Lanthanide Complexes of Disulfoxide Ligands with Varied Configurations: Influence of Lanthanide Contraction on the Structures of the Complexes

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Four new disulfoxide-Ln^{III} complexes, $[Ln(\mathbf{L})_2(NO_3)_3]_n$ {Ln = La (**1**), $n = n$; Ln = Gd (**2**), Dy (**3**) and Yb (**4**), $n = 2$}, have been prepared by the reaction of $Ln(NO_3)_3\cdot nH_2O$ with *meso*-1,3-bis(ethylsulfinyl)propane (*meso*-**L**) in methanol/triethylorthoformate, and their solid-state structures were characterized by IR spectroscopy, elemental analyses and X-ray diffraction. Complex **1** is a 1D double-bridged chain in which the La^{III} ions are ten-coordinate and the **L** ligands adopt both *meso* and *rac* configurations, and a bis-monodentate bridging coordination mode. While complexes **2**–**4** have isostructural dinuclear structures, in which the Ln^{III} ions are nine-coordinate and the ligands show two types of coordination fashions and configurations: bis-monodentate bridging with a *meso*-configuration, and monodentate coordination with a *rac*-configuration. The structural differences between **1** and **2**–**4** indicate the influence of lanthanide contraction on the complex structures. In addition, a change in configuration of the ligand occurs when it reacts with metal ions.
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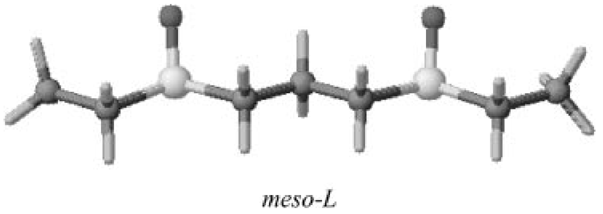
Introduction

Metal-organic architectures continue to be a subject of intense current interest,[1] because of their fascinating structural diversities and potential applications, such as in functional materials.[2] The rare earth coordination compounds may have interesting luminescence and magnetic properties,[3] and lanthanide cations usually have high coordination numbers and exhibit coordination diversity and flexibility.[4] As is well known, the structures of metal-organic architectures are influenced by many factors, such as the coordination nature of the metal ions and ligands, and reaction conditions etc.[5] Lanthanide contraction is also such a factor that affects the structures of the complexes, and is a significant research topic not only in structural control but also in the theoretical exploration of the electronic configuration of lanthanide elements.[6]

In recent years, we synthesized many metal-organic coordination compounds using flexible disulfoxide ligands,[7] which are a type of ditopic bridging ligands and have many intriguing features, such as a bidentate ditopic nature, and diastereomeric *meso* and *rac* forms. Some successful examples have shown that such ligands are able to generate unusual coordination polymers with unique structures that are governed not only by the spacer lengths and terminal groups of the ligands but also by counter anions and even solvents used in the synthesis.[7] As a continuation of such investigations, we report herein the synthesis and structures of a series of disulfoxide lanthanide complexes, $[Ln(\mathbf{L})_2(NO_3)_3]_n$ {Ln = La (**1**) $n = n$; Ln = Gd (**2**), Dy (**3**) and Yb (**4**), $n = 2$; **L** = 1,3-bis(ethylsulfinyl)propane} (for the *meso* isomer, see Scheme 1). The effect of lanthanide contraction on the structures of the complexes will also be discussed.



Scheme 1.

Results and Discussion

Syntheses and General Characterization

The *meso*-**L** ligand melts in a narrow temperature range of 101–103 °C, which indicates that it is a pure *meso* isomer. Complexes **1**–**4** were prepared by the reactions of *meso*-**L** with $Ln(NO_3)_3\cdot nH_2O$ in MeOH at room temperature with the use of triethylorthoformate as a dehydrating reagent. The results of the elemental analysis are consistent with the molecular formula evaluated by X-ray diffraction analyses for **1**–**3**, and complex **4** has a similar composition to that of complexes **2** or **3**. Such complexes are soluble in DMF and DMSO and slightly soluble in CH_3OH and CH_3CN, but almost insoluble in H_2O and acetone. The IR spectrum

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of **1** has a $\nu_{S=O}$ band at 986 cm^{-1}; this band occurs at a lower frequency than that of the free ligand (1017 cm^{-1}). The peak at this frequency disappeared in **1** indicating that all the O atoms of the ligands are coordinated to the La^{III} ions.[8] While in the spectra of **2**–**4**, vibration peaks at around 986 and 1010 cm^{-1} were observed, which indicates the partial coordination of the O atoms of the S=O entities. These results are further confirmed by X-ray structural determinations. In addition, the existence of chelating bidentately coordinated nitrate anions in the complexes was also confirmed by their IR spectra.

Structural Descriptions and Discussion

Complexes **1**–**3** were characterized by X-ray crystallography. The selected bond lengths and angles are listed in Table 1 and Table 2.

The X-ray single crystal structure reveals that complex $[La(\mathbf{L})_2(NO_3)_3]_n$ (**1**) has a 1D, double-bridging chain structure. As shown in Figure 1, the La^{III} center binds to ten O atoms, four from S=O moieties of four distinct **L** ligands and six from three chelating coordinated nitrate anions. The overall geometry is best described as a distorted bi-capped square anti-prism with two O atoms of two distinct nitrate anions in the capped positions. As listed in Table 1, the bond lengths of the La–O bonds that involve the O atoms of the four bis-monodentate **L** ligands are different [2.378(5)–2.656(5) Å with a mean value of 2.522(5) Å], perhaps as a result of steric hindering. The La–O bond lengths of the chelating nitrate anions are in the range 2.579(3)–2.749(4) Å with an average value of 2.667(4) Å, which is longer than that of the disulfoxide ligands. The *cis* bond angles around the La^{III} ion lie in a range from 47.0(2) to 85.1(2)°.

Table 1. Selected bond lengths [Å] and angles [°] for $[La(\mathbf{L})_2(NO_3)_3]_n$ (**1**).[a]

La(1)–O(1)[b]	2.601(5)	La(1)–O(7)	2.602(5)
La(1)–O(2)	2.656(5)	La(1)–O(8)	2.749(4)
La(1)–O(3)	2.378(5)	La(1)–O(9)	2.579(3)
La(1)–O(4)[b]	2.451(3)	La(1)–O(11)	2.705(5)
La(1)–O(6)	2.683(5)	La(1)–O(12)	2.684(3)
O(1)[b]–La(1)–O(2)	76.2(2)	O(3)–La(1)–O(8)	71.2(2)
O(1)[b]–La(1)–O(4)[b]	75.8(2)	O(4)[b]–La(1)–O(9)	73.7(1)
O(1)[b]–La(1)–O(6)	80.9(2)	O(4)[b]–La(1)–O(8)	69.3(2)
O(1)[b]–La(1)–O(9)	72.1(1)	O(6)–La(1)–O(7)	47.0(2)
O(1)[b]–La(1)–O(11)	70.9(1)	O(6)–La(1)–O(9)	70.9(1)
O(2)–La(1)–O(3)	84.2(2)	O(6)–La(1)–O(11)	62.2(2)
O(2)–La(1)–O(4)[b]	76.7(1)	O(6)–La(1)–O(12)	70.4(1)
O(2)–La(1)–O(11)	64.1(2)	O(7)–La(1)–O(8)	65.9(2)
O(2)–La(1)–O(12)	77.9(2)	O(7)–La(1)–O(9)	77.5(2)
O(3)–La(1)–O(4)[b]	85.1(2)	O(7)–La(1)–O(12)	63.9(2)
O(3)–La(1)–O(7)	78.7(2)	O(8)–La(1)–O(9)	46.6(1)
O(3)–La(1)–O(12)	72.2(2)	O(11)–La(1)–O(12)	46.4(1)

[a] Only those related to the higher occupancy part of the disordered atoms are listed. [b] Symmetry code: $x - 1/2, -y - 3/2, z - 1/2$.

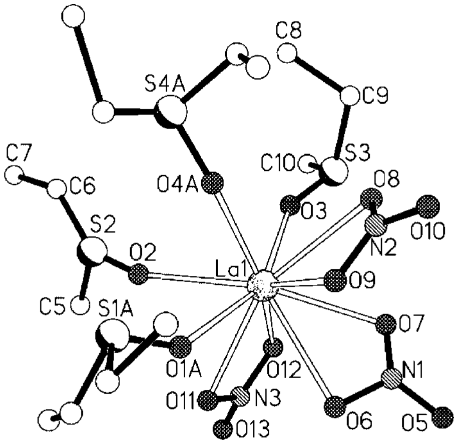


Figure 1. A view of the coordination environment of the La^{III} center in **1** (symmetry code A: $x - 1/2, -y - 3/2, z - 1/2$). The hydrogen atoms and lower occupancy part of the disordered atoms were omitted for clarity).

Table 2. Selected bond lengths [Å] and angles [°] for $[Ln(\mathbf{L})_2(NO_3)_3]_2$ (Ln = Gd, **2**; Dy, **3**).[a]

	2	**3**		**2**	**3**
Ln(1)–O(1)	2.331(2)	2.303(3)	Ln(1)–O(11)	2.505(3)	2.485(3)
Ln(1)–O(2)	2.323(2)	2.298(3)	Ln(1)–O(12)	2.494(2)	2.465(3)
Ln(1)–O(3)	2.306(2)	2.275(3)	S(1)–O(1)	1.515(3)	1.519(3)
Ln(1)–O(5)	2.465(3)	2.437(3)	S(2)–O(2)	1.531(2)	1.528(3)
Ln(1)–O(6)	2.512(2)	2.488(3)	S(3)–O(3)	1.529(2)	1.525(3)
Ln(1)–O(8)	2.522(3)	2.497(3)	S(4)–O(4)	1.472(5)	1.470(5)
Ln(1)–O(9)	2.489(3)	2.443(3)			
O(1)–Ln(1)–O(2)	81.99(8)	81.8(1)	O(3)–Ln(1)–O(8)	73.65(8)	73.2(1)
O(1)–Ln(1)–O(5)	89.72(9)	90.3(1)	O(3)–Ln(1)–O(12)	79.86(8)	80.3(1)
O(1)–Ln(1)–O(6)	76.30(8)	76.3(1)	O(5)–Ln(1)–O(6)	50.79(9)	51.7(1)
O(1)–Ln(1)–O(9)	77.33(8)	77.7(1)	O(5)–Ln(1)–O(11)	74.44(9)	74.1(1)
O(1)–Ln(1)–O(11)	73.38(8)	72.8(1)	O(5)–Ln(1)–O(12)	72.36(9)	72.5(1)
O(2)–Ln(1)–O(3)	82.51(9)	82.3(1)	O(8)–Ln(1)–O(9)	50.75(8)	51.0(1)
O(2)–Ln(1)–O(6)	77.99(8)	77.4(1)	O(8)–Ln(1)–O(12)	74.1(1)	73.9(1)
O(2)–Ln(1)–O(8)	77.44(9)	77.2(1)	O(9)–Ln(1)–O(11)	72.5(1)	72.7(1)
O(2)–Ln(1)–O(9)	80.37(9)	80.7(1)	O(9)–Ln(1)–O(12)	89.40(9)	88.4(1)
O(3)–Ln(1)–O(5)	80.75(9)	80.5(1)	O(11)–Ln(1)–O(12)	50.49(8)	51.1(1)
O(3)–Ln(1)–O(6)	76.23(8)	76.0(1)			

[a] Only those related to the higher occupancy part of the disordered atoms are listed.

In complex **1**, the ligands **L** act as bis-monodentate bridges to link the adjacent metal centers, and two such ligands link two La^{III} centers to form a 16-membered ring, which expends along the crystallographic *a* direction to form a 1D intercrossed, double-bridging chain (Figure 2). The distance between two metal centers within the ring unit is 8.898 Å. The S atoms of the ligands in **1** are disordered, each of which are refined over two positions with the occupying ratio of 6:4. Based on the higher occupation part, the ligands adopt three kinds of configurations: the *R*,*S*, *R*,*R*, and *S*,*S* forms (Figure 2); the same side chain takes one kind of configuration, either *meso* or *rac*. For the *rac* ligands, the *S*,*S* and *R*,*R* forms are arranged alternatively. The synchronous existence of two kinds of configurations in the complex reveals that the disulfoxide ligand **L** inverts part of its original configuration from *R*,*S* to either the *R*,*R* or the *S*,*S* form. The O coordination adopts a *trans*-*trans* arrangement; the La–O–S–C torsion angles range from 94.0(8) to 174.8(2)° (containing the atoms of the disordered parts). In addition, such 1D chains are parallel to each other in the crystal.

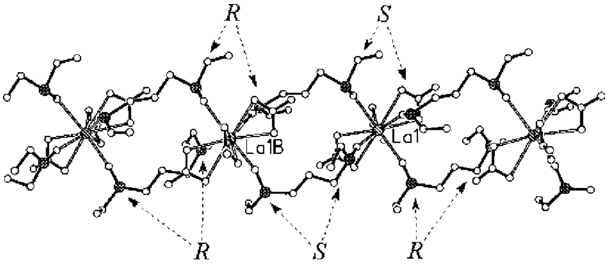


Figure 2. The 1D chain structure of **1** showing the configurations of the S atoms. The hydrogen atoms and lower occupancy part of the disordered atoms were omitted for clarity.

Complexes **2** and **3** are isostructural and the structures are composed of neutral dinuclear [Ln(**L**)$_2$(NO$_3$)$_3$]$_2$ (Ln = Gd, Dy, respectively) entities. The central metal ion is nine-coordinate and binds to three O atoms of distinct **L** ligands and six O atoms of chelating nitrate groups to give a highly disordered, tricapped, trigonal prism configuration (Figure 3). The Ln–O bond lengths involving the S=O and bidentate nitrate groups are in the normal ranges (Table 2), and lie in a more narrow range than those of **1**. The *cis* bond angles around the Ln^{III} ions range from 50.49(8) to 89.72(9)° for **2** and 51.0(1) to 90.3(1)° for **3**, respectively. As shown in Figure 4, in the binuclear entity, the two metal centers are linked by two bis-monodentate bridging ligands to form a twisted 16-membered ring with an Ln···Ln separation of 8.287 Å for **2** and 8.265 Å for **3**. It is interesting to note that the ligands **L** exhibit two kinds of coordination modes: bis-monodentate bridging and monodentate, which is a rare case in disulfoxide complexes.[7c] One of the S atoms of each monodentate disulfoxide is disordered in **2** and **3** (the occupying ratio is 9:1). On the basis of the main part of the disordered entities, the ligands adopt three kinds of configurations, *R*,*S*, *S*,*S*, and *R*,*R* forms (*meso* and *rac*) in **2** and **3**: two monodentate ligands adopt the *R*,*R* and *S*,*S* form, and two bridging ligands adopt the *meso* form. The two S atoms of the bridging ligands around the same metal center adopt the same *S* or *R* configuration, but differ from that of the mono-coordinated one. Thus, as a whole, complexes **2** and **3** are mesomeric. The O=S···S=O quasi-torsion angles between two sulfoxide groups of the ligands are 101.5 and 102.9° for the bridging ligands, and 22.8 and 22.5° for the mono-coordinated ligand in **2** and **3**, respectively. All the O coordinations adopt a *trans*-*trans* arrangement, which is exhibited by the M–O–S–C torsion angles of 109.1–143.4° for **2** and 108.5–144.4° for **3**. In addition, such dinuclear molecules are arranged in an interparallel superposition fashion in the crystal.

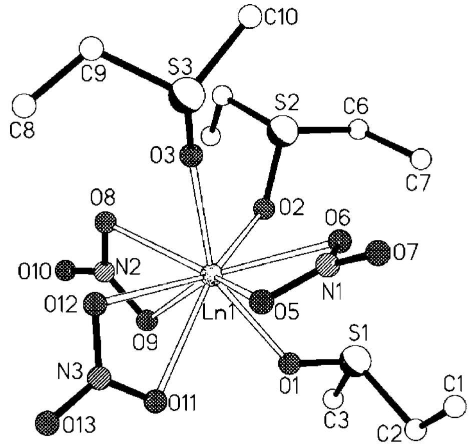


Figure 3. A view of the coordination environment of the Ln^{III} center in **2** and **3**. The hydrogen atoms and lower occupancy part of the disordered atoms were omitted for clarity.

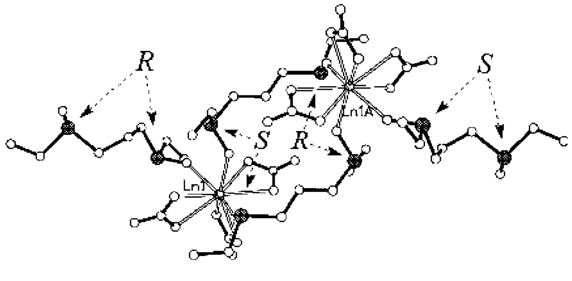
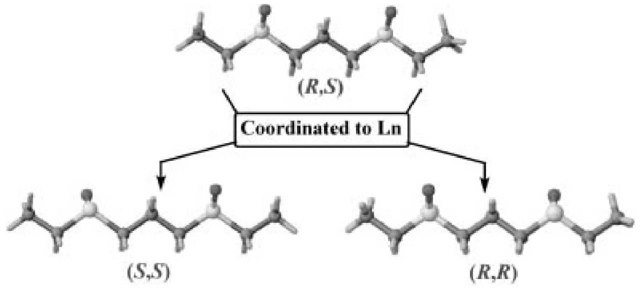


Figure 4. Dinuclear structures of **2** and **3** showing the configurations of the S atoms. The hydrogen atoms and lower occupancy part of the disordered atoms were omitted for clarity.

It should be noted that a partial configuration change of ligand **L** was observed at room temperature from *meso* to *rac* form (Scheme 2) when it reacted with lanthanide nitrate to form complexes with three stereoisomeric forms of the ligands. In some earlier investigations,[7a,9] a configurational change of the sulfoxide entities seems to occur at elevated temperatures (ca. 70–80 °C). This indicates that a metal-assisted configuration change of the disulfoxide compound may happen at room temperature.



Scheme 2.

The structural differences between **1** and **2** and **3** may be attributed to the difference in the lanthanide ion radii, i.e. lanthanide contraction. In **1**, the La^{III} ion is larger so that it can adopt a ten-coordination mode that can lead to the coordination of four O atoms from the S=O groups. While in **2** and **3**, the radius of Gd^{III} [and Dy^{III}] is smaller than that of La^{III}, so only three sulfoxide O donors take part in the coordination. Thus, **1** has a 1D structure but **2** and **3** are dinuclear.

XRPD Results; Isostructural Determination of 3 and 4

In order to further confirm if **3** and **4** have similar structures, as well as if the crystal structure of **3** is truly representative of its bulk material, X-ray powder diffraction (XRPD) experiments were carried out on the as-synthesized samples. The XRPD experimental patterns of **3** and **4**, and the computer-simulated patterns of **3** are shown in Figure 5. From the simulated and experimental patterns, we can consider that the synthesized bulk material and the as-grown crystals are almost the same for complex **3**, although there are a few unindexed diffraction lines and lines that are slightly broadened relative to those simulated from the single-crystal data. From the similar XRPD experimental patterns of **3** and **4** together with the elemental analysis results and IR spectra, we can conclude that **3** and **4** should have similar structures.

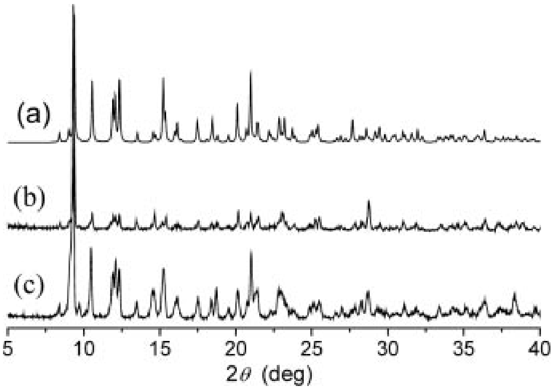


Figure 5. Powder X-ray diffraction patterns of **3** and **4**: (a) the simulated result of **3**, (b) the experimental result of **3**, and (c) the experimental result of **4**.

In addition, a suitable comparison can be made between **4** and a reported Yb^{III} complex, $[Yb(\mathbf{L}')_{1.5}(NO_3)_3]_n$,[7a] with a similar disulfoxide ligand, 1,2-bis(ethylsulfinyl)ethane (**L′**). Although **L′** has a shorter spacer than **L**, the resulted complex has a 1D single-bridging chain structure. The structural difference may be attributed to the spacer lengths of the ligands.

In summary, a series of new Ln-disulfoxide complexes with 1D or dinuclear structures have been obtained by assembling $Ln(NO_3)_3$ and a flexible disulfoxide ligand. The structural differences between these complexes show the influence of lanthanide contraction on the structures of the complexes. The ligands exhibit different configurations in the complexes, which is interesting for the investigation of disulfoxide metal complexes. In addition, a change in configuration of the ligand at room temperature has been observed when it reacts with Ln^{III} ions.

Experimental Section

Materials and General Methods: All reagents for synthesis and analyses were of analytical grade and used as received. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. IR spectra (KBr pellets) were recorded with a FT-IR 170SX (Nicolet) spectrometer. ^1H NMR spectra were measured on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C with tetramethylsilane as the internal reference. Melting point measurements were measured on an X-4 melting point meter.

Synthesis of the Ligand: 1,3-Bis(ethylsulfinyl)propane was synthesized according to a similar method reported previously[10] by oxidizing the bis(thio) precursor 1,3-bis(ethylthio)propane (obtained by the reaction of 1,3-bis(bromo)propane with sodium ethylthiolate). The *meso* isomer was separated from the isomeric mixture products by fractional crystallization from acetone. Yield: 50%. M.p. 101–103 °C. ^1H NMR ($CDCl_3$): δ = 2.66–2.78 (m, 8 H, $–CH_2–S–CH_2–$), 2.35 (t, 2 H, $C–CH_2–C$), 1.37 (t, 6 H, $CH_3–$) ppm. IR: 2963 (s), 1427 (m), 1042 (m), 1017 (s), 974 (m), 785 (m), 650 (m) cm^{-1}.

Synthesis of Complexes 1–4: The four complexes were prepared at room temperature according to the following method. A solution of $Ln(NO_3)_3 \cdot nH_2O$ (0.3 mmol) in methanol (10 mL) was added to a solution of *meso*-**L** (171 mg, 0.6 mmol) in methanol/triethylorthoformate (2:3, 15 mL). The reaction mixture was stirred for about 30 min and filtered to give a colorless solution. Slow solvent evaporation of the resulting solution gave rise to white solid products that contained a few colorless single crystals suitable for X-ray analysis.

$[La(L)_2(NO_3)_3]_n$ (1): Yield: 85 mg, 40%. $C_{14}H_{32}LaN_3O_{13}S_4$ (717.58): calcd. C 23.43, H 4.49, N 5.86; found C 23.11, H 5.02, N 5.65. IR: 2975 (m), 2938 (m), 2506 (w), 1987 (w), 1730 (w), 1631 (w), 1473 (s), 1410 (m), 1384 (s), 1315 (s), 1291(s), 1131 (w), 1027 (s), 986 (s), 967 (s), 816 (m), 780 (w), 736 (m), 627 (w) cm^{-1}.

$[Gd(L)_2(NO_3)_3]_2$ (2): Yield: 97 mg, 44%. $C_{14}H_{32}GdN_3O_{13}S_4$ (735.92): calcd. C 22.85, H 4.38, N 5.71; found C 22.33, H 5.54, N 5.95. IR: 2976 (m), 2940 (m), 2508 (w), 1988 (w), 1732 (w), 1633 (w), 1476 (s), 1410 (m), 1384 (s), 1317 (s), 1296 (s), 1131 (w), 1029 (s), 1009 (m), 986 (s), 968 (s), 817 (m), 779 (w), 739 (m), 629 (w) cm^{-1}.

$[Dy(L)_2(NO_3)_3]_2$ (3): Yield: 104 mg, 47%. $C_{14}H_{32}DyN_3O_{13}S_4$ (741.17): calcd. C 22.69, H 4.35, N 5.67; found C 22.25, H 5.25, N 5.86. IR: 2976 (m), 2941 (m), 2509 (w), 1989 (w), 1733 (w), 1630 (w), 1487 (s), 1410 (m), 1384 (s), 1318 (s), 1299 (s), 1131 (w), 1030

Table 3. Crystallographic data and structure refinement summary for complexes **1**–**3**.

	$[La(\mathbf{L})_2(NO_3)_3]_n$ (**1**)[a]	$[Gd(\mathbf{L})_2(NO_3)_3]_2$ (**2**)	$[Dy(\mathbf{L})_2(NO_3)_3]_2$ (**3**)
Empirical formula	$C_{14}H_{32}LaN_3O_{13}S_4$	$C_{28}H_{64}Gd_2N_6O_{26}S_8$	$C_{28}H_{64}Dy_2N_6O_{26}S_4$
Formula weight	717.58	735.92	1482.33
Temperature [K]	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	Cc	$P2_1/n$	$P2_1/n$
a [Å]	18.526(7)	11.800(4)	11.787(4)
b [Å]	10.819(4)	18.281(6)	18.177(6)
c [Å]	16.532(6)	13.182(4)	13.059(4)
β [°]	122.546(5)	99.201(5)	99.393(5)
Volume [Å^3]	2793(2)	2807(2)	2761(2)
Z	4	2	2
Crystal size [mm]	0.26 × 0.20 × 0.18	0.26 × 0.20 × 0.20	0.28 × 0.24 × 0.20
$D_{calcd.}$ [g cm^{-3}]	1.706	1.741	1.783
μ [mm^{-1}]	1.889	2.720	3.071
$F(000)$	1448	1476	1484
θ range [°]	2.29–26.40	2.07–26.40	2.74–26.43
Reflections measured	6301	15823	15652
Unique reflections	3135	5718	5644
R_{int}	0.0504	0.0464	0.0270
Parameters	376	352	361
Goodness of fit on F^2	1.025	1.016	1.033
R[b]/wR[c]	0.0529/0.1341	0.0453/0.1153	0.0278/0.0650
$\Delta_{max,\ min}$ [e Å^{-3}]	0.672, –0.652	0.831, –0.893	0.981, –0.579

[a] The "twin" refinement was used [Flack parameter = 0.35(2)]. [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)]^{1/2}$.

(s), 1011 (m), 986 (s), 968 (s), 817 (m), 779 (w), 741 (m), 630 (w) cm^{-1}.

$[Yb(L)_2(NO_3)_3]_2$ (4): Yield: 88 mg, 39%. $C_{14}H_{32}YbN_3O_{13}S_4$ (751.70): calcd. C 22.37, H 4.29, N 5.59; found C 21.51, H 5.14, N 6.19. IR: 2977 (m), 2941 (m), 2513 (w), 1992 (w), 1735 (w), 1630 (w), 1487 (s), 1409 (m), 1384 (s), 1323 (s), 1299 (s), 1131 (w), 1032 (s), 1010 (s), 990 (s), 969 (s), 816 (m), 778 (w), 745 (m), 630 (w) cm^{-1}.

X-ray Crystallography: Single-crystal X-ray diffraction for **1**–**3** was carried out with a Bruker Smart 1000 diffractometer. Intensities of reflections were measured by using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) with ω-φ scan mode at room temperature. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied by using the SADABS program.[11] The structures were solved by direct methods by combining successive difference Fourier syntheses.[12] The final refinement was performed by full-matrix least-squares methods on F^2 with the SHELXL-97 program package.[12] For **1**, the ligand is highly disordered, and some C and S atoms were refined in two different positions (occupation ratio 6:4) and restrained. In **2** and **3**, some S and O atoms were also refined in two different positions with partial occupation factors of 0.9 and 0.1, respectively. Some hydrogen atoms of the ligands in **1**–**3** cannot be added due to the above-mentioned disorder. All added hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analysis are summarized in Table 3. CCDC-252924–252926 contain the supplementary crystallographic data for **1**–**3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The X-ray powder diffraction patterns (XRPD) of **3** and **4** were recorded on a Rigaku D/Max-2500 diffractometer, operated at 40 kV and 100 mA, by using a Cu-target tube and a graphite monochromator. Fixed scatter and divergence slits of 1° and a 0.3-mm receiving slit were used. The intensity data were recorded by continuous scan in a $2\theta/\theta$ mode from 3° to 60°, with a step size of 0.02° and a scan speed of 8° min^{-1}. Simulation of the XRPD spectra was carried out by the single-crystal data and diffraction-crystal module of the commercially available Cerius2 program.[13]

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