

STRUCTURE AND THERMAL STABILITY OF THE BENZO-15-CROWN-5 WITH LANTHANUM (III) BROMIDE COMPLEX

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ABSTRACT

The reaction of benzo-15-crown-5 ($C_{14}H_{20}O_5$) ligand with $La(NO_3)_3 \cdot 7H_2O$ in the presence of HBr has resulted in the production of an exotic sandwich complex, $[LaC_{28}H_{36}Br_4O_{10}][3Br]$. The crystal system is triclinic with space group $P\bar{1}$, $a = 12.5834(14) \text{ \AA}$, $b = 13.5816(16) \text{ \AA}$, $c = 13.8403(16) \text{ \AA}$, $\alpha = 70.751(2)^\circ$, $\beta = 66.773(2)^\circ$ and $\gamma = 67.631(2)^\circ$. The cation comprises of the lanthanum atom coordinated to two crowns via three oxygen atoms from each crown in a η^3 -sandwich fashion. The two phenyl groups of the crown are brominated. The La-O_{Ligand} bond lengths are between 2.857(7) and 2.949(7) Å. The trianion $[3Br]^{3-}$ is linear with Br-Br bond lengths of 2.518(2) and 2.560(2) Å respectively. The molecule is stabilized by intermolecular interactions of the type $C-H \cdots Br$ to form dimers and are arranged parallel to bc face.

Keywords: lanthanum, benzo-15-crown-5, hydrogen bonding, bromination, x-ray structure

INTRODUCTION

Since the synthesis of the "crown" ether compounds by Pedersen several years ago, and his observation of their ion binding properties, a great deal of interest has been focused on them [1]. This is because of the possible chemical and biological applications of their unusual complexation, solvation and transport effect [2]. The investigations of the thermodynamic of these process have been explained [3] as well as studies of their molecular structure using X-ray crystallography [4], NMR spectroscopy [5] and infrared [6]. Lanthanide complexes have played an important role in special materials because of their optical, electronic, magnetic and biological properties [7-9].

Bromination is reaction of organometallic compounds with molecular bromines usually result in cleavage of any metal-carbon s-bonds that are present, although in some cases where suitable higher than oxidation states of the metal accessible, oxidative addition at the metal center may be observed without metal-carbon bond cleavage [10]. The bromine into organic molecules is an important and fundamental reaction in organic chemistry, owing to the considerable commercial

importance of such compounds [11]. It can be used as a potent antitumor, antibacterial, antifungal, antineoplastic, antiviral and antioxidising agents. Beside that also as industrial intermediates in the manufacture of pharmaceuticals and agrochemicals [12-15]. The traditional bromination using elemental bromine shows a maximum of 50% atom efficiency in terms of bromine consumption [11]. This process is more expensive and generates a large quantum of hydrogen bromide (HBr) for disposal. The generated HBr is used either in the preparation of value added brominated product or waste which will caused a series of environmental problems [11]. The present complex is the product of the reaction of benzo-15-crown-5 ($C_{14}H_{20}O_5$) with $La(NO_3)_3 \cdot 7H_2O$ in the presence of HBr. The reaction is accomplished by the addition of bromine at phenyl rings together with the complexation of lanthanum to oxygen atoms of the crown rings. The present study will mainly focus on the synthesis, chemical characterizations and structural features of these complex by X-ray crystallography, TGA, IR and NMR spectroscopy.

EXPERIMENTAL SECTION

All reagents were commercially available and used without any further purification: Benzo-15-

crown-5 ($C_{14}H_{20}O_5$) ($\geq 99\%$) and $La(NO_3)_3 \cdot 7H_2O$ (99%) from Fluka, HBr (48 %) from Ajax Chemicals, Australia.

Elemental analyses were performed on Control Equipment Corporation Model 250-XA, USA. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Infrared spectra were obtained of KBr pellets in the region of 4000 – 400 cm^{-1} . The NMR spectra were recorded on Bruker 300 MHz spectrometer. Melting point of the complexes was determined using a Gallenkamp melting point apparatus. Thermal stability of the complexes were determined using a Perkin-Elmer TGA-7 series under nitrogen atmosphere at scan rate of 30.0 $^{\circ}C/min$.

Lanthanum nitrate (1 mmol), benzo-15-crown-5 (1 mmol) was added drop-wise to 1 mL HBr (12.5 mmol) dissolved in 15 mL acetonitrile-methanol (3:1 v/v) until clear solution was obtained. The resulting mixture was covered with parafilm where small holes were made to control the solvent evaporation. The clear solution changed to orange after 2 days, then recrystallization was conducted in acetonitrile-methanol (1:1 v/v) after the evaporation of the first solvent mixture. After several days, single crystals (orange) were obtained. Elemental analysis revealed the formation of 2:1 = (Ligand: Lanthanide). Found (Calc.): C28.09 (27.30); H, 3.50 (2.93)% with melting point 145.3 - 188.0 $^{\circ}C$.

X-ray crystallography

A single crystal, measuring up to 0.52 \times 0.39 \times 0.29 mm^3 , was mounted on a glass fiber with epoxy cement. A summary of the crystallographic data for the $[LaC_{28}H_{36}Br_4O_{10}][3Br]$ complex at 293 K is summarized in Table 1. The crystal data were collected with a 2K-SMART APEX CCD diffractometer using graphite-monochromator, Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) with a detector distance of 6 cm and swing angle of -35° . A hemisphere of the reciprocal space was covered by the combination of three sets of exposures. Each set had a different θ angle ($0.88; 180^{\circ}$) and each exposure of 10 sec, covered 0.3° in ω . Crystal decay was monitored by repeating 50 initial frames at the end of the data collection and analyzing the intensity of duplicate reflections, and was found to be negligible. The structure was solved by direct methods and refined by least square on F_o^2 using the SHELXTL software package [16, 17].

RESULTS AND DISCUSSION

X-ray structural studies

The crystal system is triclinic with space group $P\bar{1}$, $a = 12.5834(14) \text{ \AA}$, $b = 13.5816(16) \text{ \AA}$, $c = 13.8403(16) \text{ \AA}$, $\alpha = 70.751(2)^{\circ}$, $\beta = 66.773(2)^{\circ}$ and $\gamma = 67.631(2)^{\circ}$ (Table 1). The compound is a salt type complex, $[LaC_{28}H_{36}Br_4O_{10}]^{3+}[3Br]^{3-}$ (Fig.1).

Table 1 Crystallography data of the $[LaC_{28}H_{36}Br_4O_{10}][3Br]$ complex

Parameter	
Molecule formula	$C_{28}H_{36}Br_7LaO_{10}$
Molecular weight	1230.85
Unit cell dimensions	$a = 12.5834(14) \text{ \AA}$ $b = 13.5816(16) \text{ \AA}$ $c = 13.8403(16) \text{ \AA}$ $\alpha = 70.751(2)^{\circ}$ $\beta = 66.773(2)^{\circ}$ $\gamma = 67.631(2)^{\circ}$
Crystal system, Space group	Triclinic, $P\bar{1}$
Volume	$1964.7(4) \text{ \AA}^3$
Z, Density (calculated)	2, 2.081 mg/m^3
Absorption coefficient	8.253 mm^{-1}
θ range for the data collection ($^{\circ}$)	1.64 – 26.00
F(000)	1172
Limiting indices	$-15 \leq h \leq 15$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
R (int)	0.0469
Reflection collected/unique	22866 / 7716
Data / Restraints / parameter	7716 / 0 / 417
Goodness-of-fit on F^2	1.079
Final R indices [$ I > 2\sigma(I) $]	$R1 = 0.0620$, $wR2 = 0.1757$
R indices (all data)	$R1 = 0.1092$, $wR2 = 0.1945$
Largest diff. peak and hole	1.294 and $-0.919 \text{ e. \AA}^{-3}$

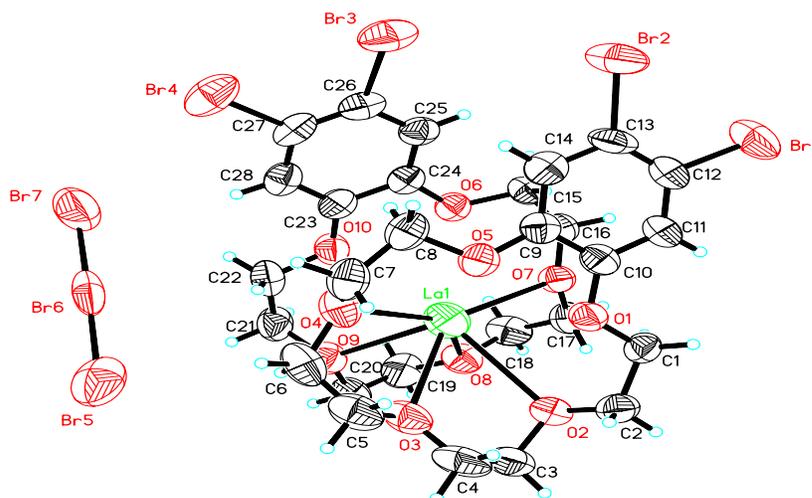


Fig. 1 Molecular structure of $[\text{LaC}_{28}\text{H}_{36}\text{Br}_4\text{O}_{10}][3\text{Br}]$ with 50% probability level

Table 2 Selected Bond Lengths (Å) and Bond Angles ($^\circ$) in the $[\text{LaC}_{28}\text{H}_{36}\text{Br}_4\text{O}_{10}][3\text{Br}]$ complex

Bond	Length (Å)
La1–O2	2.949(7)
La1–O3	2.857(7)
La1–O4	2.889(7)
La1–O7	2.885(7)
La1–O8	2.915(7)
La1–O9	2.915(7)
Br1–C12	1.885(7)
Br1–C13	1.896(7)
Br1–C26	1.909(7)
Br1–C27	1.894(7)
Br5–Br6	2.518(2)
Br6–Br7	2.560(2)
Bond	Angles ($^\circ$)
O3–La1–O2	59.30(18)
O4–La1–O2	113.8(2)
O7–La1–O2	82.18(18)
O8–La1–O2	77.56(19)
O9–La1–O2	108.9(2)
O3–La1–O4	60.74(18)
O3–La1–O7	141.4(2)
O3–La1–O8	104.6(2)
O3–La1–O9	79.6(2)
O4–La1–O7	150.5(2)
O4–La1–O8	143.6(2)
O4–La1–O9	84.88(19)
O7–La1–O9	114.3(2)
O8–La1–O9	58.98(17)
Br5–Br6–Br7	179.16(5)

The cation comprises of two brominated benzo-15-crown-5 ($\text{C}_{14}\text{H}_{18}\text{O}_5$) ligands coordinated to lanthanum atom via three oxygen atoms from each ring, O2, O3, O4, O7, O8 and O9 in a sandwich

fashion (Fig.1). The La–O bond lengths of the sandwich type structure are between 2.857(7) and 2.949(7) Å. The bond lengths and angles of the ligand are in normal ranges (Table 2). The crown rings are somewhat in gauche conformation. The tribromide anion $[3\text{Br}]^{3-}$ is linear with Br5–Br6–Br7 bond angle of $179.16(5)^\circ$. The difference in bond length of Br5–Br6 and Br6–Br7 are of 2.518(2) and 2.560(2) Å respectively, indicates the probability of a d^2sp^3 hybridization.

In the crystal structure, the molecules are linked by intermolecular interactions, C8–H8B \cdots Br5 (symmetry code (i) $1-x, 1-y, 1-z$; $A\cdots H = 2.86$ Å, $A-H\cdots D = 143^\circ$) to form dimers and arranged parallel to bc face (Fig. 2).

IR spectra

The IR spectra of the complex shows a sharp band at 649s cm^{-1} [18], exhibiting C–Br bonding (Fig. 3). The C–H vibration of the phenyl ring at 1505 cm^{-1} was shifted to lower frequency (1497 cm^{-1}) upon complexation. The $\nu(\text{C–O})$ vibration band at 1256 cm^{-1} is shifted towards lower wave numbers, indicated that the ether oxygen atoms were involved in the coordination to lanthanum(III) ion. The C=C vibration mode of the phenyl ring is shifted to a higher frequencies (1630s cm^{-1}) in relation to the free ligand (1618s cm^{-1}), indicating that phenyl rings are involved in the bromination reaction. Electrophilic bromination with phenyl ring occurs exclusively at positions meta and para to the ether bond [19].

$^1\text{H NMR}$ spectra

The spectra of B15C5 and its complex in the ether region are more complex due to the greater

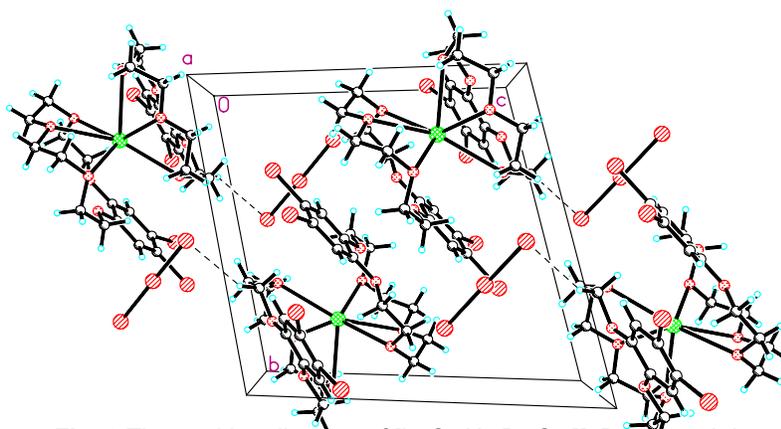


Fig. 2 The packing diagram of $[\text{LaC}_{28}\text{H}_{36}\text{Br}_4\text{O}_{10}][3\text{Br}]$ viewed down a axis

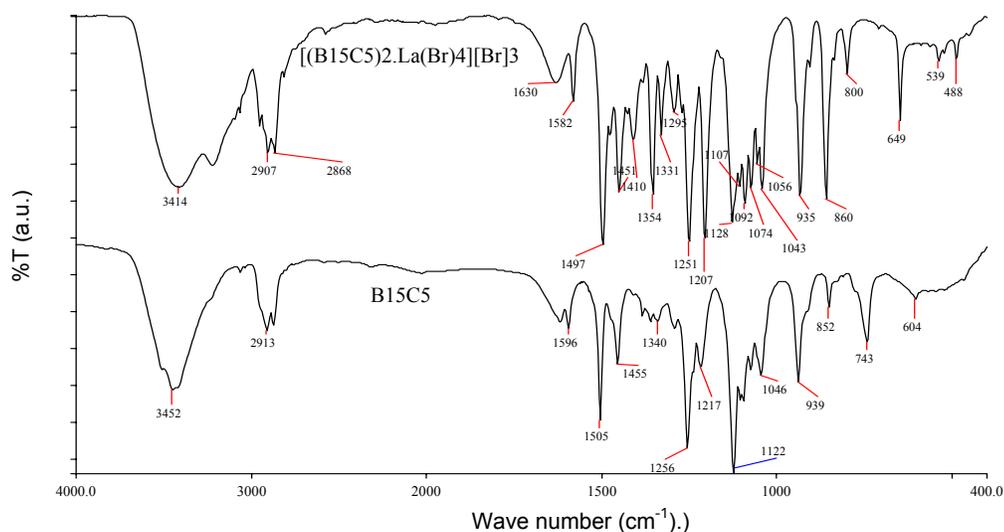


Fig. 3 IR spectrum of the B15C5 ligand and the $[\text{LaC}_{28}\text{H}_{36}\text{Br}_4\text{O}_{10}][3\text{Br}]$ complex

Table 3 IR band characteristic

Compound	$\nu\text{C-H}$ (Aromatic)	$\nu\text{C-H}$ (methylene)	$\nu\text{C=C}$	$\nu\text{C-O}$	$\nu\text{C-O-C}$	$\nu\text{C-Br}$
Ligand	3452b	2913m	1618s	1256s	1122s	-
Complex	3414-3225b	2906s	1630m	1251s	1128s	649s

number of chemically nonequivalent ether fragments (Fig. 4). The ^1H NMR spectra of the B15C5 ligand in CDCl_3 consist four peaks in the ether region at 3.767s (4H), 3.904s (4H), 4.130 (8H) and another peak due to the aromatic protons at 6.896 (4H) ppm downfield from Me_4Si . While, the spectra of $[\text{LaC}_{28}\text{H}_{36}\text{Br}_4\text{O}_{10}][3\text{Br}]$ complex showed four peaks at δ : 3.755s (4H), 3.901 (4H), 4.108 (8H) and 7.079s (2H) ppm. However, upon complexation, the ether groups (CH_2) are shifted to an upfield, whereas the signal of the phenyl ring is shifted to a downfield ($\Delta\delta$: -0.184 ppm) towards ligand and also with greater intensity. After

complexation, the phenyl ring only contains 2H because the others replaced by two Br^- anion.

Thermal gravimetry

The decomposition of the ligand and its complex was carried out in the range from begins at 30 to 700°C . The ligand has decomposed with two steps. In the first step the ligand lost 97.313% of its weight, which exhibited ether bond ring. The phenyl groups were lost at 324°C . Upon complexation, the complex decomposed in three steps. At the first the tribromide was decomposed, then at $205\text{-}700^\circ\text{C}$ two B15C5 ligand and La(III) ion have (Fig. 5).

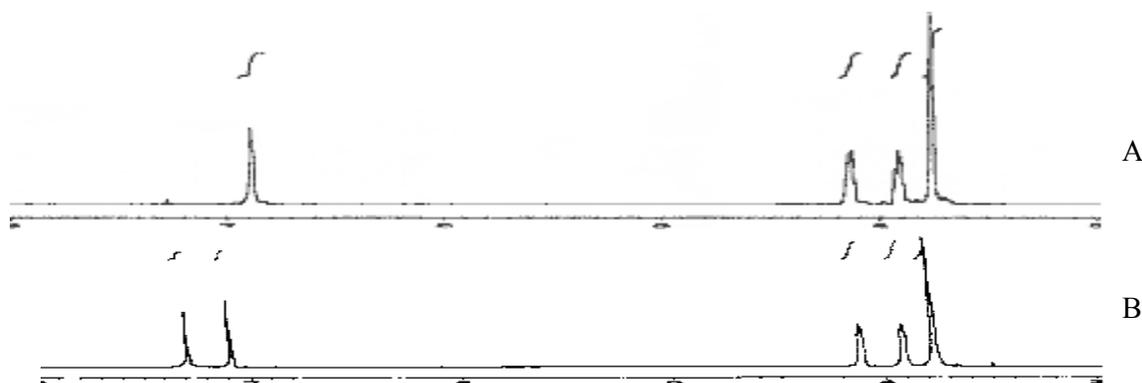


Fig. 4 A comparison between the 300 MHz ^1H NMR spectra of the B15C5 ligand (A) and the $[\text{LaC}_{28}\text{H}_{36}\text{Br}_4\text{O}_{10}][\text{Br}_3]$ complex (B). Both are dissolved in 1mL CDCl_3 solution. The peak at 7.279 ppm is referred to the solvents. Shifts are relative to Me_4Si .

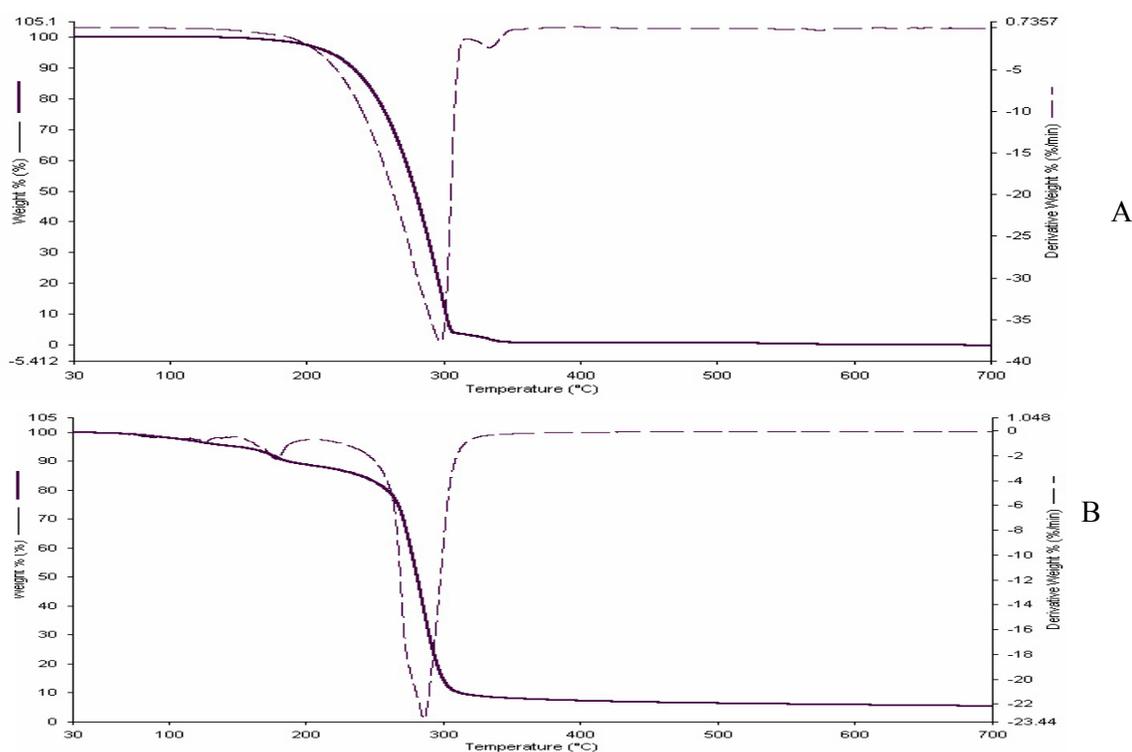


Fig. 5 The thermogram of the starting material (B15C5) (A) and the $[\text{LaC}_{28}\text{H}_{36}\text{Br}_4\text{O}_{10}][3\text{Br}]$ Complex (B). Scanning rate: $20.0^\circ\text{C}/\text{min}$, sample weight, B15C5: 10.571 g and complex: 10.596 g in nitrogen atmosphere.

CONCLUSION

In the presence of HBr, the $\text{La}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ complex with benzo-15-crown-5 ($\text{C}_{14}\text{H}_{18}\text{O}_5$) with bromination at the phenyl ring was formed. The lanthanum is coordinated to six oxygen atoms from the two crown rings forming a η^3 -sandwich like compound. The La(III) complex is balanced by a linear $[\text{Br}_3]^{3-}$ anion.

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