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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

Preparation and Properties of Some Complex Compounds of Thorium tetranitrate With Organic Ligands

by

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19

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

Preparations and Properties of Some Complex Compounds of Thorium tetranitrate With Organic Ligands

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ABSTRACT

The interaction of thorium tetranitrate with some organic ligands, which were used before with thorium tetrachloride was investigated. The effect of the anionic part of the metal compound on the nature and composition of the formed complexes were discussed. Study of the infrared spectra measured over 400–650 cm–1 region and thermal analysis in the range 25–800° C were carried out. Conductivity measurementes for the soluble complexes were done.

INTRODUCTION

Thorium tetranitrate forms a series of double salts of the type $Th(NO_3)_4, 2M^INO_3.nH_2O$, where $M^I = NH_4$, K, Rb or Cs. These compounds resemble those of Ce(IV) and may contain $[Th(NO_3)_6]^{-2}$ anion. A second series, $Th(NO_3)_4, 2M^{II} (NO_3)_2. 8H_20$ is formed with bivalent metal ions, where M^{II} is Mg, Zn, Ni or Co(1) The Mg salt has been shown to contain the 12 coordinated anion with chelated NO_3 groups.(2)

It is well established that many transition metal nitrates form complexes with organic ligands containing nitrogen or oxygen atoms.(3–8) However, the interactions of ligands with thorium tetranitrate has been little investigated.[9] This is probably because the system has received little attention, rather than because of the instability of the formed complexes.

It is reported that thorium tetranitrate reacts with 1,2-diethoxy ethane and antipyrene to give the complexes $Th(NO_3)_4, 3C_6H_{14}0_2,3H_2O$ and $Th(NO_3)_4.5C_{11}H_{12}N_2O$, respectively. The coordination number of thorium was not obvious in the two cases.

In the present communication, the complexes formed between thorium tetranitrate and some oxygen- and nitrogen-cotaining ligands were studied. The ligands were those described in the experimental part.

EXPERIMENTAL

Material and Methods: Thorium tetranitrate hexahydrate and tetrahydrate, BDH analar grade, were used without further purification. Attempt dehydration either by heating or by azeotropic distillation were unsuccessful, as the compounds decomposed.

Organic solvents were dried ad purified by conventional methods.[10]

Infrared spectra were recorded (in nujol or KBr) using a Unicam SP 200 G infrared spectrophotometer. Calibration of frequency reading was made with a polystyrene film. Conductivities were measured using an electronic switchgear bridge model MC-2 with balance indicator, details and methods of calculation were given before.[11] Thermal analyses technique was as previously mentioned. ([12], [13])

Analysis of carbon, hydrogen and nitrogen were carried out by the Microanalytical laboratory of El-Nasr Company. Analysis of phosphorus was determined by A. Bernhardt of Mulheim, Ruhr-Germany.

Organic Ligands: Some of the aromatic derivatives of nitrogen and phosphorus were prepared by the methods described previously.(8,12) The other ligandes used were analar grade materials.

Preparation of the compounds:

Equimolar amounts of thorium nitrate and the ligand solutions were mixed well in ethyl acetate, EtAc., as a solvent. The product was filtered, washed with the solvent and dried, then subjected to analysis and investigation. It was found that using excess of the organic ligand improved the yield, but did not affect the coordination number of the formed complex.

RESULTS:

The compound obtained from the reactions of equimolar amounts of 1,2 -bis (diphenylphosphino) ethane, DIPhOS ethane, and thorium nitrate was proved by analysis and ir not to be diphenylphospihno ethane complex but the corresponding dioxide adduct, Th $(NO_3)_4$, 1.5 DiPhOS ethane dioxide, which decomposed at 180–190 °C and melted at 200 °C. An authentic sample of this complex, $Th(NO_3)_4$, 1.5 DiPhOS ethane dioxide, was obtained on using DiPhOS ethane dioxide as a ligand; even on using excess of the latter.

Attempted preparation of complexes of thorium nitrate wth diphenylphosphino ethane or the corresponding diphosphine disulphide were unsuccessful, and the ligand in the latter case was recovered unchanged. This is in conformity with the earlier findings.[5'6]

The reactions of $Th(NO_3)_4$with dimethyl-bipyridyl, DM-bipy., and tripyridyl. tripy., in ethyl acetate applying the mole rations 1:1 and 1:2, gave complex compounds of the formula, $Th(NO_3)_4$, 1.5L where L stands for the organic ligands used.

Complexes of the type, $Th(NO_3)_4$, 2L,nH_20 were obtained with dimethyl-o-phenanthroline; DM-phen., bipyridyl; bipy., pyrazine and pipyridine; pipy., where n either 6 or 4 molecules. Recrystallisation of the products obtained with pyridine-N-oxide and o-phenanthroline-phen., from ethyl acetate gave the complexes $Th(NO_3)_4$, 2py-N-oxide, EtAc. and Th $(NO_3)_4$, 2phen, 2EtAc.

The complex compounds obtained during the present work are air stable white crystalline compounds which are insoluble in most organic solvents tried, except those used for conductivities.The only water-soluble complex obtained was that of picolinic acid, ($Th(NO_3)_4$, 4picolinic, $4H_20$.

Analytical data are given in Table 1.

Table (1)

	Required %				Found %		
	C	H	N/P	Formula	C	H	N/P
1. Th $(N0_3)_4$, 1.5DiPh0S ethane dioxide	41.6	3.2	8.25	$C_{39}H_{36}N_40_{15}P_3Th$	41.5	3.5	8.2
2. $Th(N0_3)_4$, 2phen.,2EtAc							
3. $Th(N0_3)_4$, 2DM-phen	37.8	3.2	11.0	$C_{32}H_{32}N_80_{16}Th$	36.2	3.2	10.9
$4H_20$	34.7	3.3	11.6	$C_{28}H_{32}N_80_{16}Th$	34.3	3.3	11.0
4. $Th(N0_3)_4$, 2bipy.,$4H_20$	27.8	2.8	13.0	$C_{20}H_{24}N_80_{16}Th$	27.8	3.1	12.3
5. $Th(N0_3)_4$,1.5-DM-bipy.	28.5	2.4	12.9	$C_{18}H_{18}N_70_{12}Th$	27.7	2.8	12.6
6. $Th(N0_3)_4$,1.5tripy.	32.5	2.0	14.3	$\frac{1}{2}(C_{45}H_{33}N_{17}0_{14}Th_2)$	31.9	3.2	13.6
7. $Th(N0_3)_4$,2dipy. amine	29.2	2.2	17.0	$C_{20}H_{18}N_{10}0_{12}Th$	28.8	2.4	15.9
8. $Th(N0_3)_4$,2pyrazine, $6H_20$	12.8	2.7	15.0	$C_8H_{20}N_80_{18}Th$	12.1	2.6	14.2
9. $Th(N0_3)_4$,2pipy.,$6H_20$	15.8	4.5	11.1	$C_{10}H_{34}N_60_{18}Th$	15.0	3.4	10.4
10. $Th(N0_3)_4$, 2py. N-oxide, EtAc	22.2	2.4	11.1	$C_{14}H_{18}N_60_{16}Th$	22.3	3.8	10.6
11. $Th(N0_3)_4$, 4picolinic acid, $4H_20$	27.6	2.7	10.7	$C_{24}H_{28}N_80_{24}Th$	27.4	2.9	10.3

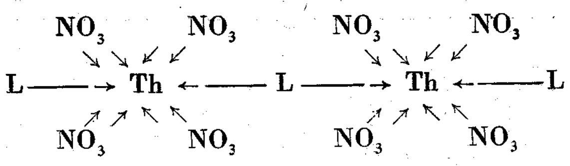
DISCUSSION

Infrared Spectra:

The infrared absorption spectrum of thorium nitrate tetrahydrate (fig 1) shows six absorption bands in the region 4000–650 cm^{-1} The bands at 1550-1490 cm^{-1} $(\surd_1)$, 810 cm^{-1} $(\surd_6)$, 1040–1030 cm^{-1} $(\surd_3)$, 1310–1280 cm^{-1} $(\surd_4)$, 745 cm^{-1} $(\surd_3)$ and 705 cm^{-1} $(\surd_5)$. Absorption by water[14] occurs in the regions 3500–3100 cm^{-1} and 1630 cm^{-1}, (Fig. 1). The chemical properties[15] and infrared spectrum show that thorium nitrate tetrahydrate is covalent. It is not easy to decide whether the nitrate groups are uni-or bidentate on the bases of infrared study alone. Ueki *et al*[16] have studied the X-ray analysis of $Th(NO_3)_4$, $5H_20$ and concluded that the thorium metal is within bonding distance of eleven oxygen atoms, three from water molecules and eight from four nitrate groups which function as bidentate ligands.

The P=0 absorption band in DiPhOS ethane dioxide is reported[8,17] to be at 1190 cm^{-1}. The spectrum of the complex, $Th(NO_3)_4$, 1.5DiPhOS ethane dioxide, shows two strong bands at 1130 and 1080 cm^{-1}, (Fig. 2). The lowering of this band from the pure ligand as found in other cases [5,18] is attributed to coordination through oxygen. The splitting may account for the different mode of coordination of this ligand to thorium(IV).[6]

The stoichiometry of this complex can be explained if bridging takes place as in the proposed structures



In such complex one of the ligand molecules acts as a bidentate ligand and donation occurs through both oxygen atoms.

Similar structure for the adducts obtained with dimethyl acetamide (d m a) has been suggested on the basis of the infrared spectrum of the complex.[19,20]

No evidence could be found for the formation of a simple adduct of the type Th $(NO_3)_4$, DiPhOS ethane (or DiPHOS ethane disulphide). This is probably because of the low donor strengths of the phosphorus and sulphur atoms with respect to thorium (IV).

In the spectrum of free pyridine-N-oxide, the frequency of the N-O gruop occurs at 1180 cm^{-1}. This band shifts to 1310 cm^{-1}, on complexing with thorium tetranitrate. The ligand in this complex is considered to be coordinated to thorium (IV) through the N—O group, (Fig.3).

Similarly, the C=O stretching band at 1720 cm^{-1} in free picolinic acid shifts to lower frequency on complexing with thorium nitrate, whereas the C=N vibration band at 1610 cm^{-1} is not altered. Thus, it is concluded that picolinic acid is linked to the thorium (IV) nitrate through its carboxylic group.

The spectra of the other complexes formed between Th (IV) nitrate and N-donors are too complicated to allow any band assignments. It was not easy to distinguish between the absorption bands of the coordinated ligands and that of the nitrate as they interfer. Similar results are reported.[21]

Thermal Analysis:

The thermal stability of thorium tetranitrate complexes was investigated over the range 25–800 °C. It was found that these complexes decompose on heating. The molecular weigths of the intermediate compounds are calculated from the graphs The final products, after heating up to 800 °C are usually ThO_2, Th or ThO $(NO_3)_2$. Table (2) indicates the effect of heat on some thorium tetranitrate complexes.

Table (2)

Thermal Decomposit on of Some Thorium tetramitrate Complexes

Temp (C)	Mobs.	Formula		Mcal.
Th $(N0_3)_4$, *1. 5 Diphos ethane dioxi de*				
26–80	1125.7	Th $(N0_3)_4$, 1.5 Diphos ethane dioxide		1125.7
120–160	1075	Th $(N0_3)_4$, 1.5 Diphos ethane	(A)	1077.6
480–800	450.3	$Th0_2$, Ph_2 P	(B)	449
Th $(N0_3)_4$, *2-0-phen., 2EtAcx*				
25–80	1016.7	Th $(N0_3)_4$, 2-0-phen., 2EtAc		1016.7
440–800	270	$Th0_2$	(C)	264
Th $(N0_3)_4$, *2DM-0-phen., 4*H_20				
26–80	968.6	Th $(N0_3)_4$, 2DM-0-phen., $4H_20$		968.6
100–140	926.5	Th $(N0_3)_4$, 2DM-0-phen., $2H_20$	(D)	932.6
320–340	694.9	Th $(N0_3)_4$, 0-phen;, $2H_20$	(E)	696.2
440–800	273.7	$Th0_2$	(F)	264
Th $(N0_3)_4$, *1.5 tripy.*				
25–120	829.96	Th $(N0_3)_4$, 1.5 tripy.		829.96
400–800	224.1	Th	(G)	232.04
Th $(N0_3)_4$, *2 dipy. amine*				
26–140	822.46	Th $(N0_3)_4$, 2 dipy. amine		822.46
420–800	310	mix.	(H)	
Th $(N0_3)_4$, *2py. N-oxide, EtAc*				
25–200	758.3	Th $(N0_3)_4$, 2py. N-oxide, EtAc		758.3
300–800	265.4	$Th0_2$	(J)	264
Th $(N0_3)_4$, *4picolinic acid, 4*H_20				
80–100	1044.6–981.9	Th $(N0_3)_4$, 4picolinic acid		972.6
210–240	835.7	Th $(N0_3)_4$, 3picolinic acid (K)		849.33
500–800	376.1	Th0 $(N0_3)_2$	(L)	372
Th $(N0_3)_4$, *2pipy. 6*H_20				
25–80	758	Th $(N0_3)_4$, 2pipy., $6H_20$		758.4
460–800	485	Th $(N0_3)_4$		480

Where Mobs. = The observed molecular weight.

Mcal. = The calculated molecular weight.

The letters indicate intermediate stages.

Conductivity Measurements:

Within the solubility limits of the complexes obtained, the molar conductivities of millimolar solutions at infinite dilution in acetonitrile and dimethyl formamide have been measured (Table 3). The values reported could indicate the number and type of ions in solution.[21'23]

As indicated in Table 3, the complexes which are soluble in acetonitrile behave as weak electrolytes.

When dimethylformamide was used as a solvent, all the adducts which are soluble in this solvent behave as weak electrolytes, except

Table (3)

Conductivities of Some Thorium tetranitrate Complexes In Different Solvents

Compound	MeCN chm^{-1} cm^{2}	DMF
Th $(N0_3)_4$, 1.5 Diphos ethane dioxide	W	—
Th $(N0_3)_4$, 2 o-phen.), 2EtAc	—	65
Th $(N0_3)_4$, 1.5 (2,2',2' tripy.)	W	—
Th $(N0_3)_4$, 2bipy., $4H_20$	—	W
Th $(N0_3)_4$, 1.5 DM-bipy.	—	W
Th $(N0_3)_4$, 2-Dipy. amine	—	W
Th $(N0_3)_4$, 2 (py. N-oxide), EtAc	—	73
Th $(N0_3)_4$, 4 (picolinic acid), 4 H_20	—	136

the complexes , Th($NO_3)_4$, 2- phen., 2 EtAc and Th$(NO_3)_4$, 2-py.- N-oxide , EtAc behave as strong electrolytes in dimetthylformamide. This is presumably due to the presence of the ethyl acetate molecules. The complex formed between thorium nitrate and picolinic acid, Th $(NO_3)_4$, 4-picolinic, $4H_2O$ is also behaving as strong electrolyte in dimethylformamide.

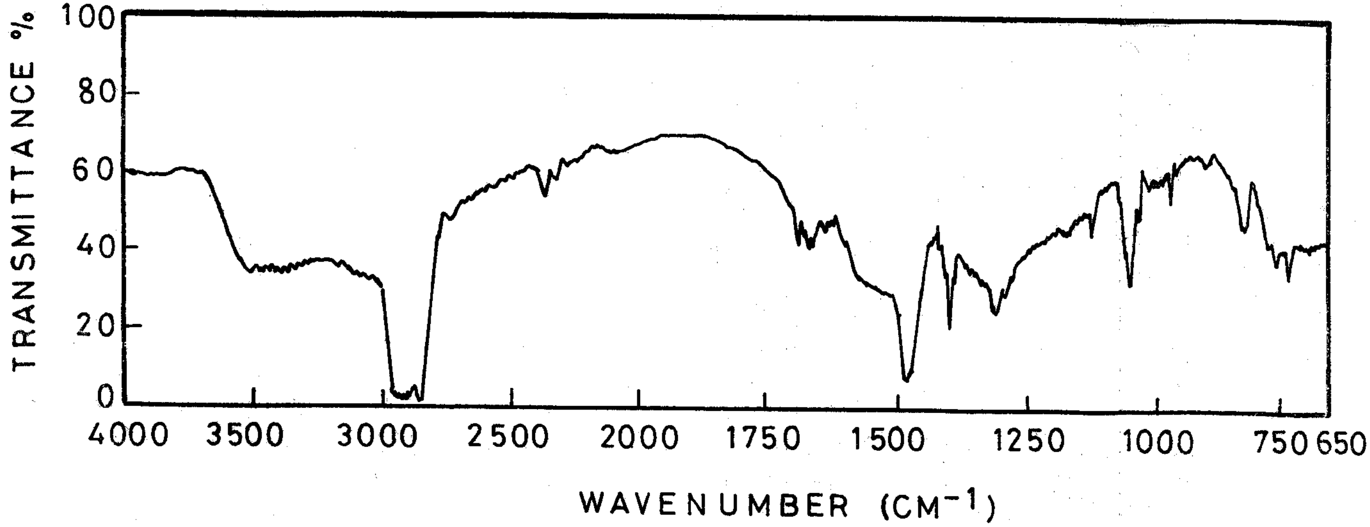


Fig. (1) The infrared spectrum of thorium nitrate tetrahydrate

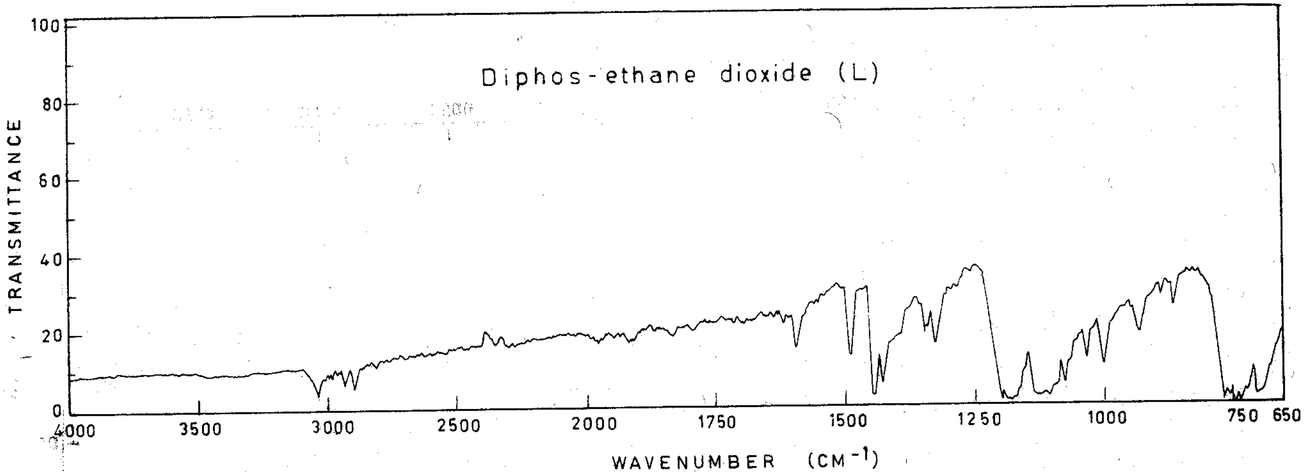

Diphos-ethane dioxide (L)
TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
650
WAVENUMBER (CM^{-1})

Fig. (2-a)

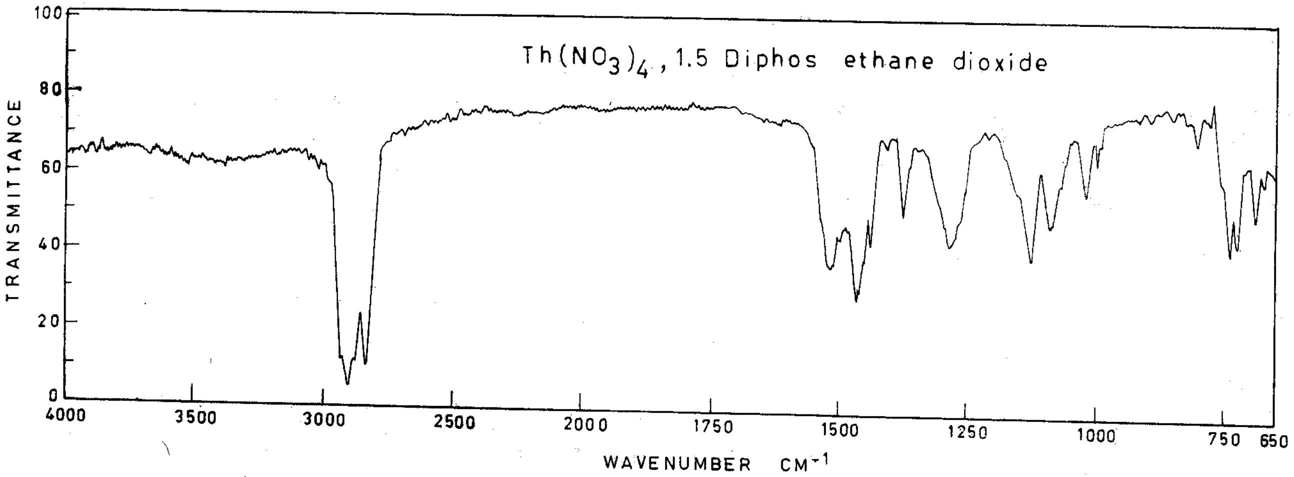

Th$(NO_3)_4$, 1.5 Diphos ethane dioxide
TRANSMITTANCE
100
80
60
40
20
0
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
650
WAVENUMBER CM^{-1}

Fig. (2-b)

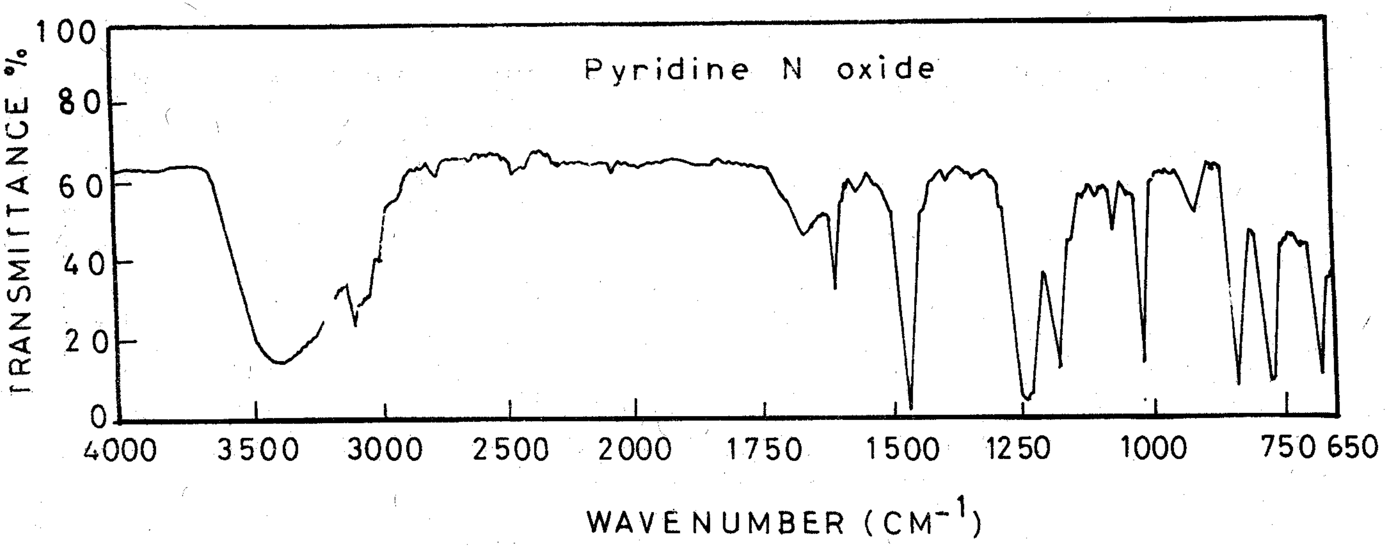


Fig (3 - a) The infrared spectrum of pyridine - N - oxide

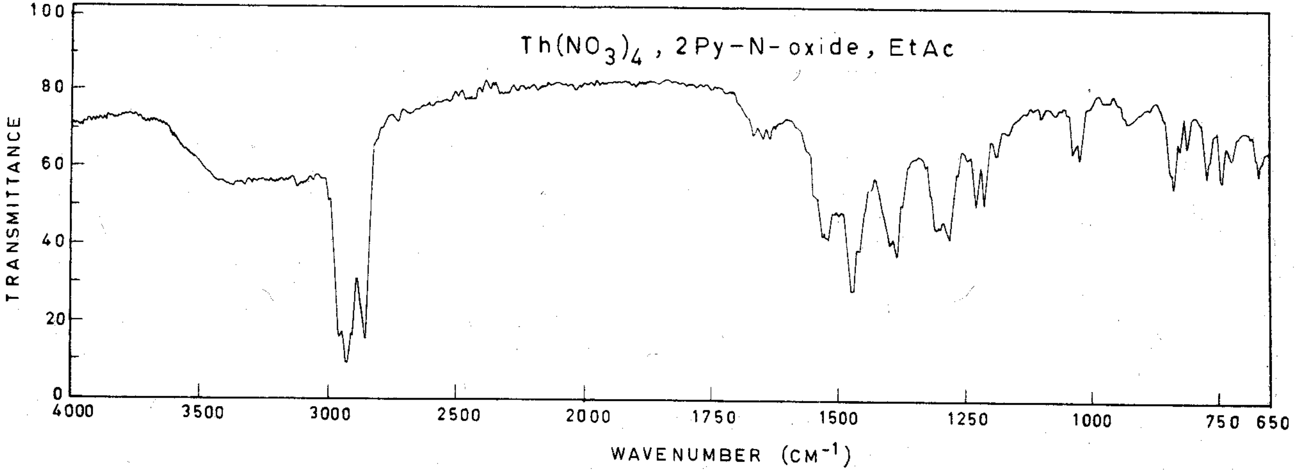


Fig.(3-b)

Fig (3- b) The infrared spectrum of pyridine N oxide.

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