

Note

X-Ray Structure of 8-Quinolinolato Lanthanide Complex: (8-Quinolinolato)bis(2,6-di-*tert*-butyl-4-methylphenoxy)samarium

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The heteroleptic (8-quinolinolato)bis(2,6-di-*tert*-butyl-4-methylphenoxy)samarium complex was synthesized and characterized by elemental analysis, IR spectrum and X-ray diffraction analysis. The complex is a five-coordinate dimer. Each 8-quinolinolato oxygen atom links two samarium atoms as a bridge and the Sm—N bond is a typical donor bond.

Keywords samarium, 8-quinolinolato, aryloxo, crystal structure

Introduction

8-Hydroxyquinoline is a classical chelating agent for transition metals and lanthanides. Recently metal complexes incorporating 8-quinolinolato ligands have received more and more attention. The research interest probably arises from two aspects. First, 8-quinolinolato metal complexes have been found promising as photosensitized luminescent materials.^{1,2} Second, 8-hydroxyquinoline usually grants metal complexes good reactivity.³⁻⁶ As we study lanthanide complexes with this ligand, it is found that there are few structures elucidating how a 8-quinolinolato ligand coordinates with a lanthanide atom. Complexes of (QuO)₃Ln [Ln = Sc, La, Pr, Eu, Yb; QuO = 8-quinolinolato] were prepared much early,⁷ but they are completely insoluble in any solvents. Mixed-ligand complexes of Cp_nLn(OQu)_{3-n} [n = 1, 2; Ln = Nd, Yb; Cp = cyclopentadienyl] were reported soluble in tetrahydrofuran (THF),⁸ but no single crystal X-ray diffraction analysis has been made. So we turned to synthesize soluble het-

eroleptic (8-quinolinolato)bis(aryloxo)samarium [aryloxo = 2,6-di-*tert*-butyl-4-methylphenoxy] complex and structurally characterize it.

Experimental

General

All operations were performed under pure Ar with rigorous exclusion of air and water using Schlenk techniques. THF was predried with CaCl₂ and distilled from sodium benzophenone ketyl before use. Melting point was determined in sealed argon-filled capillaries and uncorrected. Metal analysis was carried out by complexometric titration. Carbon, hydrogen and nitrogen analyses were performed by direct combustion. IR spectra were recorded on a Magna 550 spectrometer as KBr pellets.

Preparation of [(QuO)(ArO)₂Sm]₂ (Qu = C₉H₆N-8, Ar = C₆H₂Bu^t-2,6-Me-4)

To a suspension of SmCl₃ (0.4785 g, 1.862 mmol) in 15 mL of THF was added ArONa (3.773 mmol) in 5 mL of THF. The reaction mixture was stirred for about five minutes and the SmCl₃ solid power gradually disappeared. Then QuONa (1.938 mmol) in 3 mL of THF was added. The color of the mixture changed from yellow-green to orange-red. After it was stirred for two days, the mixture was centrifugalized. The obtained clear solution

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was concentrated and stored at 5 °C. Yellow crystals of $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$ (0.8099 g, 58.7%) were obtained. M. p. (dec.) 172–175 °C; FT-IR (KBr) ν : 2959(s), 1570(m), 1501(s), 1466(s), 1431(s), 1385(s), 1319(s), 1231(m), 1153(m), 1119(m), 864(w), 771(w), 729(w) cm^{-1} . Anal. calcd for $\text{C}_{78}\text{H}_{104}\text{N}_2\text{O}_6\text{Sm}_2$: C 63.97, H 7.16, N 1.91, Sm 20.54; found C 63.61, H 7.18, N 1.74, Sm 20.30.

X-Ray crystallography

A yellow crystal of approximate dimensions 0.50 mm \times 0.40 mm \times 0.10 mm was mounted in a glass fiber under pure argon. Measurements were made on a SMART APEX CCD diffractometer with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.071073$ nm) radiation. The data were collected at temperature of 293(2) K to maximum θ value of 26.51°. The crystal structure belongs to triclinic, space group $P-1$ with cell dimensions: $a = 1.0608(3)$ nm, $b = 1.4763(5)$ nm, $c = 1.5138(5)$ nm, $\alpha = 91.822(3)^\circ$, $\beta = 104.165(4)^\circ$, $\gamma = 110.335(4)^\circ$, $V = 2.1374(12)$ nm^3 , $Z = 1$, $D_{\text{calcd}} = 1.321$ g/cm^3 , $F(000) = 884$, $(\Delta\rho)_{\text{max}} = 1.011$, $(\Delta\rho)_{\text{min}} = -0.541$, $(\Delta/\rho)_{\text{max}} = 1.122$, $S = 1.146$. The structure was solved by direct method and refined by full-matrix least squares method using SHELXL-97 software package. The absorption is corrected by multi-scan method using SADABS procedure. The hydrogen atoms were located and refined from geometric consideration. The final agreement factors are $R_1 = 0.0350$ and $wR_2 = 0.0905$ on 7264 unique data [$I > 3\sigma(I)$] and $R_1 = 0.0432$ and $wR_2 = 0.1003$ on 8152 total data.

Results and discussion

Synthesis of $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$

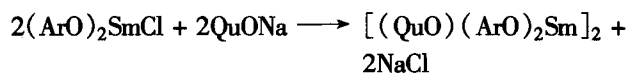
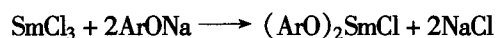
$(\text{QuO})_3\text{Ln}$ (Ln = Sc, La, Pr, Eu, Yb) can be conveniently prepared by reaction of metal nitrate and 8-hydroxyquinoline in slightly basic solutions.⁹ Unfortunately they are completely insoluble in any solvents. When the three 8-quinolinolato groups were partially substituted by other ligands such as cyclopentadiene, the solubility of the complexes may be improved. $\text{Cp}_n\text{Ln}(\text{OQu})_{3-n}$ ($n = 1, 2$; Ln = Nd, Yb) can be readily synthesized by

metathesis reaction of Cp_3Ln and 8-hydroxyquinoline.⁸ They were reported to be soluble in THF, but no molecular structures have been characterized.

To understand the coordination details, we try to synthesize soluble 8-quinolinolato lanthanides. Complexes of $\text{Cp}_n\text{Ln}(\text{OQu})_{3-n}$ ($n = 1, 2$; Ln = Sm) are found insoluble in normal solvents in our experiment. Considering that complexes of $(\text{IND})_n\text{Ln}(\text{OQu})_{3-n}$ ($n = 1, 2$; Ln = Nd, Sm) (IND = indenyl) are also insoluble,¹⁰ we began to synthesize heteroleptic samarium 8-quinolinolato/aryloxide complex.

Reaction of SmCl_3 with two molar ratio of ArONa and equivalent QuONa affords the expected complex of $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$ in a yield of 58.7% (Scheme 1). But attempt to prepare $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$ by the reaction of $\text{Cp}_2\text{Sm}(\text{OQu})$ and ArOH is unsuccessful.

Scheme 1



Complex of $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$ is soluble in THF. It is thermally stable and decomposes at about 172 °C, but it is sensitive to air and moisture.

X-Ray diffraction analysis indicates that one molecule of $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$ coexists with three uncoordinated benzene unexpectedly in a unit cell. The benzene may come from the contaminated THF solvent. However, the result of elemental analysis is more consistent with the formula $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$ without benzene. The uncoordinated benzene must be very easy to be lost under vacuum.

Molecular structure of $[(\text{QuO})(\text{ArO})_2\text{Sm}]_2$

The crystal structure and stereogram of the complex packing in a crystal unit cell are shown in Figs. 1 and 2. Selected bond distances and angles are listed in Table 1. The complex is a dimer. One samarium atom is coordinated to two aryloxo oxygen atoms, two 8-quinolinolato oxygen atoms and one 8-quinolinolato nitrogen atom. Each 8-quinolinolato oxygen atom links two samarium atoms as a bridge.

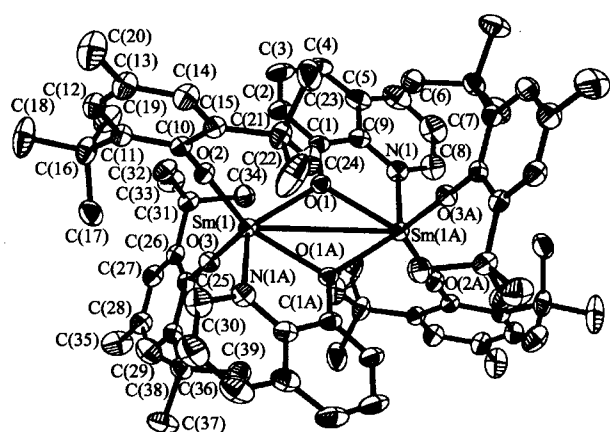


Fig. 1 ORTEP view of the title complex.

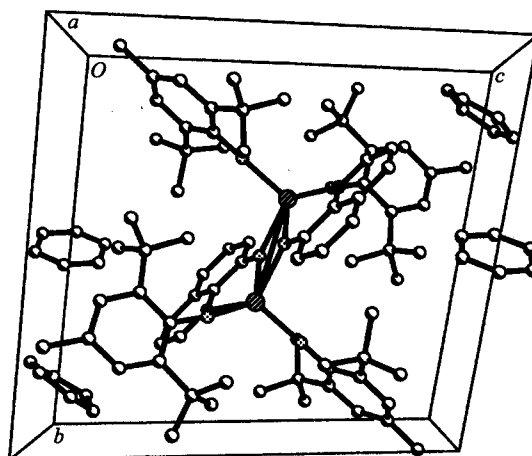


Fig. 2 Packing diagram of the title complex.

Table 1 Selected bond distances [nm] and angles [°] for the complex

Bond	Distance (nm)	Bond	Distance (nm)	Bond	Distance (nm)
Sm(1)—O(1)	0.2357(3)	Sm(1)—O(1A)	0.2393(3)	Sm(1)—O(2)	0.2154(3)
Sm(1)—O(3)	0.2146(3)	Sm(1)—N(1A)	0.2523(3)	C(1)—C(2)	0.1360(6)
C(2)—C(3)	0.1411(7)	C(3)—C(4)	0.1357(8)	C(4)—C(5)	0.1412(8)
C(5)—C(6)	0.1414(8)	C(6)—C(7)	0.1341(10)	C(7)—C(8)	0.1400(8)
C(5)—C(9)	0.1419(6)	C(1)—C(9)	0.1433(6)	C(8)—N(1)	0.1331(6)
C(9)—N(1)	0.1362(6)	C(1)—O(1)	0.1347(4)		
Bond	Angle (°)	Bond	Angle (°)		
O(1)—Sm(1)—O(2)	107.38(10)	O(1)—Sm(1)—O(3)	107.84(10)		
O(1A)—Sm(1)—O(2)	131.22(9)	O(1A)—Sm(1)—O(3)	106.53(10)		
O(1)—Sm(1)—O(1A)	68.04(10)	O(2)—Sm(1)—O(3)	120.07(10)		
N(1A)—Sm(1)—O(1)	128.45(10)	N(1A)—Sm(1)—O(1A)	66.22(11)		
N(1A)—Sm(1)—O(2)	86.25(11)	N(1A)—Sm(1)—O(3)	106.79(11)		
Sm(1)—O(1)—Sm(1A)	111.96(10)	Sm(1)—O(2)—C(10)	164.0(2)		
Sm(1)—O(3)—C(25)	179.5(3)				

The Sm—O(2) and Sm—O(3) bond distances, 0.2154(3) and 0.2146(3) nm respectively, are consistent with those in $(\text{ArO})_2(\text{THF})_2\text{SmI}$ [0.2153(7) nm] and $[(\text{ArO})_2(\text{THF})\text{Sm}(\mu\text{-Cl})_2]$ [0.2110(7)—0.2135(6) nm].¹¹ The Sm—O(1) bond distance of 0.2357(3) nm is comparable with that in $[(\text{ArO})_2(\text{DME})\text{Sm}]_2[\mu\text{-}\eta^4\text{-(PhN)OCCO(NPh)}]$ [0.2318(7) nm].¹² The Sm—N bond [0.2523(3) nm] is in agreement with a donor bond, for the Sm—N donor bond distance for a five-coordinated Sm^{3+} is expected to be 0.24–0.26 nm.^{13,14} The Sm(1)—O(3)—C(25) three atoms are almost in a line, but Sm(1)—O(2)—C(10) atoms are not. This bent phenomenon is normal for aryloxo lanthanides. The angle of Sm(1)—O(2)—C(10) [164.0(2)°] is consistent with that in $[(\text{ArO})_2(\text{THF})-$

$\text{Sm}(\mu\text{-Cl})_2]$ [165.1(6)°]. Each 8-quinolinolato group is planar, but the two groups are not coplanar. Neither of them are coplanar with Sm(1)—O(1)—Sm(1A)—O(1A) four atoms. The main structure feature can be described as Fig. 3.

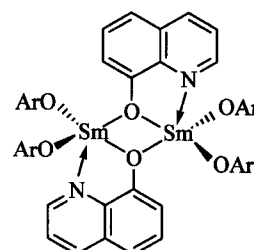


Fig. 3 Bond fashion of the title complex.

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