The First (Trisulfoxide)metal Complexes: Synthesis and Crystal Structures of the 1D Lanthanide Coordination Polymers $[Ln(L)(MeOH)(NO_3)_3]_n$ and $\{[La(L)(DMF)_5](ClO_4)_3\}_n$ [L = 1,3,5-Tris(ethylsulfinyl)-2,4,6-trimethylbenzene, Ln = La^{III} and Nd^{III}]

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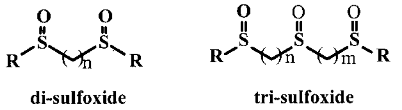
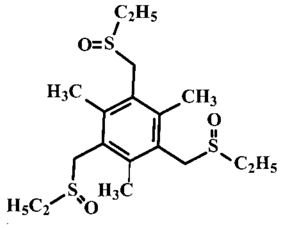
A new trisulfoxide ligand, 1,3,5-tris(ethylsulfinyl)-2,4,6-trimethylbenzene (L), was designed and synthesized, and treated with $Ln(NO_3)_3$ or $Ln(ClO_4)_3$ to produce three coordination polymers: $[Ln(L)(MeOH)(NO_3)_3]_n$ [where Ln = La^{III} (**1**); Nd^{III} (**2**)] and $\{[La(L)(DMF)_5](ClO_4)_3\}_n$ (**3**). Solid-state structures of all three complexes were determined by single-crystal X-ray diffraction. The three complexes have 1D helical-chain structures and complexes **1** and **2** are isostructural. To the best of our knowledge, these coordination polymers are the first examples of (trisulfoxide)metal complexes.

Introduction

In recent years, much effort has been invested in attempts to design and synthesize metal-organic coordination polymers having specific network topologies and potential applicable properties.[1,2] In this regard, the studies performed by us and others[3] on the construction of coordination architectures using flexible disulfoxide ligands and metal ions as building blocks have acquired some interesting results. We are, therefore, interested in further exploiting the multisulfoxide ligands. Such ligands may produce interesting coordination polymers because of their multiple coordination modes. As a continuation of this study, we designed a new trisulfoxide ligand, 1,3,5-tris(ethylsulfinyl)-2,4,6-trimethylbenzene (L) (see structure shown below), which is a simple tridentate ligand. Since each S atom is an asymmetric center, the tridentate L molecule should be a chiral bridging ligand. Therefore, the ligand may be used to construct non-centric framework polymers (or chiral crystals). To the best of our knowledge, (trisulfoxide)metal complexes have not yet been reported and the lanthanide complexes presented here are the first structurally characterized examples of metal complexes with such ligands. Herein, we report the synthesis and crystal structures of three novel lanthanide complexes with L, $[Ln(L)(CH_3OH)(NO_3)_3]_n$ [where Ln = La (**1**); Nd, (**2**)] and $\{[La(L)(DMF)_5](ClO_4)_3\}_n$ (**3**).





L

Results and Discussion

Synthesis and General Characterization

The ligand L was synthesized according to a similar method used for the synthesis of disulfoxide[4] and the product might have been a mixture containing several isomers of the trisulfoxides. The attempts for separation were not successful so the mixture was used directly to prepare the metal complexes. The IR data of L show the characteristic band of the sulfinyl group (S=O) at 1022 cm^{-1} and the C−S stretching vibration at 756 cm^{-1}.[5]

The complexes **1−3** were prepared by the reaction of L with $Ln(NO_3)_3{\cdot}nH_2O$ or $Ln(ClO_4)_3{\cdot}nH_2O$ in the presence of triethyl orthoformate (see Scheme 1). The 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 of each complex has a $\nu_{S=O}$ band at around 1000 cm^{-1}, which is shifted to a lower frequency than that of the free ligand (1022 cm^{-1}), indicating that the

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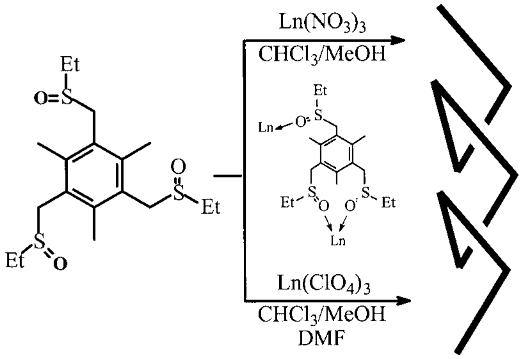
oxygen is coordinated to the Ln^{III} ions.[5] The existence of nitrate and perchlorate anions in the complexes was also confirmed by the IR spectra.



Scheme 1. Schematic representation of the formation of **1**−**3**

Description of the Crystal Structures

Complexes **1** and **2**, $[Ln(L)(CH_3OH)(NO_3)_3]_n$ [where Ln = La^{III} (**1**); Nd^{III} (**2**)], have isostructural, neutral helical-chain structures, with only minor differences in their geometry parameters, which reflect the normal lanthanide contraction. The coordination environments of the Ln^{III} centers in **1** and **2** are shown in Figure 1 (top, with **1** as a representative). Each Ln^{III} center is coordinated to three oxygen atoms of two distinct L ligands (one is mono-*O* and the other is chelating), six oxygen atoms of three bidentate nitrate groups and one oxygen atom of methanol to form a 4,4-bicapped square-antiprism geometry. Due to the small bite angle of the nitrate group, its oxygen atoms are closer than those of two independent L ligands, which makes their complexes have higher coordination numbers. In **1** and **2** the smallest chelating angles of the nitrate groups are 45.25° for **1** [O(9)−La(1)−O(7)] and 45.07° for **2** [O(32)−Nd(1)−O(31)]. Otherwise, one relatively short and one longer Ln−O (NO_3^-) bond [La(1)−O(9) = 2.629(6) Å and La(1)−O(7) = 2.926(7) Å for **1**, Nd(1)−O(32) = 2.541(6) Å and Nd(1)−O(31) = 2.947(6) Å for **2**] also show the binding of the oxygen atoms of this nitrate group, with the smaller chelating angle, to the Ln^{III} ions. In particular, for the La(1)−O(7) and Nd(1)−O(31) bonds, the interactions between the metal and the oxygen atom are week. The lengths of the bonds [2.436(6)−2.498(6) Å for **1** and 2.365(5)−2.437(5) Å for **2**] between the oxygen atoms of the sulfoxide moieties and the Ln^{III} ions are within the expected ranges and similar to those found in disulfoxide analogues,[3f] but significantly shorter than those of the nitrate groups [2.611(7)−2.926(7) Å for **1** and 2.541(6)−2.958(6) Å for **2**] or methanol [2.553(6) Å for **1** and 2.488(4) Å for **2**] in the same complex.

In **1** and **2**, each L links two adjacent Ln^{III} ions to form a 1D helical chain and the shortest Ln···Ln intrachain distance is 11.113 Å for **1** and 11.017 Å for **2**, as shown in Figure 1 (middle). In the chain the alternating Ln centers are located in a straight line and the alternating phenyl groups of the ligands are parallel to each other, while the dihedral angle between two adjacent phenyl planes (namely, around one Ln center) is 66.6° for **1** and 64.5° for **2**, respectively. The 1D helical chain is related by a 4_1 helical axis, which passes through the alternating Ln^{III} ions. Furthermore, in the crystal packing of **1** and **2** the 1D chains are arranged parallel to each other in the *a* and *b* directions, respectively, to form planes. However, the chains in the adjacent planes are perpendicular to each other (see Figure 1 bottom).

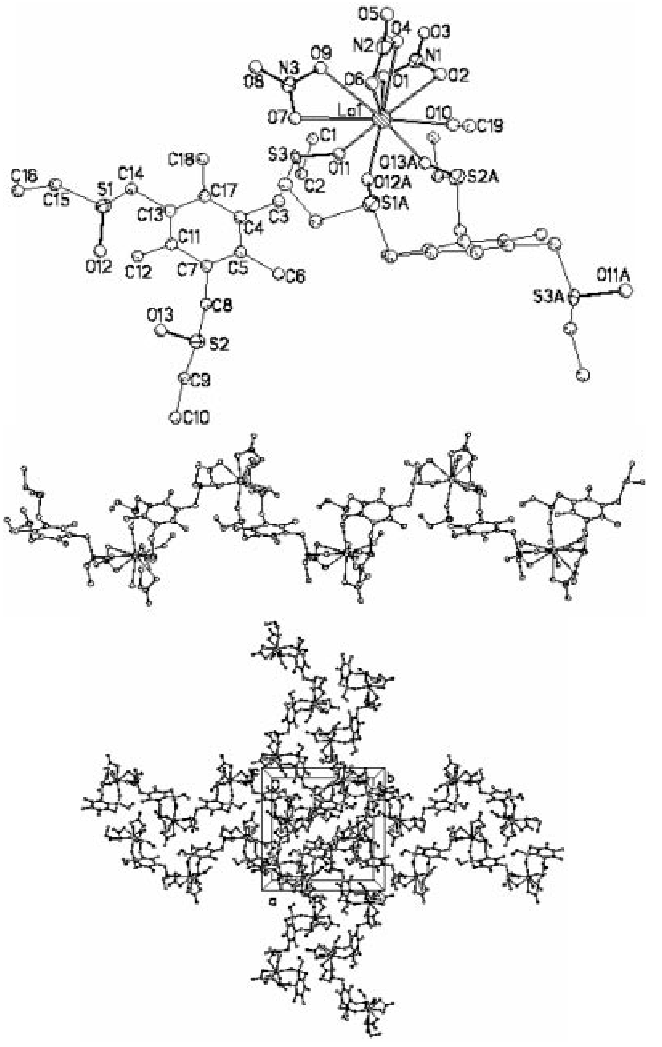


Figure 1. (Top) View of **1** showing the coordination environment of the center ion, (middle) the helical-chain structures of **1** (or **2**) and (bottom) crystal packing diagram in **1** (or **2**), only one position of the disordered sets of S atoms is shown

The structure of **3** ($\{[La(L)(DMF)_5](ClO_4)_3\}_n$) consists of cationic, helical chains and perchlorate anions. Each chain contains the structural units $[La(L)(DMF)_5]^{3+}$, which are linked by L bridges. In each $[La(L)(DMF)_5]^{3+}$ unit, the La^{III} center is coordinated to eight oxygen atoms, of which three from two distinct L ligands and five from DMF (see Figure 2 top). The geometry of the La center approximates to a square antiprism. In **3** the La−O bond lengths are in the range of 2.4506(2)−2.5806(2) Å and are in the normal La−O bond-length range of eight-coordinate La^{III} complexes. The three distances of La−O(L) are basically equal and the average value is 2.4713(5) Å, which is slightly longer than that in **1** [2.4573(6) Å].

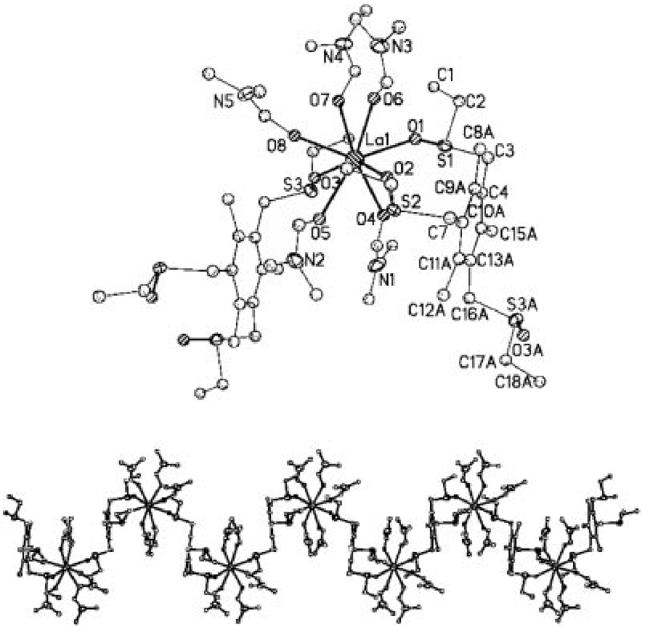


Figure 2. (Top) View of **3** showing the coordination environment of the center ion and (bottom) the helical-chain structure of **3**, only one position of the disordered sets of S atoms is shown

In **3**, the L ligands act as bridges that link adjacent metal ions to form a helical chain (see Figure 2 bottom) with an La···La separation of 10.313 Å. Within the chain, the alternating La^{III} ions are in a straight line, as in **1** and **2**, but all the phenyl groups are parallel to each other and related by a 2_1 helical axis, in contrast to **1** and **2**. Another difference is that in **3** all the chains are arranged parallel to each other along the *c* axis and the perchlorate ions are located among these chains.

In **1**−**3** the ligand is multidentate and displays two kinds of coordination mode: chelate bridging and mono-*O*-bridging. Each L ligand uses two of the sulfinyl moieties to chelate one Ln^{III} center to form a 10-membered ring and uses other one to bridge an adjacent Ln^{III} center. In **1**−**3**, although the trisulfoxide ligand is chiral due to its three S atoms displaying *S*,*R*,*R* (or *S*,*R*,*S*) configurations, in the crystal the presence of a 1:1 disorder for the sulfur atom (S, S$'$) of one of the sulfoxide moieties makes the configurations offset each other, which means that the complexes as a whole are not chiral. The S=O bond lengths are normal for sulfoxide moieties coordinated to metal ions and are similar to those in di- or mono-sulfoxide analogues.[6] In addition, and similarly to the lanthanide complexes with disulfoxide,[3c,3d] in **1**−**3** there are large M−O−S angles (140.1−168.8° for **1**, 143.6−156.1° for **2** and 147.1−150.6° for **3**) probably due to the high coordination number of the lanthanide ions, and the coordination configurations of the ligands are *trans*−*trans* (C−S−O−M torsion angles are 90−270°) as those in the previously reported disulfoxide lanthanide complexes.[3c−3g]

In summary, three 1D lanthanide-coordination polymers with trisulfoxide ligands were synthesized and structurally characterized. In the complexes, the trisulfoxide ligand shows tridentate linkage as well as mono-*O*-bridging and chelate-bridging coordination modes. Similarly to the disulfoxide ligands, the trisulfoxide ligands also act as bridges to link adjacent metal ions, which may allow the complexes to have higher dimensions. To the best of our knowledge, this is the first report on a trisulfoxide ligand used as a building block to construct coordination polymers. This study may not only open up a new researching domain for developing multisulfoxide-coordination chemistry, but will also offer a new type of organic building block for the construction of metal-organic coordination polymers.

Experimental Section

All the reagents used for synthesis and analyses were of analytical grade and used as received. Hydrated lanthanide nitrate and perchlorate were prepared from the corresponding oxides. Elemental analyses were performed on a Perkin−Elmer 240C analyzer. IR spectra (KBr pellets) were taken on an FT-IR 170SX (Nicolet) spectrometer. ^{1}H NMR spectra were measured on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C with tetramethylsilane as the internal reference. The melting point measurement was taken on an X-4 melting point meter.

Syntheses of the Ligand: 1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene was prepared according to a reported procedure.[7] 1,3,5-Tris(ethylthio)-2,4,6-trimethylbenzene was synthesized by the similar literature method.[8]

1,3,5-Tris(ethylsulfinyl)-2,4,6-trimethylbenzene (L): L was synthesized following a procedure similar to our previous work for synthesizing disulfoxides.[4] Nitric acid (63 %, 2 mL) was added dropwise to a vigorously stirred solution of 1,3,5-tris(ethylthio)-2,4,6-trimethylbenzene (10.3 g, 0.03 mol) in benzene (50 mL). After stirring for 24 h, the resulting mixture was added to a 15 % sodium hydrogen carbonate solution to adjust the pH value to ca. 7. The solid product was filtered and washed with distilled water, ethanol and diethyl ether successively. Yield 6.1 g, 52 %. M.p. 233−242 °C (mixture of isomers). $C_{18}H_{30}O_3S_3$ (390.15): calcd. C 55.35, H 7.74; found C 55.01, H 7.22. IR (cm^{-1}): 2887 (w), 2546 (w), 1455 (w), 1278 (m), 1022 (s), 962 (m), 864 (m), 756 (m), 689 (m), 639 (w), 580 (w). ^{1}H NMR (300 MHz): δ = 1.40 (t, 9 H, S−CH_2−*CH_3*), 2.82 (s, 9 H, Ph−*CH_3*), 4.04 (q, 6 H, S−*CH_2*−CH_3), 4.31 (s, 6 H, S−*CH_2*−Ph) ppm.

Preparation of Complexes: Caution! While we have experienced no problems in handling Ln^{III} perchlorates, these compounds should be handled with great caution because of their potential for explosion.

$[Ln(L)(CH_3OH)(NO_3)_3]_n$ [Ln = La (1); Nd (2)]: Triethyl orthoformate (3 mL) was added to a solution of L (117 mg, 0.3 mmol) in $CHCl_3$ (4 mL) and the mixture was stirred for ca. 20 min. Then $Ln(NO_3)_3\cdot nH_2O$ (0.2 mmol) in anhydrous methanol (4 mL) was added to the above mixture and further stirred at 70−80 °C for about 4 h. The mixture was cooled to room temperature and filtered. The filtrate was allowed to stand at room temperature for ca. one week and single crystals suitable for X-ray analysis were obtained. For **1**, yield 87 mg, 39 % based on L. $C_{19}H_{34}LaN_3O_{13}S_3$ (747.58): calcd. C 30.53, H 4.58, N 5.62; found C 30.11, H 4.27, N 5.40. IR (cm^{-1}):

2917 (m), 2426 (w), 1636 (m), 1456 (m), 1384 (s), 1043 (m), 1001 (s), 970 (m), 839 (w), 678 (m). For **2**, yield 77 mg, 34 % based on L. $C_{19}H_{34}NdN_3O_{13}S_3$ (752.91): calcd. C 30.31, H 4.55, N 5.58; found C 30.14, H 4.21, N 5.24. IR (cm^{-1}): 2941 (m), 2426 (w), 1638 (s), 1457 (m), 1384 (s), 1042 (m), 1000 (s), 970 (m), 637 (m).

$\{[La(L)(DMF)_5](ClO_4)_3\}_n$ (3): Triethyl orthoformate (2 mL) was added to a solution of L (78 mg, 0.2 mmol) in $CHCl_3$ (3 mL) and the mixture was stirred for 20 min. $La(ClO_4)_3 \cdot nH_2O$ (0.2 mmol) in anhydrous methanol (3 mL) was added to the mixture and a precipitate immediately appeared. The mixture was further stirred at about 60 °C for 30 min. Then, DMF was slowly added until the precipitate dissolved and the solution was filtered. The slow diffusion of diethyl ether into the filtrate resulted in the formation of single crystals in 23 % yield. $C_{33}H_{65}Cl_3LaN_5O_{20}S_3$ (1193.34): calcd. C 33.21, H 5.49, N 5.87; found C 33.04, H 5.21, N 5.48. IR (cm^{-1}): 2981 (m), 1647 (m), 1457 (w), 1384 (m), 1141 (s), 1121 (s), 1086 (m), 1001 (s), 636 (m).

Crystal Structure Determinations: Single-crystal X-ray diffraction measurements of **1−3** were carried out at 293(2) K on a Bruker−Smart 1000 CCD area detector with Mo-K_α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-square methods based on F^2 using the SHELXS-97 program.[9] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were added theoretically. In **1−3** one of the three sulfur atoms in each crystallographic asymmetry unit displays positional disorder, and was refined in a statistical two-site occupancy. CCDC-217187 to -217189 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].

Crystal Data for 1: Tetragonal, space group $I4_1/cd$, $a = b = 18.215(4)$, $c = 36.89(1)$ Å, $V = 12241(5)$ Å^3, $Z = 16$, final refinement $[I > 2\sigma(I)]$: $R1 = 0.0392$, $wR2 = 0.0882$.

Crystal Data for 2: Tetragonal, space group $I4_1/cd$, $a = b = 17.9931(2)$, $c = 36.7875(6)$ Å, $V = 11910.0(3)$ Å^3, $Z = 16$, final refinement $[I > 2\sigma(I)]$: $R1 = 0.0621$, $wR2 = 0.1565$.

Crystal Data for 3: Monoclinic, space group $P2_1/c$, $a = 11.897(4)$, $b = 27.391(8)$, $c = 16.288(5)$ Å, $\beta = 91.841(5)°$, $V = 5305(3)$ Å^3, $Z = 4$, final refinement $[I > 2\sigma(I)]$: $R1 = 0.0660$, $wR2 = 0.1417$.

Acknowledgments

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