Inorganica Chimica Acta 453 (2016) 128–134

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Research paper

Structural elucidation, EPR and magnetic interpretation of lanthanide (Ln = La, Nd, Sm) compounds with 4,4′-bipyridine and 2-sulfoterephthalate

Amitabha Datta [a,*], Kuheli Das [b], Shruti Mendiratta [c], Chiara Massera [d], Eugenio Garribba [e], Jui-Hsien Huang [a,*], Sandeep B. Mane [c], Chittaranjan Sinha [b,*], M. Salah El Fallah [f]

[a] Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan
[b] Department of Chemistry, Jadavpur University, Kolkata 700032, India
[c] Institute of Chemistry, Academia Sinica, Nankang, Taipei 115, Taiwan
[d] Dipartimento di Chimica, Università degli Studi di Parma, Viale delle Scienze 17/A, 43124 Parma, Italy
[e] Dipartimento di Chimica e Farmacia, and Centro Interdisciplinare per lo Sviluppo della Ricerca Biotecnologica e per lo Studio della Biodiversità della Sardegna, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy
[f] Departament de Química Inorgànica and Institute of Nanoscience (IN2UB) and Nanotechnology, Universitat de Barcelona, Av. Diagonal 645, Barcelona 08028, Spain

ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form 26 July 2016
Accepted 10 August 2016
Available online 12 August 2016

Keywords:
Lanthanides
Crystal structure
Emission
EPR
Magnetic property

ABSTRACT

A series of three lanthanide compounds, namely, {[La(**stp**)(bipy)(H_2O)]·H_2O}$_n$ (**1**), {[Nd(**stp**)(bipy)(H_2O)]·2H_2O}$_n$ (**2**), and {[Sm(**stp**)(bipy)(H_2O)]·H_2O}$_n$ (**3**) has been synthesized through the reaction of 2-sulfoterephthalic acid monosodium salt Na(H_2**stp**), trivalent lanthanide nitrate [Ln(NO_3)$_3$·6H_2O] and N-donor ancillary co-ligand, 4,4′-bipyridine (bipy). As a result of the potential coordination modes of the **stp** ligand and the bipy co-ligand, the aforementioned compounds are arranged in a 2-D network, as evidenced by single-crystal X-ray diffraction technique. In all the three compounds, the Ln ion presents a distorted tricapped trigonal-prismatic coordination geometry. The EPR measurements evidence a diamagnetic behaviour of compound **1** (La^{3+}) whereas there exhibits a weak antiferromagnetic coupling between paramagnetic Ln^{3+} ions (Nd^{3+} and Sm^{3+}) for compounds **2** and **3**. This is also supported by the magnetic data obtained for compounds **1–3**. The encapsulation of the lanthanide coordination polymers displays a moderate luminescent property.

1. Introduction

Coordination polymers and the related metal–organic frameworks (MOFs) have been in the focus of research efforts during the past decade [1]. Their hybrid nature, composed of metal ions or clusters connected with organic linkers, gives rise to properties derived from these two components separately, as well as from their combination. Indeed, several cooperative properties, such as porosity [2,3], magnetism [4], photoluminescence [5], or nonlinear optical properties [6] can stem from these families of hybrid materials. In this respect, the most important parameters that can be fine-tuned to obtain MOFs with different properties are i) the choice of the metal centers, with a particular attention towards their electronic state and coordination geometry; ii) the use of organic ligands to create different 3D networks of desired topology. Thus, specific structural and physicochemical characteristics at the molecular level can be translated into prescribed bulk properties for solid-state materials. In this context, there has been current interest in using polycarboxylates as anionic linking groups to support neutral, stable polymeric coordination open frameworks [7–9]. However, much of the work has so far focused on coordination polymers containing transition metals [10,11], while rare-earth metal compounds have received less attention [12–14]. The construction of supramolecular networks containing lanthanide ions as connectors is particularly attractive because of the magnetic and electronic properties of 4f ions, which should result in the application of lanthanide polymers in sensors, lighting devices, and optical storage [14–18]. In contrast to the fruitful production of metal-organic frameworks (MOFs) with d block transition metal ions, the design and control over high dimensional lanthanide-based frameworks is currently a formidable task owing to their high and variable coordination numbers and flexible coordination environments [19–21]. On the other hand, lanthanide ions, with

* Corresponding authors.
E-mail addresses: amitd_ju@yahoo.co.in (A. Datta), juihuang@cc.ncue.edu.tw (J.-H. Huang), c_r_sinha@yahoo.com (C. Sinha).

http://dx.doi.org/10.1016/j.ica.2016.08.018
0020-1693/

their high coordination flexibility and their lack of preferential geometries, are good candidates to provide unique opportunities for the discovery of unusual network topologies [22–25], thus leading us to this interesting and challenging field. So far, much work is focused on using multi-carboxylate ligands to prepare lanthanide-containing MOFs [26–35].

Recent research into nano-scale magnetic materials has led to lanthanide ions becoming prime candidates in the synthesis of coordination compounds. This can be partly attributed to their inherently large spin–orbit coupling, thus leading to significant magnetic anisotropy [36–38]. Such anisotropy is known to lead to a magnet-like behaviour of slow relaxation of the magnetization in these systems. The magnetic orbitals in lanthanide ions are located in the core 4f orbitals; thus, super-exchange pathways generally play a minimal role in the magnetic interactions [39–41]. Recent research, however, determined that the large anisotropy and non-negligible magnetic moments of lanthanide ions compensate for the weak exchange coupling and have yielded single molecular materials with the highest spin reversal barriers to date [42,43].

With the aim of producing materials exhibiting either physical or magnetic properties, the rigid but nonsymmetrical 2-sulfoterephthalate (**stp**), a bifunctional dicarboxylate/sulfonate ligand has been used as one bridging organic tecton, in combination with N-donor co-ligands and lanthanides to produce coordination polymers. Previously, some of us have reported a zinc polypseudorotaxane and a 3D copper coordination polymer based on the combined use of 2-sulfoterephthalate and the rigid, nitrogen-containing 4,4′-bipyridine (bipy) ligand as building blocks (Scheme 1) [44,45]. The **stp** ligand dispenses a diverse range of potential coordination and bridging modes, due to the presence of both the carboxylate and the sulfonate donorgroups [46,47]. Following these earlier studies, attention has now been focused on the preparation of a series of lanthanide compounds with these two versatile ligands. Hence, the synthesis, structural diversity, EPR and magnetic properties of new lanthanide compounds are described herein.

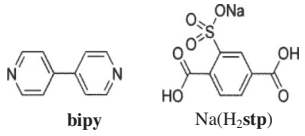
2. Experimental

2.1. Materials

2-sulfoterephthalic acid monosodium salt Na(H_2**stp**) and 4,4′-bipyridine(Acros Organics) were used as received without further purification. $La(NO_3)_3{\cdot}6H_2O$, $Nd(NO_3)_3{\cdot}6H_2O$ and $Sm(NO_3)_3{\cdot}6H_2O$ were purchased from Aldrich.

2.2. Physical measurements

Microanalytical data (C, H, and N) were collected on a Perkin–Elmer 2400 CHNS/O elemental analyzer. FTIR spectra were recorded on a Perkin-Elmer RX-1 spectrophotometer in the range 4000–400 cm^{-1} as KBr pellets. Solid state emission measurements were performed on a F-4500 FL spectrophotometer using 5.0 nm slit width, scan speed of 1200 nm/min, and PMT voltage of 700 V. EPR spectra were recorded at room (298 K) or liquid nitrogen temperature (77 K) using an X-band (9.4 GHz) Bruker EMX spectrometer equipped with a HP 53150A microwave frequency counter. Magnetic susceptibility measurements for the compounds were carried out on polycrystalline samples, at the Servei de Magnetoquímica of the Universitat de Barcelona, with a Quantum Design SQUID MPMS-XL susceptometer apparatus working in the range 2–300 K under magnetic field of approximately 10000 G for compound **1**, 3000 G for compound **2** and 5000 G for compound **3**. Diamagnetic corrections were estimated from Pascal Tables.



Scheme 1. Ligands employed to generate coordination networks; 4,4′-bipyridine (left) and 2-sulfoterephthalic acid monosodium salt (right).

2.3. Synthesis of the compounds

2.3.1. Synthesis of {[La(*stp*)(bipy)(H_2O)]·H_2O}$_n$(*1*)

A methanolic solution (20 mL) of 2-sulfoterephthalic acid monosodium salt (0.0402 g, 0.15 mmol) was mixed with another methanolic solution (20 mL) of 4,4′-bipyridyl (0.2191 gm, 1.4 mmol), and the resulting solution was stirred for 15 min. La $(NO_3)_3{\cdot}6H_2O$ (0.1299 g, 0.3 mmol)was dissolved in 20 mL of water in a separate beaker. Six milliliters of this mixed ligand solution was slowly and carefully layered above 3 mL of metal solution using 2 mL of buffer (1:1 of water and MeOH) in a glass tube. After 1 week, colourless rectangular-shaped crystals were obtained on the wall of the tube; they were washed with a methanol–water (1:1) mixture and dried in air. Yield: 0.044 g. Anal. Calc. for $C_{18}H_{15}N_2O_9SLa$: C, 37.64; H, 2.63; N, 4.88. Found: C, 37.91; H, 2.72; N, 5.23%. IR (KBr, cm^{-1}): 3357 (s br), 2493 (w), 1611 (s br), 1491 (s), 1239 (w br), 1177 (w), 1168 (s br), 1075 (s br), 1017 (s), 873 (w br), 791 (s br), 621 (s), 542 (s), 533 (s), 464 (s).

2.3.2. Synthesis of {[Nd(*stp*)(bipy)(H_2O)]·2H_2O}$_n$(*2*)

The synthetic procedure to obtain compound **2** was similar to that used for **1**; $Nd(NO_3)_3{\cdot}6H_2O$ (0.1314 g, 0.3 mmol) was used instead of $La(NO_3)_3{\cdot}6H_2O$. Yield: 0.119 g. Anal. Calc. for $C_{18}H_{17}N_2O_{10}SNd$: C, 36.17; H, 2.87; N, 4.69. Found: C, 36.33; H, 2.69; N, 4.88%. IR (KBr, cm^{-1}): 3361 (s br), 2498 (w), 1616 (s br), 1489 (s), 1228 (w br), 1169 (w), 1147 (s br), 1069 (s br), 1024 (s), 849 (w br), 789 (s br), 615 (s), 539 (s), 456 (s), 433 (s).

2.3.3. Synthesis of {[Sm(*stp*)(bipy)(H_2O)]·H_2O}$_n$ (*3*)

The synthetic procedure to obtain compound **3** was similar to that used for **1**; $Sm(NO_3)_3{\cdot}6H_2O$ (0.1332 g, 0.3 mmol) was used instead of $La(NO_3)_3{\cdot}6H_2O$. Yield: 0.051 g. Anal. Calc. for $C_{18}H_{15}N_2O_9SSm$: C, 36.91; H, 2.58; N, 4.78. Found: C, 37.07; H, 2.73; N, 4.93. IR (KBr, cm^{-1}): 3346 (s br), 2478 (w), 1633 (s br), 1512 (s), 1236 (w br), 1191 (w), 1171 (s br), 1047 (s br), 1039 (s), 866 (w br), 781 (s br), 643 (s), 541 (s), 459 (s), 428 (s).

2.4. Structural determination

Crystal data and experimental details for data collection and structure refinement are reported in Table 1. The crystal structures of compounds **1–3** were determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at 293(2) K on a Bruker Breeze (**1**), at 190(2) K (**2**) and at 293(2) K (**3**) on a Bruker APEX II (MoKα radiation λ = 0.71073 Å) both equipped with a CCD area detector and a graphite monochromator. The raw frame data were processed using SAINT and SADABS to yield the reflection data file [48,49]. The structures were solved by Direct Methods using the SIR97 program [50] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program [51] in the WinGX suite v.1.80.05 [52]. All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were either located in the difference Fourier map, or included in the refinement at idealized geometry (C–H 0.95 Å) and refined "riding" on the corresponding parent atoms. Some positive residual electron density was found located around the metals