, N. Murase, H. Yamamoto. *J. Org. Chem.*, **58**, 2938 (1993).

[9] D. Braga, L. Maini, F. Grepioni, A.D. Cian, O. Felix, J. Fischer, M.W. Hosseini. *New J. Chem.*, **24**, 547 (2000).

[10] C.Y. Su, B.S. Kang, H.Q. Liu, Q.G. Wang, T.C.W. Mak. *Chem. Commun.*, 1551 (1998).

[11] C.V.K. Sharma, R.D. Rogers. *Chem. Commun.*, 83 (1999).

[12] J.W. Ko, K.S. Min, M.P. Suh. *Inorg. Chem.*, **41**, 2151 (2002).

[13] P. Lightfoot, A. Snedden. *J. Chem. Soc., Dalton Trans.*, 3549 (1999).

[14] M.-L. Tong, X.-M. Chen, X.-L. Yu, T.C.W. Mak. *J. Chem. Soc., Dalton Trans.*, 5 (1998).

[15] L.R. MacGillivray, R.H. Groeneman, J.L. Atwood. *J. Am. Chem. Soc.*, **120**, 2676 (1998).

[16] X.-M. Chen, M.-L. Tong, Y.-J. Luo, Z.-N. Chen. *Aust. J. Chem.*, **49**, 853 (1996).

[17] M.-L. Tong, X.-M. Chen, B.-H. Ye, L.-N. Ji. *Angew. Chem. Int. Ed. Engl.*, **38**, 2237 (1999).

[18] T.L. Hennigar, D.C. MacQuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko. *Angew. Chem. Int. Ed. Engl.*, **36**, 972 (1997).

[19] Y.-B. Dong, H.-Y. Wang, J.-P. Ma, D.-Z. Shen, R.-Q. Huang. *Inorg. Chem.*, **44**, 4679 (2005).

[20] L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi. *J. Chem. Soc., Chem. Commun.*, 2755 (1994).

[21] A. Garcia-Raso, J.J. Fiol, S. Rigo, A. Lopez-Lopez, E.E. Molins, E. Borras, G. Alzuet, J. Borras, A. Castineiras. *Polyhedron*, **19**, 991 (2000).

[22] Z. Zheng, R. Wang. *Comments Inorg. Chem.*, **22**, 1 (2000) and references cited therein.

[23] B.-L. An, M.-L. Gong, K.-W. Cheah, J.-M. Zhang, K.-F. Li. *Chem. Phys. Lett.*, **385**, 345 (2004).

[24] B.-L. An, M.-L. Gong, J.-M. Zhang. *J. Mol. Struct.*, **687**, 1 (2004).

[25] H. Sigel, A. Sigel (Eds.), *MetalIons in Biological Systems: The Lanthanides and their Inter-Relations with Biosystems*, Vol. 40, Marcel Dekker, Basel (2003).

[26] H. Li, M. Guo, H. Tian, F.Y. He, G.H. Lee, S.M. Peng. *J. Solid State Chem.*, **179**, 3511 (2006).

[27] O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy. *Acc. Chem. Res.*, **31**, 474 (1998).

[28] K.T. Al-Rasoul, M.G.B. Drew. *Acta Crystallogr., Sect. C*, **43**, 2081 (1987).

[29] F.T. Edelmann. *Coord. Chem. Rev.*, **253**, 343 (2009).

[30] Bruker Advanced X-ray Solutions. *SMART for WNT*/2000 (*Version 5.628*), Bruker AXS Inc., Madison, Wisconsin, USA (1997–2002).

[31] Bruker Advanced X-ray Solutions. *SAINT* (*Version* 6.45), Bruker AXS Inc., Madison, Wisconsin, USA (1997–2003).

[32] G.M. Sheldrick. *SHELXS-97 and SHELXL-97*, Göttingen University, Germany (1997).

[33] (a) L.J. Farrugia. *J. Appl. Crystallogr.*, **30**, 565 (1997); (b) Mercury 1.4.1, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (2001–2005).

[34] N. Rahahlia, B. Benmerad, A. Laidoudi, S. Dahaoui, C. Lecomte. *J. Mol. Struct.*, **833**, 42 (2007).

[35] L.-P. Zhang, T.C.W. Mak. *Polyhedron*, **22**, 2788 (2003).