

$[\text{H}_2\text{en}]_2\{\text{La}_2M(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}, \text{Ni}$): First organically templated $3d-4f$ mixed metal sulfates

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Abstract

The first organically templated $3d-4f$ mixed metal sulfates, $[\text{H}_2\text{en}]_2\{\text{La}_2M(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}$ **1**, Ni **2**) have been synthesized and structurally determined from non-merohedrally twinned crystals. The two compounds are isostructural and their structures feature a three-dimensional anionic network formed by the lanthanum(III) and nickel(II) ions bridged by sulfate anions. The La(III) ions in both compounds are 10-coordinated by four sulfate anions in bidentate chelating fashion, and two sulfate anions in a unidentate fashion. The transition metal(II) ion is octahedrally coordinated by six oxygens from four sulfate anions and two aqua ligands. The doubly protonated ethylenediamine cations are located at the tunnels formed by 8-membered rings (four La and four sulfate anions).

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1. Introduction

Materials with open-framework and microporous structures are promising candidates for hybrid composite materials in electro-optical and sensing applications in addition to their potential applications in the areas of catalysis, ion exchange, intercalation chemistry, photochemistry, and materials chemistry [1,2]. For the past two decades, this research field has been dominated by silicates [3], phosphates [1] and carboxylates [4]. Although a three-dimensional organically templated zinc sulfate was reported in 1970 by Morimoto and Lingafelter, the study of metal open architectures making use of oxy-anions of group 16 elements started to be flourishing only after Rao's works on the

preparation of organically templated open-framework cadmium sulfates a few years ago [5]. Organically templated vanadium, nickel, cobalt and iron sulfates have been also characterized by Rao's group [6]. Organically templated lanthanide and actinide sulfates exhibit a very different structural chemistry from those of transition metal ones. Uranium sulfates with different organic templates have been structurally established by O'Hare et al. [7]. An open framework solid of scandium sulfate–phosphate was reported by Wright's group [8]. One-, two- and three-dimensional organically templated lanthanum(III) sulfates have also been structurally characterized [9], and the open frameworks isolated are closely related to the “structure directing” template cations as well as the reaction conditions. No organically templated $3d-4f$ mixed-metal sulfates have been reported so far. $3d-4f$ mixed-metal coordination polymers and cluster compounds have been extensively

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studied due to their interesting magnetic properties, and a wide range of organic ligands has been used as the bridge for lanthanide and transition metal ions [4c,10–13]. We deem that the sulfate group can also act as the 3d–4f metal linker. Organically templated 3d–4f mixed metal sulfates have several advantages over normal 3d–4f mixed coordination compounds in that the inorganic open framework of metal sulfates are usually thermally much more stable and the use of the “structure directing” template allows more structurally controlled designing and synthesis. Our such research efforts lead to $[\text{H}_2\text{en}]_2\{\text{La}_2\text{M}(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}$ **1**, Ni **2**), the first organically templated 3d–4f mixed metal sulfates. Herein we report their syntheses, crystal structures, and physical properties.

2. Experimental section

2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 15 °C/min under an O₂ atmosphere. IR spectra were recorded on a Magna 750 FT-IR spectrometer photometer as KBr pellets in the 4000–400 cm⁻¹. X-ray powder diffraction data were collected on an X'Pert-MPD diffractometer using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) over the 2θ range of 5–65° with a step size of 0.05° and a counting time of 0.6 s per step. The generator voltage is 40 kV and the tube current is 40 mA. Magnetic susceptibility measurements on polycrystalline samples of compounds (0.12945 g for the La–Co compound and 0.05799 g for the La–Ni compound) were performed with a PPMS-9T magnetometer at a field of 1 T in the range of 2.0–300 K. The raw data were corrected for the susceptibility of the container and the diamagnetic contributions of the sample using Pascal's constants.

2.2. Preparation of $[\text{H}_2\text{en}]_2\{\text{La}_2\text{M}(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}$ **1**; Ni **2**)

Both compounds were synthesized under solvothermal conditions. 0.353 g of $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$, 0.237 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (or 0.234 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and 0.632 g of $[\text{H}_2\text{en}]\text{SO}_4$ were dissolved in 6.48 ml 2-Methyl-1-propanol under vigorous stirring for 4 h. Then 1 ml of sulfuric acid (1 mol/L) was added. The resultant mixture with a molar composition of $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$): $5\text{H}_2\text{SO}_4$: 4en: 70 2-methyl-1-propanol was sealed into 23 ml teflon-lined autoclave and heated at 160 °C for 4 days. The initial and final pH values of the solution are 1.5 and 2.5,

respectively. Pink crystals of $(\text{H}_2\text{en})_2[\text{La}_2\text{Co}(\text{H}_2\text{O})_2(\text{SO}_4)_6]$ and green crystals of $(\text{H}_2\text{en})_2[\text{La}_2\text{Ni}(\text{H}_2\text{O})_2(\text{SO}_4)_6]$ were obtained in a 72.0% and 70.5% yield, respectively (based on La). Both compounds are single phases, the measured XRD powder patterns are in agreement with the ones simulated from the single crystal data. Elemental analysis for $(\text{H}_2\text{en})_2[\text{La}_2\text{Co}(\text{H}_2\text{O})_2(\text{SO}_4)_6]$ ($M_r = 1073.38$): C 4.54%, H 2.25%, N 5.28%, S 17.72%. Calc.: C 4.48%, H 2.24%, N 5.52%, S 17.90%. IR data (KBr, cm⁻¹): 3368 (w), 3172(br), 1630(w), 1506(m), 1400 (m), 1096(s), 816(w), 736(w), 660(m), 605(m). Elemental analysis for $(\text{H}_2\text{en})_2[\text{La}_2\text{Ni}(\text{H}_2\text{O})_2(\text{SO}_4)_6]$ ($M_r = 1073.16$): C 4.55%, H 2.31%, N 5.31%, S 17.76%. Calc.: C 4.48%, H 2.25%, N 5.22%, S 17.92%. IR data (KBr, cm⁻¹): 3366 (w), 3174(br), 1631(w), 1507(m), 1402 (m), 1097(s), 815(w), 737(w), 662(m), 606(m).

2.3. X-ray crystallographic study

Data collections for **1** and **2** were performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$), operating at 50 kV and 40 mA at –93 °C controlled with Crysosream Controller 700. Absorption corrections by using program SADABS was applied. Both crystals used for data collection were found to be non-merohedrally twinned and GEMINI program (Version 1.0) was thus applied [14]. For **1**, the reflections from the two domain components were used for the structural solution and refinements. The twin refinements were performed with *SHELXL97* using the data in *HKLF5* format and refinement of batch scale factors [14]. Symmetry equivalent reflections were not merged and all measured intensities were treated as independent

Table 1
Crystal data and structure refinements for compounds **1** and **2**

Compound	1	2
Formula	C ₄ H ₂₄ CoLa ₂ N ₄ O ₂₆ S ₆	C ₄ H ₂₄ NiLa ₂ N ₄ O ₂₆ S ₆
fw	1073.38	1073.16
Space group	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ / <i>c</i>
<i>a</i> /Å	9.473(4)	9.412(3)
<i>b</i> /Å	10.056(4)	9.967(3)
<i>c</i> /Å	13.114(5)	13.034(4)
β /°	91.304(7)	91.427(7)
<i>V</i> (Å ³)	1248.9(8)	1222.3(7)
<i>Z</i>	2	2
<i>D</i> _{calcd.} (g cm ⁻³)	2.854	2.916
μ (mm ⁻¹)	4.642	4.834
Measured reflections	6100	2809
Independent reflections	6100	2809
Observed reflections	4741	2115
GOF on <i>F</i> ²	1.031	1.149
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0602/0.1462	0.0782/0.1540
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0783/0.1591	0.1077/0.1647

^a $R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|$, $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2\}^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

Compound 1			
La(1)–O(23)	2.429(5)	La(1)–O(21)#1	2.532(5)
La(1)–O(34)	2.535(5)	La(1)–O(14)#2	2.552(6)
La(1)–O(32)#3	2.598(5)	La(1)–O(33)	2.604(6)
La(1)–O(11)	2.635(6)	La(1)–O(13)	2.734(7)
La(1)–O(31)#3	2.861(5)	La(1)–O(12)#2	2.981(7)
Co(1)–O(22)#4	2.037(6)	Co(1)–O(22)	2.037(6)
Co(1)–O(1W)	2.098(6)	Co(1)–O(1W)#4	2.098(6)
Co(1)–O(12)#4	2.143(7)	Co(1)–O(12)	2.143(7)
Hydrogen bonds			
N(1)...O(1w) #4	3.016(11)	N(1)–H(1d)...O(1w)#4	145.4
N(2)...O(24)	2.856(10)	N(2)–H(2e)...O(24)	170.6
Compound 2			
La(1)–O(23)	2.431(9)	La(1)–O(34)	2.508(9)
La(1)–O(21)#1	2.510(9)	La(1)–O(14)#2	2.543(8)
La(1)–O(33)	2.571(9)	La(1)–O(32)#3	2.581(8)
La(1)–O(11)	2.603(9)	La(1)–O(13)	2.703(9)
La(1)–O(31)#3	2.836(8)	La(1)–O(12)#2	3.013(9)
Ni(1)–O(22)#4	2.024(9)	Ni(1)–O(22)	2.024(9)
Ni(1)–O(1W)	2.054(9)	Ni(1)–O(1W)#4	2.054(9)
Ni(1)–O(12)	2.075(9)	Ni(1)–O(12)#4	2.075(9)
Hydrogen bonds			
N(1)...O(1w) #5	3.006(14)	N(1)–H(1d)...O(1w)#5	144.8
N(2)...O(24) #6	2.867(14)	N(2)–H(2e)...O(24) #6	172.4

Symmetry transformations used to generate equivalent atoms: #1 $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; #2 $x, -y - \frac{1}{2}, z - \frac{1}{2}$; #3 $-x - 1, y + \frac{1}{2}, -z + \frac{3}{2}$; #4 $-x, -y, -z + 2$.

data in the refinement. All non-hydrogen atoms were refined anisotropically, except for O(32), N(2) and C(1) atoms. For **2**, only reflections from the domain component were used for structural solution and refinement and all non-hydrogen atoms were refined anisotropically, except O(12), O(21), O(32) and C(1) atoms, which were refined isotropically. The positions for all hydrogen atoms were added by calculation, and their contributions were included in the structure factor calculations. Crystallographic data and structural refinements for compounds **1** and **2** are summarized in Table 1. Relevant bond distances and angles are listed in Table 2.

CCDC 261771 and 261772 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

3. Results and discussion

3.1. Crystal structure descriptions for $[H_2en]_2\{La_2M(SO_4)_6(H_2O)_2\}$ ($M = Co$ **1**, Ni **2**)

$[H_2en]_2\{La_2M(SO_4)_6(H_2O)_2\}$ ($M = Co$ **1**, Ni **2**) represent the first organically templated 3d–4f mixed metal

sulfates. The two compounds are isostructural and their structures feature a three-dimensional network formed by La(III) and M(II) ions interconnected through bridging sulfate anions. The structure of compound **1** is discussed in detail as an example. As shown in Fig. 1, the La(III) ion is 10-coordinated by four sulfate anions in bidentate chelating fashion, and two sulfate anions in a unidentate fashion. The La–O distances range from 2.429(5) to 2.981(7) Å. These La–O distances are comparable to those reported in other organically templated lanthanum(III) sulfates [9]. The Co(II) ion located on an inversion center is octahedrally coordinated by four sulfate anions in a unidentate fashion and two aqua ligands. Co–O distances are in the range of 2.037(6)–2.143(7) Å, which are comparable to those reported [6]. The three sulfate anions adopt three different coordination modes. The S(1)O₄ is pentadentate, it chelates with two La(III) ions bidentately and also bridges to a Co(II) ion. O(12) is a bidentate metal linker. The S(3)O₄ is tetradentate, it chelates bidentately with two La(III) ions. The remaining sulfate group is tridentate, and bridges with two La(III) ion and a Co(II) ion. O(24) remains non-coordinated (Fig. 1).

The interconnection of Co(II) and La(III) ions through bridging and chelating sulfate groups lead to a three-dimensional open framework with tunnels along *c*-axis (Fig. 2). These tunnels are formed by 8-member rings (four La(III) and four sulfate groups). The cavity of these 8-member apertures is estimated to be $4.4 \times 3.3 \text{ \AA}^2$ based on crystal structure data. The template cations are located at the above tunnels. Both amine groups of the template cation are protonated and are involved in hydrogen bonding with non-coordination sulfate oxygen (O(24) and the aqua ligand (O(1w)).

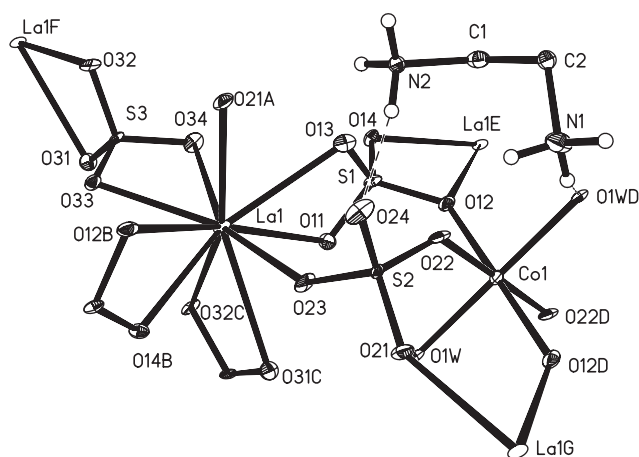


Fig. 1. ORTEP representation of the selected unit in $[H_2en]_2\{La_2Co(SO_4)_6(H_2O)_2\}$ showing the coordination geometries around La and Ni atoms. Thermal ellipsoids are drawn at 50% probability. Hydrogen bonds are drawn as dotted lines. Symmetry codes for the generated atoms: (a) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$ (b) $x, -y - \frac{1}{2}, z - \frac{1}{2}$ (c) $-x - 1, y + \frac{1}{2}, -z + \frac{1}{2}$ (d) $-x, -y, -z + 2$ (e) $x, -y - \frac{1}{2}, z + \frac{1}{2}$ (f) $-x - 1, y - \frac{1}{2}, -z + \frac{3}{2}$ (g) $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

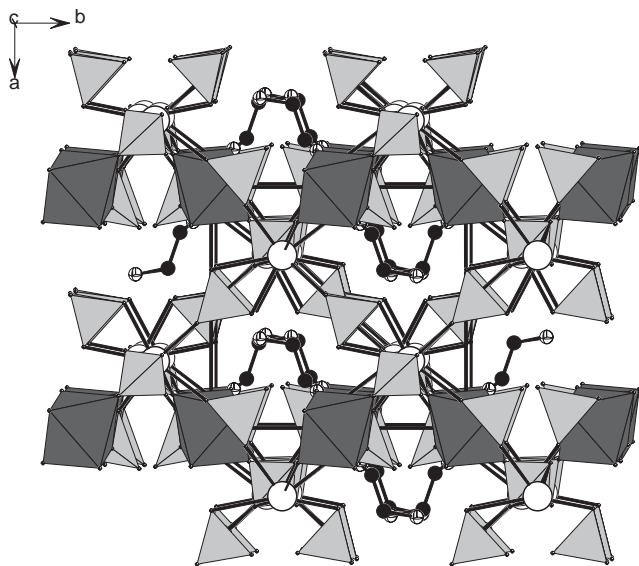


Fig. 2. View of the structure of $[\text{H}_2\text{en}]_2\{\text{La}_2\text{Co}(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ down the c -axis. The CoO_6 octahedra and sulfate tetrahedra are shaded in dark and light gray, respectively. La, C, N and O atoms are drawn as open, black, octahed and crossed circles, respectively.

The hydrogen bond distance and angle for $\text{N}(1)\text{---}\text{H}(1\text{d})\text{---}\text{O}(1\text{wd})$ (symmetry code: $-x, -y, 2-z$) are 3.016(11) Å and 145.4° , respectively. The other hydrogen bond, $\text{N}(2)\text{---}\text{H}(2\text{e})\text{---}\text{O}(24)$ is much stronger (2.856(10) Å and 170.6°) (Table 2). The 3D framework constructed by the lanthanum(III) and sulfate groups in $[\text{H}_2\text{en}]_2\{\text{La}_2M(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}$ **1**, Ni **2**) is different from those of $[\text{H}_2\text{pip}]\{\text{La}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2\}$, $[\text{H}_2\text{en}]_2\{\text{Ln}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2\}$ ($\text{Ln} = \text{La}, \text{Pr}$ or Nd) and $[\text{H}_2\text{pip}]\{\text{Nd}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2\}$ with a smaller SO_4/Ln ratio [9c,9e]. In $[\text{H}_2\text{pip}]\{\text{La}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2\}$, the La(III) ions are in 10- and 9-fold coordination geometries, respectively. $[\text{H}_2\text{en}]_2\{\text{Ln}_2(\text{SO}_4)_5(\text{H}_2\text{O})_2\}$ ($\text{Ln} = \text{La}, \text{Pr}$ or Nd) contain both 8- and 16-membered apertures, whereas the structure of $[\text{H}_2\text{pip}]\{\text{Nd}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2\}$ is composed of 8- and 12-membered apertures [9c,9e]. It should be also noted that $[\text{H}_2\text{en}]_3\{\text{La}_2(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ with same SO_4/Ln ratio with that in $[\text{H}_2\text{en}]_2\{\text{La}_2M(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}, \text{Ni}$) has a layered structure [9c].

3.2. IR studies

The IR spectra of compounds **1** and **2** show the typical sharp peaks for ethylenediamine in the region $1400\text{--}1600\text{ cm}^{-1}$. The absorption bands in the region $3400\text{--}3100\text{ cm}^{-1}$ are due to the aqua ligands. The bands associated with the sulfate anions appear at 1096 and 605 cm^{-1} for compound **1**, and 1097 and 606 cm^{-1} for compound **2**. Absorption bands at 816 cm^{-1} (for **1**) and 815 cm^{-1} (for **2**) can be assigned to the La–O vibration [9b].

3.3. Magnetic property studies

Magnetic properties of $[\text{H}_2\text{en}]_2\{\text{La}_2M(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}$ **1**, Ni **2**) have been studied. A plot of χ_m versus T is shown in Fig. 3. The effective magnetic moments of 4.56 (for **1**) and $3.30\ \mu_B$ (for **2**) at room temperature are significantly larger than those for the expected spin-only values of the Co^{2+} and Ni^{2+} ions (Co^{2+} , $S = \frac{3}{2}$, $\mu_{\text{eff}} = 3.87\ \mu_B$ and Ni^{2+} , $S = 1$, $\mu_{\text{eff}} = 2.83\ \mu_B$), which can be attributed to the spin-orbital interactions. Non-linear fitting of the susceptibility data according to $\chi = C/(T-\theta) + \chi_0$ gave Weiss constants of $-0.79(2)$ and $-2.62(2)\text{ K}$ respectively for the cobalt and nickel compounds, respectively, indicating a weak antiferromagnetic interaction between magnetic centers. Such weak antiferromagnetic interactions are expected since the magnetic centers are well-separated from each other (8.263(1) and 8.204(1) Å, respectively for compounds **1** and **2**).

3.4. TGA study

TGA analyses indicate that compounds **1** and **2** are stable up to 150 and 167°C , respectively (Fig. 4). Then both of them exhibit three main overlapping steps of weight losses. The first step corresponds to the release of the two aqua ligands and partial removal of the template cations. The observed weight losses are 5.4% and 5.1% for compounds **1** and **2**, respectively. The second step corresponds to the complete removal of the template cations and the loss of two molecules of SO_3 . The intermediate compounds thus formed are $\text{La}_2(\text{SO}_4)_3 + M(\text{SO}_4)$ ($M = \text{Co}, \text{Ni}$). The observed residual weight of 67.0% (for **1**) and 65.5% (for **2**) are very close to the calculated values (67.17% and 67.16%, respectively). During the third step, the compounds are further decomposed. The final residuals at 1000°C are La_2MO_4 ($M = \text{Co}, \text{Ni}$) based on XRD powder studies (La_2NiO_4 JCPDS file card no. 11–557). The total weight losses at

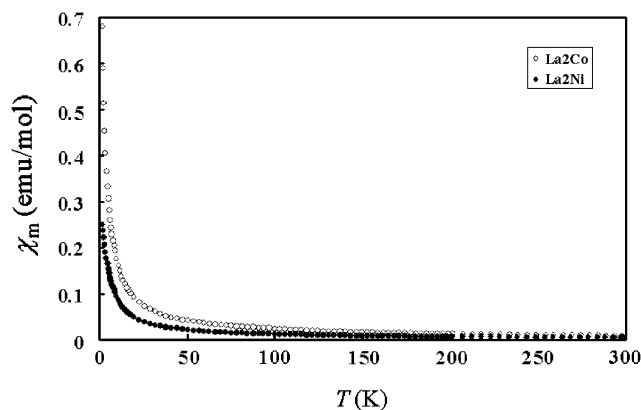


Fig. 3. Plot of χ_m versus T for $(\text{H}_2\text{en})_2[\text{La}_2M(\text{H}_2\text{O})_2(\text{SO}_4)_6]$ ($M = \text{Co}$ **1**, Ni **2**).

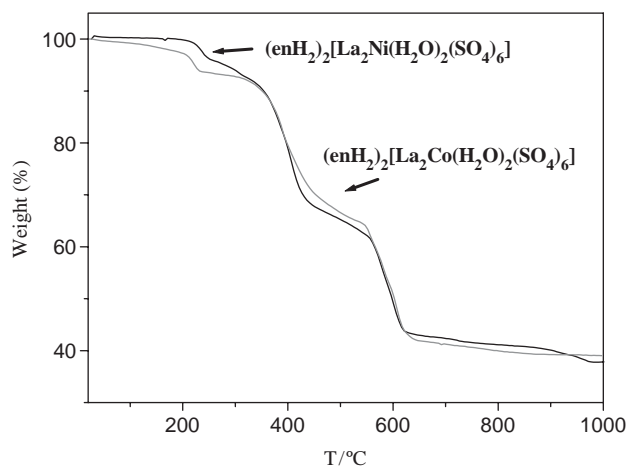


Fig. 4. TGA curves of $(\text{H}_2\text{en})_2[\text{La}_2\text{M}(\text{H}_2\text{O})_2(\text{SO}_4)_6]$ ($M = \text{Co}$ **1**, Ni **2**).

1000 °C are 60.9% (for **1**) and 62.2% (for **2**), which are close to the calculated values of 62.6% (for **1**) and 62.7% (for **2**).

4. Conclusion

In summary, we have prepared the first organically templated *3d–4f* mixed metal sulfates, $[\text{H}_2\text{en}]_2\{\text{La}_2\text{M}(\text{SO}_4)_6(\text{H}_2\text{O})_2\}$ ($M = \text{Co}$ **1**, Ni **2**). Their structures feature a three-dimensional network of lanthanum nickel sulfate with tunnels occupied by the template cations. Future research efforts will be devoted to the syntheses, crystal structures and magnetic studies of other *3d–4f* mixed metal sulfates in which both types of metal ions are paramagnetic.

Acknowledgments

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