

# COMPARISON BETWEEN THERMAL ANALYSIS AND MASS SPECTROSCOPIC STUDIES OF URANYL OXINATES

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## Abstract

The 5,7-dichloro, 5,7-dibromo, 5,7-diiodo and 5,6-dinitro derivatives of oxine (ligands  $L_1$ – $L_4$ ) were used to prepare uranyl chelates ( $A_1$ – $A_4$ ). Thermal analysis (DTA) and mass spectroscopic studies were performed. The stoichiometries of the chelates were determined by elemental analysis, molecular weight determination applying an  $\alpha$ -spectroscopic liquid scintillation counter and mass spectral measurements. The uranyl:ligand ratios were found to be 1:1 for  $A_1$ , 1:3 for  $A_2$ , 1:2 (monohydrate) for  $A_3$ , and 1:2 for  $A_4$ . The correlation between the thermal analysis and mass spectra was examined. The activation energy required for each step of thermal degradation of the ligands and chelates was calculated. The natures of most of the molecular ions obtained in the mass spectra were also explained.

**Keywords:** complexes, MS, thermal analysis, uranyl oxinates

## Introduction

Complexation reactions between uranyl ion and various ligands containing hydroxy groups, e.g. oxines and other phenolic compounds, have been reported previously [1–15]. A number of physicochemical methods of analysis were used, such as thermal analysis [1–3], X-ray analysis [4] and different spectroscopic techniques [7–10]. The mode of chelation in these compounds has been discussed [1, 2]. Spectrophotometric determination of uranium in its ores on the basis of these studies has also been performed [7, 8].

In the present article, uranyl complexes of certain substituted oxines are studied and their mass spectra are correlated with their thermal analysis in an attempt to shed light on their structure. Different mass spectra techniques, e.g. electron ionization (EI) and fast bombardment (FAB), were applied [12–16].

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The FAB technique promotes the formation of more molecular ions than EI, which facilitates a clearer identification of these chelates in comparison with thermal analysis.

## Experimental

All chemicals used were of analytical grade (BDH). The ligands used for the preparation of chelates  $A_1$ – $A_4$  were 5,7-dichloro-, 5,7-dibromo-, 5,7-diiodo- and 5,7-dinitro-8-hydroxyquinoline (oxine) denoted  $L_1$ – $L_4$ , respectively. These oxine derivatives were prepared, purified and recrystallized from suitable solvents by Abd El-Gany [17]. The solid complexes  $A_1$ – $A_4$  were prepared by the addition of calculated masses of the ligands in a suitable solvent to aqueous solutions containing suitable amounts of uranyl nitrate (BDH), using a recommended procedure [18]. The chelates were crystallized and dried. Their elemental microanalysis were performed in Cairo University Microanalytical Center; the data are recorded in Table 1. The uranium contents of these chelates were determined by using a Beckmann liquid scintillation counter  $\alpha$ -spectrometer, using 0.0875 g, 0.0947 g, 0.1153 g and 0.0861 g of  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$ , respectively, in 25 ml nitric acid solution. These measurements were made in the FU Institute of Inorganic Chemistry at the University of Berlin (Germany). From the obtained concentrations of U ( $\text{mol L}^{-1}$ ), the molecular weights of these chelates were calculated (Table 1).

The FT-IR spectra of the chelates were also recorded from KBr discs on a Perkin-Elmer FT-IR 1650 instrument.

DTA of the ligands  $L_1$ – $L_4$  and chelates  $A_1$ – $A_4$  were performed at the Radiation Technology Centre, Nuclear Authority, Nasr City, Cairo, Egypt, using a Shimadzu 30 thermal analyzer at a heating rate of  $10^\circ\text{C min}^{-1}$  in an inert atmosphere of argon and xenon.

**Table 1** Elemental analysis and some characters of uranyl-oxine derivative complexes  $A_1$ – $A_4$

Compound	Colour	X	C	H	N	M.W.	U
$A_1$ , $\text{UO}_2\cdot L_1$	orange	14.66 (13.99)	32.4 (33.0)	1.5 (1.6)	4.2 (4.5)	484 (482)	49.2 (49.0)
$A_2$ , $\text{UO}_2\cdot 3L_2$	brown	20.70 (21.0)	28.3 (28.2)	1.31 (1.29)	3.66 (3.20)	1145 (1142)	20.78 (20.32)
$A_3$ , $\text{UO}_2\cdot L_3\cdot \text{H}_2\text{O}$	deep brown	23.31 (23.21)	18.86 (18.50)	0.92 (0.90)	2.58 (2.50)	1081 (1083)	22.1 (22.01)
$A_4$ , $\text{UO}_2\cdot 2L_4$	brown		42.77 (42.50)	1.98 (1.90)	16.63 (16.40)	505 (508)	47.13 (46.99)

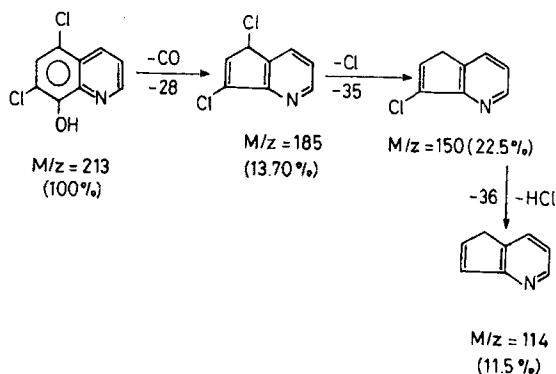
$L_1 = \text{C}_9\text{H}_5\text{Cl}_2\text{NO}$ , M.W.=214,  $L_2 = \text{C}_9\text{H}_5\text{Br}_2\text{NO}$ , M.W.=301,  $L_3 = \text{C}_9\text{H}_5\text{I}_2\text{NO}$ , M.W.=397,  
 $L_4 = \text{C}_9\text{H}_5\text{N}_3\text{O}_5$ , M.W.=235. X=Cl, Br, I.

The values in parenthesis are the found values.

The mass spectra of the ligands and their chelates were analysed by the EI technique at 80 eV, threshold output=0.8 V and peak detection=0.02 V, and by the FAB technique, spectrum (6–10) averaged, POS FAB, CH5DF, threshold output=0.1 V and peak detection=0.01 V.

## Results and discussion

DTA curves for the dichlorooxine  $L_1$  and its uranyl chelate  $A_1$  are presented in Fig. 1. The curve  $L_1$  exhibits a pronounced exothermic base shift at 50 to 125°C, which reflects the increase in heat capacity of the ligand  $L_1$  and its sensitivity to heating. It is followed by a sharp exothermic peak at 120°C, which may be related to a crystalline rearrangement. The curve shows another exothermic base shift starting at 150°C, which indicates another increase in heat capacity of the new crystalline shape of this ligand. The endothermic peak at 172°C indicates the melting of this compound (*m.p.* of  $L_1$  is 179°C) [17, 19, 20]. This requires an energy of activation  $E^*=2.72 \text{ kJ mol}^{-1}$ , and the order of the process is found to be 0.701 with standard deviation=0.224 and coefficient of variation 0.48% (applying the method recommended by Zayed *et al.* [21]). The curve finally shows an endothermic peak at 280°C, followed by a very steep endothermic base shift, which may be explained by the loss of excited parts of the ligand (e.g.  $\text{Cl}_2$ , HCl and/or CO) and a decrease in heat capacity of the remaining oxide. The energy required for this step is found to be  $4.45 \text{ kJ mol}^{-1}$  and its order is 1.0. The mass spectrum of the ligand  $L_1$  (Fig. 2) demonstrates a molecular ion of  $m/e=215$  of abundance 100%, which relates to the actual mass of the ligand  $\text{C}_9\text{H}_5\text{Cl}_2\text{NO}$  (M.W.=214). The scheme of decomposition of the ligand may be tentatively given [22] by (Scheme 1)



Scheme 1

Loss of the fragments CO, Cl and HCl explains the thermal behaviour of this ligand.

The DTA of chelate  $A_1$  reveals a small exothermic base shift at the beginning of heating. It starts at 60°C, reflecting the sensitivity of  $L_1$  to heating in the

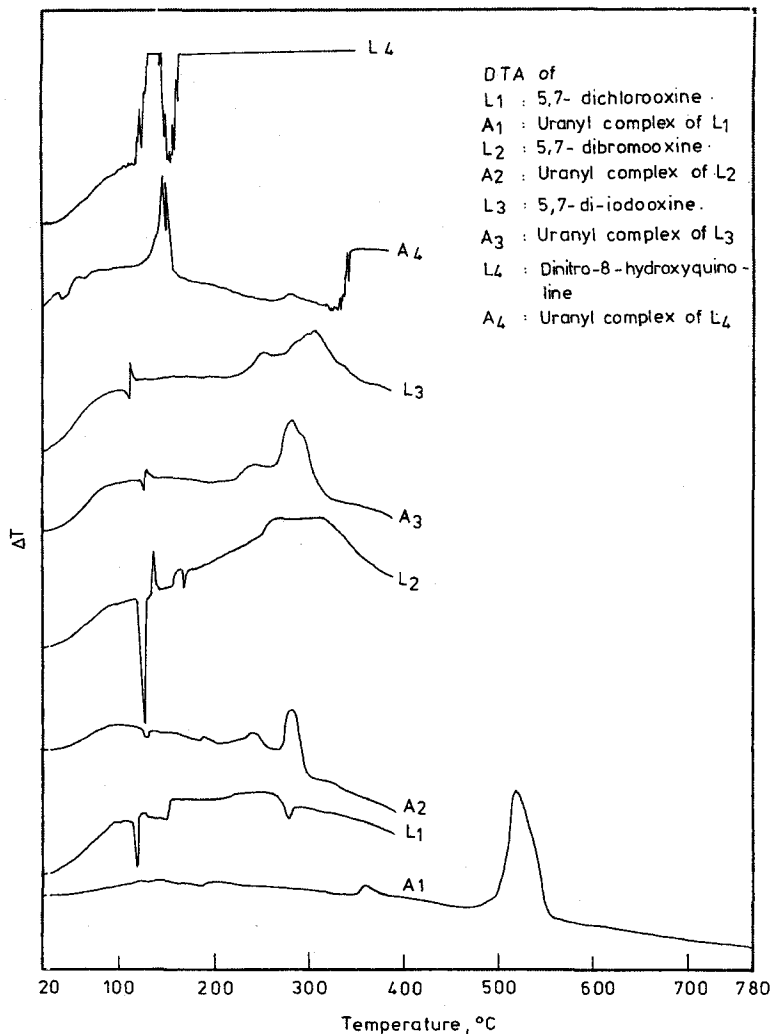
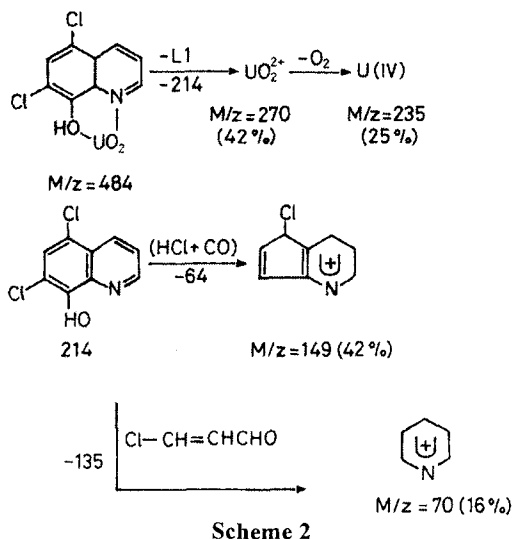


Fig. 1 DTA curves of some oxine ligands ( $L_1$ – $L_4$ ) and their uranyl complexes ( $A_1$ – $A_4$ )

chelate  $A_1$ . It also exhibits an endotherm at 180–184°C, which may be due to partial melting of this complex. The exotherm at 359°C may be related to chemical changes such as bond breaking. The broad exotherm at 500–548°C may be an indicator of the cleavage of some part of the chelate. The final steep broad endothermic base shift may be explained by the loss of excited parts (HCl, Cl<sub>2</sub> and CO) of the chelate, leaving a stable residue of the uranyl oxine complex with lower heat capacity.

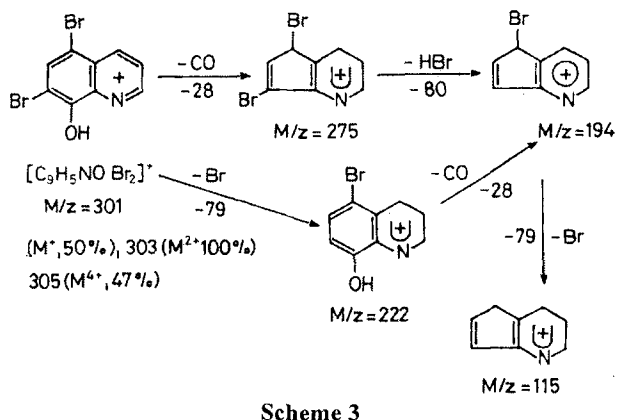
The energy required for these mass losses, as calculated from the DTA data, is found to be 5.04 kJ mol<sup>-1</sup>; the order is 1.50 and SD=0.888.

The mass spectrum by the FAB-POS technique of complex  $A_1$  dissolved in DMSO (dimethyl-sulphoxide) in xenon atmosphere is shown in Fig. 2. The scheme of decomposition of this chelate can be tentatively given [22] by Scheme 2.



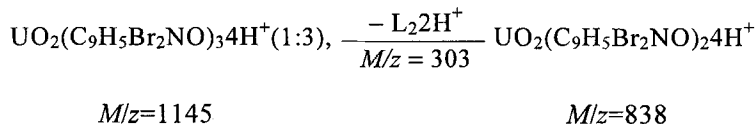
The DTA curves for the  $L_2$  are shown in Fig. 1 ( $L_2$ ). It displays an exothermic base shift at 40–110°C, related to the increase in heat capacity of  $L_2$ . This is followed by a sharp endothermic peak at 130°C, which may be related to thermal loss of Br or HBr. Next come a series of exo- and endothermic processes, which may be attributed to other fragmentations and physical or chemical changes. The activation energies and orders of these thermal changes are found to be 5.2, 1.57 and 1.69 kJ mol<sup>-1</sup>, with orders of 1.0, 1.0 and 0.667, respectively.

The mass spectrum of  $L_2$  is given in Fig. 3. The Scheme 3 representing the mass fragmentation revealed by the EI technique is



The DTA of chelate  $A_2$ , illustrated in Fig. 3, shows an exothermic base shift, as expected for this kind of chelate, at 30–70°C, followed by sharp endothermic peaks at 133 and 190°C, which may be attributed to partial melting of the complex or the loss of Br, HBr and/or CO. The broad exothermic peaks may be related to chemical changes in  $A_2$  after these losses. The steep endothermic base shift from 290 to 400°C may be explained by the low heat capacities of the final products of decomposition of the chelate. The activation energies required for these successive steps are found to be 2.87 and 2.73 kJ mol<sup>-1</sup>, with orders of 2.0 and 1.5, respectively.

The mass spectrum of  $A_2$  found by means of the EI technique and heating at 120°C is given in Fig. 3. The decomposition can be tentatively represented by



followed by fragmentation of  $L_2 2\text{H}^+$  ( $M^{2+}/z=303$ ) as previously explained.

Heating of chelate  $A_2$  at 400°C and use of the EI technique indicates that the mass of chelate  $A_2=1144$ , i.e.  $\text{UO}_2(\text{C}_9\text{H}_5\text{Br}_2\text{NO})_3 3\text{H}^+$ , which is confirmed by the EI technique at 120°C. The mass spectrum also demonstrates the loss of one

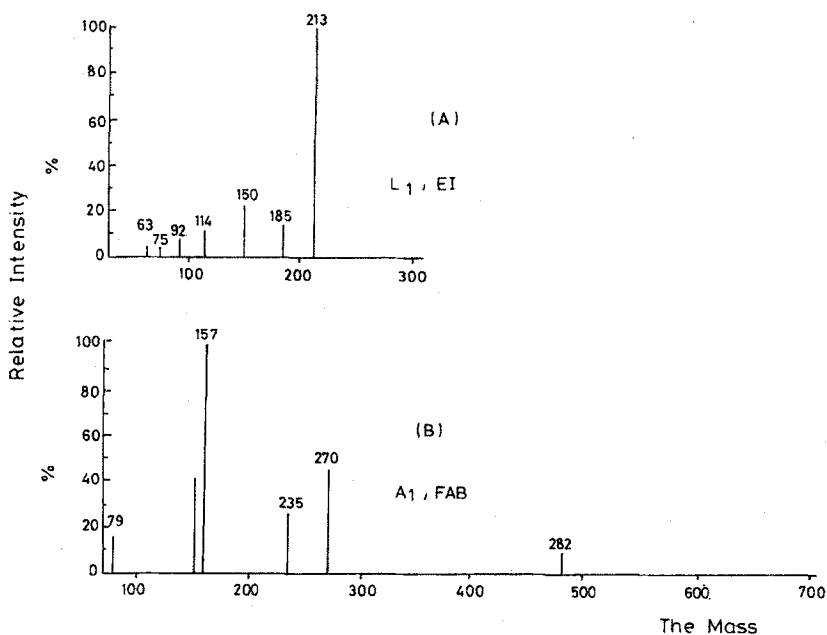


Fig. 2 Mass spectra obtained by both EI and FAB techniques for (A) 5,7-dichlorooxine,  $L_1$ ; (B) the uranyl-5,7-dichlorooxine obtained,  $A_1$

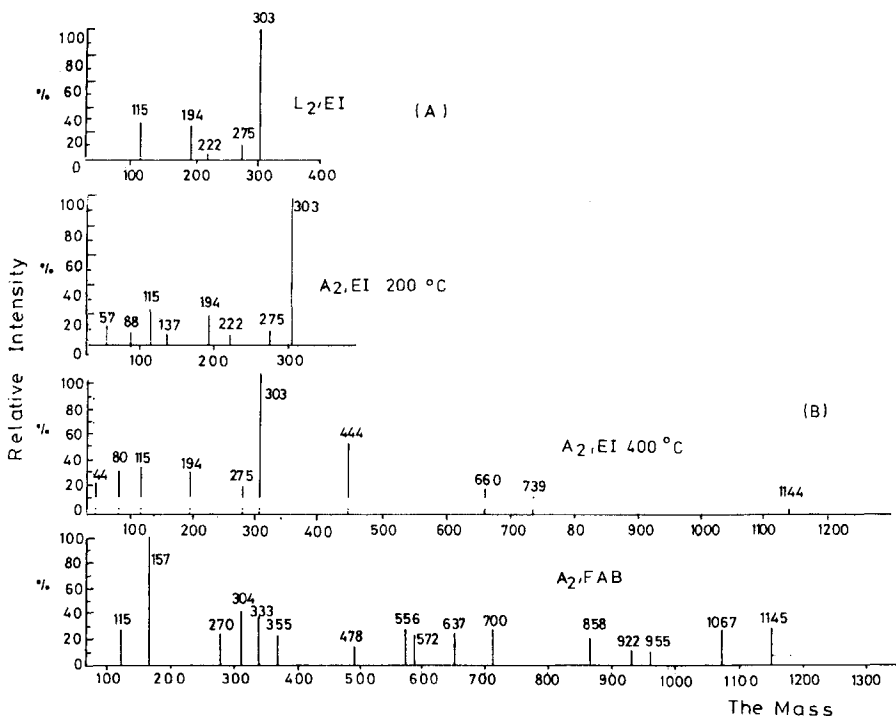
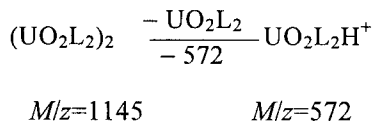


Fig. 3 Mass spectra obtained by both EI and FAB techniques for (A) 5,7-dibromooxine,  $L_2$ ; (B) the uranyl-5,7-dibromooxine obtained,  $A_2$

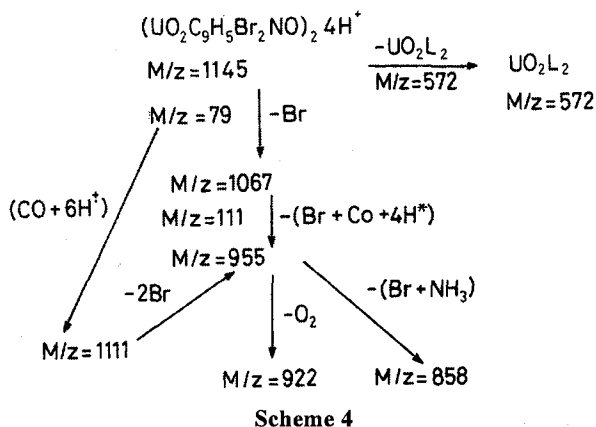
molecule of ligand, which decomposes to give more or less similar fragments as discussed previously.

The mass spectrum of  $A_2$  obtained by the FAB-POS technique, in DMSO/glyc./xenon (5/11611- $H_4$ ) is shown in Fig. 3. It indicates  $M/z=1145$  with the same general formula  $M^{4+}$ ,  $UO_2(C_9H_5Br_2NO)_2 \cdot 4H^+$ . This mass spectrum can be explained by the same scheme as previously mentioned, but the appearance of the molecular ion with  $M/z=572$  is due to the residue of  $UO_2L_2$ . This means that this complex may have the formula  $(UO_2L_2)_2$ ,  $M/z=1145$ , and its decomposition is tentatively given by

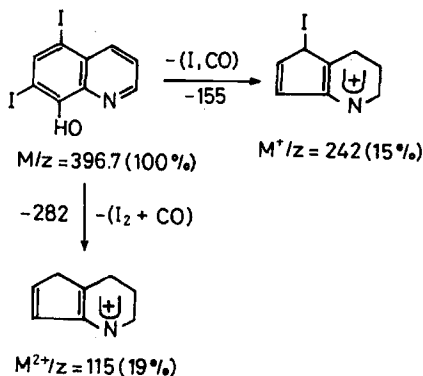


The appearance of the other possible molecular ions can be explained by the decomposition of the bridged complex according to the suggested Scheme 4.

The DTA pattern of  $L_3$  is shown in Fig. 1 ( $L_3$ ). It shows an exothermic base shift in a similar manner as obtained for  $L_1$  and  $L_2$ . This is followed by a sharp



endothermic peak at 120°C, which may be due to melting of the ligand or the loss of iodine. It is also followed by a broad exothermic peak in the temperature range 280–358°C, which indicates the possible vigorous fragmentation of the ligand. The energy required for these changes is 0.162 and 0.64 kJ mol<sup>-1</sup>, with orders of zero and 0.5, respectively. These fragments are identified from the mass spectrum of this ligand as given in Fig. 4, during heating at 250°C and application of the EI technique in an inert atmosphere. The following scheme may be postulated:

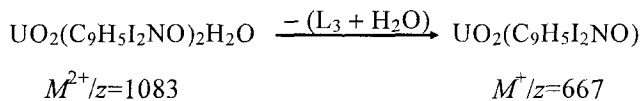


**Scheme 5**

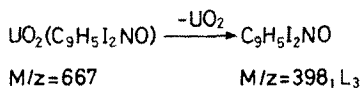
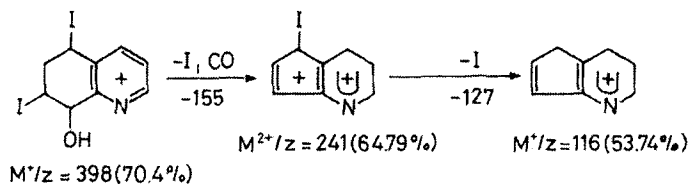
The DTA data on chelate  $A_3$  are depicted in Fig. 1 ( $A_3$ ). There is an endothermic peak at 136°C, and immediately an exothermic one at 137°C, which may reflect the loss of iodine and CO from the ligand. The broad exotherms at 230–330°C may be explained by other vigorous exothermic processes in  $A_3$ . The overall activation energy required for all changes in  $A_3$  during heating up to 400°C is found to be 0.526 kJ mol<sup>-1</sup>. This is more or less equal to that required for all the changes in  $L_3$ . This means that the changes in  $A_3$  mainly involve those



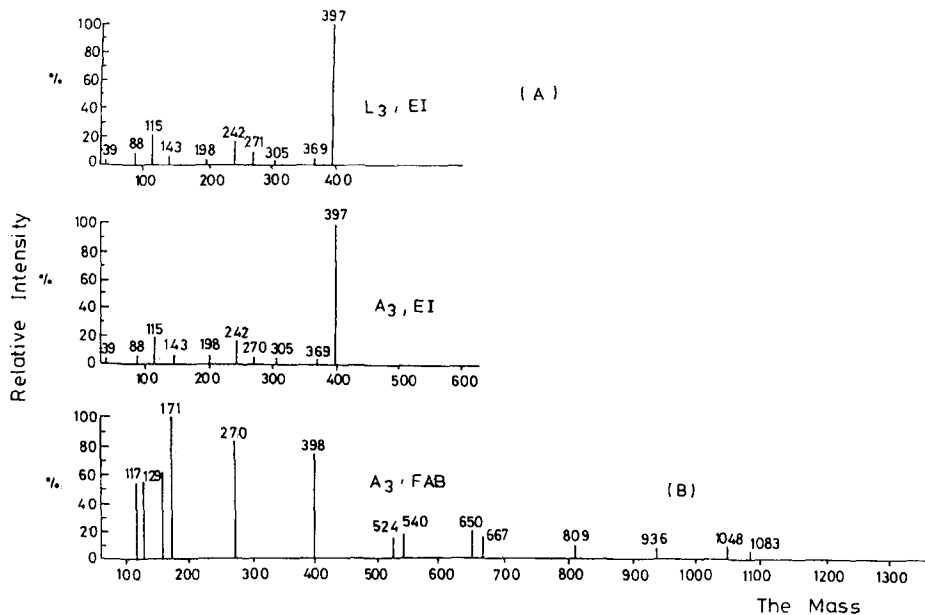
occurring in  $L_3$ . Most of these changes are explained by the mass spectrum (Fig. 4) of  $A_3$  in DMSO/glyc./xenon with heating at  $400^\circ\text{C}$ , obtained by the FAB-POS technique. The mass spectrum of  $A_3$  can be explained by the decomposition



This means that this chelate has the M:L stoichiometry 1:2 or 1:1 after heating. The decomposition may be explained by Scheme 6.



Scheme 6

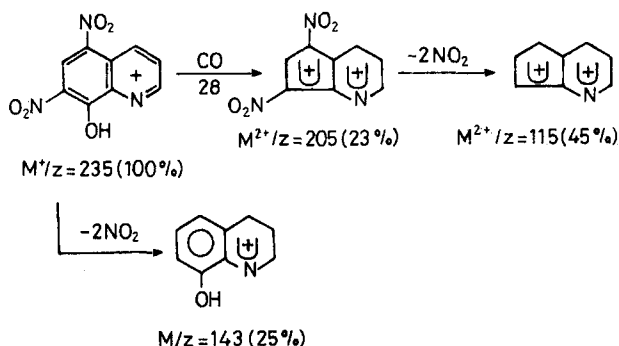


**Fig. 4** Mass spectra obtained by both EI and FAB techniques for (A) 5,7-diiodooxine,  $L_3$ ; (B) the uranyl-5,7-diiodooxine obtained,  $A_3$

Therefore, it is concluded that the chelate decomposes into its constituents, and the resulting free ligand  $L_3$  is fragmented as previously explained.

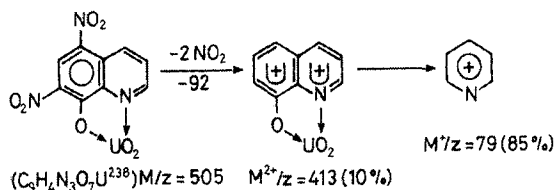
The DTA data on  $L_4$  in Fig. 1 ( $L_4$ ) demonstrate a distinct exothermic base shift between 20 and 140°C. This is followed by a series of exotherms and endotherms that cannot be easily followed by the recorder. This means that this ligand is very sensitive to heating. The activation energy required for all these changes is 0.669 kJ mol<sup>-1</sup>, with an overall order of 0.667.

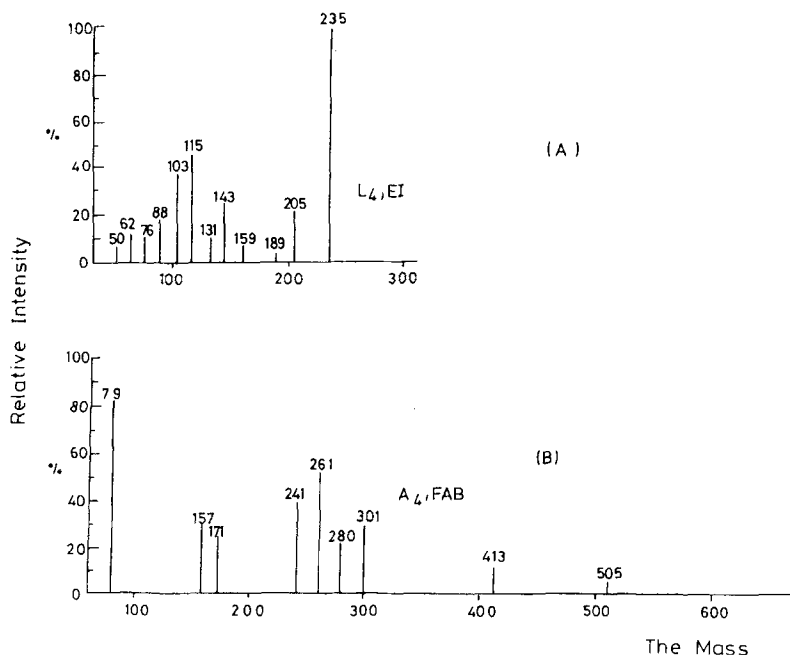
The mass spectrum of  $L_4$ , obtained by using the EI technique at 80 eV and heating at 150°C, is shown in Fig. 5. This spectrum can be explained by the decomposition (Scheme 7)



The DTA curves of  $A_4$  are shown in Fig. 1 ( $A_4$ ). As for  $L_4$ , there is an exothermic base shift from 20 to 140°C, followed by sharp exo- and endothermic peaks at 150–180°C. In the range 180–340°C, there is a steep broad endotherm, and finally various sharp exo- and endotherms at 340–370°C. These changes may be explained by the increase in heat capacity of the chelate with increase of temperature, followed by vigorous loss of NO<sub>2</sub> and CO from  $L_4$ . The activation energies required for all of these changes are found to be 0.737 and 1.08 kJ mol<sup>-1</sup>, with an order of 1.0 in each case.

The mass spectrum of  $A_4$ , obtained by applying the FAB-POS technique in DMSO/glyc./xenon and heating at 400°C, is shown in Fig. 5. It gives a mass of 505, i.e. an M:L stoichiometry of 1:1 for  $A_4$ ; the general formula is C<sub>9</sub>H<sub>4</sub>N<sub>3</sub>O<sub>7</sub>U<sup>238</sup>. This mass spectrum can be explained in terms of the following proposed Scheme 8:





**Fig. 5** Mass spectra obtained by both EI and FAB techniques for (A) 5,7-dinitrooxine,  $L_4$ ; (B) uranyl-5,7-dinitrooxine obtained,  $A_4$

A comparison of the fragments formed from both  $L_4$  and  $A_4$  clearly indicates that the first step of decomposition of both involves the release of  $\text{NO}_2$ . The other fragments from  $A_4$  are related to the decomposition of the remaining part of the oxine ligand. The new fragment appearing here is the pyridine moiety.

The FT-IR spectra [23, 24] of the chelates are used only to confirm the bonding of the phenolic oxygen and the nitrogen of the oxine skeleton to the uranyl ion. The frequencies in the range  $500\text{--}600\text{ cm}^{-1}$  relate to such bonding. The frequencies at  $420\text{--}450\text{ cm}^{-1}$  are due to the  $\text{C-X}$  ( $X=\text{Cl, Br, I}$ ) groups.

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