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Research paper

Lanthanide coordination polymers with N-methyliminodipropionic acid: Synthesis, crystal structures and luminescence

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ABSTRACT

The synthesis, crystal structures and luminescence of a novel family of lanthanide polymer complexes with general formula $[Ln_2(Hmidp)_3(H_2O)_3](ClO_4)_3{\cdot}6H_2O$ (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Tm; H_2midp = N-methyliminodipropionic acid) are reported. The compounds were obtained by direct reaction of H_2midp and lanthanide(III) perchlorate in aqueous solution. The choice of the conditions of synthesis were selected from speciation studies. The structure of the polymer complexes contains bimetallic cationic units $[Ln_2(Hmidp)_3(H_2O)_3]^{3+}$ in which one of the Ln ions is eight-coordinated and the other nine-coordinated, linked by carboxylate bridges. This is expanded to a 2D network through carboxylate linkers. The solid state luminescence of the Eu complex was observed and an average lifetime value of 0.5 ms was verified for the red emitting $^5D_0$ excited state.

1. Introduction

Exploration of the assembly of lanthanide metal-organic frameworks has become an interesting field of research [1]. This is due to the intriguing architectures exhibited, as well as the various potential applications. These compounds have been tested as luminescent, catalytic, sensor, and gas storage materials [2–6]. The design and synthesis of lanthanide metal-organic compounds remains a challenge because the self-assembly process is affected by many factors. The size of the metal ion (which can determine the coordination geometry), the flexibility of the ligand, the metal to ligand molar ratio during the preparation, solvent, pH value and the presence of counterions are among the most influential factors [7–10].

Polycarboxylate ligands can link lanthanide ions into novel structures with dimensionality from 0D to 3D. One factor that causes the variation in the final structure is the possibility of several coordination modes of carboxylate groups in the complexes with lanthanide ions. Coordination modes η^1, η^2, μ_2-$\eta^1\eta^1$ (O,O), μ_2-$\eta^1\eta^1$ *ZZ*, μ_2-$\eta^1\eta^1$ *EE*, μ_2-$\eta^1\eta^1$ *ZE*, μ_2-$\eta^2\eta^1$, μ_3-$\eta^2\eta^1$, μ_3-$\eta^2\eta^2$ are observed, and other intermediate modes are not uncommon [11]. We have been interested in the preparation of polynuclear complexes with aminopolycarboxylates, such as iminodiacetic acid (H_2ida) [12], iminotripropionic acid (H_3ntp) [13], and benzyliminodiacetic acid ($H_2bzlida$) [14] under acidic conditions. The nitrogen atom can be protonated under these conditions, which prevents its coordination to the metal. This facilitates the polytopic capability of the aminopolycarboxylate.

This work explores the coordination of N-N-methyliminodipropionic acid (H_2midp, Fig. 1) as a flexible ligand towards lanthanide ions. This derivative of iminodipropionic acid has been rarely used as ligand in coordination chemistry. A single report describes the preparation of $[Cu(midp)(H_2O)]{\cdot}H_2O$ [15]. The ligand is fully deprotonated and the structure is a 1D chain. With this in mind, we performed potentiometric studies to choose the pH and molar ratio (ligand to metal) in which stable species are formed. Then, hydrothermal syntheses were carried out to isolate seven novel polynuclear species with general formula $[Ln_2(Hmidp)_3(H_2O)_3](ClO_4)_3{\cdot}6H_2O$ (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Tm). The complexes were characterized by X-ray diffraction. We have also measured photoluminescence excitation and emission spectra, and excited state lifetimes of the Eu compound.

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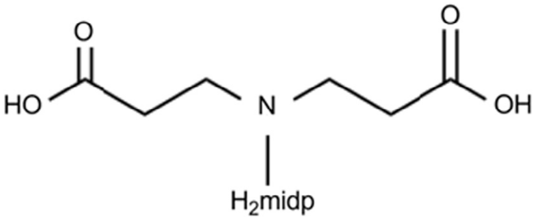

Fig. 1. *N*-methyliminodipropionic acid.

2. Experimental

2.1. Materials and methods

All laboratory chemicals were reagent grade, from commercial sources. Ln_2O_3 (Ln = Nd, Sm, Eu, Gd, Dy, Ho and Tm 99.9% from Aldrich), $CeCl_3 \cdot 7H_2O$ (98% from Carlo Erba) or $LnCl_3 \cdot 6H_2O$ (Ln = Sm, Gd, Yb, 99–99.9% from Aldrich) were used as metal sources. All solvents were distilled prior to use.

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

The infrared spectra, of 1% KBr pellets, were obtained in a Bomen MB 102 FT-IR spectrophotometer. Elemental analysis (C, H) were performed on a Flash 2000 instrument. Thermal analyses were carried out on a Shimadzu TGA-50 instrument with a TA 50I interface, using a platinum cell and nitrogen atmosphere. Experimental conditions were 0.5 °C min^{-1} temperature ramp rate and 50 mL min^{-1} nitrogen flow rate. The room temperature excitation and emission spectra were recorded in a HORIBA Jobin Yvon spectrofluorimeter model SPEX Fluorolog 3, equipped with a CW xenon lamp (450 W) and PPD photocounting detector. The spectra were corrected for the intensity distribution of the lamp, and the response functions of the monochromators and detector. For the excited state lifetimes, excitation was done with a pulsed xenon lamp. All the measurements were done for the complexes in solid state, using a flat cuvette and front face excitation and collection.

The X-ray powder diffraction (XRPD) data were obtained for all the samples using a Rigaku ULTIMA IV powder diffractometer, operating in Bragg Brentano geometry. The radiation corresponds to CuKα (λ = 1.5418 Å), monochromatized with a germanium crystal bent diffraction beam. The data was collected over the 2θ range 5.00–60.00°, in steps of 0.02°, using a scintillation detector. Fixed slits of 2/3° were used for data collection to prevent beam spillage outside the 2 cm long sample (along the beam-path) at low angles.

NMR spectra were obtained on a Bruker Avance DPX-400 instrument. Proton chemical shifts (δ) are reported in ppm downfield from TMS as an internal reference.

2.2. Synthesis

2.2.1. N-methyliminodipropionic acid (H_2midp)

This compound was prepared by a slight modification of a reported protocol [16]. Acrylic acid (0.44 mol) was added to 20 mL of an 8 mol L^{-1} solution of methylamine in ethanol (0.16 mol). The mixture was refluxed overnight. The product precipitated as a white solid which was filtered and washed with cold ethanol. H^1 NMR (δ, ppm, DMSO-d_6): 2.26 (s; 3 H), 2.38 (t; 4 H; J = 7.1 Hz), 2.68 (t; 4 H; J = 7.1 Hz). Yield 65%. Anal. Calc. for $C_7H_{13}NO_4$: C, 48.0; N, 8.0; H, 7.5%. Found: C, 48.1; N, 7.8; H, 7.5%.

2.2.2. $[Ln_2(Hmidp)_3(H_2O)_3](ClO_4)_3 \cdot 6H_2O$ (Ln = Nd(1), Sm(2), Eu(3), Gd (4), Dy(5), Ho(6), Tm(7))

Ln_2O_3 (0.25 mmol) was dissolved in 60% $HClO_4$ (0.18 mL), under gentle heating and adding a few drops of water, if necessary. Then, H_2midp (87.6 mg, 0.50 mmol) dissolved in 5 mL water was added. In the resulting solution, the pH value was adjusted to 4–5 with NaOH. The resulting suspension was filtered (to remove a small amount of unreacted lanthanide oxide) and allowed to evaporate at room temperature. After three to four weeks, prismatic plaque crystals were obtained, filtered off, washed with water and dried in air. Yield 25–45%. Anal. Calc. for $C_{21}H_{54}Nd_2N_3O_{33}Cl_3$ (**1**): C, 19.8; N, 3.3; H, 4.3%. Found: C, 20.1; N, 3.3; H, 4.2%. Anal. Calc. for $C_{21}H_{54}Sm_2N_3O_{33}Cl_3$ (**2**): C, 19.6; N, 3.3; H, 4.2%. Found: C, 19.9; N, 2.9; H, 4.1%. Anal. Calc. for $C_{21}H_{54}Eu_2N_3O_{33}Cl_3$ (**3**): C, 19.6; N, 3.3; H, 4.2%. Found: C, 20.0; N, 2.8; H, 4.2%. Anal. Calc. for $C_{21}H_{54}Gd_2N_3O_{33}Cl_3$ (**4**): C, 19.4; N, 3.2; H, 4.2%. Found: C, 19.7; N, 2.9; H, 4.0%. Anal. Calc. for $C_{21}H_{54}Dy_2N_3O_{33}Cl_3$ (**5**): C, 19.3; N, 3.2; H, 4.2%. Found: C, 19.6; N, 3.2; H, 3.4%. Anal. Calc. for $C_{21}H_{54}Ho_2N_3O_{33}Cl_3$ (**6**): C, 19.2; N, 3.2; H, 4.1%. Found: C, 19.3; N, 3.2; H, 3.8%. Anal. Calc. for $C_{21}H_{54}Tm_2N_3O_{33}Cl_3$ (**7**): C, 19.1; N, 3.2; H, 4.1%. Found: C, 19.4; N, 3.1; H, 3.8%. IR peaks (cm^{-1}) associated to the midp ligand appear at: 1705(vs), 1601 (s), 1477(s), 1420(vs), 1377(s), 1334(s) (free ligand); 1593vs), 1568(vs), 1449(s), 1398(s), 1327(m), 1313(m) (**1**); 1593(vs), 1568 (vs), 1449(s), 1398(s), 1327(m), 1313(m) (**2**); 1593(vs), 1568(vs), 1449(s), 1398(s), 1327(m), 1313(m) (**3**); 1593(vs), 1568(vs), 1449 (s), 1398(s), 1327(m), 1313(m) (**4**); 1593(vs), 1568(vs), 1449(s), 1398(s), 1327(m), 1313(m) (**5**); 1593(vs), 1568(vs), 1449(s), 1398 (s), 1327(m), 1313(m) (**6**); 1593(vs), 1568(vs), 1449(s), 1398(s), 1327(m), 1313(m) (**7**).

2.2.3. Single-crystal structure determination

X-ray diffraction data of single crystals of **1** and **5** were collected with an Agilent SuperNOVA diffractometer with microfocus X-ray using Cu Kα radiation (λ = 1.54184 Å). CrysAlisPro [17] software was used to collect, index, scale and apply analytical absorption correction based on the faces of the crystal. The structures were solved by dual-space algorithm using SHELXT program [18]. Fourier recycling and least-squares refinement were used for the model completion with SHELXL-2014 [19]. All non-hydrogen atoms have been refined anisotropically, and all hydrogen atoms have been placed in geometrically suitable positions and refined riding with isotropic thermal parameter related to the equivalent isotropic thermal parameter of the parent atom. The hydrogen atoms were geometrically positioned with C—H = 0.93 Å and Uiso(H) = 1.2 Ueq(C). The perchlorate anions present a higher thermal disorder in both structures and they have not been easy to model. Besides, the Hmidp ligands exhibit structural disorder at lower temperature for structure **5**. A high degree of disorder is present for both compounds, even when the data collection was performed at low temperature (150 K). In general, hydration water molecules are disordered and their occupancy factor was fixed to half in order to keep their thermal factors under control. This prevented the location of their hydrogen atoms, and gave short contacts between some of water molecules. Also, some of hydrogens atoms from hydration water molecules could not be located due to this fact. The geometrical analysis of interactions in the structure was performed with PLATON [20] and Olex2 [21] program. Crystal data, collection procedures and refinement results are summarized in Table S1.

2.3. Equilibrium studies

The standard HCl solutions were prepared by diluting Merck standard ampoules. Me_4NOH solutions were prepared from $Me_4NOH \cdot 5H_2O$ (97% from Sigma). Acid and base stock solutions were standardized against sodium borate and potassium hydrogen phthalate, respectively. All the solutions were prepared with analytical grade water (18 μS cm^{-1}) and were freed of carbon dioxide by bubbling with Ar(g).