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Note

Novel Five-Connected Lanthanide(III)–Bis(sulfinyl) Coordination Polymers Forming a Unique Two-Dimensional ($^3_4$, 5) Network

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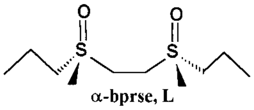
Introduction

Crystal engineering and construction of coordination polymers with fascinating structural topologies have attracted great attention in recent years due to their potential as functional materials.[1] So far, most of the work reported in the literature has been focused on the coordination polymers of d-block transition metal elements.[2] The lanthanide ions generally display variable and high coordination numbers, the energy differences between the various coordination geometries are small,[3] and they show low stereochemical preference.[4] Therefore, the use of lanthanide ions as nodes for the construction of coordination polymers with desired structures is more difficult than their d-block metal analogues, and this makes them attractive for the construction of novel and unusual networks.

We report herein two novel lanthanide(III) coordination polymers consisting of unusual five-connected lanthanum nodes, with a flexible *meso*-bis(sulfinyl) bridging ligand, 1,3-bis(*n*-propylsulfinyl)ethane (α-bprse, **L**), forming a unique and unprecedented two-dimensional ($^3_4$, 5) network, which has been predicated by Wells.[5] Our consideration for using flexible bis(sulfinyl) as bridging ligand is as follows: (a) Their pyramidal S atoms are asymmetric centers that can introduce acentric sites into the resulted crystals. (b) Their backbone and terminal groups could be changed easily; thus, the structures of their complexes might be adjusted easily by ligand modifications.[6b] (c) Such ligands are likely to be widely relevant in the context of a vast variety of metal moieties, while their chemistry is still less developed.[6]



α-bprse, L

Experimental Section

All reagents and solvents were commercially available and used as received. Elemental analysis was carried out on a Perkin-Elmer 240 elemental analyzer, and IR spectra were recorded on a Nicolet 170 SX FT-IR spectrometer.

Synthesis of Ligand and Complexes. The ligand was synthesized according to the method described previously.[7]

[$Ln_2(\mu$-$L)_5(NCS)_6]_n$ (Ln = Nd, Yb, Corresponding to **1** and **2**). Triethyl orthoformate (2 mL) was added to the methanol solution (2 mL) of **L** (0.75 mmol), and the mixture was stirred for 10 min. Hydrated lanthanide thiocyanate (0.25 mmol) in anhydrous methanol (5 mL) was added dropwise to the above solution, and the mixture was stirred at 70−80 °C for 4 h and then filtered. After the slow evaporation of the solvent, the complex was appeared as a precipitate and was obtained by filtration, washed with acetone, and dried in a vacuum. The single crystals of **1** and **2** suitable for X-ray analysis were obtained by recrystallization of the corresponding precipitates from methanol.

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Table 1. Crystallographic Data for Complexes **1** and **2**

param	**1**	**2**
empirical formula	$C_{23}H_{45}N_3O_5S_8Nd$	$C_{23}H_{45}N_3O_5S_8Yb$
fw	844.34	873.14
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.105(2)	8.9752(6)
b, Å	12.472(3)	12.4973(8)
c, Å	17.450(4)	17.1536(10)
α, deg	97.639(4)	97.0230(10)
β, deg	96.240(5)	95.5590(10)
γ, deg	97.378(5)	96.9410(10)
V, Å^3	1931.9(8)	1883.4(2)
Z	2	2
T, K	298(2)	298(2)
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.452	1.540
μ, mm^{-1}	1.809	2.960
R_1	0.0411	0.0339
wR	0.1103	0.0853

$[Nd_2(\mu\text{-}L)_5(NCS)_6]_\infty$, 1. Yield: 42%. Anal. Calcd for $C_{23}H_{45}N_3O_5S_8Nd$: C, 32.70; H, 5.34; N, 4.98. Found: C, 32.74; H, 5.40; N, 4.78. IR (KBr, cm^{-1}): 2966 m, 2064 vs ($\nu_{C=N}$), 1637 w, 1459 w, 1384 w, 999 vs ($\nu_{S=O}$), 759 w, 670 w.

$[Yb_2(\mu\text{-}L)_5(NCS)_6]_\infty$, 2. Yield: 40%. Anal. Calcd for $C_{23}H_{45}N_3O_5S_8Yb$: C, 31.21; H, 5.10; N, 4.80. Found: C, 31.13; H, 4.81; N, 4.71. IR (KBr, cm^{-1}): 2965 m, 2076 vs ($\nu_{C=N}$), 1637 w, 1459 w, 1384 w, 1008 s, 984 vs ($\nu_{S=O}$), 761 w, 670 w.

X-ray crystallography. Single-crystal X-ray diffraction measurements of **1** (0.10 × 0.15 × 0.30 mm^3) and **2** (0.05 × 0.15 × 0.20 mm^3) were carried out with a Bruker Smart 1000 diffractometer at room temperature. Intensities of reflections were measured using graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) with the ω scan mode in the range of $1.19 \leq \theta \leq 25.03°$ (for **1**) and $1.66 \leq \theta \leq 25.03°$ (for **2**). The structures were solved by direct methods (SHELXS-97),[8] and the Ln^{III} ions were located from E-maps. 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 by the SHELXL-97 program package. Hydrogen atoms were included in calculated position and refined with isotropic thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1 and in the Supporting Information.

Results and Discussion

Synthesis and General Characterization. The Ln^{III} (Ln = Nd, Yb, corresponding to complexes **1** and **2**) thiocyanate complexes of **L** were synthesized by the direct reaction between $Ln(NCS)_3 \cdot nH_2O$ and **L** in methanol in the presence of triethyl orthoformate. Both **1** and **2** showed similar IR spectra in which characteristic bands assignable to $\nu_{S=O}$ (~990 cm^{-1}) and $\nu_{C=N}$ (~2060 cm^{-1}) were observed, indicating that **L** binds Ln^{III} through its oxygen atoms of the sulfoxide groups and thiocyanate binds the metal ions with its nitrogen atom.[9] Elemental analyses revealed the components of **1** and **2** to be $Ln_2\mathbf{L}_5(NCS)_6$. The La^{III}, Pr^{III}, Gd^{III}, and Ho^{III} complexes have also been prepared and obtained as powder, and elemental analysis also revealed their components to be the same as those of **1** and **2**; however, single crystals of these complexes suitable for X-ray analysis have not been obtained and their structural motifs are not clear.

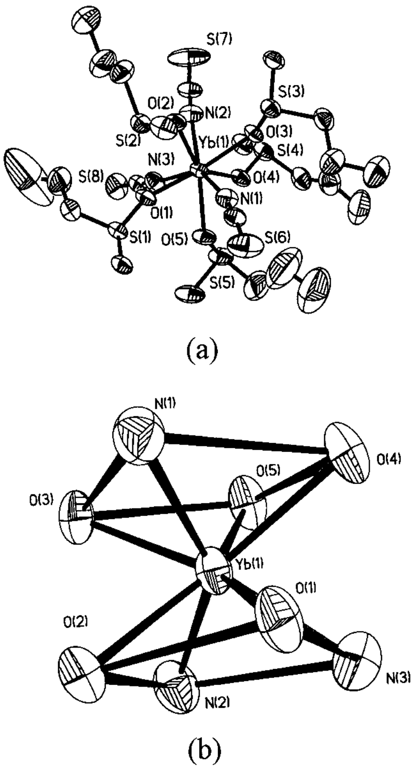

Figure 1. ORTEP view of the mononuclear segment of **2** (a) and the metal coordination environment in **2** (b).

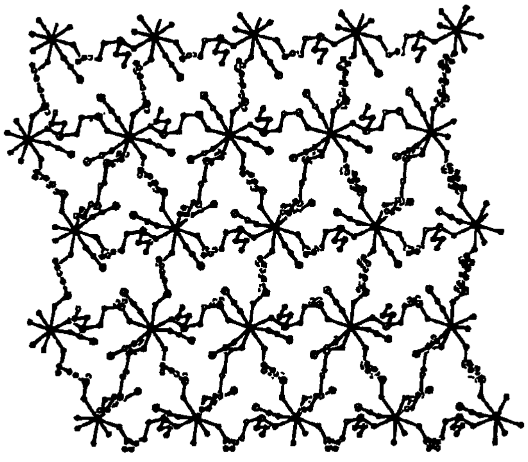

Figure 2. Two-dimensional network of **2** forming a $(\genfrac{}{}{0pt}{}{3}{4}, 5)$ net.

Crystal Structure. The crystal structures of **1** and **2** are isostructural (Figures 1 and 2 show the structure of **2**). They all have unique two-dimensional framework containing eight-coordinated Ln^{III} centers (Figure 1). Each Ln^{III} ion is surrounded by five oxygen atoms from five distinct **L** ligands and three nitrogen atoms of three SCN$^-$ anions, and each Ln^{III} ion is in a distorted square antiprism coordination environment (Figure 1b). The metal−oxygen bonds are in the ranges 2.410(4)−2.475(4) and 2.293(3)−2.380(3) Å for **1** and **2**, respectively, and the Ln−N bonds are 2.534(5)−2.538(5) and 2.398(4)−2.411(4) Å for **1** and **2**, respectively, all being normal coordination bonds. The differences of bond

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1** and **2**

Compound **1**			
Nd(1)−O(5)	2.410(4)	Nd(1)−O(4)	2.475(4)
Nd(1)−O(3)	2.423(4)	Nd(1)−N(1)	2.534(5)
Nd(1)−O(2)	2.458(4)	Nd(1)−N(2)	2.538(5)
Nd(1)−O(1)	2.459(4)	Nd(1)−N(3)	2.538(5)
O(5)−Nd(1)−O(3)	145.30(13)	O(4)−Nd(1)−N(1)	137.87(16)
O(5)−Nd(1)−O(2)	139.58(13)	O(5)−Nd(1)−N(2)	75.43(17)
O(3)−Nd(1)−O(2)	70.41(13)	O(3)−Nd(1)−N(2)	108.59(17)
O(5)−Nd(1)−O(1)	72.84(13)	O(2)−Nd(1)−N(2)	73.28(16)
O(5)−Nd(1)−N(1)	120.55(17)	O(1)−Nd(1)−N(3)	112.81(17)
O(3)−Nd(1)−N(1)	77.13(17)	O(4)−Nd(1)−N(3)	75.38(17)
O(2)−Nd(1)−N(1)	75.74(17)	N(1)−Nd(1)−N(3)	72.26(19)
Compound **2**			
Yb(1)−O(1)	2.293(3)	Yb(1)−O(5)	2.380(3)
Yb(1)−O(4)	2.313(3)	Yb(1)−N(1)	2.398(4)
Yb(1)−O(3)	2.349(3)	Yb(1)−N(3)	2.403(5)
Yb(1)−O(2)	2.358(3)	Yb(1)−N(2)	2.411(4)
O(1)−Yb(1)−O(4)	145.23(11)	O(3)−Yb(1)−N(1)	73.44(13)
O(1)−Yb(1)−O(3)	139.36(12)	O(2)−Yb(1)−N(1)	80.85(14)
O(1)−Yb(1)−O(2)	73.07(11)	O(1)−Yb(1)−N(3)	75.63(14)
O(1)−Yb(1)−O(5)	74.99(12)	O(2)−Yb(1)−N(3)	112.53(15)
O(4)−Yb(1)−O(5)	73.08(12)	O(5)−Yb(1)−N(3)	75.69(15)
O(3)−Yb(1)−O(5)	119.46(12)	N(1)−Yb(1)−N(3)	142.43(15)
O(2)−Yb(1)−O(5)	143.38(11)	O(1)−Yb(1)−N(2)	120.03(15)
O(1)−Yb(1)−N(1)	75.38(14)	O(4)−Yb(1)−N(2)	77.95(14)

length in the two complexes are due to lanthanide contraction. The bond angles around each metal center range from 70.41(13) to 83.52(17)° for **1** and from 70.67(11) to 83.45(14)° for **2** (Table 2), indicating that the metal centers in the two complexes have nearly the same configurations.

Each Ln^{III} ion in **1** and **2** is linked to five other metal atoms by the bis(sulfinyl) bridges, and the consequence of these combined interactions is the formation of a unique five-connected coordination network containing two types of macrometallacyclic array (see Figure 2). One type is a 28-membered macrocyclic ring with quadrilateral grid formed by four metal centers and four **L** ligands, and the other type is a 21-membered macrocyclic ring with triangle grid made up by three metal centers and three **L** ligands. The distances of Ln−Ln in the 28-membered quadrilateral grid are 9.105 and 9.255 Å for **1** and 8.975 and 9.188 Å for **2**, respectively, and those in the 21-membered triangle grid are 9.105, 9.353, and 9.772 Å for **1** and 8.975, 9.202, and 9.684 Å for **2**, respectively.

The most striking feature of the structure of **1** and **2**, in which the ligand (**L**) adopts different conformations to link different metal centers, is the formation of a unique and unprecedented five-connected two-dimensional $({}^{3}_{4}, 5)$ net which refers to a kind of five-connected two-dimensional net in which the “shortest circuits” formed around each connecting node are 3-gons and 4-gons. Three 3-gons and two 4-gons are adopted around each Ln^{III} node. To our knowledge, there are only a few known five-connected nets,[10] of which two have Ag^{I} metal nodes,[10a,b] one has Na^{I} metal nodes, and two have La^{III} nodes.[10d]

In summary, a unique and unprecedented two-dimensional neutral coordination polymer-forming $({}^{3}_{4}, 5)$ topological net consisted of two types of macrometallacycles has been constructed from a flexible bis(sulfinyl) ligand **L** and Ln^{III} thiocyanate. To our knowledge, this is the third five-connected lanthanide network[10d] and the first characterized $({}^{3}_{4}, 5)$ net. Our success in the construction of unusual coordination networks using bis(sulfinyl) ligands as bridging ligands indicates a new direction for the development of novel coordination polymers with unusual topologies. Since **L** has *RS* configuration, the network of **1** and **2** is mesomeric. Further studies using bis(sulfinyl) ligands with *SS* or *RR* configurations for construction of chiral networks and systematic studies on such ligands by varying their backbones, as well as studies on the properties and functionality of such complexes, are under way in our laboratory.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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