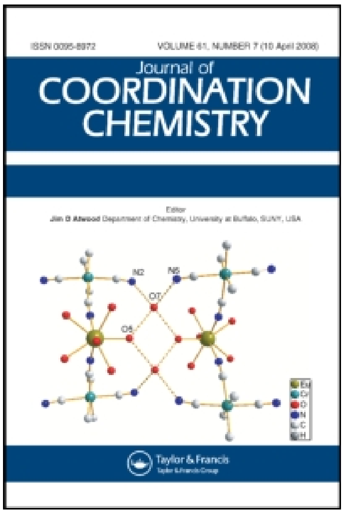

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Synthesis and crystal structure of a 1D disulfoxide-lanthanide(III) complex $\{[La(L)_2(DMF)_4](ClO_4)_3\}_n$ [L = 1,6-bis(ethylsulfinyl)hexane]

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A new disulfoxide-La(III) complex $\{[La(\mathbf{L})_2(DMF)_4](ClO_4)_3\}_n$ (**1**) has been prepared by the reaction of $La(ClO_4)_3 \cdot nH_2O$ and a flexible disulfoxide ligand, 1,6-bis(ethylsulfinyl)hexane (**L**), and characterized by elemental analysis, IR and single-crystal X-ray diffraction analysis (monoclinic system, space group $C2/c$, with $a = 24.94(2)$, $b = 12.012(8)$, $c = 20.81(1)$ Å, $\beta = 117.57(1)^\circ$, $V = 5527(6)$ Å^3 and $Z = 4$). The crystal structure consists of polymeric chains of $\{[La(\mathbf{L})_2(DMF)_4]^{3+}\}_n$ cations and ClO_4^- anions. In the cation of **1**, each La(III) center is coordinated to eight O atoms from four distinct **L** ligands and four DMF molecules to give a square antiprism coordination geometry. The adjacent two La(III) ions are linked by two **L** ligands, which adopt bis-monodentate O-coordination bridging mode to form a double-bridging zigzag chain containing 22-membered macrocycles.

Keywords: Crystal structure; Chain polymeric complex; Disulfoxide ligand; La(III)

1. Introduction

The synthesis and characterization of metal-organic coordination polymers has been an active research field in recent years [1–5]. Transition metal ions and rigid bridging ligands, such as 4,4′-bipyridine, are often used as connecting nodes and linkers, respectively, in such research [6–9]. In recent years, our attention has mainly been focused on the construction of metal complexes using flexible organic ligands such as bridging disulfoxides [10–12] or dithioethers [13–15] as building blocks/linkers. Disulfoxide compounds are ditopic multifunctional ligands, having intriguing features: the inherent chiral property of the sulfur atom, the diastereomeric *meso* and *rac* forms, coordination mode multiplicity and the possible configuration inversion of sulfur

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atoms after coordination. Such features may lead to metal-coordination complexes with unpredictable structures. On the other hand, the ability of lanthanide elements to adopt coordination numbers from six to twelve provides a rich and variable structural chemistry. Some disulfoxide-Ln(III) complexes with unique structures have been reported [10, 16, 17] in which the bridging linkages (spacers) of the ligands have up to four C atoms between two S=O moieties. As a continuation of our investigations, we use a new disulfoxide ligand, 1,6-bis(ethylsulfinyl)hexane (**L**, chart 1) with a longer spacer (six C atoms between two S=O groups) to react with $La(ClO_4)_3 \cdot nH_2O$ in the presence of DMF, to obtain a new 1D disulfoxide-La(III) complex, $\{[La(\mathbf{L})_2(DMF)_4](ClO_4)_3\}_n$ (**1**). Herein we report the synthesis and crystal structure of this complex.

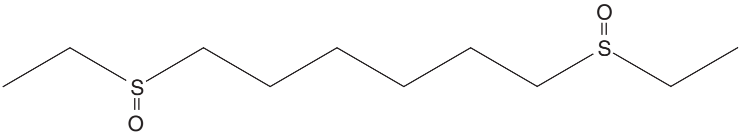

Chart diagram.

2. Experimental

2.1. *Materials and general methods*

All commercially available reagents for synthesis and analyses were of analytical grade and used as received. $La(ClO_4)_3 \cdot nH_2O$ was prepared by dissolving La_2O_3 (99.95%) in $HClO_4$. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellets) were taken on 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 taken on an X-4 melting point apparatus.

2.2. *Synthesis of 1,6-bis(ethylsulfinyl)hexane (L)*

2.2.1. 1,6-bis(ethylthio)hexane. Potassium hydroxide (~80%, 7.2 g, 0.1 mol) and ethyl mercaptan (6.3 g, 0.1 mol) were dissolved in anhydrous ethanol (70 mL) at ~60°C, then 1,6-dibromohexane (12.2 g, 0.05 mol) was added to the solution with stirring over 30 min. The mixture was cooled to room temperature and filtered to remove KBr. Then the solvent was removed under reduced pressure from above filtrate, the crude product was dissolved in chloroform (80 mL) and washed with 5% potassium hydroxide solution and distilled water, then dried over $MgSO_4$. The product was obtained after the solvent was evaporated. Yields: 85%.

2.2.2. 1,6-bis(ethylsulfinyl)hexane (L). To a vigorously stirred solution of 1,6-bis(ethylthio)hexane (6.2 g, 0.03 mol) was added dropwise nitric acid (~40%, 9 mL). After stirring for 24 h, the resulting mixture was adjusted to pH 7 by 15% sodium hydrogen carbonate solution and the solid product was filtered, washed with distilled water and dried. The *meso* isomer was separated from the isomeric mixture of products by fractional crystallization from acetone. Yield: 50%. m.p. 84 ~ 86°C. Anal. Calcd (%) for $C_{10}H_{22}S_2O_2$ (238.40): C, 50.38; H, 9.30. Found: C, 49.96; H, 9.50. ^{1}H NMR ($CDCl_3$): δ 2.61 ~ 2.74 (m, 8H, $-CH_2-S-CH_2-$), 1.80 (q, 4H, $S-C-CH_2-C$), 1.52 ~ 1.55 (m, 4H, $C-C-CH_2-CH_2-C-C-$), 1.35 (t, 6H, CH_3-). IR (KBr pellet, cm^{-1}): 2921s, 2861m, 1466m, 1264w, 1084m, 1013s, 785w, 731w, 656w, 459w.

2.3. *Synthesis of* $\{[La(L)_2(DMF)_4](ClO_4)_3\}_n$ *(1)*

A solution of $La(ClO_4)_3 \cdot nH_2O$ (0.2 mmol) in MeOH (10 mL) was added to a stirred solution of **L** (95 mg, 0.4 mmol) in methanol/triethylorthoformate (1 : 1, 20 mL) to immediately give white solid. Then, DMF was slowly added to the mixture until the solid dissolved completely. The solution was filtered and diffused slowly with Et_2O to yield colorless single crystals suitable for X-ray analysis in ~50% yield after ca three days. m.p. ~135°C (dec.). Anal. Calcd (%) for $C_{32}H_{72}LaCl_3N_4O_{20}S_4$ (1206.44): C, 34.62; H, 6.54. Found: C, 34.13; H, 6.78. ^{1}H NMR (CD_3OD): δ 7.99 (s, 1H, N–COH), 3.00 (s, 6H, $N-CH_3$), 2.79 ~ 3.04 (m, 4H, $-CH_2-S-CH_2-$), 1.81 (t, 2H, $S-C-CH_2-C$), 1.57 (t, 2H, $C-C-CH_2-C-C-C$), 1.33 (t, 3H, $C-CH_3$). IR (KBr, pellet, cm^{-1}): 2937m, 1664s, 1457w, 1087s, 997s, 626m.

Caution. Although we experienced no problems in this work, perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution.

2.4. *Crystal structure determination*

Single crystal X-ray diffraction was carried out on a Bruker Smart 1000 diffractometer. Intensities of reflections were measured using graphite monochromated Mo-Kα radiation with ω–ϕ scan mode in the range of $2.00 < \theta < 26.47°$. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using the SADABS program [18]. The structure was solved by direct methods [19]. The La(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 the SHELXL-97 program package [20]. Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on the parent atoms. Some of the oxygen atoms of the perchlorate ions are disordered, and were refined in two occupation parts and restrained. Crystallographic data and experimental details for structural analysis are summarized in table 1, fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in table 2 and selected bond lengths, angles and torsion angles are presented in table 3, respectively.

3. Results and discussion

3.1. *Synthesis and general characterization*

Complex **1** was prepared by the reaction of **L** with $La(ClO_4)_3 \cdot nH_2O$ in methanol/DMF using triethylorthoformate as a dehydrating reagent. The results of elemental analyses

Table 1. Crystal data and structure refinement summary for the complex **1**.

CCDC deposit no.	CCDC-252406
Empirical formula	$C_{32}H_{72}LaCl_3N_4O_{20}S_4$
Formula weight	1206.44
Space group	$C2/c$
a (Å)	24.94(2)
b (Å)	12.012(8)
c (Å)	20.81(1)
β (°)	117.57(1)
Volume (Å^3)	5527(6)
Z	4
D_{Calcd} (g/cm^3)	1.450
T (K)	293(2)
λ (Mo-K$_\alpha$) (Å)	0.71073
μ (mm^{-1})	1.136
F (000)	2496
Range of h, k, l	−23/31, −15/13, −25/23
Reflections collected/unique	15392/5593 [$R_{\mathrm{int}} = 0.0731$]
Max. and min. transmission	0.8216 and 0.7881
Data/restraints/parameters	5593/4/309
Goodness-of-fit on F^2	0.969
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0647$, $wR_2 = 0.1449$
R indices (all data)	$R_1 = 0.1339$, $wR_2 = 0.1767$
Largest diff. peak and hole (e/Å^3)	0.971 and −0.686

are consistent with the molecular formula evaluated by X-ray diffraction analyses. The complex is 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 of **1** has a $\nu_{S=O}$ band at 997 cm^{-1}, shifted to lower frequency than that of the free ligand (1013 cm^{-1}), indicating that all oxygen atoms of the disulfoxide ligands have coordinated to La(III) [21, 22]. In addition, the existence of ClO_4^- anions and coordinated DMF entities in the complex was also confirmed by the IR spectrum.

3.2. *Crystal structure*

The crystal structure of complex **1** shows that it consists of cationic 1D chains $\{[La(\mathbf{L})_2(DMF)_4]^{3+}\}_n$ and ClO_4^- anions. In the cationic chain, the La(III) center located on the inversion center is coordinated to eight oxygen donors from four distinct **L** ligands and four DMF molecules (figure 1). The coordination geometry of the La(III) ion can best be described as a slightly distorted square antiprism, with the *cis* angles (acute angles) ranging from 71.8(2) to 77.1(2)°. As shown in table 2, the La–O bond lengths depend markedly on the nature of oxygen atoms, and were divided into two groups: those for the sulfoxide oxygen atoms having an average value of 2.454(5) Å and those for DMF at 2.509(5) Å. In all cases, the carbonyl and sulfoxide groups substantially retain their double bond character with the mean C=O and S=O bond distances of 1.208(5) and 1.521(5) Å, respectively.

As shown in figure 2, in **1** each La(III) ion is bridged by four **L** ligands to two adjacent La(III) ions to result in an infinite 1D double-bridging chain containing 22-membered $(La\mathbf{L})_2$ macrometallocycles. In each such macrocycle the La···La distance is 10.305 Å, and the spacer chains (six C atoms) of the two bridging ligands are almost parallel with each other. The dihedral angle of the two rings (based on the four S atoms in each) around one La(III) center is 76.0°, while such rings are

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 1. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	X/a	Y/b	Z/c	U_{eq}
La(1)	0	9904(1)	2500	50(1)
S(1)	1396(1)	11463(2)	2820(1)	89(1)
S(2)	545(1)	8102(2)	4102(1)	72(1)
Cl(1)	0	5000	0	121(1)
Cl(2)	2273(1)	9618(3)	1195(2)	110(1)
N(3)	973(3)	12794(5)	4111(3)	78(2)
N(4)	1115(3)	6920(5)	2248(4)	82(2)
C(3)	764(4)	11792(6)	3910(4)	69(2)
C(4)	970(4)	7950(6)	2324(4)	73(2)
C(11)	1019(11)	12921(12)	1783(10)	261(12)
C(12)	1433(5)	12163(9)	2094(6)	120(4)
C(13)	2105(4)	10781(8)	3162(5)	96(3)
C(14)	2183(4)	9984(8)	3754(5)	101(3)
C(15)	2759(4)	9378(9)	4028(6)	115(3)
C(21)	−257(5)	8672(10)	4596(6)	125(3)
C(22)	404(4)	8371(8)	4859(4)	97(3)
C(23)	1349(4)	7851(7)	4574(5)	89(2)
C(24)	1501(5)	6868(9)	5085(6)	127(4)
C(25)	2112(4)	6493(8)	5417(5)	101(3)
C(31)	744(5)	13720(8)	3625(5)	119(3)
C(32)	1479(5)	13025(9)	4832(5)	129(4)
C(41)	831(5)	6018(8)	2409(7)	137(4)
C(42)	1522(5)	6672(9)	1962(6)	127(4)
O(1)	928(2)	10537(4)	2478(3)	79(1)
O(2)	479(2)	9233(4)	3754(2)	75(1)
O(3)	350(2)	11550(4)	3319(3)	77(1)
O(4)	617(2)	8215(4)	2537(3)	83(2)
O(5)	2445(9)	10642(14)	1339(7)	328(11)
O(6)	1786(8)	9638(11)	578(10)	379(15)
O(7)	2239(11)	9185(19)	1710(12)	401(14)
O(8)	2643(8)	8900(20)	1129(11)	405(15)
O(9)	−65(11)	5554(17)	581(10)	163(7)*
O(9′)	320(30)	4260(40)	567(13)	280(20)*
O(10)	623(9)	5000(40)	250(20)	227(15)*
O(10′)	260(30)	6040(30)	120(30)	304(19)*

*The disordered occupation ratio, 1 : 1.

Table 3. Selected bond lengths [Å], bond angles and torsion angles [°] for complex **1***.

La(1)–O(1)	2.457(5)	La(1)–O(4)	2.527(5)
La(1)–O(2)	2.451(5)	S(1)–O(1)	1.529(5)
La(1)–O(3)	2.490(5)	S(2)–O(2)	1.512(5)
O(1)–La(1)–O(2)	97.1(2)	O(2)–La(1)–O(4)	73.4(2)
O(1)–La(1)–O(3)	74.5(2)	O(2)–La(1)–O(2A)	141.6(2)
O(1)–La(1)–O(4)	71.5(2)	O(2)–La(1)–O(3A)	146.5(2)
O(1)–La(1)–O(1A)	144.0(2)	O(2)–La(1)–O(4A)	76.0(2)
O(1)–La(1)–O(2A)	94.6(2)	O(3)–La(1)–O(4)	127.0(2)
O(1)–La(1)–O(3A)	77.1(2)	O(3)–La(1)–O(3A)	74.9(3)
O(1)–La(1)–O(4A)	144.5(2)	O(3)–La(1)–O(4A)	132.4(2)
O(2)–La(1)–O(3)	71.8(2)	O(4)–La(1)– O(4A)	73.1(3)
C(12)–S(1)–O(1)–La(1)	125.9(5)	C(23)–S(2)–O(2)–La(1)	118.0(5)
C(13)–S(1)–O(1)–La(1)	131.9(5)	O(1)–S(1)···S(2B)–O(2B)	22.8
C(22)–S(2)–O(2)–La(1)	137.6(5)		

*Symmetry codes: A: $-x$, y, $-z+1/2$; B: $-x+1/2$, $-y+3/2$, $-z+1$.

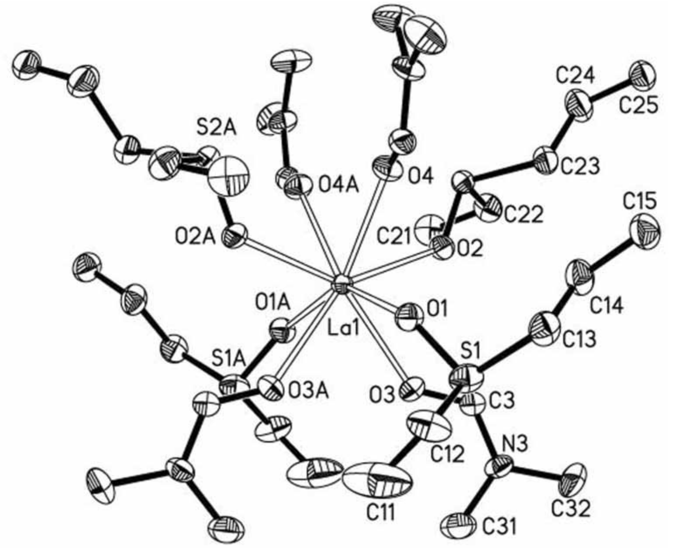

Figure 1. A view of the coordination environment of La(III) in **1**, with 30% probability for the ellipsoids and all hydrogen atoms omitted for clarity.

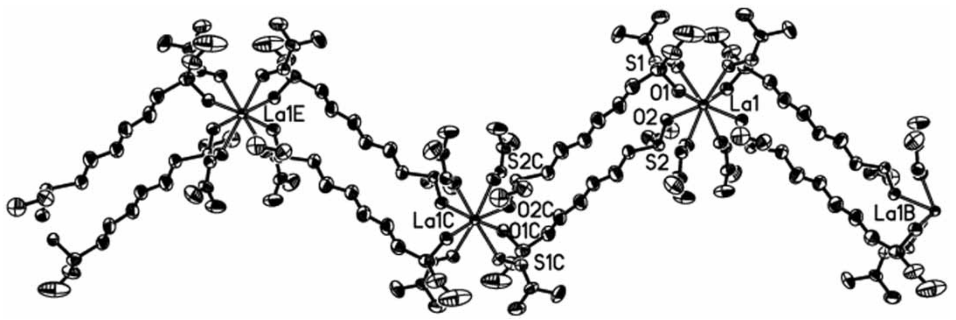

Figure 2. The 1D double-bridging cationic chain of **1** (symmetry codes, B: $x-1/2$, $3/2-y$, $z-1/2$; C: $1/2-x$, $3/2-y$; E: $1-z$, $1-x$, y, $3/2-z$).

parallel to each other. **L** ligands adopt the bis-monodentate O-coordination bridging mode to link La(III) ions, with the similar situation usually found in other disulfoxide-Ln complexes [16, 17]. Around each La(III), two pairs **L** and DMF lie in opposite directions respectively. The La(III) ions in the chain are up and down and the chain has a zig-zag orientation with the La···La···La angle of 128.5°. In **1**, all disulfoxide ligands possess *S*, *R* geometry and the quasi-torsion angle of O=S···S=O is 22.8°. The O coordination of sulfoxide group adopts a *trans–trans* arrangement with the M–O–S–C torsion angles ranging from 118.0(5) to 137.6(5)° (table 2). In addition, in **1** such 1D double-bridging chains stack parallel along the (1 0 1/2) direction, and the face-to-face stacking of those rings produces channels when viewed along the *b* direction (figure 3). The ClO_4^- ions reside between the chains.

Comparing complex **1** with a related disulfoxide-La(III) complex, $\{[La(\mathbf{L}')_2(DMF)_4](ClO_4)_3\}_n$ (**2**) [16] [$\mathbf{L}'$ = 1,4-bis(phenylsulfinyl)butane], which has a 2D (4,4)

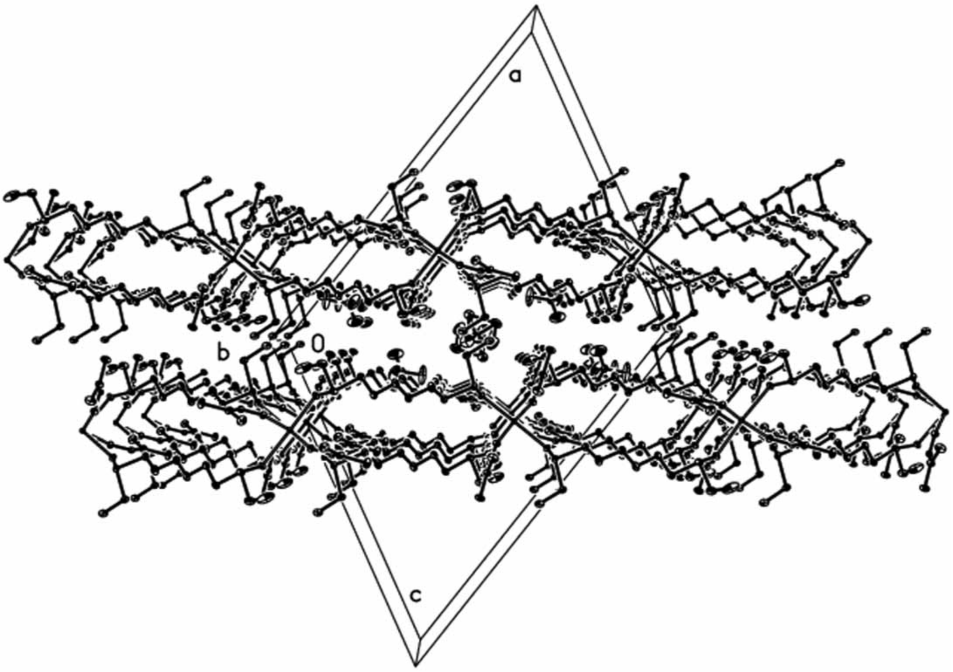

Figure 3. The crystal packing diagram showing the chains arranged parallel to each other.

framework structure, the spacer length and terminal groups of such disulfoxide ligands have important effects on the structures of their La(III) complexes. In **2**, the ligand **L′** has a larger terminal group and a shorter spacer (four C atoms between S=O moieties) than those in **L**, and these factors may cause **2** to form a 2D sheet.

In summary, we have obtained a new 1D double-bridging chain complex by assembling the $La(ClO_4)_3$ and a flexible disulfoxide ligand. The structure is different than the previously reported complex of a related disulfoxide ligand with shorter spacer, which shows the influence of the spacer length and terminal groups of ligands on the structures of complexes.

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