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Formation and Crystal Structure of a Polymeric La(H_2salen) Complex

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Introduction

Coordination chemistry of lanthanide(III) Schiff base complexes has been extensively studied in the past two decades.[1−3] Considerable work has concentrated on Ln(III) complexes with *N*,*N*′-ethylene bis(salicylideneimine) (H_2salen).[4−13] Depending on the preparative procedures, a number of Ln(III) H_2salen (salen) complexes with different compositions have been reported, including $Ln_2(salen)_3$,[4,5,12] $[Ln_2(H_2salen)_3(NO_3)_4](NO_3)_2·3H_2O$,[6] Eu(Hsalen)(salen),[10] $Ln(H_2salen)X_3·nH_2O$, $Ln_2(H_2salen)_3X_6·nH_2O$, $Ln(H_2salen)_2X_3·nH_2O$, and $Ln(H_2salen)_3X_3·nH_2O$ ($X = Cl, Br$; $n = 0−2$).[11] Despite the large number of such complexes, most of the structures were proposed on the basis of the compositions and spectroscopic data. Very little crystallographic evidence is available so far as to the coordination mode of the Schiff base ligand.

We report here the formation and crystal structure of a polymeric lanthanum H_2salen complex, $[La(H_2salen)(NO_3)_3(MeOH)_2]_n$, a composition not reported before. To our best knowledge, this is the first report of the X-ray crystal structure of lanthanide complexes with neutral H_2salen ligands.

Experimental Section

General. All chemicals were reagent grade and were used as received. NMR spectra were recorded on a Varian 400 spectrometer, infrared spectra on a Nicolet-SX FT-IR spectrophotometer, and UV spectra on a Hewlett-Packard 845X spectrophotometer. H_2salen was prepared from salicylaldehyde and ethylenediamine by routine methods.

Synthesis of $[La(H_2salen)(NO_3)_3(MeOH)_2]_n$. To a solution of H_2salen (0.500 g, 1.9 mmol) in $MeOH/CH_2Cl_2$ (40 mL/10 mL) was slowly added 0.774 g (1.9 mmol) of $La(NO_3)_3$ hydrate in 10 mL of MeOH at room temperature. The initial bright yellow solution turned immediately into a light brown color upon addition of $La(NO_3)_3$. A yellow precipitate formed gradually during 2 h of stirring. The solid (0.680 g) was collected by filtration and washed with CH_2Cl_2. The filtrate was concentrated to half of the initial volume. After addition of CH_2Cl_2 and standing for 2−3 h, a second portion of the product was afforded (0.230 g) with a combined yield of 73%. Found: C, 33.17; H, 3.25; N, 10.98. Calcd for $C_{18}H_{24}LaN_5O_{13}$: C, 32.89; H, 3.68; N, 10.65. Mp 261 °C (dec). ^1H NMR (CD_3OD, 400 MHz): 3.27 (s, 6H), 3.91 (s, 4H), 6.75 (m, 4H), 7.23 (m, 4H), 8.39 (s, 2H) ppm. IR (KBr): 3589 (w), 1644 (vs, w), 1603 (vs), 1528 (s), 1480 (s, w), 1432 (s, w), 1377 (s), 1325 (s, sh), 1315 (s), 1281 (s), 1225 (s), 1144 (s), 1028 (s), 1000 (m), 900 (m), 852 (m), 799 (m), 762 (s), 733 (m), 566 (s) cm^{-1}. UV−vis (MeOH): λ_{max} (ϵ): 210 (6.1×10^3), 242 (2.3×10^2), 256 (2.0×10^2), 319 (4.5×10) nm.

Table 1. Crystal Data and Structure Refinement

empirical formula	$C_{18.5}H_{25}ClLaN_5O_{13}$
fw	699.79
cryst syst	monoclinic
space group	$P2(1)/n$
a, Å	8.6049(4)
b, Å	15.2542(7)
c, Å	22.3577(11)
α, deg	90
β, deg	96.3130(10)
γ, deg	90
V, Å^3	2916.9(2)
Z	4
d_{calc}, g cm^{-3}	1.594
cryst size, mm	$0.28 \times 0.28 \times 0.08$
h, k, l range	−11 to 11, 0 to 19, 0 to 28
θ range, deg	1.62−28.28
$F(000)$	1396
goodness of fit on F^2	0.972
final R indices ($I > 2\theta(I)$)	$R1 = 0.0437$, $wR2 = 0.1236$
R indices (all data)	$R1 = 0.0716$, $wR2 = 0.1535$

X-ray Analysis. Crystals suitable for X-ray determination were obtained from a $MeOH/CH_2Cl_2$ solution at room temperature. Crystallographic data were collected at room temperature on a Siemens automated P4/CCD diffractometer with graphite-monochromated Mo Kα radiation. A hemisphere of data (1390 frames) were collected at 10 s/frame and integrated with the manufacturer's SMART and SAINT software, respectively. Cell constants were refined with SAINT. Absorption corrections were applied using Sheldrick's SADABS program and the structures were solved and refined using the program of SHELXS-86 and SHELXL-93.[14] 16 053 total data were averaged to yield 6169 ($R_{int} = 0.043$) independent reflections. The compound crystallized as a polymeric complex repeating through a crystallographic 2_1 axis. One-half molecule of distorted methylene chloride was present in the asymmetric unit. Crystal data and a summary of the crystallographic analysis are presented in Table 1.

Results and Discussion

Formation of $[La(H_2salen)(NO_3)_3(MeOH)_2]_n$. Formation of the title La−H_2salen complex was readily achieved by the reaction of $La(NO_3)_3$ hydrate with equivalent Schiff base H_2salen in $MeOH/CH_2Cl_2$ at room temperature (Scheme 1). Methylene dichloride was used here to increase the solubility of H_2salen. The immediate color change of the H_2salen solution upon addition of $La(NO_3)_3$ solution indicated instant occurrence of the coordination. Most of the product precipitated out during the stirring. Isolation of additional amount of the product could be accomplished by addition of CH_2Cl_2 to the concentrated filtrate. Unlike other previously reported lanthanide H_2salen complexes, the title complex had considerable solubility in methanol. This allowed crystals suitable for X-ray analysis to be obtained with a mixed solvent system of $MeOH/CH_2Cl_2$.

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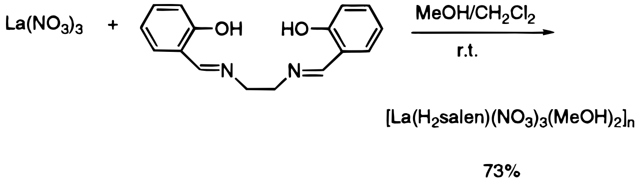
10.1021/ic9810539 CCC: $18.00

Scheme 1



Characterization and Spectroscopic Studies. The complex was studied with ^{1}H NMR, IR, and elemental analysis to have an empirical formula of La(H$_2$salen)(NO$_3$)$_3$(MeOH)$_2$, which was later confirmed by X-ray crystallography. In the ^{1}H NMR spectrum, a singlet attributed to the CH$_3$ groups of the two methanol molecules in the complex appeared at 3.27 ppm, 0.03 ppm upfield than the corresponding solvent peak of CD$_3$OD. This suggested that the two methanol molecules, instead of existing as inclusion solvent molecules, were coordinated to the La(III) ion. Moreover, the exchanging rate between the coordinated methanol (CH$_3$OH) molecules and CD$_3$OD was relatively slow as revealed by ^{1}H NMR, indicating a rather small dissociation constant of the complex in methanol. Although the H$_2$salen displayed only little differences in chemical shifts compared with the ^{1}H NMR spectrum of the free H$_2$salen, the differences in the IR spectrum were evident. The complex showed an O$-$H stretching frequency around 3590 cm^{-1}. The broad band centered at ca. 2650 cm^{-1} (due to the intramolecular hydrogen bond in free H$_2$salen[15]) was not observed. This indicated that the intramolecular hydrogen bond was opened up by the complexation of the metal. Coordination of the phenolic oxygen was also indicated by a significant decrease in the C$-$O stretching frequency ($\Delta\bar{\nu} \sim 50$ cm^{-1}). Due to the complication of the absorption around the region 1600$-$1660 cm^{-1}, it is hard to judge from the IR spectrum whether there was any coordination occurring for the nitrogen atoms of the imine functionalities.

UV spectrum of the complex provided further information in solution. The complex showed a new absorption band in methanol at 242 nm, which was absent both for the free ligand and La(NO$_3$)$_3$. Apparently this new band was attributed to the electron transfer between the metal center and the coordinated ligand. The UV spectrum in acetonitrile was just identical to that in methanol, though the solubility of the complex in acetonitrile was considerably lower. However, when measured in DMSO, the UV spectrum of the complex displayed no new band. It appeared just as a simple combination of the corresponding spectra of the free ligand and La(NO$_3$)$_3$. These observations indicated that complex was stable both in methanol and acetonitrile, but dissociated to give the free ligand in DMSO, which is a strong solvating agent.

Crystal Structure of the Complex. The complex has a ten-coordinated metal center as shown in Figure 1. The lanthanum ion was coordinated with two phenolic oxygen atoms, three bidentate nitrate ions and two molecules of methanol. Unlike previously reported halide complexes,[11] no coordination took place through the imine nitrogen atoms. Instead, the two phenolic oxygen atoms, which were believed to be uncoordinated in the corresponding halide complexes, were coordinated respectively to two La atoms. Thus each H$_2$salen molecule acted in this manner as a bridge between two La atoms. Recently, due to their significance in crystal engineering, there has been considerable interest in polymeric metal complexes.[16-20] As mentioned above, by the bridging of H$_2$salen, the complex formed a polymeric structure related by a 2$_1$ screw axis passing between C(8) and C(9). There were two parallel polymeric chains extending along the *b* direction (Figure 2). However, the solution structure of the complex is not yet very clear, although the simplicity of the ^{1}H NMR, which reflected a symmetric structure, seemed to suggest a polymeric form also in solution. Further studies are in progress to better understand the solution structure and behaviors of the title complex.

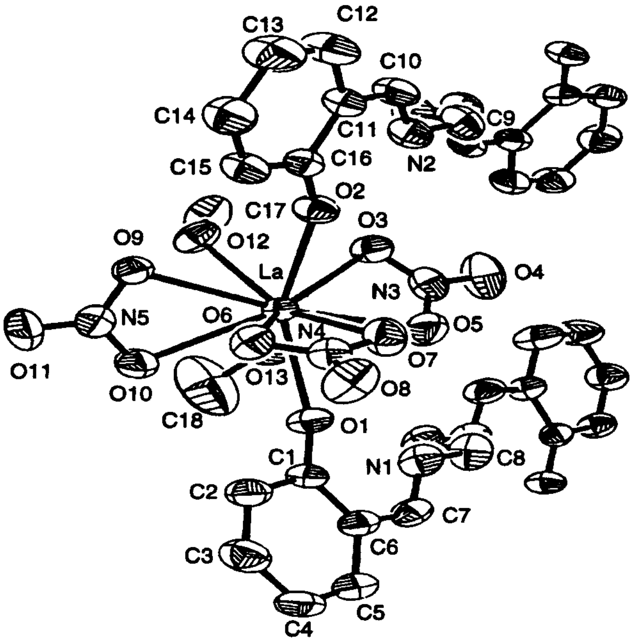


Figure 1. Structural skeleton of the asymmetric unit of [La(H$_2$salen)(NO$_3$)$_3$(MeOH)$_2$]$_n$ with thermal ellipsoids at the 50% probability level.

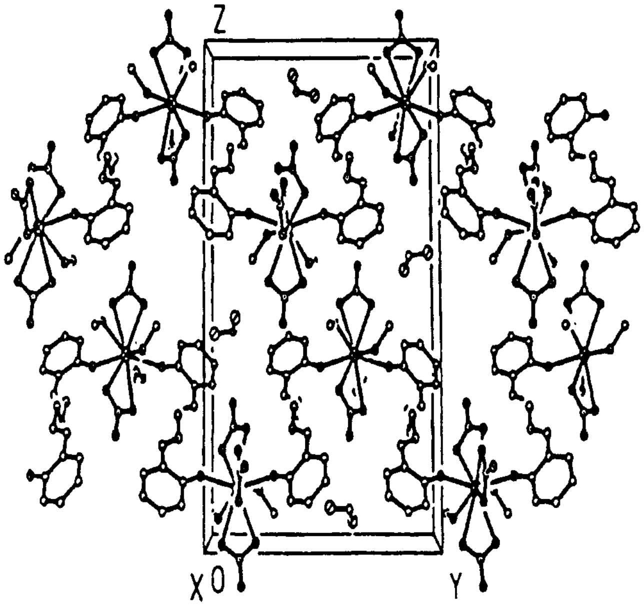


Figure 2. Packing drawing showing the polymeric chains.

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Table 2. Selected Bond Lengths (Å) and Angles (deg)[a]

La(1)−O(1)	2.447(3)	La(1)−O(2)	2.413(4)
La(1)−O(10)	2.614(4)	La(1)−O(12)	2.588(4)
La(1)−O(13)	2.611(4)	La(1)−O(5)	2.674(4)
La(1)−O(3)	2.674(4)	La(1)−O(6)	2.681(4)
La(1)−O(9)	2.688(4)	La(1)−O(7)	2.699(4)
C(1)−O(1)	1.286(6)	C(16)−O(2)	1.299(6)
C(6)−C(7)	1.401(7)	C(7)−N(1)	1.300(7)
O(2)−La(1)−O(1)	144.5(2)	O(2)−La(1)−O(12)	78.44(13)
O(2)−La(1)−O(10)	125.98(12)	O(12)−La(1) −O(10)	79.97(13)
O(1)−La(1)−O(10)	74.84(13)	O(1)− La(1)−O(13)	71.82(13)
O(12)−La(1)−O(13)	69.56(13)	O(10)−La(1)−O(13)	79.67(13)
O(2) −La(1)−O(5)	93.79(14)	O(1)−La(1)−O(5)	69.96(13)
O(2)−La(1)−O(3)	70.13(11)	O(1)−La(1)−O(3)	112.68(12)
O(5)−La(1)−O(3)	47.04(13)	O(1)−La(1)−O(6)	76.99(12)
O(12)−La(1)−O(6)	127.07(12)	O(12)−La(1)−O(9)	63.13(11)
O(10)−La(1)−O(9)	48.37(12)	O(6)−La(1)−O(7)	47.39(12)
C(1)−O(1)−La(1)	151.2(3)	C(16)−O(2)−La(1)	149.5(3)
O(4)−N(3)−O(3)	122.7(5)	O(4)−N(3)−O(5)	115.7(4)

[a] Numbers in parentheses are estimated standard deviations in the least-significant digits.

Selected bond lengths and bond angles are listed in Table 2. The two La−O (methanolic) bonds are of similar length, 2.588(4), 2.611(4) Å respectively, while La−O (nitrate) distances are in the range 2.614(4)−2.699(4) Å (average 2.672 Å). The phenolic C−O bonds here, C(1)−O(1) (1.286(6) Å) and C(16)−O(2) (1.299(1) Å), were notably shorter than those in the related free ligands.[21] This is believed to be caused by the coordination of the phenolic oxygen to La(III) ion.

The bond lengths of two La−O (phenolic) bonds are 2.447(4) and 2.413 (4) Å respectively. They are very close to those observed in $[La(H_2L)(H_2O)_4]Cl_3$ (H_2L = *N*,*N*′-ethylene-3,3′-(3,6-dioxactane-1,8-diyldioxy)bis(2-hydroxybenzylideneimine)) where the La was also ten-coordinated and the average La−O (phenolic) distance was 2.452 Å.[22] In another related ten-coordinated complex $[La(H_3L)(H_2O)](ClO_4)_3$ the average La−O (phenolic) distance was reported to be 2.468 Å (H_3L was a Schiff base derived from tris(2-aminoethyl)amine and 2,6-diformyl-4-methylphenol).[23] In all these complexes, the Schiff base ligands remained as overall neutral molecules. One may thus tend to believe that the phenolic hydroxyl groups remained un-ionized when coordinated to the La^{3+} (the authors did not mention in refs 22 and 23 the ionization nature of the phenolic hydroxyl groups). If this is the case, the La−O(phenolic) distances are expected to be longer than the corresponding La−O distances where the phenolic hydroxyl groups are deprotonated. However, the La−O(phenolic) distances observed here are very close to the value (2.42 Å) found in a ten-coordinated salicylidene tris(α-aminoethyl)amine (L) complex $La(L)(CF_3SO_3)$ in which the phenolic hydroxyl group was evidently ionized.[24] When using other related crystallographic data for comparison, they are found to be even shorter than a predicted average La−O distance (2.53 Å) for ionized phenolic hydroxyl group which is based on the data from the complexes $[Er(salen)_2]^-[pipH]^+$ [7] and $Y(salen)[N(SiMe_3)_2](THF)$[25] after correction for differences in metal ionic radii and coordination number. These observations, together with the notably short phenolic C−O distances, seem to suggest that the phenolic hydroxyl groups most likely exist as deprotonated forms in all the three complexes $La(H_2salen)(NO_3)_3(MeOH)_2$, $[La(H_2L)(H_2O)_4]Cl_3$, and $[La(H_3L)(H_2O)](CO_4)_3$ as mentioned above. It is probably true that upon coordination to La^{3+}, the phenolic hydroxyl groups ionized with dramatically increased acidity; the protons, after ionization, resided on the imine nitrogen atoms, leaving the whole Schiff base ligand remaining as a neutral molecule.

In summary, we have demonstrated that lanthanum nitrate reacts with H_2salen in $MeOH/CH_2Cl_2$ to afford a novel polymeric chain complex, the first example of lanthanide H_2salen complexes which has been fully characterized and studied by both spectroscopic method and X-ray crystallography. The unusual coordination pattern of H_2salen revealed by X-ray analysis provides valuable information for structural studies of other related lanthanide complexes.

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Supporting Information Available: Listings of experimental crystallographic parameters, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for the title complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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