

## Alkaline earth metal complexes of 17-membered oxa-azamacrocycles derived from $\alpha$ -diketones and 1,13-diamino-4,7,10-trioxatridecane

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**Abstract :** 1 + 1 Cyclocondensation of 1,13-diamino-4,7,10-trioxatridecane with  $\alpha$ -diketones such as 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione and 3,4-hexanedione in the presence of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  ions as templates yields a series of complexes of the type  $[MLX]X$  (where  $M = Mg^{II}$ ,  $X = Cl^-$ ;  $M = Ca^{II}$ ,  $Sr^{II}$  and  $Ba^{II}$ ,  $X = NCS^-$ ;  $L = N_2O_3$  type macrocycle having 17-membered ring). The resulting complexes have been characterized by elemental analyses, conductance measurements and IR,  $^1H$  NMR and FAB mass spectral studies.

**Keywords :** Macrocyclic complexes, alkaline earth metals, IR spectra,  $^1H$  NMR spectra, FAB mass spectra.

### Introduction

Application of oxa-azamacrocycles as sensors for cations, anions and molecular scaffolds for materials and biological models<sup>1-8</sup> and the interest toward molecular recognition and activation of anionic or neutral substrates<sup>9-13</sup> have prompted us to investigate the chemistry of oxa-azamacrocycles. Earlier, oxa-azamacrocyclic complexes of transition metals have been synthesized in our laboratories and their biological studies have been reported<sup>14-16</sup> and in the present paper synthesis of a series of alkaline earth metal complexes of oxa-azamacrocycles derived from 1,13-diamino-4,7,10-trioxatridecane and  $\alpha$ -diketones such as 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione or 3,4-hexanedione are described.

### Experimental

$MgCl_2 \cdot 6H_2O$  (Himedia),  $CaCl_2 \cdot 2H_2O$  (Merck),  $SrCl_2 \cdot 6H_2O$  (Merck) and  $BaCl_2 \cdot 2H_2O$  (Merck) used were of AR grade. 1,13-Diamino-4,7,10-trioxatridecane (Merck), 2,3-butanedione (Aldrich), 2,3-pentanedione (Fluka), 2,3-hexanedione (Aldrich), 3,4-hexanedione (Fluka) were used as such and *n*-butanol and methanol were distilled before use. Magnesium, calcium and strontium were determined volumetrically by EDTA using Eriochrome Black T as indicator and barium was determined gravimetrically as  $BaSO_4$ <sup>17</sup>. Nitrogen was determined by Kjeldahl's method. IR spectra were re-

corded as KBr pellets in the region 400-4000  $cm^{-1}$  on a Shimadzu-8400 spectrophotometer.  $^1H$  NMR spectra were recorded in  $DMSO-d_6$  on a JEOL AL-300 spectrometer at 300 MHz using TMS as reference. Conductances in DMSO were determined using Systronics Direct Reading Conductivity Meter-304. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 Mass spectrometer/Data system using Argon/Xenon (6 kV, 10 mA) as the FAB gas.

#### Synthesis of macrocyclic complexes :

##### (a) Synthesis of $Mg^{II}$ complexes of 17-membered $N_2O_3$ macrocycles :

To a butanolic solution of  $MgCl_2 \cdot 6H_2O$  (965 mg, 4.74 mmol in 10 ml *n*-butanol), a butanolic solution of 2,3-hexanedione (541 mg, 4.74 mmol in 10 ml *n*-butanol) was added. Then a butanolic solution of 1,13-diamino-4,7,10-trioxatridecane (1.05 g, 4.74 mmol in 10 ml *n*-butanol) was added to this under continuous stirring. The contents were stirred for 6 h and the solid obtained was filtered, washed with *n*-butanol and dried *in vacuo*.  $Mg^{II}$  complex of 17-membered diazatrioxa macrocycle was isolated. Similar method was adopted for the synthesis of  $Mg^{II}$  complexes of macrocycles derived from 2,3-butanedione, 2,3-pentanedione or 3,4-hexanedione and 1,13-diamino-4,7,10-trioxatridecane.

**(b) Synthesis of  $\text{Ca}^{\text{II}}$  complexes of 17-membered  $\text{N}_2\text{O}_3$  macrocycles :**

To a butanolic solution of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (896 mg, 6.09 mmol in 15 ml *n*-butanol), a butanolic solution of 2,3-hexanedione (695 mg, 6.09 mmol in 10 ml *n*-butanol) was added. To this reaction mixture, a butanolic solution of 1,13-diamino-4,7,10-trioxatridecane (1.34 g, 6.09 mmol in 10 ml *n*-butanol) was added under continuous stirring. As no solid appeared, a methanolic solution of potassium thiocyanate (592 mg, 6.09 mmol in 10 ml methanol) was added. The contents were stirred for 8 h and the temperature was maintained at 70 °C throughout the course of the reaction. The solid obtained was filtered, washed with *n*-butanol and dried under *vacuo*. Similar method was adopted for the synthesis of  $\text{Ca}^{\text{II}}$  complexes of macrocycles derived from 2,3-butanedione, 2,3-pentanedione or 3,4-hexanedione and 1,13-diamino-4,7,10-trioxatridecane.

**(c) Synthesis of  $\text{Sr}^{\text{II}}$  complexes of 17-membered  $\text{N}_2\text{O}_3$  macrocycles :**

$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  (966 mg, 3.62 mmol) was dissolved in minimum amount of water and 10 ml *n*-butanol. The butanolic solution of 2,3-hexanedione (413 mg, 3.62 mmol in 10 ml *n*-butanol) was added. Then a butanolic solution of 1,13-diamino-4,7,10-trioxatridecane (798 mg, 3.62 mmol in 15 ml *n*-butanol) was added dropwise under continuous stirring. As no solid appeared, a methanolic solution of potassium thiocyanate (352 mg, 3.62 mmol in 15 ml methanol) was added under continuous stirring. The stirring was continued for 10 h. The solid obtained was filtered, washed with *n*-butanol and dried *in vacuo*. Similarly, the reactions of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  with 1,13-diamino-4,7,10-trioxatridecane and 2,3-butanedione, 2,3-pentanedione or 3,4-hexanedione were carried out and the  $\text{Sr}^{\text{II}}$  complexes of 17-membered diazatrioxa macrocycle were isolated.

**(d) Synthesis of  $\text{Ba}^{\text{II}}$  complexes of 17-membered  $\text{N}_2\text{O}_3$  macrocycles :**

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (987 mg, 4.04 mmol) was dissolved in ethanol-water (1 : 1) and an ethanolic solution of 2,3-hexanedione (461 mg, 4.04 mmol) was added. Then an ethanolic solution of 1,13-diamino-4,7,10-trioxatridecane (890 mg, 4.04 mmol in 10 ml ethanol) was added dropwise under continuous stirring. As no solid appeared, a methanolic solution of potassium thiocyanate (392 mg

4.04 mmol in 10 ml methanol) was added. After 15 min a precipitate appeared. Stirring was continued for 10 h. The solid obtained was filtered, washed with ethanol and dried *in vacuo*. Similar method was adopted for the synthesis of  $\text{Ba}^{\text{II}}$  complexes of macrocycles derived from 2,3-butanedione, 2,3-pentanedione or 3,4-hexanedione and 1,13-diamino-4,7,10-trioxatridecane.

**Results and discussion**

The reactions of metal chlorides with 1,13-diamino-4,7,10-trioxatridecane and different  $\alpha$ -diketones such as 2,3-butanedione, 2,3-pentanedione, 2,3-hexanedione and 3,4-hexanedione in 1 : 1 : 1 molar ratios resulted in the formation of metal complexes of 17-membered  $\text{N}_2\text{O}_3$  macrocycles (Fig. 1). The resulting complexes were obtained as brown or white solids. On heating they do not melt but decompose. These are insoluble in chloroform, carbon tetrachloride and ether but soluble in DMSO. The

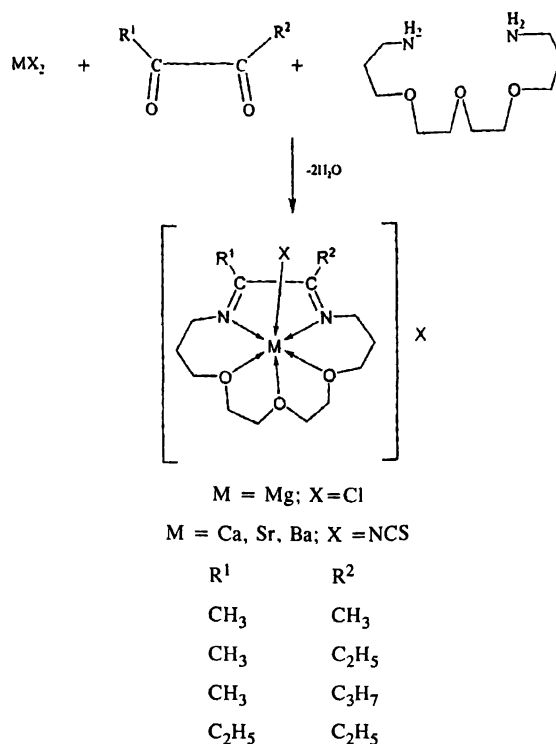


Fig. 1. Synthesis of macrocyclic complexes.

analyses and characteristics of the complexes are recorded in Table 1. The molar conductances of the complexes indicate their 1 : 1 electrolytic nature<sup>18</sup>.

**Table 1.** Analyses and characteristics of the macrocyclic complexes

Complex	Colour and decomp. temp. (°C)	Yield (%)	Analyses (%) :		Molar cond. (Ω <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			Found/(Calcd.)		
			M	N	
[Mg{(Me) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }Cl]Cl	White (210)	31	6.54 (6.65)	7.51 (7.65)	69
[Mg{(Me)(Et)[17]dieneN <sub>2</sub> O <sub>3</sub> }Cl]Cl	White (168)	29	6.23 (6.40)	7.24 (7.36)	71
[Mg{(Me)(Pr)[17]dieneN <sub>2</sub> O <sub>3</sub> }Cl]Cl	White (189)	29	6.15 (6.17)	7.06 (7.11)	73
[Mg{(Et) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }Cl]Cl	White (204)	33	6.09 (6.17)	7.10 (7.11)	79
[Ca{(Me) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (209)	24	9.24 (9.38)	6.58 (6.57)	58
[Ca{(Me)(Et)[17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (217)	18	9.07 (9.10)	6.27 (6.36)	64
[Ca{(Me)(Pr)[17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (180)	30	8.74 (8.82)	6.12 (6.16)	68
[Ca{(Et) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (173)	26	8.79 (8.82)	6.09 (6.16)	62
[Sr{(Me) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	Brown (201)	35	18.40 (18.48)	5.80 (5.91)	59
[Sr{(Me)(Et)[17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	Light brown (187)	21	18.24 (18.30)	5.79 (5.84)	55
[Sr{(Me)(Pr)[17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (207)	31	17.68 (17.78)	5.63 (5.67)	71
[Sr{(Et) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (189)	34	17.39 (17.44)	5.59 (5.67)	67
[Ba{(Me) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	Brown (193)	27	26.19 (26.24)	5.29 (5.34)	63
[Ba{(Me)(Et)[17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (205)	24	25.42 (25.55)	5.16 (5.21)	75
[Ba{(Me)(Pr)[17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (168)	28	24.80 (24.88)	5.01 (5.07)	58
[Ba{(Et) <sub>2</sub> [17]dieneN <sub>2</sub> O <sub>3</sub> }NCS]NCS	White (185)	41	24.79 (24.88)	4.99 (5.07)	71

*Infrared spectra :*

The IR spectra of M<sup>II</sup> macrocyclic complexes do not exhibit any band corresponding to the free primary diamine (3200–3400 cm<sup>-1</sup>) or free keto group (~ 1700 cm<sup>-1</sup>) which suggest the complete condensation of the amino group with the keto group<sup>19,20</sup>. All the complexes show a medium intensity band in the region 1580–1640 cm<sup>-1</sup> which can be assigned to  $\nu(\text{C}=\text{N})$ <sup>21,22</sup>. All the complexes show bands in the region ~ 420–440 cm<sup>-1</sup> which may be assigned to  $\nu(\text{M}-\text{N})$  vibrations<sup>23</sup>. N-Bonded thiocyanate

stretching frequencies are observed at 2040–2070 cm<sup>-1</sup>. The lowering of these frequencies in Ca<sup>II</sup>, Sr<sup>II</sup> and Ba<sup>II</sup> complexes as compared to that reported for free thiocyanate (2100 cm<sup>-1</sup>) supports the coordination of the thiocyanate group to the metal atom through nitrogen atom. Fenton and Cook<sup>24</sup> reported N-bonded thiocyanate stretching frequencies at 2063, 2073 and 2081 cm<sup>-1</sup> in Ca<sup>II</sup>, Sr<sup>II</sup> and Ba<sup>II</sup> complexes respectively, of the macrocycle 3,15,21-triaza-6,9,12-trioxabicyclo[15.3.1]heneicos-1[21],2,5,17,19-pentene.

*<sup>1</sup>H NMR spectra :*

<sup>1</sup>H NMR spectra of four complexes [Mg{(CH<sub>3</sub>)<sup>d</sup>-(CH<sub>2</sub><sup>c</sup>CH<sub>2</sub><sup>b</sup>CH<sub>3</sub><sup>a</sup>)[17]dieneN<sub>2</sub>O<sub>3</sub>}Cl]Cl (I), [Ca{(CH<sub>3</sub><sup>a</sup>-CH<sub>2</sub><sup>c</sup>)<sub>2</sub>[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS (II), [Sr{(CH<sub>3</sub>)<sup>d</sup>-(CH<sub>2</sub><sup>c</sup>CH<sub>2</sub><sup>b</sup>CH<sub>3</sub><sup>a</sup>)[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS (III) and [Ba{(CH<sub>3</sub><sup>a</sup>CH<sub>2</sub><sup>c</sup>)<sub>2</sub>[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS (IV) were recorded in DMSO-*d*<sub>6</sub>. A peak at δ 2.49 ppm is observed in the spectra of all the complexes due to the residual methyl protons of the solvent DMSO-*d*<sub>6</sub>. Free diamine shows a peak at δ 1.43 ppm due to -NH<sub>2</sub> protons which disappears in the spectra of macrocyclic complexes confirming the condensation of -NH<sub>2</sub> groups of the amine residue with the C=O groups of the ketone residue to give macrocycles having C=N linkages. In the spectra of macrocyclic complexes the -NCH<sub>2</sub> (α) and -OCH<sub>2</sub> protons merge together and a peak is observed in the region δ 2.76–2.78 ppm. The β-CH<sub>2</sub> protons of the amine residue appear in the region δ 1.78–1.98 ppm. In 1,2,8,9-tetraphenyl-3,7-diazaduohepta-2,7-diene-1,9-dione (KIM, Fig. 2) the α-CH<sub>2</sub> protons have been reported to appear

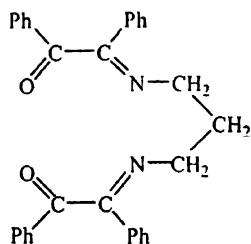


Fig. 2. KIM.

as a triplet at δ 3.63 ppm and β-CH<sub>2</sub> protons as a quintet at δ 2.11 ppm<sup>25</sup>. The free macrocycles have not been isolated during the present investigations but they are expected to exhibit the -NCH<sub>2</sub> (α) and β-CH<sub>2</sub> protons almost at the same positions as reported for KIM. As compared to KIM in all the macrocyclic complexes, the peaks of -NCH<sub>2</sub> (α) and β-CH<sub>2</sub> protons are observed at higher field. This high-field shift of these protons confirms the coordination of the nitrogen and oxygen atoms of the macrocycle to the metal atom. In free 2,3-hexanedione [CH<sub>3</sub><sup>d</sup>COCOCH<sub>2</sub><sup>c</sup>CH<sub>2</sub><sup>b</sup>CH<sub>3</sub><sup>a</sup>], the CH<sub>3</sub><sup>a</sup> protons exhibit a triplet at δ 1.05 ppm, CH<sub>2</sub><sup>b</sup> protons a multiplet at δ 1.12 ppm, CH<sub>2</sub><sup>c</sup> protons a triplet at δ 2.72 ppm and CH<sub>3</sub><sup>d</sup> protons a singlet at δ 2.35 ppm. In free 3,4-hexanedione [CH<sub>3</sub><sup>a</sup>CH<sub>2</sub><sup>c</sup>COCOCH<sub>2</sub><sup>c</sup>CH<sub>3</sub><sup>a</sup>], the CH<sub>3</sub><sup>a</sup> protons appear

as a triplet at δ 1.10 ppm and the CH<sub>2</sub><sup>c</sup> protons as a quartet at δ 2.77 ppm. In all the complexes, CH<sub>3</sub><sup>a</sup> protons of the ketone moiety give rise to a triplet at δ 0.84–0.87 ppm. In complexes I and III, the CH<sub>2</sub><sup>b</sup> protons of the propyl group appear as a multiplet at δ 1.21 and 1.24 ppm, the CH<sub>2</sub><sup>c</sup> protons as a triplet at δ 1.35 and 1.37 ppm and CH<sub>3</sub><sup>d</sup> protons as a singlet at δ 1.23 and 1.62 ppm respectively. In complexes II and IV, the CH<sub>2</sub><sup>c</sup> protons appear as a quartet at δ 1.30 and 1.24 ppm respectively. High field shifting of CH<sub>2</sub><sup>c</sup> and CH<sub>3</sub><sup>d</sup> protons in the complexes confirms the coordination of the nitrogen atoms of C=N groups of the macrocycles to the metal atoms. However, CH<sub>3</sub><sup>a</sup> and CH<sub>2</sub><sup>b</sup> protons are very slightly shifted as these are away from the C=N groups and are not affected much by coordination.

*FAB mass spectra :*

The FAB mass spectra of [Ca{(Et)<sub>2</sub>[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS, [Sr{(Me)<sub>2</sub>[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS, [Sr{(Et)<sub>2</sub>[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS, [Ba{(Me)(Et)[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS and [Ba{(Me)(Pr)[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS have been recorded using NBA matrix. Peaks at *m/z* 136, 137, 154, 289 and 307 are due to matrix. All the complexes show peaks corresponding to molecular ions [M]<sup>+</sup> and free macrocycles [L]<sup>+</sup>, which confirm the formation of the macrocyclic complexes. Peaks due to [M+H]<sup>+</sup> and [L+H]<sup>+</sup> have also been observed. In addition to the peaks due to the molecular ions and the macrocycles, the spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the macrocycles and their complexes. The fragmentation pattern for the complex [Sr{(Me)<sub>2</sub>[17]dieneN<sub>2</sub>O<sub>3</sub>}NCS]NCS is given in Fig. 3. The complex **a** exhibits molecular ion [M]<sup>+</sup> peak at *m/z* 474 (47.22%). Fragments **b** and **c** are formed due to the successive loss of two NCS groups from molecular ion **a** and appear at *m/z* 416 (16.66%) and *m/z* 358 (27.77%) respectively. There are two possible pathways for the fragmentation of the complex :

**Pathway [A] :** In this pathway, the metal ion remains attached with the macrocycle framework and step by step loss of CH<sub>3</sub> groups from **c** gives peaks at *m/z* 343 (16.66%) and 328 (13.88%) due to the species **d** and **e** respectively. Loss of Sr from the species **e** finally gives the species **h**, *m/z* 240 (25%).

**Pathway [B] :** In this pathway, the metal ion may be

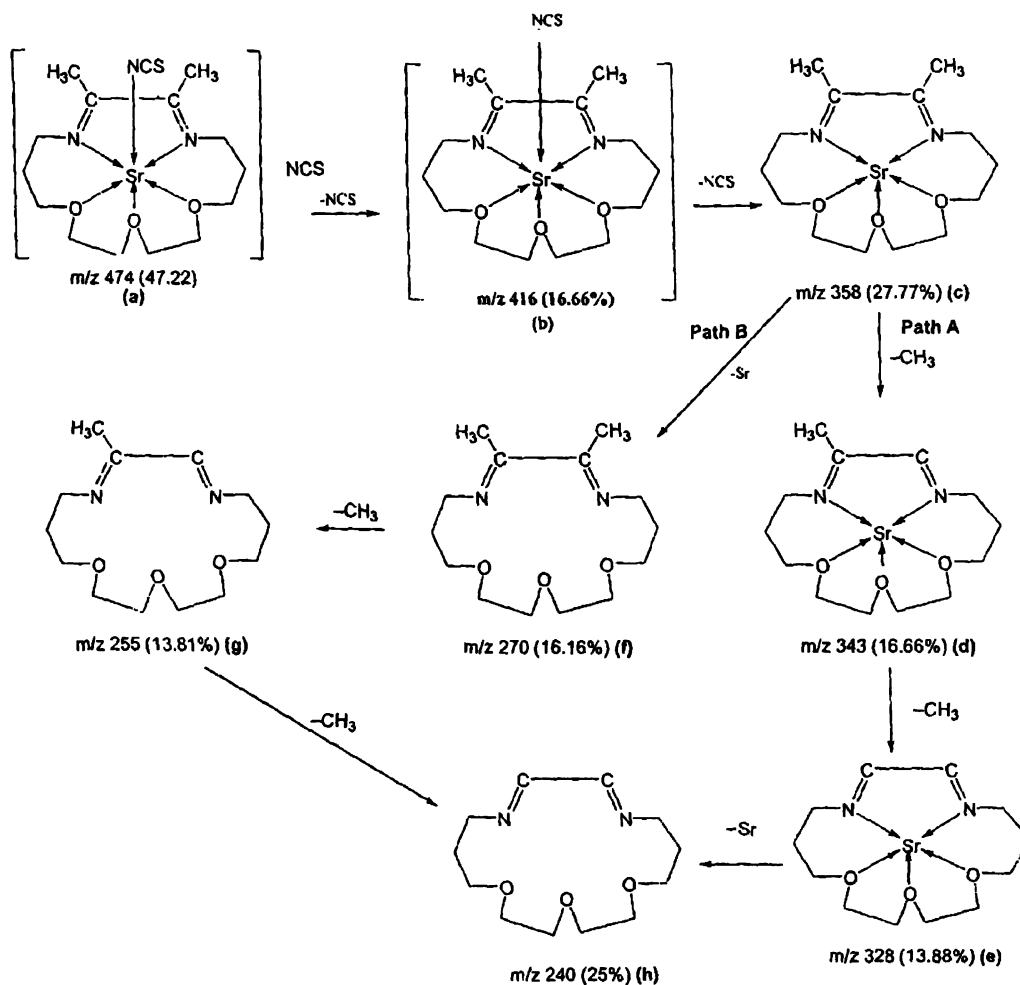


Fig. 3. Fragmentation pattern of  $[\text{Sr}\{(\text{Me})_2[17]\text{dieneN}_2\text{O}_3\}\text{NCS}]\text{NCS}$ .

lost from the macrocyclic complex in the beginning and a peak at  $m/z$  270 (16.16%) appears due to the free macrocycle f. Subsequent loss of  $\text{CH}_3$  group from the macrocycle gives peak at  $m/z$  255 (13.81%) and 240 (25%) due to the species g and h respectively. Thus the mass spectral studies strongly support the formation of macrocyclic complexes and their structures.

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