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Note

Novel Lanthanide(III) Coordination Polymers with 1,4-Bis(phenyl-sulfinyl)butane Forming Unique Lamellar Square Array: Syntheses, Crystal Structures, and Properties

Xian-He Bu,[*,†,‡] Wei Weng,[†] Miao Du,[†] Wei Chen,[†] Jian-Rong Li,[†] Ruo-Hua Zhang,[†] and Li-Juan Zhao[§]

Departments of Chemistry and Physics, Nankai University, Tianjin 300071, P. R. China, and The State Key Lab of Rare Earth Material Chemistry and Applications, Peking University, Beijing 100871, P. R. China

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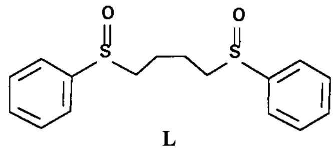
Introduction

The construction of organized molecular architectures containing lanthanide ions is a theme of considerable current interest in supramolecular and material chemistry owing to potential applications as new materials.[1] Our studies[2] on the metal complexes with a flexible bis(sulfinyl) show several interesting features for such ligands: their propensity to form multidimensional coordination polymers with both transition metals and rare earth elements in which the metal ions act as nodes forming macrometallocyles, and their preference for O-bonding in "hard acid" metal complexes, such as Ln^{III}, Cu^{II},[2c,3] and Sn^{II},[4] and for σ-bonding (*S*-bonding) which is prevalent only in soft Ru^{III}, Pt^{II}, and Pd^{II} complexes.[5,6] Such structurally flexible ligands have the possibility to form diverse extended networks which might be influenced and controlled by the length of the spacer units[2c] and the template anions. Furthermore, lanthanide networks, especially when studied across the whole series, are relatively unexplored compared to transition metal coordination systems.[1h,i] As a continuation of our study, we report herein the syntheses, crystal structures, and luminescent and magnetic properties of a novel series of Ln^{III} coordination polymers with 1,4-bis(phenylsulfinyl)butane (**L**, Chart 1) that form a unique lamellar square array.

Chart 1



L

Experimental Section

General Information. Most of the starting materials and solvents for syntheses were commercially available and were used as received. IR and electronic spectra were recorded on a Nicolet Magna-IR 750 spectrometer and a Hitachi UV-3010 spectrometer, respectively. TG-DTA curves were recorded on a Dupont thermal analyzer. Elemental analyses were obtained on an Elementar Vario EL analyzer. ^{1}H NMR spectra were carried out on a Varian UNITY-plus spectrometer at 25 °C with tetramethylsilane as internal reference.

Preparations. *Caution!* While we have experienced no problems in handling Ln^{III} perchlorate, these should be handled with great caution because of the potential for explosion.

1,4-Bis(phenylsulfinyl)butane. The ligand, 1,4-bis(phenylsulfinyl)butane (**L**), was prepared according to our previous work[7] and purified by fractional recrystallization from acetone. Anal. Calcd for C$_{16}$H$_{18}$S$_2$O$_2$: C, 62.74; H, 5.88. Found: C, 62.50; H, 5.62. Mp 84−86 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.27−7.59 (m, 10H, Ph), 2.73−2.79 (m, 4H, −CH$_2$), 1.71−1.93 (m, 4H, −CH$_2$). Selected IR (KBr pellet, cm^{-1}): 2986w, 1440m, 1035s, 742m, 690m.

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[*] Corresponding author. E-mail: buxh@nankai.edu.cn. Fax: +86-22-23530850.

[†] Department of Chemistry, Nankai University.

[‡] Peking University.

[§] Department of Physics, Nankai University.

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Table 1. Crystallographic Data and Structural Refinement Summary for **1**−**3** and **6**

	1	**2**	**3**	**6**
formula	$[LaL_2(DMF)_4](ClO_4)_3{\cdot}CHCl_3$	$[PrL_2(DMF)_4](ClO_4)_3{\cdot}2H_2O$	$[EuL_2(DMF)_4](ClO_4)_3{\cdot}2H_2O$	$[YL_2(DMF)_4](ClO_4)_3{\cdot}8H_2O$
M_r	1461.86	1380.52	1391.57	1436.62
space group	P_4/ncc	P_4/ncc	P_4/ncc	P_4/ncc
a (Å)	15.8110(8)	15.7124(7)	15.6617(8)	15.5776(7)
b (Å)	15.8110(8)	15.7124(7)	15.6617(8)	15.5776(7)
c (Å)	28.283(2)	28.4342(19)	28.468(2)	28.4289(16)
V (Å^3)	7070.5(7)	7019.8(6)	6983.0(7)	6898.6(6)
D_c (g/cm^3)	1.373	1.306	1.324	1.383
Z	4	4	4	4
R_1	0.0527	0.0501	0.0475	0.0830
wR	0.1504	0.1581	0.1221	0.2047

[LnL$_2$(DMF)$_4$](ClO$_4$)$_3$. The general procedure for complex preparation was as follows: triethylorthoformate (2 mL) was added to the $CHCl_3$ solution (5 mL) of **L** (230 mg, 0.75 mmol), and the mixture was stirred for ∼20 min. Then, $Ln(ClO_4)_3{\cdot}nH_2O$ (0.25 mmol) in anhydrous methanol (10 mL) was added dropwise to the mixture, and a precipitate soon appeared. The mixture was further stirred at 70−80 °C for 4 h. Then, DMF (2 mL) was added, and the precipitate dissolved. The solution was filtered, and the filtrate was allowed to evaporate slowly at room temperature for several days, until microcrystals were obtained. Single crystals suitable for X-ray analyses were obtained by further recrystallization from DMF and $CHCl_3$.

[LaL$_2$(DMF)$_4$](ClO$_4$)$_3$·CHCl$_3$ (1). Yield: 48%. Anal. Calcd for $C_{45}H_{65}Cl_6LaN_4O_{20}S_4$: C, 36.97; H, 4.48; N, 3.83. Found: C, 37.34; H, 4.11; N, 3.64. IR (KBr pellet, cm^{-1}): 2944w, 1644vs, 1445m, 1379m, 1090vs, 1003m, 989vs, 761m, 624m.

[PrL$_2$(DMF)$_4$](ClO$_4$)$_3$·2H$_2$O (2). Yield: 45%. Anal. Calcd for $C_{44}H_{68}Cl_3PrN_4O_{22}S_4$: C, 38.27; H, 4.93; N, 4.05. Found: C, 38.41; H, 5.19; N, 4.36. IR (KBr pellet, cm^{-1}): 2945w, 1644vs, 1444m, 1384m, 1093vs, 1002m, 989vs, 761m, 623m.

[EuL$_2$(DMF)$_4$](ClO$_4$)$_3$·4H$_2$O (3). Yield: 40%. Anal. Calcd for $C_{44}H_{72}Cl_3EuN_4O_{22}S_4$: C, 37.97; H, 4.89; N, 4.03. Found: C, 37.62; H, 4.57; N, 3.81. IR (KBr pellet, cm^{-1}): 2946w, 1673s, 1647vs, 1444m, 1384m, 1093vs, 1004m, 991s, 757m, 627m.

[GdL$_2$(DMF)$_4$](ClO$_4$)$_3$·4H$_2$O (4). Yield: 47%. Anal. Calcd for $C_{44}H_{72}Cl_3GdN_4O_{24}S_4$: C, 36.87; H, 5.03; N, 3.91. Found: C, 36.64; H, 4.76; N, 3.89. IR (KBr pellet, cm^{-1}): 2950w, 1670m, 1647vs, 1443m, 1383m, 1093vs, 1003m, 992s, 758m, 628m.

[TbL$_2$(DMF)$_4$](ClO$_4$)$_3$·3H$_2$O (5). Yield: 52%. Anal. Calcd for $C_{44}H_{70}Cl_3TbN_4O_{23}S_4$: C, 37.30; H, 4.94; N, 3.96. Found: C, 37.37; H, 4.81; N, 4.33. IR (KBr pellet, cm^{-1}): 2950w, 1668m, 1646vs, 1443m, 1383m, 1094vs, 1003m, 991s, 758m, 628m.

[YL$_2$(DMF)$_4$](ClO$_4$)$_3$·8H$_2$O (6). Yield: 56%. Anal. Calcd for $C_{44}H_{80}Cl_3YN_4O_{28}S_4$: C, 36.78; H, 5.61; N, 3.90. Found: C, 36.44; H, 5.92; N, 3.99. IR (KBr pellet, cm^{-1}): 2947w, 1655m, 1444m, 1389m, 1087vs, 1012m, 995m, 753m, 626s.

Luminescence and Magnetic Measurements. The luminescent spectra were measured on powder samples and in solution (10^{-3} M in CH_3CN or DMF) at room temperature using a model FIII AI Fluorolog-2 spectrofluorometer, recording in the λ range 550−720 nm (**3**) and 450−700 nm (**5**). Variable-temperature magnetic susceptibilities (4.2−300 K) of **4** were measured on a model CF-1 vibrating-sample magnetometer. Diamagnetic correction was made with Pascal's constant for all the constituent atoms, and the magnetic moments were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_m T)^{1/2}$.

X-ray Crystallography. Intensities of reflections were measured on a Bruker Smart 1000 CCD diffractometer at room temperature using graphite monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å, ω mode, θ range 1.44−25.03° for **1**, 1.83−25.03° for **2**, 1.43−25.03° for **3**, and 3.61−26.03° for **6**, respectively). Semiempirical absorption corrections were applied using the SADABS program. All the structures were solved by direct methods.[8] Ln^{III} atoms were located from E-maps, and the other non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods on F^2 using SHELXL-97 program package.[8] Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

Results and Discussion

Syntheses and General Characterization. The complexes were prepared by the reaction of $Ln(ClO_4)_3{\cdot}nH_2O$ with **L** and DMF in $CH_3OH/CHCl_3$ in the presence of triethylorthoformate to dehydrate. TGA studies showed that all the complexes are stable in air and that the loss of solvent molecules takes place at ∼100−130 °C. The starting point of decomposition was ∼230 °C. All the complexes are soluble in DMF and DMSO, slightly soluble in CH_3OH and CH_3CN, and almost insoluble in H_2O. Their IR spectra indicated that **L** binds Ln^{III} through its O atoms of the sulfinyl moieties, and the S═O bond stretching frequencies (989−995 cm^{-1}) are lower than that in the free ligand (1035 cm^{-1}). The perchlorate anions are uncoordinated.[9]

Descriptions of the Crystal Structures. The X-ray crystal structures of **1**−**3** and **6** showed that these complexes are isomorphous (see Table 1) and isostructural. Each complex consists of polymeric $\{[LnL_2(DMF)_4]^{3+}\}_\infty$ cation, ClO_4^-, or guest solvent molecules. Each Ln^{III} is bonded to four O atoms from four distinct **L** ligands and four DMF molecules (see Figure 1; the Eu complex is shown as an example). The O atoms of the sulfinyl moieties and carbonyl groups are arranged at the corners of the square antiprism, and each Ln^{III} ion is located at the 4-fold axis. The Ln−O distances fall into two distinct groups: the bond lengths of the O atoms in sulfinyl groups and those of the carbonyl groups of DMF, decreasing with the contraction of the ionic radii of Ln^{III} (see Table 2). The central Ln^{III} ion displays a slightly distorted square antiprism coordination geometry (Figure 1b), and the degree of the distortion decreases from La^{III} to Y^{III}. In all cases, the sulfinyl and carbonyl groups substantially retain their double bond character.

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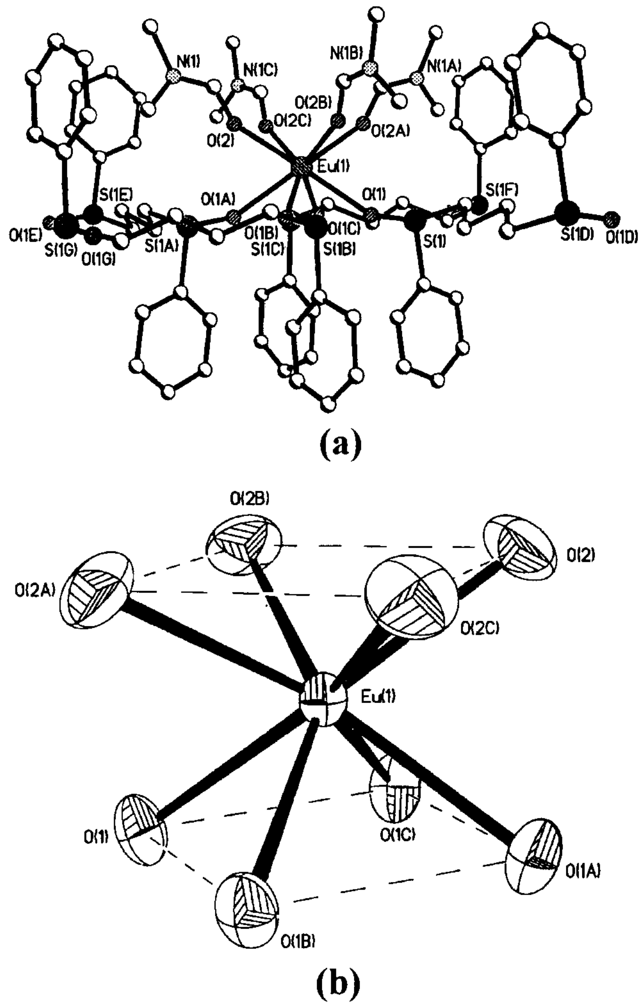

Figure 1. (a) ORTEP view of the mononuclear segment of the Eu^{III} complex. (b) Coordination environment around each Eu^{III} ion. Other complexes are isostructural.

Table 2. Selected Bond Distance (Å) and Angles (deg) for Complexes **1**−**3** and **6**

	1	2	3	6
Ln(1)−O(1)	2.497(4)	2.438(4)	2.395(4)	2.354(4)
Ln(1)−O(2)	2.489(5)	2.444(5)	2.396(4)	2.342(4)
O(1)−Ln(1)−O(1C)	69.97(10)	70.81(10)	71.28(10)	71.64(10)
O(2)−Ln(1)−O(2C)	77.39(10)	75.84(12)	75.10(11)	75.05(12)
O(1)−Ln(1)−O(1A)	108.37(19)	108.37(19)	111.0(2)	111.7(2)
O(2)−Ln(1)−O(2A)	124.3(2)	120.7(3)	119.1(2)	119.0(3)
O(2)−Ln(1)−O(1A)	74.40(15)	75.44(17)	76.17(16)	76.64(16)
O(2)−Ln(1)−O(1)	144.68(16)	144.94(17)	144.44(16)	143.25(16)
O(2)−Ln(1)−O(1C)	78.74(16)	79.26(17)	79.06(16)	78.07(17)
O(2)−Ln(1)−O(1B)	137.92(16)	138.9(17)	139.84(16)	143.25(16)

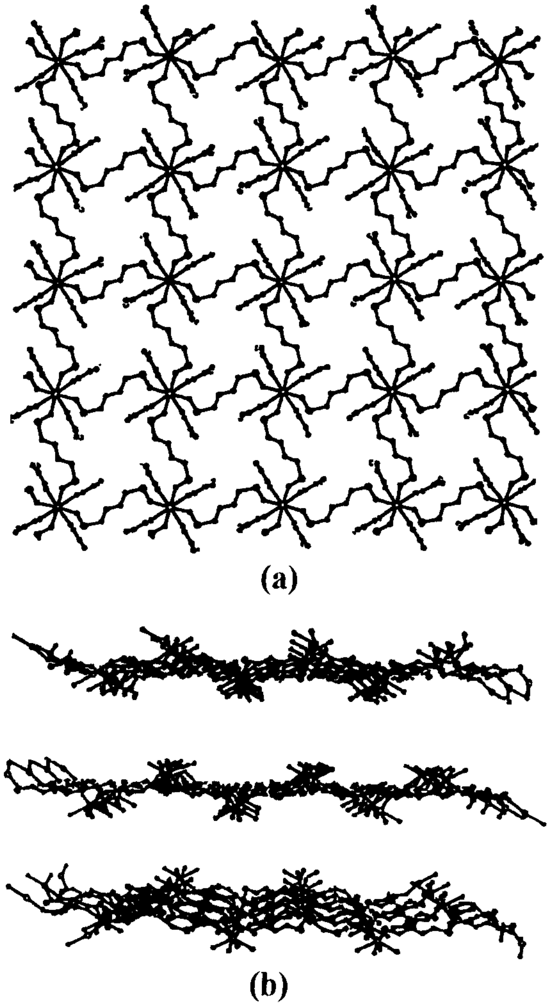

Figure 2. (a) Top view of the square-grid array of the complexes (phenyl groups, hydrogen atoms, solvent, and ClO_4^- were omitted for clarity). (b) Side view of the sheets.

As shown in Figure 2a, each Ln^{III} is bridged by four **L** ligands to four adjacent Ln^{III} centers which results in an infinite noninterpenetrated 2D (4,4) network.[10] **L** and DMF bind the Ln^{III} ions from opposite directions in adjacent Ln−Ln chains along the *a* axis. Therefore, the Ln^{III} positions in adjacent Ln−Ln chains are up and down from the 2D sheets (see Figure 2b). The structures comprise infinite square grids with 36-membered $(LnL)_4$ macrometallocycles, and each grid contains four Ln^{III} atoms. One ClO_4^- anion is situated in the cavity of the grid probably to serve as template for the formation of the square grid, while the other two ClO_4^- anions are sandwiched between layers to keep electric balance.

Although we have not analyzed the crystal structures of the complexes of the whole Ln^{III} series, the four crystal structures could be representative of the three groups of the Ln^{III} series[1i] (Y^{III} is usually regarded as belonging to the group of the heavy Ln^{III}). We could thus conclude that the complexes of **L** with the whole Ln^{III} perchlorate series are isomorphous and isostructural.

Comparing this series of complexes with $[Ln\mathbf{L}(NO_3)_3]_\infty$ (Ln = La, Nd and Eu),[2a,b] we find that the complexes reported herein have the same 8-coordination for the whole lanthanide series in a square antiprism coordination environment, while the $[Ln\mathbf{L}(NO_3)_3]_\infty$ series comprise neutral complexes and have different coordination numbers (10-coordination for the La^{III} and Nd^{III} complexes forming 1D coordination polymers and 9-coordination for the Eu^{III} complex forming a 2D network).[2a,b] *These striking differences indicate that the counteranions have a very important role in controlling the structures of such complexes.*

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Luminescence Properties of 3 (Eu^{III}) and 5 (Tb^{III}). Compounds **3** and **5** exhibit intense luminescence in the solid state. Excitation at 394 (for **3**) or 377 nm (for **5**) results in intense emission (see Supporting Information). For **3**, four emission bands are resolved corresponding to the transitions from the $^5D_0$ excited state to ^7F_J ($J = 1-4$), and the 3-fold degeneracy of the $^7F_1$ free-ion state is not split. The $^5D_0 - {}^7F_2$ manifold consists of two peaks, and the $^5D_0 - {}^7F_4$ manifold exhibits two peaks at different energies. The intensity of $^5D_0 - {}^7F_2$ and $^5D_0 - {}^7F_1$ is almost equivalent. The results indicate that the site symmetry is not too far from D_{4d},[11] which is in agreement with the structural data. The emission spectrum of **5** contains four bands corresponding to the transitions from the $^5D_4$ excited state to ^7F_J ($J = 3-6$) levels. The luminescences of **3** and **5** were also retained in CH_3CN and DMF. Compound **3** shows remarkable spectral changes in relative intensities ($^5D_0 - {}^7F_2/{}^5D_0 - {}^7F_1$) and in the appearance of $^5D_0 - {}^7F_0$ on passing from solid to solution probably because the solvents may affect the coordination environments of Eu^{III} ions, and the site symmetry of Eu^{III} in solution may thus be lowered. In addition, the spectral changes of **5** from solid to solution are not obvious.

Magnetic Properties of 4. Magnetic susceptibility measurements on the Gd^{III} complex (**4**) were made on a solid sample in the 4.2−300 K range (see Supporting Information). According to the crystal structure data of related complex **3**, the distance between the adjacent Gd^{III} ions in **4** should be larger than 10 Å. Therefore, the intramolecular magnetic interaction can be omitted, and the treatment of the magnetic data is performed according to the following equation:[12]

$$\chi(J) = Ng_J^2\beta^2 J(J+1)/3kT + 2N\beta^2(g_J - 1)(g_J - 2)/3\lambda \quad (1)$$

The Gd^{III} ion has a $^8S_{7/2}$ ground state, which is located at 3×10^{-4} cm^{-1} below the first excited state and is not perturbed by crystal field effects, and it has no orbital angular momentum. The Zeemann factor g_J is equal to 2, and the TIP term appearing on the right-hand side of eq 1 is negligible. The magnetic susceptibility should obey the Curie law ($\chi_m = 21N\beta^2/kT$), and the experiment data are in line with this. At 293 K, the effective magnetic moment is 8.02 μ_B, and $\chi_m T$ is equal to 8.04 cm^3 K mol^{-1}, being slightly higher than the calculated value (7.94 μ_B and 7.70 ± 0.05 cm^3 K mol^{-1})[12,13] for the free ion ground state ($^8S_{7/2}$) of Gd^{III}. The change of $\chi_m T$ is in the range 7.78 ± 0.92 cm^3 K mol^{-1} from 300 to 4.2 K. When T is further lowered below 8.5 K, the $\chi_m T$ decreases slightly and reaches 6.86 cm^3 K mol^{-1} at 4.2 K, probably because of a small zero-field splitting within the $^8S_{7/2}$ state.

In summary, a series of Ln^{III} coordination polymers with a flexible bis(sulfinyl) ligand, **L**, forming a unique non-interpenetrated 2D (4,4) net has been reported. The coordination number of the Ln^{III} ions across the whole Ln^{III} series remains unchanged, and all the complexes of this series are isomorphous and isostructural. Thus, the correlation between the ionic radii and the Ln^{III}−O interatomic distances in the whole Ln^{III} series becomes possible. The Ln−$O_{S=O}$ or Ln−$O_{C=O}$ bond distances and the Ln−Ln nonbond distances decrease with the contraction of the ionic radii of Ln^{III}. Further studies toward the construction of novel lanthanide networks with interesting properties and structures are under way in our laboratory.

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Supporting Information Available: Four X-ray crystallographic files in CIF format, the luminescence spectra and data for **3** and **5**, and the magnetic diagram of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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