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Insights into the Complexation of Lanthanides with Dibenzyl-Diaza-18-Crown-6 Ethers

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Abstract: ***The investigation aimed to enhance the understanding of the coordination chemistry of lanthanide elements with aza-crown ethers. A group of lanthanide metal complexes with the general formula $[Ln(SCN)_3(C_{26}H_{38}N_2O_4)]$ (Ln^{3+}= La^{3+}, Nd^{3+}, Eu^{3+}) and $[Ln(NO_3)_5.H_2O(C_{26}H_{38}N_2O_4)]$ (Ln^{3+}= La^{3+}, Nd^{3+}, Gd^{3+}) has been synthesized and their structures in solution were determined using variable-temperature ^1H NMR spectroscopy. The interactions between the donor atoms and the central atom were clearly reflected in the chemical shifts of protons on the crown moiety. Notably, the chemical shifts of protons adjacent to oxygen atoms were less sensitive to temperature variations compared to those of protons adjacent to nitrogen atoms. Additionally, the chemical shifts were found to depend on the type of anion and the ionic radius of the guest molecule. The ^1H NMR analysis provided a compelling explanation for the selectivity of this type of ligands toward lanthanum compared to other lanthanide elements. These findings confirmed that La^{3+} behaves distinctly in its complexes with dibenzo-diaza-18-crown-6 (DD18C6) compared to other lanthanide elements of similar composition.***

Keywords: lanthanides, crown ethers, host-guest, complexation, coordination

1. Introduction

The strong interaction between metal ions and cyclic polyether complexing agents often enables the formation of crystalline salts that incorporate the complexed cation as an integral part of the crystal structure. Several crystal structures of these complexes have been analyzed, providing valuable insights into the cationic complex, its interaction with the anion, and the solvent used during crystallization. Designing ligands that create stable lanthanide (III) complexes not only facilitates further exploration of the coordination properties of lanthanide metal ions but also enables chemists to utilize the unique properties of these complexes.

Mixed donor atom (N,O) crown ethers, known as aza-crown ethers, have attracted significant interest from researchers [1-6]. These compounds offer a new perspective on cation and anion complexation chemistry due to their combination of oxygen and nitrogen donor atoms [7]. Consequently, they can coordinate with a broader range of cations compared to purely oxygen-containing or nitrogen-containing crowns, making them the subject of extensive studies [4,7].

Over the past decade, the field of synthetic saturated oxa-aza macrocyclic compounds has expanded significantly [8-10]. Mixed oxa-aza macrocyclic receptors have garnered considerable interest due to their ability to coordinate both cations and anions, particularly in their polyprotonated forms. A critical focus of this research is the coordination of crown ether ligands, especially six-membered ring crown ethers, with metal ions [11-15]. Consequently, numerous derivatives have been developed for various successful applications. Their high selectivity for complexation makes them valuable ligands for studying the coordination properties of lanthanide metal ions. Stable complexes with these ions have been reported, laying the groundwork for further exploration of their coordination chemistry. Understanding how the structure and dynamics of ligand frameworks influence the stability and other physicochemical properties of lanthanide metal ions is essential, particularly through the synthesis of macrocyclic complexes using identical ligand frameworks [16].

Previous research indicates that the selectivity of these ligands is significantly affected by several factors, such as cavity size, macrocycle rigidity, the number and properties of donor atoms, and the nature of the counter-anion [17,18]. Notably, cavity sizes of 15 and 18 members, with 5 or 6 donor atoms, have been found to be particularly suitable for lanthanide ions [19,20]. As a result, 18C6 and its derivatives were synthesized along with their complexes with lanthanide metal ions, and their structures were characterized using techniques such as elemental analysis, X-ray crystallography, and IR spectrometry. Additionally, their thermodynamic and thermal properties were investigated [21-23]. Significant advances in understanding the thermodynamic and kinetic properties of several metal ions-crown ether complexes since the early discovery of these complexing agents were reported.

Despite numerous reported crown ether complexes, there is limited information about their geometric structure in solution. X-ray crystallographic studies have shown that the ether oxygens arrange themselves in a planar, symmetrical configuration around the complexed cation. Consequently, research has focused on investigating the coordination number and its potential variations across the lanthanide series [. Additionally, NMR and electron spectroscopic studies have provided evidence of covalent bonding in some organometallic complexes involving heavier lanthanides. Most trivalent lanthanide ions are paramagnetic; causing significant chemical shifts in the ^1H NMR signals of protons near the metal center. This broadening of resonances in organic molecules interacting with paramagnetic complexes has resulted in the widespread use of paramagnetic lanthanide-containing species as NMR shift reagents [24-26].

In our previous studies, we reported on the complexation of dibenzo-diaza-crown ether (DD18C6) with lanthanide metal ions. A 1:1:3 complexes [DD18C6/Ln/$(SCN)_3$] (La, Nd, Eu, Dy) [27-29], and 1:1:5 [DD18C6/Ln/$(NO_3)_3(NO_3)_2$] (La, Nd, Gd) [30], with the total coordination number for the central metal ion being equal to 9 and 11 for both types of complexes have been reported, respectively. The solid-state data indicated that the Ln^{3+} (La, Nd, Eu) ion in the thiocyanate complexes was located in the geometrical center of the crown ether molecule and was monohedrally coordinated to four O atoms and two N atoms of the macrocycle, along with three thiocyanate ligands. In the nitrate complexes, no direct interaction between the crown ether and the guest lanthanide nitrates was observed. However, the unique selectivity of these ligands toward La^{3+} had opened avenue for further investigations on the stoichiometric behavior of these ligands as well as lanthanide elements [20].

This study aims to explore the temperature-dependent coordination behavior of DD18C6 with various lanthanide salts in solution and to clarify the distinct selectivity exhibited by La^{3+} using NMR spectroscopy. Understanding how DD18C6 selectively binds lanthanides under varying conditions provides insights valuable for designing tailored ligands in analytical, medical, and separation sciences.

2. Experimental

Chemicals and Reagents

The ligand, N,N'-dibenzyl-4,13-diaza-18-crown-6 (DD18C6) (**Figure 1**) was obtained from Aldrich. Lanthanide nitrates ($La(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, and $Dy(NO_3)_3 \cdot 5H_2O$) and potassium thiocyanate were purchased from Alfa. Hexadeuterated dimethyl sulfoxide (DMSO-d_6) was used as NMR solvent.

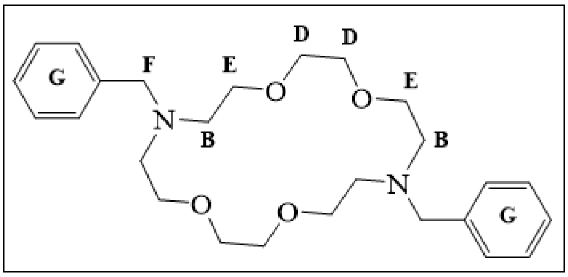

Figure 1: N, N'-dibenzyl-4,13-diaza-18-crown-6 (DD18C6)

Instrumentations

Infrared (IR) spectra were recorded with a Perkin Elmer System 200 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were conducted with a Perkin Elmer TGA-7 series thermal analyzer under a nitrogen atmosphere. Additionally, HNMR measurements were performed using a Bruker 300 MHz AC-P superconducting NMR spectrometer.

Synthesis of the complexes.

All the targeted lanthanide-DD18C6 complexes were prepared as reported previously [27-30]. Seven complexes (i.e. $La(SCN)_3$DD18C6 (C1), $Nd(SCN)_3$DD18C6 (C2), $Eu(SCN)_3$DD18C6 (C3), $Dy(SCN)_3$DD18C6 (C4), $[La(NO_3)_5.H_2O]$DD18C6 (C5), $[Nd(NO_3)_5.H_2O]$DD18C6 (C6) and $[Gd(NO_3)_5.H_2O]$DD18C6 (C7) complex were synthesized and characterized.

3. Results and Discussion

The isolation of lanthanide complexes featuring uncharged, oxygen-containing ligands like crown ethers has been documented [31,32]. However, there is limited information regarding lanthanide complexes with thiocyanates and nitrates that incorporate mixed donor atom ligands. In this study several crystalline complexes of DD18C6 with lanthanide elements with the general formula $[Ln(SCN)_3(C_{26}H_{38}N_2O_4)]$ (Ln= La^{3+}, Nd^{3+}, Eu^{3+}) and $[Ln(NO_3)_5.H_2O.(C_{26}H_{38}N_2O_4)]$ has been synthesized, resulting in shiny, colorful crystals of the studied species (**Table 1**). Complexes formed with lanthanide thiocyanate developed more rapidly and yielded better results than those made with lanthanide nitrate, suggesting that thiocyanate is a more favorable counterion for these complexes. This preference for thiocyanate over nitrate may be due to the greater flexibility of the thiocyanate anion, which allows for the formation of more linear-chain compounds that can easily accommodate the metal ion and fit into the cavity of the crown ether. [31,33]

Table 1: Some of the characteristics of the DD18C6 complexes with lanthanide (III) elements.

Complex		Mass* (g/mol)	M.P. (°C)	Color	%Yield	Ref.
C1	$La(SCN)_3C_{26}H_{38}N_2O_4$	755.74	293	Colorless	18	27
C2	$Nd(SCN)_3C_{26}H_{38}N_2O_4$	761.07	332	Pale violet	10	29
C3	$Eu(SCN)_3C_{26}H_{38}N_2O_4$	768.79	304	Yellowish	13	29
C4	$Dy(SCN)_3C_{26}H_{38}N_2O_4$	779.33	324	Cream	10	34
C5	$[La(NO_3)_5.H_2O]C_{26}H_{38}N_2O_4$	909.54	150	Colorless	12	34
C6	$[NdNO_3)_5.H_2O]C_{26}H_{38}N_2O_4$	914.88	148	Pale violet	9	30
C7	$[Gd(NO_3)_5.H_2O]C_{26}H_{38}N_2O_4$	927.89	167	Colorless	8	34

(*): Calculated mass

Characterization of the complexes.

IR-spectra of Ln-DD18C6 complexes

The infrared analysis of the studied complexes proved the bond formation between the metal ion and the ligand. The vibrational modes of the ligand experience substantial shifts and splitting upon complexation. Tables 2 and 3 present some of the IR bands that undergo significant changes upon the complexation of the ligand with lanthanide metal ions. The data confirm the complexation of $Ln(SCN)_3$ with the targeted crown ether. The strong absorption bands at approximately 949, 950, 951, and 950 cm^{-1} for the same complexes also indicate the presence of coordinated thiocyanate groups, while the absorption bands at 496, 497, 495, and 491 cm^{-1} correspond to out-of-plane bending involving the $(SCN)^-$ groups. [35,36] These findings regarding the lanthanide thiocyanate complexes are consistent with N-bonded NCS- anions. [36]

The IR-spectra of the nitrate showed some different peaks that can clearly be distinguished from that of the parent ligand. Shifting in the vibration of some functional groups on the ligand have been observed upon complexation with lanthanide ions. All nitrate groups absorption bands are characteristics of coordinated nitrate. Five vibration modes of nitrate groups were observed. The absorption bands on the IR spectra of the complexes (C5-C7) (i.e. 1737-1764, 1735-1739, 1312-1303, 1035-1033 cm^{-1} and 818-821 cm^{-1} regions) are assigned to the $\nu(NO_2)$ ($\nu_2 + \nu_5$ or ν_6), ν_l, ν_4, ν_2) and $\nu(NO)(\nu_3)$ vibrations [22] respectively of the chelating bidentate nitrate ion.

Table 2: The IR absorption of the Ln (III) thiocyanate complexes of DD18C6 [27-30].

Ligand	**Crown Ether (cm^{-1})**						
	ν(OH)	ν(CH)	δ(CH)	ν(C-O-C)	ν(C-N-C)	δ(CH)*	ν(C=C)
	3446	3085	1495/1375	1118-1025	1251-1212	749-702	1602
Complex	**Thiocyanate complexes (cm^{-1})**						
C1	3446	3026-2853	1477/1345	1104-1026	1255-1200	734-708	1635
C2	3446	3081-2853	1475/1440	1107-1027	1256-200	734-708	1635
C3	3446	3081-2853	1475/1342	1108-1028	1256-1200	735-708	1601
C4	3446	3025-2853	1475/1341	1109-1028	1257-1200	736-708	1636
Nitrate complexes (cm^{-1})							
C5	3524	2928-2885	1467/1385	1145-1070	1249-1203	748-704	1638
C6	3565	2928-2885	1458/1385	1162-1070	1250-1204	748-704	1636
C7	3570	2926-2884	1473/1385	1164-1070	1249-1204	748-704	1635

Table 3: Characteristic IR absorption of coordinate anions (thiocyanate, nitrate) [29,30].

Complex	Coordinated thiocyanate (cm^{-1})			Coordinated nitrate (cm^{-1})					Coordinated H_2O
	ν(CN)	ν(CS)	ν(NCS)	ν_1	$\nu_2 + \nu_5$ or ν_6	ν_2	ν_3	ν_4	
C1	2044	949	496	---	---	---	---	---	---
C2	2050	950	497	---	---	---	---	---	---
C3	2048	951	495	---	---	---	---	---	---
C4	2062	950	491	---	---	---	---	---	---
C5	---	---	---	1764	1735	1033	1303	820	3250
C6	---	---	---	1737	1737	1034	1305	821	3238
C7	---	---	---	1739	1739	1035	1312	818	3241

NMR spectra of the DD18C6-Ln complexes

Significant attention has been paid to the role of f-orbital electrons in the complexation of these elements with complexing agents. However, earlier spectroscopic studies of crown ether-lanthanide complexes do not address any effects associated with the complexation of f-orbital electrons. [37, 38]

Earlier studies conformed the formation of complexes between lanthanide metal ions and their corresponding crown ether ligands. However, no clear differences among the lanthanide elements that could influence their complexation and selectivity were reported. To gain further insight into the interactions between lanthanide ions and crown ethers, we investigate the magnetic and electronic behavior of lanthanide-crown ether complexes in solution. Nuclear magnetic resonance analysis of lanthanide thiocyanates or nitrates with DD18C6 provided strong evidence of complex formation and highlighted the differences in the chemical behavior of these elements when associated with crown ethers.

The NMR spectrum of the free ligand displays seven resonance signals labeled A, B, C, D, E, F, and G (**Figure 2a**), observed in DMSO-d6, with signal (A) at 2.5 ppm. The signal at 3.35 ppm (C) corresponds to water present in the deuterated solvent. The three sets of crown ring methylene (CH_2) protons (B, D, and E) are found at 0.19, 0.99, and 1.02 ppm, respectively, relative to the solvent peak. Among these, proton groups B and E appear as triplets. In contrast, group D is a singlet. Notably, there is a significant difference of 0.83 ppm in the chemical shift between the CH_2 protons (B and E) attached to the two different donor groups (O and N) on the ring. The N-CH_2 protons (B) are shifted considerably upfield at 0.19 ppm, whereas the O-CH_2 protons (E) are shifted downfield at 1.02 ppm. These findings are consistent with previously reported methylene resonances (CH_2) of cryptates, as noted by Ramirez *et al.*[39]. These differences in the X-CH_2 (X = O, N) groups on the macrocyclic ring reflected the influence of the type of donor atom present on the ring, as well as the ligand's flexibility in solution.

All CH_2 protons have been significantly affected, with some collapsing into single broad peaks with upfield or downfield shifts upon the complexation of these metal ions with the studied crown ether. Due to the similarities in the NMR spectra of the complexes, here we present only the lanthanum spectrum (**Figure 2b**). Upon complexation of the ligand with lanthanide salts, all six signals (excluding A) from the starting material were affected. The N-CH_2 protons (B) on the ligand ring are assigned chemical shifts of 2.60, 2.68, 2.69, and 2.70 ppm for the La, Nd, Eu, and Dy complexes, respectively. These protons are shifted upfield by 0.10, 0.18, 0.19, and 0.20 ppm for the 4 complexes, compared to a shift of 0.19 ppm for the starting material. The O-CH_2 protons (E) exhibit shifts of 1.05, 1.03, and 1.04 ppm for the La, Eu, and Dy complexes, respectively; however, this peak overlaps with peak D in the Nd complex. **Table 3** presents the differences in chemical shift. Clear differences in the interaction of N-CH_2 protons (B) were observed upon ligand complexation with $La(SCN)_3$. These shifts may be related to the length of the metal-N bond. Additionally, the signal that representing water (C) is also influenced by the presence of the lanthanide metal ion. This peak was noticeably shifted downfield for the La complex, while it remained unchanged for the other complexes when compared to the starting material.

The effect of the anion on complexation was also noted. Unlike the previous $Ln(SCN)_3$ complexes, a broad downfield resonance was observed for the $La(NO_3)_3$ complexe (Figure 3). The downfield N-CH_2 (B) protons were completely overlapped due to the presence of deuterated water. In the spectra of the complexes, the O-CH_2 protons (E) shifted downfield by 1.28 to 1.30 ppm. Additionally, the slightly larger downfield shifts in the N-CH_2 (out of ring plane) protons (F) indicated a significant change in the ligand's characteristics. This change is further supported by the chemical shift of the aromatic protons on the benzene ring (G). **Table 4** illustrates the changes that occurred to the ligand protons upon complexation with lanthanide nitrate salts. The only notable change in chemical shift (Δδ) was observed for the -CH_2 protons located outside the ring (F) of the ligand. This peak was found slightly depends on the ionic radius of the lanthanide metal ions, with values of Δδ = 1.92, 1.93, and 1.95 for La, Nd, and Gd complexes, respectively. Consequently, a smaller ionic radius corresponds to a larger chemical shift (Δδ). This phenomenon suggests that when the ionic radius of the metal ion closely fits the ligand cavity, the benzyl group more effectively covers the ring, potentially influencing the coordination of the metal ion (guest) to the donor atoms within the ligand cavity, as demonstrated by X-ray crystallography [27-30].

Table 3: The chemical shift (ppm) of the $La(SCN)_3$ complexes of DD18C6

Peak	Ligand	Resonance			
		La	Nd	Eu	Dy
B	2.6876 (0.19)	2.5982 (0.10)	2.6786 (0.18)	2.6888 (0.19)	2.6986(0.20)
C	3.3528 (0.85)	3.3973 (0.90)	3.3417 (0.84)	3.3626 (0.86)	3.3570(0.86)
D	3.4902 (0.99)	3.4746 (0.97)	3.4808 (0.98)	3.4944 (0.99)	3.4996(1.00)
E	3.5232 (1.02)	3.5493 (1.05)	----	3.5274 (1.03)	3.5383(1.04)
F	3.6266 (1.13)	3.7083 (1.21)	3.6221 (1.12)	3.6294 (1.13)	3.6439(1.14)
G	7.3104 (4.81)	7.2845 (4.78)	7.3032 (4.80)	7.3190 (4.82)	7.3228 (4.82)

The chemical shifts difference (Δδ in ppm) are given in parentheses. DMSO-d_6 at 25 °C.

Table 4: The chemical shift (ppm) of the $La(NO_3)_3$ complexes of DD18C6

Peak	Ligand	Resonance			
		La	Nd	Gd	Status
B	2.6876 (0.19)	--	--	--	--
C	3.3528 (0.85)	3.3793 (0.88)	3.3524 (0.83)	3.3748 (0.87)	downfield
D	3.4902 (0.99)	3.5971 (1.10)	3.5959 (1.10)	3.6166 (1.12)	downfield
E	3.5232 (1.02)	3.7799 (1.28)	3.7760 (1.28)	3.7965 (1.30)	downfield
F	3.6266 (1.13)	4.4232 (1.92)	4.4283 (1.93)	4.4494 (1.95)	downfield
G	7.3104 (4.81)	7.4804 (4.98)	7.4787 (4.98)	7.4895 (4.99)	downfield

The chemical shift (Δδ in ppm) are given in parentheses. Peak B is overlapped by peak C.

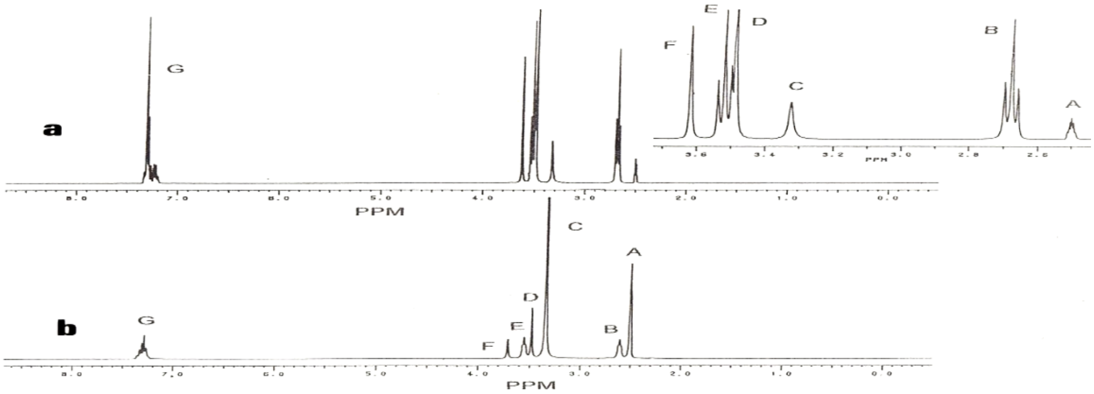

Figure 2: ^{1}HNMR spectra of (a) free ligand (DD18C6) and (b) its complexes with $La(SCN)_3$ in DMSO-d_6 solution. The peak at 2.5 ppm is referred to the solvent.

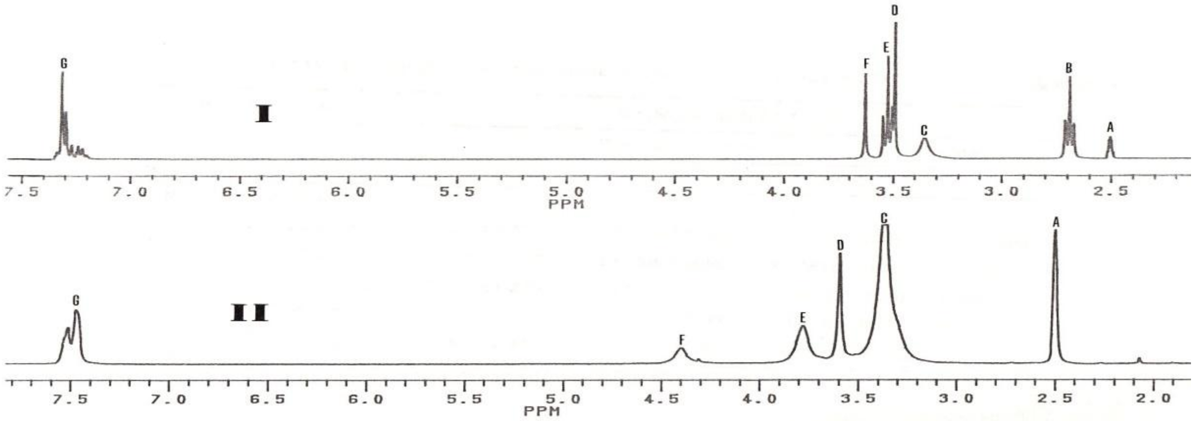

Figure 3: ^{1}HNMR spectra of DD18C6 and its complexes with $La(NO_3)_3$ in DMSO-d_6 solution. The peak at 2.5 ppm is referred to the solvent.

Effect of changes in temperature

Analysis of the dependence of chemical shifts on temperature was conducted by changing the sample temperature. This step allowed us to observe and measure changes in the rate of certain dynamic processes that affect the ^{1}HNMR spectra of the complexes. Data show that as the temperature increased, the methylene (CH_2) proton resonances of the free ligand became sharper, shifted, and displaced. **Figure 4a** displays the spectra at four different temperatures for the free ligand in DMSO-d6 solution. No significant changes in any of the CH_2 protons, either in or outside the plane of the crown ether ring, were observed. These findings reflect the high stability of the free ligand upon heating.

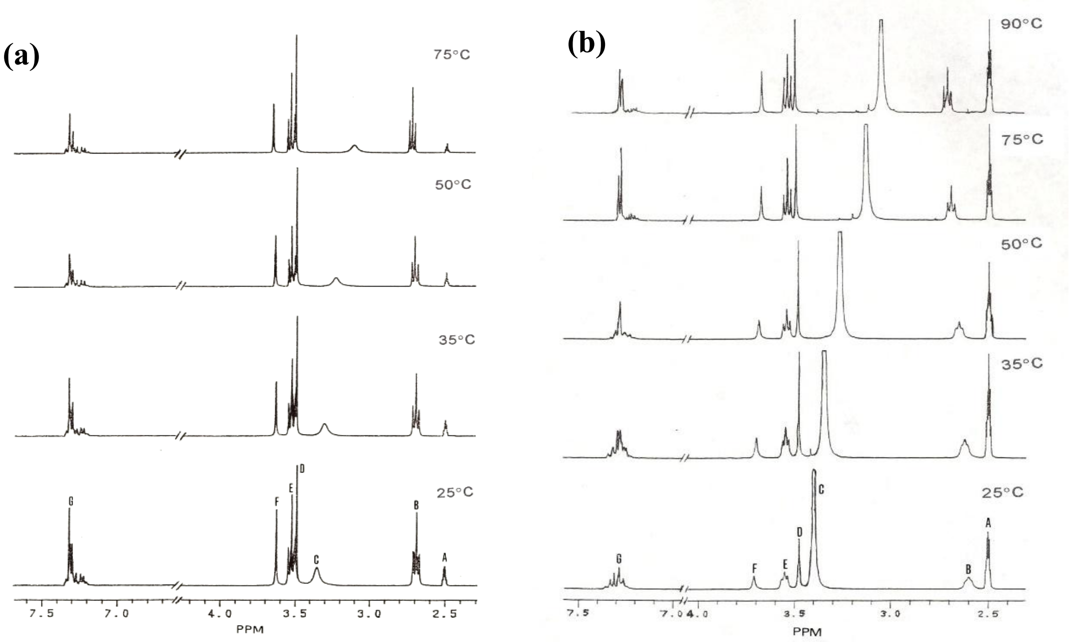

Figure 4: Temperature dependence of the ^{1}HNMR spectra for the DMSO-d_6 solution of (a) the free ligand DD18C6 and (b) $La(SCN)_3$ complex with DD18C6.

Temperature dependence of ^{1}HNMR spectra of the $Ln(SCN)_3$ complexes of DD18C6.

The study of the effect of temperature on the $Ln(SCN)_3$ complexes of DD18C6 demonstrated that complexation is temperature-dependent (**Figure 4b**). As the temperature increased, the N-CH_2 (B) protons on the ring became sharper and shifted downfield, resembling the behavior of the starting material. These changes in the chemical shift of the N-CH_2 protons may indicate that the N-Ln bond no longer exists in the solution when heated. In contrast, the O-CH_2 proton resonances (E) were only slightly affected, becoming sharper with rising temperatures. A similar trend was observed for the protons on the benzene ring (G). Additionally, a notable change occurred in the chemical shift of the deuterated water peak (C), which shifted upfield and decreased slightly in intensity, likely due to water evaporation.

A comparison of chemical shifts as a function of temperature among four thiocyanate complexes is presented in **Table5**. The table highlights a significant difference between lanthanum and other lanthanide elements. The N-CH_2 protons (B) exhibit a strong upfield shift in the La spectrum compared to both the other lanthanides and the starting material spectra. A similar trend is observed for the O-CH_2 proton (D). The shifts of these two peaks (B and D) are closely related to the ionic radius of the metal ion; specifically, a smaller ionic radius corresponds to a higher chemical shift. This relationship is also reflected in the chemical shifts of the CH protons (G) on the benzene ring. Additionally, a notable increase in temperature significantly affects the N-CH_2 (F) and O-CH_2 protons (E). The behavior of the lanthanum complex is markedly different from that of the other lanthanide complexes. Upon heating, the protons (E and F) are shifted upfield, whereas they are shifted downfield in the other lanthanide complexes. These differences in chemical shifts among the lanthanide elements indicate that the solution chemistry of the Lanthanum ion at low temperatures (25-50 °C) is distinctly different from that of other Ln^{3+} metal ions. Similar phenomena were observed in the earlier reported thermal analysis study [37].

Table 5: The effect of temperature on the chemical shift, ($\Delta\delta = \delta_{sample} - \delta_{reference}$) of the DD18C6 complexes with lanthanide metal ions.

Temp (°C)	Peak	Ligand	DD18C6.Ln(SCN)$_3$				DD18C6.[Ln(NO$_3$)$_5$.H$_2$O]		
			La	Nd	Eu	Dy	La	Nd	Gd
25	A	0	0	0	0	0	0	0	0
	B	0.1876	0.0982	0.1786	0.1888	0.1986	---	---	---
	C	0.8528	0.8973	0.8417	0.8626	0.8570	0.8793	0.8524	0.8748
	D	0.9902	0.9746	0.9808	0.9944	0.9996	1.0971	1.0959	1.1166
	E	1.0232	1.0493	---	1.0274	1.0383	1.2799	1.2760	1.2965
	F	1.1266	1.2083	1.1221	1.1294	1.1439	1.9232	1.9283	1.9494
	G	4.8104	4.7845	4.8032	4.8190	4.8228	4.9804	4.9787	4.9895
35	A	0	0	0	0	0	0	0	0
	B	0.1960	0.1205	0.1875	0.2047	0.2103	---	---	---
	C	0.8072	0.8472	0.7924	0.8111	0.8011	0.8310	0.8077	0.8244
	D	0.9950	0.9780	0.9887	1.0001	1.0037	1.0995	1.0974	1.1111
	E	1.0267	1.0475	1.0113	1.0288	1.0417	1.2875	1.2968	1.2957
	F	1.1332	1.1995	1.1286	1.1350	1.1520	1.9280	1.9283	1.9396
	G	4.8108	4.7898	4.7924	4.8106	4.8236	4.9805	4.9790	4.9780
50	A	0	0	0	0	0	0	0	0
	B	0.2100	0.1528	0.1991	0.2170	0.2256	0.8505	0.8559	0.8508
	C	0.7395	0.7695	0.7146	0.7391	0.7196	0.7600	0.7455	0.7624
	D	1.0023	0.9850	0.9922	1.0054	1.0092	1.1043	1.1024	1.1058
	E	1.0335	1.0445	1.0183	1.0475	1.0457	1.2983	1.2955	1.2979
	F	1.1445	1.1883	1.1384	1.1510	1.1635	1.9193	1.9284	1.9259
	G	4.8110	4.7978	4.8023	4.8168	4.8239	4.9805	4.970	4.9686
75	A	0	0	0	0	0	0	0	0
	B	0.2328	0.1960	0.2269	0.2385	0.2485	0.8692	0.8744	0.8591
	C	0.6215	0.6373	0.5905	0.6228	0.5826	0.6517	0.6529	0.6649
	D	1.0143	0.9975	1.0056	1.0170	1.0186	1.1120	1.1097	1.1030
	E	1.0478	1.0435	1.0314	1.0475	1.0533	1.3054	1.3060	1.2959
	F	1.1628	1.1783	1.1576	1.1699	1.1802	1.9122	1.9204	1.9041
	G	4.8124	4.7998	4.8080	4.8219	4.8235	4.9776	4.9760	4.9576
90	A	0	0	0	0	0	0	0	0
	B	---	0.2163	0.2383	0.2515	0.2614	0.8715	0.8740	0.8587
	C	---	0.5583	0.5147	0.5513	0.5026	0.6045	0.6108	0.6185
	D	---	1.0050	1.0120	1.0229	1.0250	1.160	1.1107	1.1038
	E	---	1.0445	1.0341	1.0529	1.0590	1.3073	1.3044	1.2944
	F	---	1.1780	1.1659	1.1795	1.1896	1.9033	1.9082	1.8916
	G	---	4.8052	4.8088	4.8220	4.8197	4.9743	4.9664	4.9614

A, B, C, D, E, F and G are referred to ***Figure 1***

Temperature dependence of ^{1}HNMR spectra of the Ln(NO$_3$)$_3$ complexes of DD18C6.

The impact of temperature on the lanthanide nitrate complexes is clearly illustrated in **Figure 5**. The spectra of the La(NO$_3$)$_3$ complex of DD18C6 at various temperatures were selected. At a low temperature of 25 °C, the spectrum exhibits five peaks, including the peak for deuterated water (C). All the methylene (CH_2) protons in the spectrum are fully resolved, with some appearing broadened (E and F) and others overlapping (B). As the temperature rises from 25 to 90 °C, slight changes in the chemical shifts of these peaks are observed. The most significantly affected peak is the deuterated water peak (C), which broadens and slightly disappears and shifts to the upfield region, as the case for the free ligand and the thiocyanate complexes. At approximately 50°C, the N-CH_2 protons (B) emerge as a broad, low-intensity singlet peak. When the temperature is further increased to 90 °C, this peak, along with peaks D, E, and F, sharpens and shifts closer together, moving further away from the reference peak (2.5 ppm). Notably, the N-CH_2 (B) and O-CH_2 (E) peaks appear as triplets. No changes are observed in the CH protons (D) on the benzene ring.

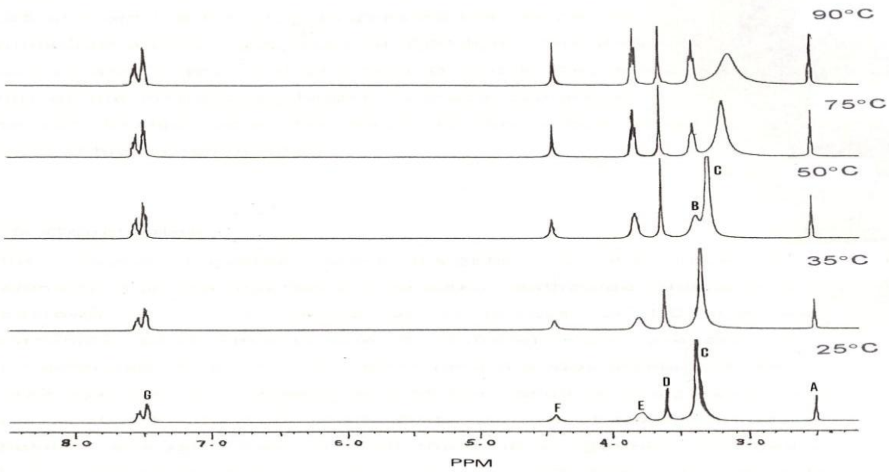

Figure 5: Temperature dependence of the ^{1}HNMR spectra for the DMSO-d_6 solution of $La(NO_3)_3$ complex with DD18C6

In comparing the studied complexes, it was observed that they exhibited slightly different behaviors in solution. Notably, the Gd-complex displayed unique characteristics. **Table 5** illustrates the impact of increasing temperature on the three lanthanide nitrate complexes of DD18C6. This difference is a clear evidence in the shifts of peaks D and F. The closer shift of the methylene protons in these complexes suggests that the coordinated molecules lack metal at higher temperatures.

4. Conclusion

The present work provided some insights into the coordination geometry and the interaction between lanthanide elements and azacrown ethers. In attempt to understand the stoichiometry of the complexes formed between DD18C6 and lanthanide metal ions ($Ln(SCN)_3/Ln(NO_3)_3$). The composition of the resulted complexes were investigated. This study deepens our understanding of how lanthanide ions interact with dibenzyl-diaza-18-crown-6 ethers, particularly in solution. Through NMR analysis, we observed that La^{3+} exhibits distinct complexation behavior compared to other lanthanides, likely due to its ionic radius and interaction with donor atoms. The study highlights how temperature and anion type influence complex stability and shifts, pointing to potential applications in designing selective lanthanide-binding systems.

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