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Note

INFRARED AND THERMAL STUDIES OF THORIUM(IV) CHELATES OF 2-ETHOXYCARBONYLAMINOPYRIDINE *N*-OXIDE

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In continuation with our studies on the complexing behaviour of different aromatic amine *N*-oxides with thorium(IV) [1–5], we have now investigated the coordinating ability of 2-ethoxycarbonylaminopyridine *N*-oxide (ECAPO) towards thorium(IV) salts and the thermal characteristics of the resulting chelates. The ligand ECAPO has three potential donor sites in tertiary amine *N*-oxygen, imino nitrogen and carbonyl oxygen. Only the oxozirconium chelate of this ligand has been reported so far [6].

EXPERIMENTAL

The ligand was prepared from 2-aminopyridine as reported earlier [7]. $Th(NO_3)_4 \cdot 4\ H_2O$ (B.D.H.) was used as supplied. Halides and perchlorate salts were prepared by the reported methods [8,9].

The metal complexes were prepared by mixing the corresponding thorium salt in absolute ethanol and a dehydrating agent and the ligand in diethyl ether. In each case, a solid product was obtained which was washed with ethanol and then with diethyl ether and dried in vacuo over P_4O_{10}.

The analyses, conductance, molecular weight, TG and DTA measurements on the complexes were made as reported previously [1].

RESULTS AND DISCUSSION

Stoichiometries of the synthesized complexes were established on the basis of elemental analysis (Table 1). The complexes are not hygroscopic in nature and are fairly stable at room temperature. The chloro, bromo, thiocyanate and nitrato complexes are nonelectrolytes (Table 1) in nitrobenzene, while

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TABLE 1

Analytical, conductivity and molecular weight data for thorium(IV) compounds of ECAPO

Compound	Th (%)		N (%)		Anion (%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$Th(ClO_4)_4 \cdot 3ECAPO$	19.50	19.72	7.32	7.14	31.20	33.84
$Th(NO_3)_4 \cdot 2ECAPO$	27.21	27.48	13.42	13.27		
$ThCl_4 \cdot 2ECAPO$	31.90	31.43	7.72	7.58	18.32	19.24
$ThBr_4 \cdot 2ECAPO$	25.06	25.32	6.32	6.11	32.72	34.93
$ThI_4 \cdot 3ECAPO$	18.40	18.04	6.72	6.53	37.20	39.50
$Th(NCS)_4 \cdot 2ECAPO$	28.48	28.01	13.76	13.52	27.21	28.01

the iodo and perchlorato complexes dissociate in this solvent. The iodo complex behaves as a 1 : 2 electrolyte, while the perchlorato complex is 1 : 4. The molecular weights in freezing nitrobenzene also support the similar electrolytic behaviour of the complexes.

Infrared

The IR spectra of ECAPO and its complexes have been recorded in the 4000–200 cm^{-1} region. Katritzky and Hands [10] have examined the IR spectra of a large number of 2-substituted pyridine *N*-oxides. Partial use of their assignments as well as the reports of others [11–14] is made for the assignment of the IR bands of the ligand and its thorium(IV) complexes. The pertinent IR data are given in Table 2. The N–O stretching frequency, observed as a strong band at 1220 cm^{-1} in the free ligand [6,15], is shifted towards a lower frequency in the complexes due to coordination of oxygen

TABLE 2

Partial IR spectral data (cm^{-1}) of thorium(IV) compounds of ECAPO

Compound	ν(N–O)	δ(N–O)	ν(C=O)	ν(M–O)
ECAPO	1220s	840m	1730s	
$Th(ClO_4)_4 \cdot 3ECAPO$	1160s	830m	1670s	390m
$Th(NO_3)_4 \cdot 2ECAPO$	1150s	832m	1665s	380m
$ThCl_4 \cdot 2ECAPO$	1160s	835m	1670s	380m
$ThBr_4 \cdot 2ECAPO$	1155s	830m	1665s	372m
$ThI_4 \cdot 3ECAPO$	1160s	835m	1660s	370m
$Th(NCS)_4 \cdot 2ECAPO$	1165s	830m	1665s	380m

Λ_{m} (ohm^{-1} cm^2 mole^{-1})	Electrolytic nature	Average M.W. in $PhNO_2$	Formula weight
98.4	1 : 4	240	1176
4.6	Non-electrolyte	820	844
3.9	Non-electrolyte	732	738
4.7	Non-electrolyte	903	916
56.4	1 : 2	405	1286
4.8	Non-electrolyte	810	828

to the metal ion [1–5]. The N–O bending in the free ligand, observed in the 840 cm^{-1} region [1–5], exhibits small shifts in the spectra of the complexes as expected. The N–H stretching frequencies occur at 3200 and 3120 cm^{-1} in the free ligand, and there is no change in these frequencies after complexation. This observation precludes the possibility of coordination through the imino nitrogen atom. The carbonyl stretching band of the COOEt moiety occurs at 1730 cm^{-1} and is shifted to lower wave number after complexation. This suggests that coordination occurs through carbonyl oxygen atom [16]. Absorptions associated with CH out-of-plane deformation modes, as expected, undergo a slight positive shift due to tightening of the aromatic ring on complexation [1,3]. The overall IR spectral evidence suggests that ECAPO acts as a bidentate ligand and coordinates through *N*-oxygen and carbonyl oxygen atoms forming a seven-membered chelate ring. The bands observed in the 400–300 cm^{-1} region are assigned as ν(M–O) [1,17,18].

In the perchlorato complex, the two strong bands at 1080 cm^{-1} (ν_3) and 620 cm^{-1} (ν_4) for perchlorate ions, indicate that tetrahedral symmetry has not been disturbed and all the perchlorate ions are not bonded to the thorium ion [1,17,18]. The absence of the ν_3 band of ionic nitrate (D_{3h}) around 1360 cm^{-1} and presence of two strong bands at 1520 and 1290 cm^{-1} in the spectrum of $Th(NO_3)_4 \cdot 2ECAPO$ suggest the covalent nature of nitrate ions in this complex [19,20]. The bidentate nature of nitrato groups has been established by comparing the spectral bands of $Th(NO_3) \cdot 2ECAPO$ with those of $Th(NO_3)_4 \cdot 5H_2O$ [21] where the bidentate character of the nitrato groups has been established by X-ray analysis [22]. In $Th(NO_3) \cdot$ 2ECAPO, the nitrato vibrations occur at 1520 (ν_1), 1290 (ν_4), 1040 (ν_2), 820 (ν_6), 760 (ν_3), and 700 (ν_5), while in $Th(NO_3)_4 \cdot 5H_2O$, the corresponding bands occur at 1520, 1290, 1030, 808, 745, 715 cm^{-1}, respectively. In thiocyanato complex, the observed frequencies at 2055 (ν C≡N), 840 (ν CS) and 465 cm^{-1} (δ NCS) are due to the *N*-bonded isothiocyanato group [4,23].

TABLE 3

Thermal data on thorium(IV) compounds of ECAPO

Compound	Decomp. temp. (°C)		Decomp. product	Wt. loss (%)		DTG peak
	Initial	Final		Found	Calcd.	
$Th(ClO_4)_4 \cdot 3ECAPO$	175	320	ThO_2	75.27	77.55	exo
$Th(NO_3)_4 \cdot 2ECAPO$	190	340	$Th(NO_3)_4$	42.22	43.12	endo
	390	510	ThO_2	67.12	68.72	exo
$ThCl_4 \cdot 2ECAPO$	185	345	$ThCl_4$	48.52	49.32	endo
	400	490	$ThOCl_2$ [a]	52.10	56.77	endo
$ThBr_4 \cdot 2ECAPO$	180	350	$ThBr_4$	38.71	39.73	endo
	410	480	$ThOBr_2$ [a]	51.06	55.45	endo
$Th(NCS)_4 \cdot 2ECAPO$	170	340	$Th(NCS)_4$	42.39	43.96	endo
	350	490	$ThO(NCS)_2$ [a]	52.92	56.03	endo

[a] Mixed with ThO_2.

The ν(Th–Cl) vibration has been assigned at ca. 250 cm^{-1} [2,24]. ν(Th–Br) and ν(Th–I) could not be assigned because they are out of the region studied here.

In conclusion, the coordination number of Th(IV) in these complexes varies from six to twelve depending on the nature of the anions.

Thermal studies

The Thermal investigations of thorium(IV) complexes with aromatic amine *N*-oxides have been carried out to a limited extent. Patel and coworkers have reported thorium (IV) perchlorato complexes of pyridine *N*-oxide [25] and quinoline *N*-oxide [26] by DTA. Agarwal et. al. [1–4,27] have reported thermal results on various thorium(IV) complexes of amine *N*-oxides. In the present work, the thermal decomposition characteristics of thorium(IV) complexes of ECAPO are reported. The results of the thermal analyses are presented in Table 3.

The TG and DTG curves of the present complexes do not show the presence of water molecules either in or out of the coordination sphere. The DTG curve of the perchlorato complex reveals only one exothermic peak at ca. 180°C. At this temperature, the complex explodes with a considerable amount of smoke due to the oxygen content of the perchlorate [25]. This behaviour is similar to other complexes of thorium(IV) with lutidine*N*-oxide [27] and 4-amino antipyrine [28]. The pyrolysis curve behaves similarly and shows that decomposition of the complex has started at 175°C and continues up to 320°C, after which the curve analysis indicates the formation of ThO_2. No stable intermediate perchlorate–ECAPO complexes have been obtained during the pyrolysis. The TG analysis of the nitrato complex shows that the complex is quite stable upto 190°C, beyond which decomposition starts and continues upto 340°C (endo peak at 200°C). Analysis of the thermogram indicates that both the ligand molecules have been lost at this stage. Finally, ThO_2 is obtained as the residual mass at 510°C. The decomposition of chloro, bromo and thiocyanato complexes are completed in two steps. In the first step, the complexes lose all the ligand molecules as shown by the break in the TG curve and the peak in the DTG curves. The final product is a mixture of oxohalide and oxide. TG or DTG studies of the iodo complex could not be carried out as this complex decomposes slowly at room temperature with evolution of iodine vapour.

Thus the thermograms of the complexes show the decomposition scheme (X = Cl, Br or NCS)

$$Th(ClO_4)_4 \cdot 3\ ECAPO \rightarrow ThO_2$$

$$Th(NO_3)_4 \cdot 2\ ECAPO \rightarrow Th(NO_3)_4 \rightarrow ThO_2$$

$$ThX_4 \cdot 2\ ECAPO \rightarrow ThX_4 \rightarrow ThOX_2 \text{ (mixed with } ThO_2\text{)}$$

In conclusion, if the minimum TG decomposition temperature is taken as a rough criterion of thermal stability, then the order of stability falls in the order $NO_3 > Cl > Br > ClO_4 > NCS$.

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