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FT-IR study of rare earth 4-aminobenzenesulfonate complexes

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Abstract

The crystal structure of lanthanum 4-amino-benzenesulfonate complex has been determined by X-ray diffraction. The crystal data indicate that lanthanum and neodymium 4-amino-benzenesulfonates are isomorphous. The FT-IR spectroscopic study of rare earth 4-amino-benzenesulfonate complexes showed that the spectra of light rare earth (La, Nd, Sm, Eu) complexes are similar and so are the spectra of heavy rare earth (Dy, Er, Y) complexes. There are remarkable differences between the spectra of light rare earth and heavy rare earth complexes. Based on above results, we infer that light rare earth (La, Nd, Sm, Eu) complexes are isomorphous and three heavy rare earth (Dy, Er, Y) complexes are of a different structure but also isomorphous.

Keywords: FT-IR spectroscopy; Rare earth complexes; 4-Aminobenzenesulfonates; Crystal structure; X-ray diffraction

1. Introduction

The sulfonate group in metal complexes may act as monodentate, bidentate chelating or tridentate ligand to different metal ions according to the property of the metal ions and the number of water molecules therein [1–3]. The coordination fashion of the sulfonate group in arylsulfonate complexes also depends on other substituting groups on the benzene ring and the number of water molecules. For example, in the hexaaqua Co^{2+} complexes of benzenesulfonate [4], the central ions are coordinated only with water molecules, and the benzenesulfonate forms hydrogen bonding with water molecules. While for tetraaqua Co aminobenzenesulfonate complexes [5], both amino and sulfonate groups participate in the coordination with Co^{2+} ions. Compared with many crystal structures of alkali, alkaline earth and transitional metal complexes of arylsulfonic acid reported in the literature [4,6–12], relatively little was known about the rare earth complexes [1,13,14]. In this paper, different compositions were found for light and heavy rare earth complexes of 4-aminobenzenesulfonic acid and also distinct differences were observed in their corresponding FT-IR spectra. The crystal structure of lanthanum 4-aminobenzenesulfonate is also presented.

2. Experimental

2.1. Synthesis

4-aminobenzenesulfonic acid was dissolved in hot

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Table 1
Elemental results of title complexes

Complexes	C		H		N	
	Cal.	Exp.	Cal.	Exp.	Cal.	Exp.
La	27.04	26.92	4.29	4.21	5.26	5.17
Nd	26.86	27.13	4.26	4.17	5.22	5.16
Sm	26.66	26.66	4.22	4.15	5.18	5.05
Eu	26.60	26.39	4.22	4.11	5.17	4.95
Tb	25.81	25.94	4.33	3.99	5.02	4.89
Dy	25.70	25.90	4.31	3.99	4.99	4.83
Er	25.56	25.95	4.28	3.56	4.97	4.82

water, lanthanide (La, Nd, Sm, Eu, Tb, Dy, Er or Y) hydroxide was added until it could not be dissolved further. After filtration, the filtrate was left under room temperature, crystals were formed after several days. For lanthanum, crystals suitable for single crystal determination were obtained.

2.2. Instruments

The elemental analysis was performed with Carlo Erba 1106 microanalysis instrument. FT-IR spectra were performed in Nujol mull on a Nicolet Magna 750 IR spectrometer.

All diffraction data were collected on a Ragaku AFC6S diffractometer, with MoKα radiation ($\lambda = 0.71073$ Å, graphite monochromator) at room temperature in $\omega - 2\theta$ scan mode. Corrections to the absorption data were made by semi-empirical method. The structure was solved by direct method with SHELXTL PLUS(VMS) program, and refined by the full-matrix least-squares method to determine the non-hydrogen atom coordinates. The coordinates of hydrogen atoms of benzene ring were located in calculated positions and the coordinates of hydrogen atoms of $-NH_2$ were calculated according to the diffraction density around the nitrogen atoms.

Table 2
Structural parameters of $LaL_3{\cdot}8H_2O$

Formula	$C_{18}H_{34}LaN_3O_{17}S_3$
M_w	799.6
Color; habit	Colorless needle
Crystal size (mm)	0.10 × 0.20 × 0.30
Crystal system	Orthorhombic
Space group	*Pbca*
a	7.985(3) Å
b	23.701(9) Å
c	32.039(8) Å
V(Å^3)	6063(4)
Z	8
Density (Mg m^{-3})	1.752

3. Results and discussion

3.1. Elemental analysis

The elemental analysis gave the following results: $LnL_3{\cdot}8H_2O$ (Ln = La, Nd, Sm, Eu), $LnL_3{\cdot}9H_2O$ (Ln = Tb, Dy, Er; L represents the *p*-aminobenzenesulfonate anion), see Table 1.

Table 3
Selected bond lengths (Å) and angles (°) in $LaL_3{\cdot}8H_2O$

La–O(2)	2.464(9)	La–O(4)	2.484(10)
La–O(10)	2.545(10)	La–O(11)	2.561(10)
La–O(12)	2.625(10)	La–O(13)	2.613(9)
La–O(14)	2.556(9)	La–O(15)	2.557(9)
La–O(16)	2.692(10)	S(1)–C(1)	1.739(13)
S(1)–O(1)	1.456(11)	S(1)–O(2)	1.461(10)
S(1)–O(3)	1.439(10)	S(2)–C(7)	1.749(14)
S(2)–O(4)	1.437(10)	S(2)–O(5)	1.442(12)
S(2)–O(6)	1.419(11)	S(3)–C(13)	1.772(15)
S(3)–O(7)	1.409(14)	S(3)–O(8)	1.433(16)
S(3)–O(9)	1.482(14)	O(2)–La–O(4)	90.4(3)
O(2)–La–O(10)	77.6(3)	O(4)–La–O(10)	138.7(3)
O(2)–La–O(11)	138.4(3)	O(4)–La–O(11)	73.1(3)
O(10)–La–O(11)	90.0(3)	O(2)–La–O(12)	70.1(3)
O(4)–La–O(12)	71.4(3)	O(10)–La–O(12)	136.1(3)
O(11)–La–O(12)	133.8(3)	O(2)–La–O(13)	136.3(3)
O(4)–La–O(13)	133.2(3)	O(10)–La–O(13)	67.4(3)
O(11)–La–O(13)	68.4(3)	O(12)–La–O(13)	120.1(3)
O(2)–La–O(14)	78.2(3)	O(4)–La–O(14)	139.2(3)
O(10)–La–O(14)	77.2(3)	O(11)–La–O(14)	137.8(3)
O(10)–La–O(14)	67.9(3)	O(13)–La–O(14)	69.6(3)
O(12)–La–O(14)	138.9(3)	O(4)–La–O(15)	76.8(3)
O(10)–La–O(15)	135.8(3)	O(11)–La–O(15)	75.2(3)
O(12)–La–O(15)	68.7(3)	O(13)–La–O(15)	68.5(3)
O(14)–La–O(15)	86.4(3)	O(2)–La–O(16)	69.0(3)
O(4)–La–O(16)	69.3(3)	O(10)–La–O(16)	69.5(3)
O(11)–La–O(16)	69.5(3)	O(12)–La–O(16)	121.8(3)
O(13)–La–O(16)	118.1(3)	O(14)–La–O(16)	137.1(3)
O(15)–La–O(16)	136.5(3)	O(1)–S(1)–O(2)	111.9(6)
O(1)–S(1)–O(3)	111.1(6)	O(2)–S(1)–O(3)	112.7(6)
O(4)–S(2)–O(5)	109.2(7)	O(4)–S(2)–O(8)	111.6(7)
O(5)–S(2)–O(6)	114.7(8)	O(7)–S(3)–O(2)	118.3(9)
O(7)–S(3)–O(9)	108.8(7)	O(8)–S(3)–O(9)	108.9(8)

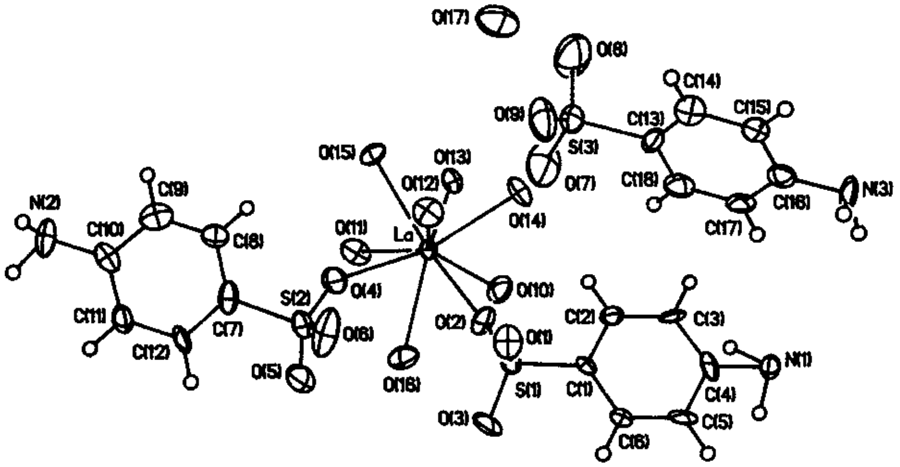

Fig. 1. The structure of $LaL_3{\cdot}8H_2O$ (L = 4-aminobenzenesulfonate anion).

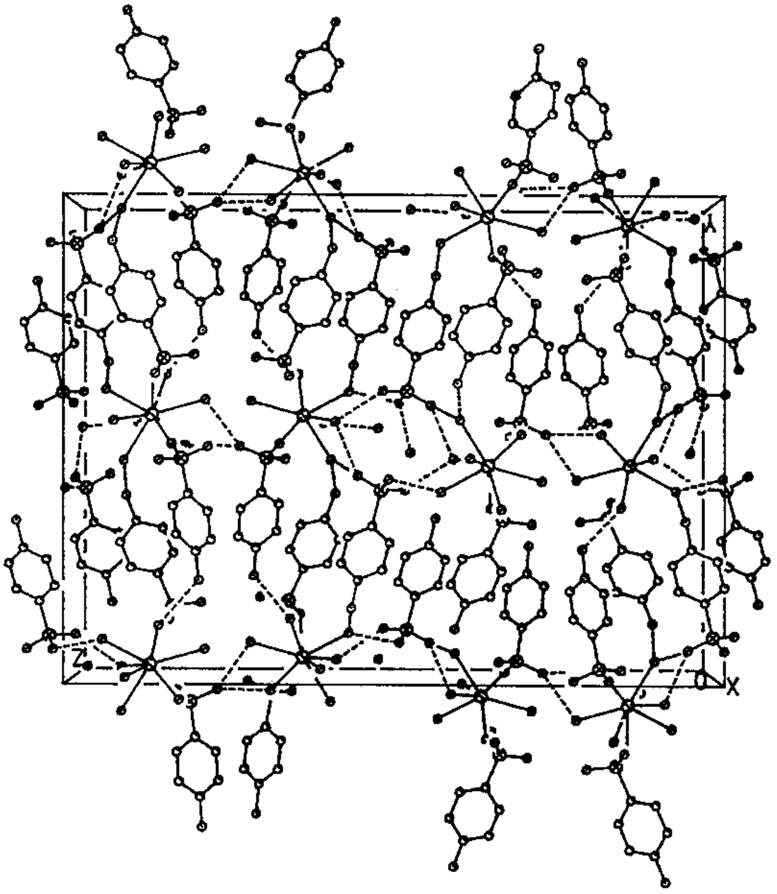

Fig. 2. Hydrogen bonding network and layer structure in $LaL_3{\cdot}8H_2O$ (L = 4-aminobenzenesulfonate anion).

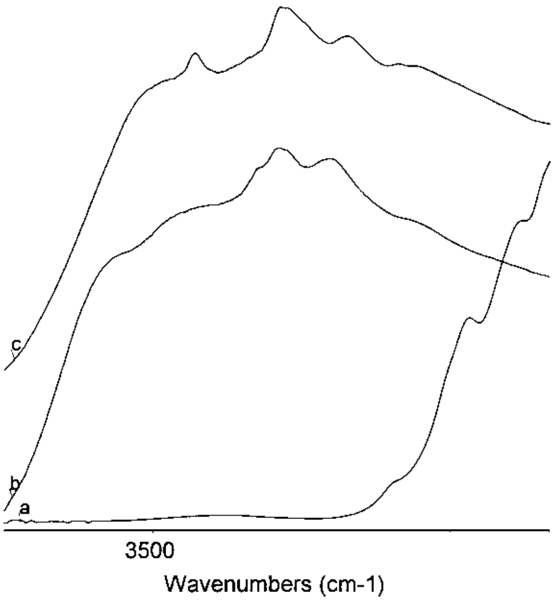

Fig. 3. FT-IR spectra of the complexes and ligand in the range of 3650–3100 cm^{-1}: (a) ligand, (b) La complex, (c) Er complex.

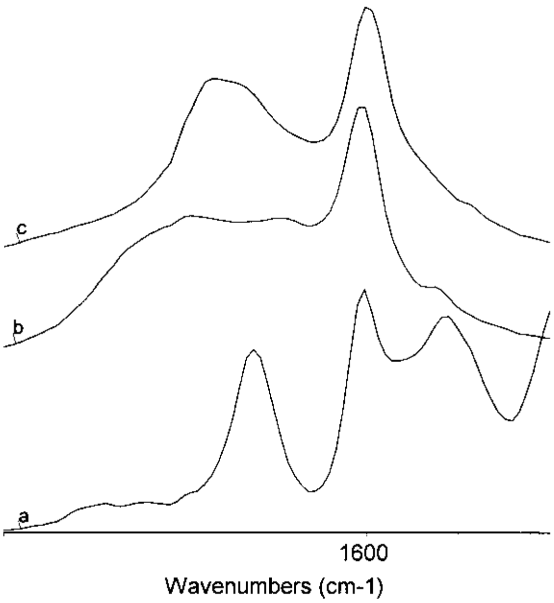

Fig. 4. FT-IR spectra of the complexes in the range of 1700–1550 cm^{-1}: (a) ligand, (b) La complex, (c) Er complex.

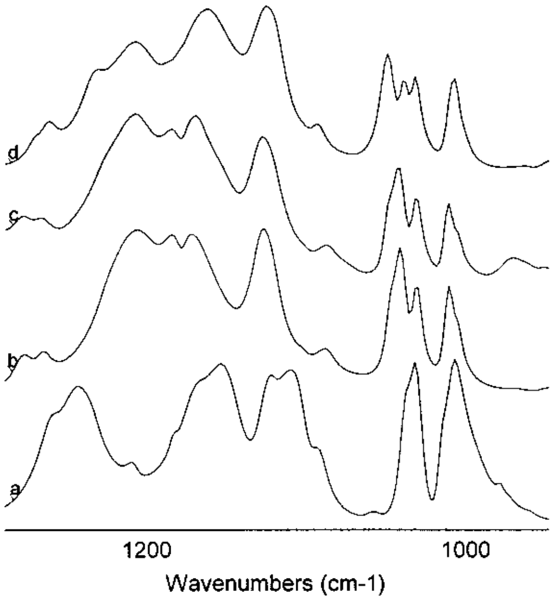

Fig. 5. FT-IR spectra of the complexes and ligand in the range of 1290–950 cm^{-1}: (a) ligand, (b) La complex, (c) Nd complex, (d) Er complex.

3.2. Crystal structure of $LaL_3 \cdot 8H_2O$

The collection parameter and data were listed in Table 2. The structure of the complexes $LaL_3 \cdot 8H_2O$ is given in Fig. 1. Selected bond lengths and bond angles are listed in Table 3. In the complex, the lanthanum atom is coordinated to two oxygen atoms from two $-SO_3^-$ groups and seven oxygen atoms from water molecules, thus the coordination number of lanthanum atom is nine, another water molecule exists as lattice water, the other 4-aminobenzenesulfonic acid molecule is not bonded to the lanthanum atom, but forms H-bonding with water molecules. The coordination geometry around the lanthanum ion is a tricapped trigonal prism. There is complicated hydrogen bonding network between $-SO_3^-$ groups, water molecules and $-NH_2$ group in the complexes. Also layer structure can be observed in the compound as shown in Fig. 2. According to the report of Staryhowwicz [13], the La and Nd complexes are isomorphous.

Compared with the sulfonate group in the complexes of $Ln(PTS)_3 \cdot 9H_2O$ [1], in which PTS is *p*-methylbenzenesulfonate anion, the geometry of sulfonate group in the complexes of $LaL_3 \cdot 8H_2O$ was

Table 4
The assignment of bands in the FT-IR spectra of ligand and the title complexes

$LnL_3{\cdot}8H_2O$				$LnL_3{\cdot}9H_2O$			Ligand	Assignments
La	Nd	Sm	Eu	Dy	Er	Y		
				3458	3458	3458		
3373	3375	3373	3377	3372	3372	3373		
3322	3321	3321	3319	3305	3304	3305		ν_{O-H}
				3253	3253	3254		ν_{N-H}
				3238	3237	3237		
1649		1651	1653	1643	1642	1642		δ_{H-O-H}
1624		1631	1632	1634			1632	δ_{H-N-H}
1602		1602	1602	1600	1600	1600	1601	$\nu_{C=C}$
				1233	1232	1232	1245	
1208	1209	1212	1211	1209	1209	1208		
1186	1187	1187	1187					ν_{as,SO_3^-}
1174	1172	1176	1175	1163	1163	1163	1155	
1129	1129	1130	1129	1127	1127	1127	1124	β_{C-H}
				1050	1051	1051		
1043	1044	1045	1046	1046	1041	1041		ν_{s,SO_3^-}
1033	1033	1033	1033	1033	1034	1033	1034	
1012	1013	1013	1012	1009	1009	1009	1009	$\beta_{C-H} + \nu_{C-S}$

distorted, especially in the non-coordinated sulfonate group, the largest difference between the angle O–S–O is 10° and the largest difference between the three S–O is 0.07 Å.

3.3. FT-IR spectra

Selected FT-IR spectra are shown in Figs. 3–5. The main absorption bands and the preliminary assignments are listed in Table 4. The IR spectra of the complexes show great difference from that of the ligand. These changes indicate the formation of these complexes. Absorption bands in the range of 3700–3100 cm^{-1} show that there are water molecules in the complexes. In the crystal of 4-aminobenzenesulfonic acid, $-NH_3^+$ exists instead of $-NH_2$, therefore there are no ν_{N-H} absorption bands in its IR spectrum, while combination broad absorption bands of H_2O and $-NH_2$ appear in the spectra of title complexes. This difference indicates that the bond between $-SO_3H$ and $-NH_2$ was destroyed, thus $-NH_2$ group appears.

The spectra of $LnL_3{\cdot}8H_2O$ (La, Nd, Sm, Eu) are similar to each other and so are the spectra of $LnL_3{\cdot}9H_2O$ (Dy, Er, Y). But there are distinct differences between the spectra of the two series of complexes, e.g. the vibrational absorption bands of H_2O and $-SO_3^-$. Remarkable differences between the absorption bands of $-SO_3^-$ group reveal its different coordination fashions in two series of complexes.

It is well-known that the property of lanthanide ions are similar. Ohki and co-workers [14] have reported that the crystal structure of $[RE(PTS)_2(H_2O)_6](PTS){\cdot}3H_2O$ (RE = Y, Sm, Gd, Dy, Ho, Er, Yb; PTS represents the *p*-methylbenzenesulfonate anion) are similar and so are their IR spectra. So it may be concluded that rare earth complexes with same composition and similar IR spectra are isomorphous. According to our result, both the IR spectra and crystal structure of La and Nd complexes are all similar, and the IR spectra of La, Nd, Sm and Eu complexes are also similar. Therefore, it is concluded that the crystal structures of Sm and Eu complexes are similar to those of La and Nd complexes. In other words, light rare earth $LnL_3{\cdot}8H_2O$ (La, Nd, Sm, Eu) complexes are isomorphous.

From the results of elemental analyses and FT-IR spectra, we can infer that the crystal structure of heavy rare earth complexes should be different from those of light rare earth complexes. Also, the same composition and the similarity of IR spectra of heavy rare earth complexes may reflect that the complexes of $LnL_3 \cdot 9H_2O$ (Dy, Er, Y) are isomorphous too.

Compared with rare earth complexes of 4-methylbenzenesulfonates whose crystal structures were similar, it can be seen that the substituting group on the benzene ring has an impact on the crystal structure of rare earth complexes.

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