

THERMAL DECOMPOSITION OF METAL COMPLEXES. XI. THERMAL PROPERTIES AND SPECTROSCOPIC CHARACTERISTICS OF THE COMPLEXES OF URANYL NITRATE WITH SEVERAL O-DONOR LIGANDS

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ABSTRACT

The thermal decompositions in the solid state of some uranyl nitrate adducts with O-donor ligands were investigated and the corresponding activation energy, E_a^\ddagger , values were calculated. The IR spectra of the adducts show that the donor ligands shift differently the antisymmetric stretching vibration of the O–U–O group. A linear correlation between E_a^\ddagger and $\bar{\nu}_3$ values was found and the corresponding equation was calculated. The results obtained indicate a lesser stability of the O-donor adducts with respect to previously studied N-donor adducts

INTRODUCTION

Many papers regarding the thermal decomposition of solid complexes have been published and it was found that conclusive experimental information about the possibility of a correlation between kinetic parameters and the strength of the metal–ligand bond can be correctly obtained if the thermal decompositions at solid state are chemically controlled processes.

The uranyl nitrate complexes with neutral ligands have been largely studied in order to correlate the structural characteristics of the complexes with the donor properties of the ligands. In particular the correlation between the spectrochemical series of the ligands and the symmetric and antisymmetric stretching vibrations $\bar{\nu}_1$ and $\bar{\nu}_3$ of the O–U–O group was attempted by several authors, but the conclusions about this correlation disagree [1–3].

In a previous paper [4] we have studied the thermal decomposition of some uranyl nitrate adducts with neutral N-donor ligands, in order to correlate the activation energy relative to the release of the neutral ligands with the donor properties of the ligand itself and with the antisymmetric stretching vibration $\bar{\nu}_3$ of O–U–O group. The linear relationship $\bar{\nu}_3 = 883 + 0.596 E_a^\ddagger$ has been found.

Following on from that study, in this paper we report the thermoanalytical and spectroscopic behaviour of uranyl nitrate adducts with the following O-donor ligands, L: water, urea, acetamide (ACAM), *N,N*-dimethylformamide (DMF), *p*-nitrosodimethylaniline (*p*-NODMA) and pyridine-*N*-oxide (PyNO). All the complexes considered have the general formula $\text{UO}_2(\text{NO}_3)_2\text{L}_2$.

EXPERIMENTAL

Reagents

Uranyl nitrate hexahydrate (FLUKA), urea (C. Erba RP), dimethylformamide (C. Erba RP), acetamide (C. Erba RP), pyridine-*N*-oxide (FLUKA) and *p*-nitrosodimethylaniline (C. Erba RP) were used.

Preparation of the solid complexes

The $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$ was prepared directly into the thermoanalyzer from the $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ in vacuum (5×10^{-2} mmHg) at room temperature. In fact under these experimental conditions, the loss of the four externally coordinated water molecules was observed, the dehydrated salt being stable. The $\text{UO}_2(\text{NO}_3)_2\text{Urea}_2$ was prepared as Bullock [2], the $\text{UO}_2(\text{NO}_3)_2(\text{DMF})_2$ was prepared as Frigerio and Coley [5] and the $\text{UO}_2(\text{NO}_3)_2(\text{ACAM})_2$ and $\text{UO}_2(\text{NO}_3)_2(\text{PyNO})_2$ complexes were both prepared by mixing, at room temperature, and in ethanolic solution, the uranyl nitrate hexahydrate with ligand in excess. The yellow precipitate obtained for both complexes was filtered, washed with ethanol and then dried at 90°C.

The $\text{UO}_2(\text{NO}_3)_2(p\text{-NODMA})_2$ was prepared as reported in the literature [6].

Analyses

The complexes obtained were analyzed. Uranium was determined according to the classical method by precipitation as ammonium diuranate and weighed as U_3O_8 . The other elements were determined by the usual methods. The analytical compositions found for the compounds obtained agree with the theoretical values. The analytical data are reported in Table 1.

Thermal measurements

The thermal decomposition processes were studied by TG and DTG curves in order to evaluate the kinetic parameters and the stoichiometry of

TABLE I
Analytical data

Donor	C%		H%		N%		U%	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
H ₂ O			0.47	0.50	6.51	6.44	55.35	55.22
Urea	4.67	4.52	1.57	1.60	16.35	16.25	46.30	46.12
ACAM	9.38	9.32	1.97	1.89	10.94	10.92	46.47	46.40
DMF	13.34	13.39	2.61	2.50	10.37	10.39	44.06	43.99
<i>p</i> -NODMA	17.65	17.59	1.86	1.82	10.29	10.37	43.74	43.91
PyNO	20.56	20.61	1.73	1.65	9.59	9.63	40.74	40.77

the decomposition reactions. The corresponding thermal effects were observed by DTA curves.

The measurements were performed using a Mettler thermoanalyzer at heating rates between 0.5 and 4°C min⁻¹ in a dynamic nitrogen atmosphere (10 l h⁻¹). A Mettler T-TD3 crucible holder, 0.3 ml platinum microcrucibles and thermally inactive Al₂O₃ as reference material were used.

Mass spectra measurements

A Balzer mass spectrometer model QMG 311 was used to analyze the evolved gases.

IR measurements

The IR spectra were obtained as KBr pellets using a Perkin-Elmer mod. 257 spectrophotometer (4000–625 cm⁻¹).

Evaluation of the activation energy, E_a[‡]

The activation energy, E_a[‡], of the thermal decomposition processes was calculated graphically after introducing the appropriate reaction order as reported in the literature [7–11].

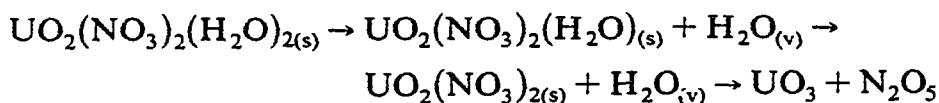
RESULTS AND DISCUSSION

Thermal measurements

In Fig. 1–6 the TG and DTG curves of the considered complexes are reported.

UO₂(NO₃)₂(H₂O)₂ (Fig. 1)

The UO₂(NO₃)₂(H₂O)₂ salt, stable up to 110°C, decomposes in two endothermic steps as reported below



UO₂(NO₃)₂urea₂ (Fig. 2)

The UO₂(NO₃)₂urea₂ compound at 198°C releases only one of two urea molecules, giving rise to the polymeric UO₂(NO₃)₂urea compound as previ-

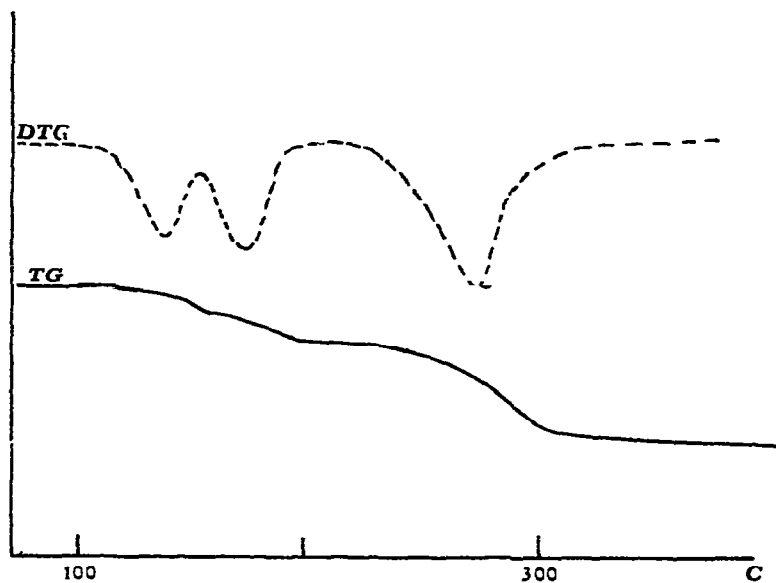


Fig. 1. Thermal behaviour of $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$.

ously reported [12], and then decomposes, exhibiting only an exothermic process, giving rise to UO_3 and gaseous products. The recorded mass spectra of the evolved gases show peaks corresponding to NO and CO_2 , thus

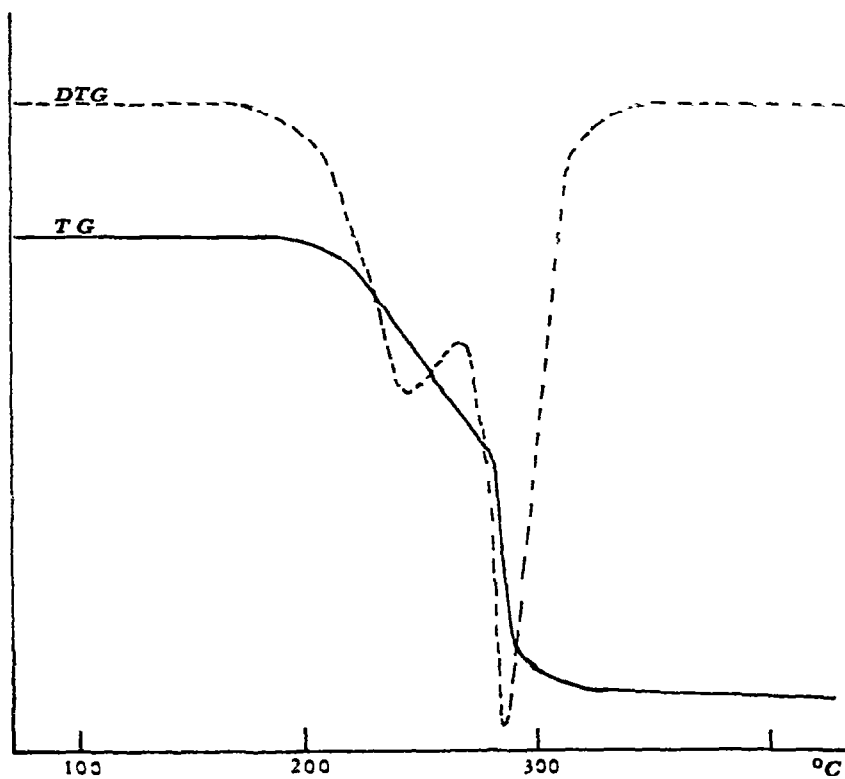


Fig. 2. Thermal behaviour of $\text{UO}_2(\text{NO}_3)_2\text{urea}_2$.

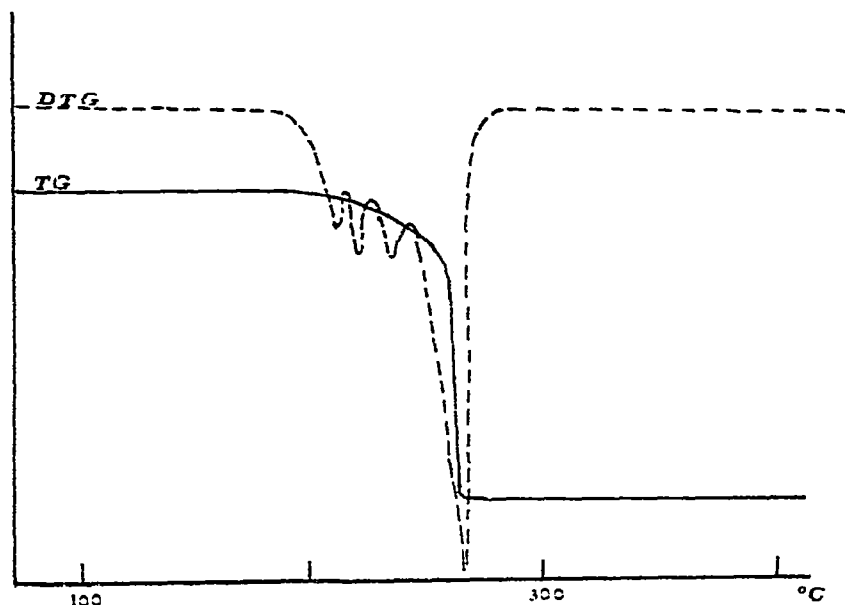


Fig. 3. Thermal behaviour of $\text{UO}_2(\text{NO}_3)_2(\text{ACAM})_2$.

indicating that redox reactions, involving both a neutral donor and an ionic ligand, occur.

$\text{UO}_2(\text{NO}_3)_2(\text{ACAM})_2$ (Fig. 3)

According to the thermoanalytical curves this compound melts at 190°C and successively decomposes. The DTG curves do not exhibit regular

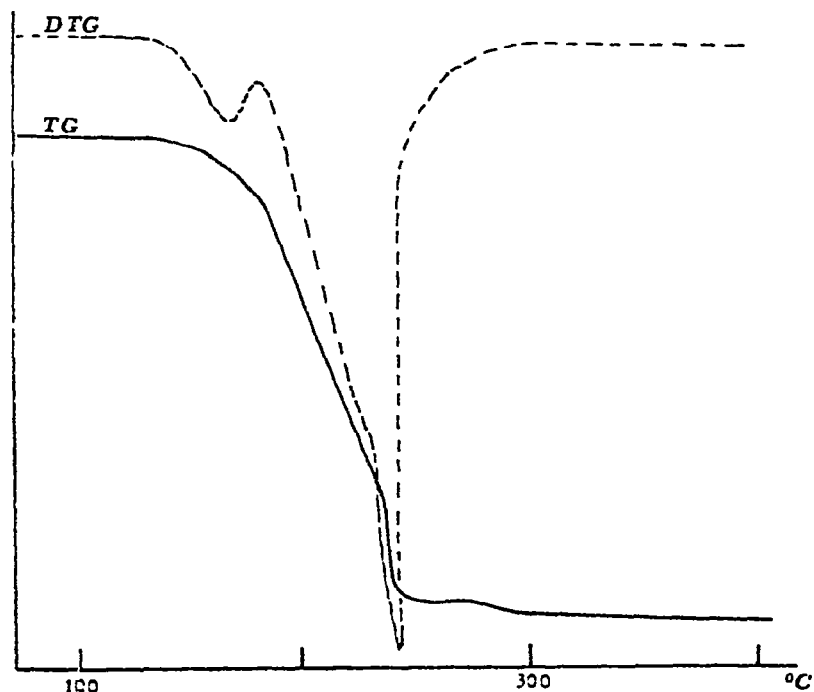


Fig. 4. Thermal behaviour of $\text{UO}_2(\text{NO}_3)_2(\text{DMF})_2$.

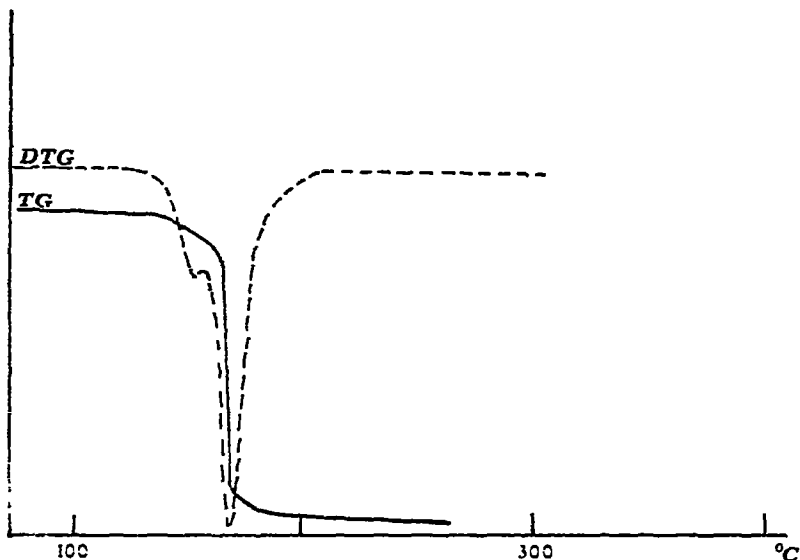


Fig. 5. Thermal behaviour of $\text{UO}_2(\text{NO}_3)_2(p\text{-NODMA})_2$.

behaviour, thus suggesting that the release of the two ACAM molecules is not a stoichiometric stepwise process. The overall process evolves as reported below

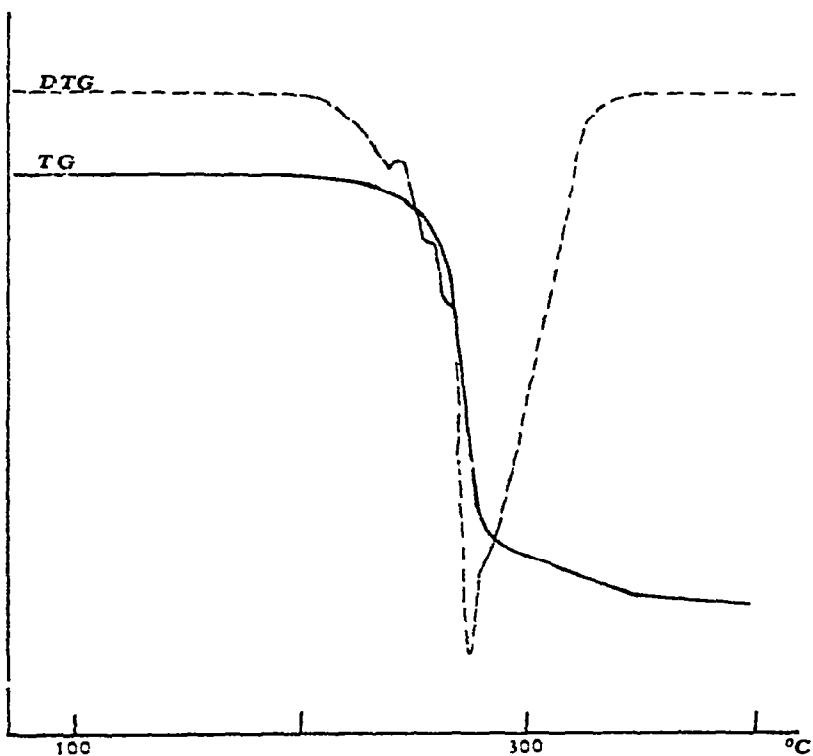
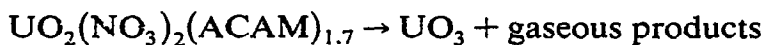
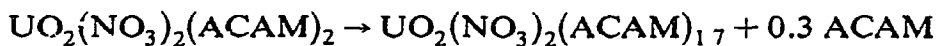
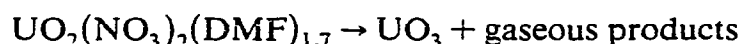
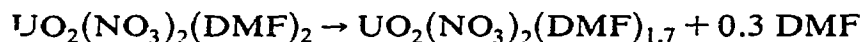


Fig. 6. Thermal behaviour of $\text{UO}_2(\text{NO}_3)_2(\text{PyNO})_2$.

According to the thermal measurements, the recorded mass spectra of the gaseous products substantiates the initial release of undecomposed ACAM; successively the intensity of the ACAM peak rapidly decreases while the CO₂ and NO peaks appear.

UO₂(NO₃)₂(DMF)₂ (Fig. 4)

Thermally stable up to 156°C, this compound decomposes in two stoichiometric steps according to the scheme



The simultaneous DTA curve substantiates that the initially endothermic process associated with the release of DMF evolves exothermically after the loss of 30% of the ligand itself.

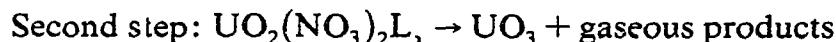
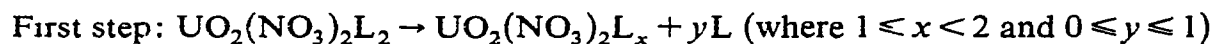
*UO₂(NO₃)₂(*p*-NODMA)₂ (Fig. 5)*

Thermally stable up to 140°C, this compound is the most reactive of the considered complexes because of the presence of the nitroso group. At a heating rate of 0.5°C min⁻¹ we observe an exothermic process (due to the release of 15% of the undecomposed ligand), followed by another thermal process with release of CO₂, NO and other gaseous products due to the simultaneous decomposition of both *p*-NODMA and nitro groups, as substantiated by the recorded mass spectra. At heating rates > 0.5°C min⁻¹ the thermal decomposition evolves explosively.

UO₂(NO₃)₂(PyNO)₂ (Fig. 6)

This adduct, thermally stable up to 200°C, decomposes exothermically in several non-stoichiometric steps, giving rise, as a final product at 500°C, to UO₃. The peaks of the recorded mass spectra show only the release of fragments of the ligands, whereas the peak relative to PyNO was not found.

It is worth noting that the thermal decomposition of the complexes examined can be generalized as follows



Depending on the ligand, the thermal effects associated with the thermal decomposition processes are reported below

Compound	1st step	x	y	2nd step
UO ₂ (NO ₃) ₂ (H ₂ O) ₂	endo	1	1	endo
UO ₂ (NO ₃) ₂ urea ₂	endo	1	1	exo
UO ₂ (NO ₃) ₂ (ACAM) ₂	endo	1.7	0.3	exo
UO ₂ (NO ₃) ₂ (DMF) ₂	endo	1.7	0.3	exo
UO ₂ (NO ₃) ₂ (<i>p</i> -NODMA) ₂	exo	1.85	0.15	exo
UO ₂ (NO ₃) ₂ (PyNO) ₂	exo	0	2	-

TABLE 2

Thermochemical data obtained from thermoanalytical curves relative to the first decomposition step and some characteristic IR absorptions (cm^{-1}) of uranyl nitrate complexes

Donor	Serial No.	T_1 ($^{\circ}\text{C}$)	E_a^{\ddagger} (kcal mole $^{-1}$) *				$\bar{\nu}_3$ (cm^{-1})
			a	b	c	d	
H ₂ O	1	110	30.6	30.8	31.4	30.9	943
Urea	2	185	35.7	35.0	34.9	35.2	952
ACAM	3	186	28.3	30.7	29.2	29.4	942
DMF	4	156	21.8	22.4	23.6	22.6	932
<i>p</i> -NODMA	5	140	9.2	10.5	8.5	9.4	908
PyNO	6	200				18.1 **	923

* a, Calculated as ref. 7; b, Calculated as ref. 8; c, Calculated as ref. 9; d, Average.

** Calculated value.

From the data obtained we think that only the first process can be associated with the linkage of the $\text{UO}_2\text{-L}$ bond. This conclusion is supported by the mass spectra of the evolved gases. The second step of the reactions represents the sum of several processes: (i) the release of H_2O or urea (from the respective complexes) associated with salt polymerization due to the filling of the coordination sphere of the uranium atom with oxygen atoms from the nitric groups; (ii) the release, with decomposition, of both neutral and ionic ligands and subsequent redox reaction of the products (as substantiated by the NO and CO_2 peaks obtained by mass spectra).

The results obtained suggest that the activation energy values, which it is possible to correlate with the antisymmetric stretching vibration $\bar{\nu}_3$ of the O-U-O group, are only those relative to the first step of the thermal decomposition of the complexes studied.

The E_a^{\ddagger} values calculated using the literature methods agree with each other and are listed in Table 2.

Infrared spectra

The IR spectra of the complexes studied have been recorded in order to investigate whether the antisymmetric stretching vibration of the UO_2 group is influenced by the nature of the donor and if a correlation between the E_a^{\ddagger} values (of the first step of the decomposition) and $\bar{\nu}_3$ is possible. In Table 2 the average E_a^{\ddagger} and corresponding $\bar{\nu}_3$ values are listed and in Fig. 7 the plot of $\bar{\nu}_3$ against E_a^{\ddagger} is reported.

The results obtained clearly indicate that a straight line represents the best fit of the points corresponding to the complexes of H_2O , urea, ACAM, DMF and *p*-NODMA. By a least squares treatment we have found that the

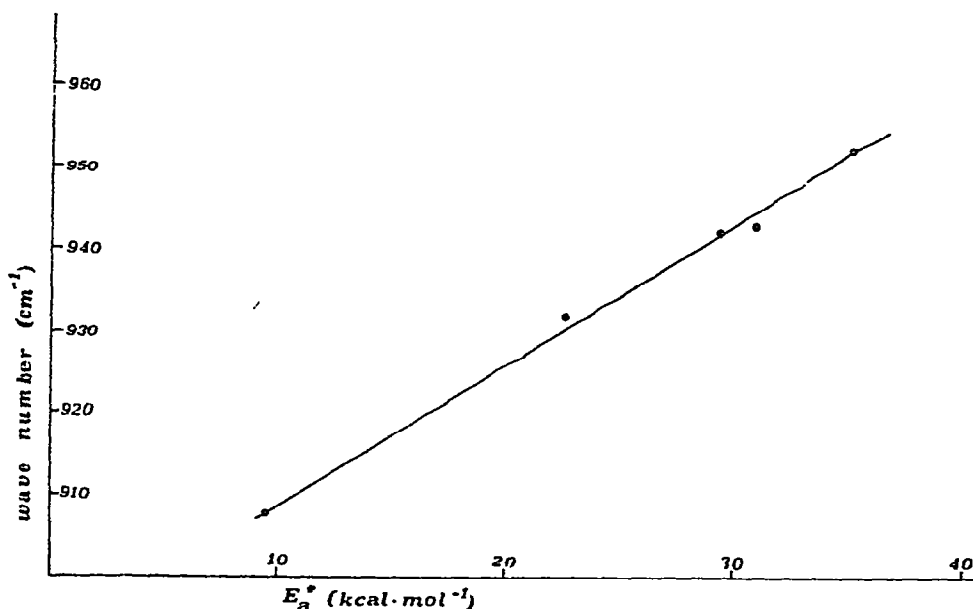


Fig. 7 Plot of $\bar{\nu}_3$ (cm^{-1}) vs. E_a^* (kcal mole^{-1}) of uranyl nitrate adducts. The serial numbers correspond to those used in Table 2

linear relationship obeys the equation

$$\bar{\nu}_3 = 892.8 + 1.67 E_a^*$$

The confidence coefficient was 0.998.

By this linear relationship we feel that it is possible to calculate the theoretical E_a^* of the Py-N-Oxide complex, utilizing the experimental $\bar{\nu}_3$ antisymmetric stretching vibration of the UO_2 group, and therefore the corresponding value is reported in Table 2.

On comparing our results with those previously obtained for the uranyl nitrate adducts with N-donor ligands [4], we note that all the activation energy values of the N-donor complexes are greater than the O-donor complexes, this indicating generically a greater stability, in the solid state, of the N-donor adducts.

Difficulties were encountered in identifying the symmetric stretching frequencies $\bar{\nu}_1$, of the O-U-O group of the complexes examined. In order to predict the position of $\bar{\nu}_1$ by the experimental $\bar{\nu}_3$, we have used a relation reported in the literature [1]

$$\bar{\nu}_1 = 21 + 0.89 \bar{\nu}_3$$

The calculated $\bar{\nu}_1$ values disagree with the experimental bands of the IR spectra, so that no correlation was attempted with E_a^* values.

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