Thermochimica Acta, 63 (1983) 363–368
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

INFRARED AND THERMAL DECOMPOSITION OF PYRIDINE *N*-OXIDE AND SUBSTITUTED PYRIDINE *N*-OXIDE COMPLEXES OF THORIUM(IV) HALIDES

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(Received 20 September 1982)

A number of workers [1–11] have investigated the coordinating ability of thorium(IV) salts with different amine *N*-oxides. Halogens are common ligands in coordination chemistry, readily forming coordinate bonds with metals. However, comparatively less is known about thorium(IV) halide complexes of the N–O donor system. Therefore, this note describes the preparation, IR spectra and the thermal decomposition characteristics of the coordination compounds formed by the interaction of thorium(IV) halides with pyridine *N*-oxide, 2-methyl-, 3-methyl-, and 4-methyl pyridine *N*-oxides.

EXPERIMENTAL

All chemicals used were of analytical grade. Various thorium(IV) salts were synthesized using methods given in the literature [12]. The ligand pyridine *N*-oxide was prepared by oxidation of pyridine using the method of Ochiai [13], while 2-, 3- and 4-methyl pyridine *N*-oxides were obtained from Aldrich Chemical Company.

Preparation of the complexes

The thorium salt was dissolved in absolute ethanol and a dehydrating agent (2-2′-dimethoxy propane), and the reaction mixture was warmed on a water bath with constant stirring. A warm ethanolic solution of the ligand was added dropwise; some compounds were precipitated after cooling while others precipitated upon addition of anhydrous diethyl ether. The compounds so formed were filtered, washed with ethanol and finally with ether, and dried in vacuo over P_4O_{10}.

0040-6031/83/$03.00

TABLE 1

Analytical and IR spectral (cm^{-1}) data of Th(IV) complexes of amine *N*-oxides

Complex	Analysis						IR absorption frequencies (cm^{-1})		
	Th		Malide		N		ν(N–O)	δ(N–O)	ν(Th–O)
	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)	Found (%)	Calcd. (%)			
$[Th(PyO)_2Cl_4]$	40.82	41.13	24.91	25.17	4.71	4.96	1200s, 1190m	845m, 830sh	395m
$[Th(PyO)_2Br_4]$	30.86	31.26	42.61	43.12	3.49	3.77	1205s, 1192m	840m, 830w	392m
$[Th(PyO)_4I_2]I_2$	20.16	20.71	44.21	45.35	5.20	5.00	1215m, 1190m	845m, 835sh	390m
$[Th(2MePyO)_2Cl_4]$	38.79	39.18	23.41	23.98	4.65	4.72	1195s, 1185m	820m	390m
$[Th(2MePyO)_2Br_4]$	29.89	30.12	40.27	41.55	3.51	3.63	1198s, 1190m	830m	385m
$[Th(2MePyO)_4I_2]I_2$	19.18	19.72	42.14	43.19	4.65	4.76	1200m, 1190m	825sh	382w
$[Th(3MePyO)_2Cl_4]$	38.90	39.18	23.21	23.98	4.59	4.72	1210s, 1195m	835m, 825sh	390m
$[Th(3MePyO)_2Br_4]$	28.71	30.12	40.19	41.55	3.49	3.63	1215s, 1198m	830m	385m
$[Th(3MePyO)_4I_2]I_2$	19.21	19.72	42.12	43.19	4.29	4.76	1220m, 1190m	835m	382w
$[Th(4MePyO)_2Cl_4]$	38.61	39.18	23.29	23.98	4.63	4.72	1180s, 1170m	830m	385m
$[Th(4MePyO)_2Br_4]$	28.52	30.12	40.21	41.55	3.59	3.63	1182s, 1172m	825m	575m
$[Th(4MePyO)_4I_2]I_2$	19.32	19.72	41.92	43.19	4.69	4.76	1190m, 1180m	835sh	370w

Physical measurements and analyses

The molar conductances of the compounds in nitrobenzene were determined using a Toshniwal conductivity bridge with cell type CL 01/02. The IR spectra (4000–650 cm^{-1}) in KBr pellets and far IR spectra (650–200 cm^{-1}) in Nujol mulls were recorded on Perkin-Elmer 621 and Beckman IR-12 spectrophotometers, respectively. Halide contents were estimated by Volhard's method. Thorium metal was estimated as the oxide in all the compounds. The DTA's were carried out in air using a DTA-02 Universal (DDR) DT analyzer with a heating rate of 10°C min^{-1}. TG was carried out on a Cahn RG-electrobalance with a linear heating rate of 6°C min^{-1} in static air.

RESULTS AND DISCUSSION

Analytical data recorded in Table 1 indicate that the interaction of Th(IV) halide with amine *N*-oxides results in the formation of complexes of the type $ThX_4 \cdot 2$ L (X = Cl, Br; L = ligand) and $ThI_4 \cdot 4$ L. All the complexes are non-hygroscopic and stable, and can be stored for a longer period, except the iodide complexes which decompose slowly at room temperature, giving off iodine vapours. The complexes are partially soluble in common organic solvents.

Due to the partial solubility of the complexes in nitrobenzene or benzene, the conductivity results are not absolutely correct. However, the conductivities of the filtrates of the solutions (in nitrobenzene) of chloro and bromo complexes were measured and the values were too low to account for any dissociation of these complexes in solution. Further, the aqueous extracts of these complexes fail to give any turbidity or precipitate with silver nitrate. On the basis of these observations and previous results, we conclude that chloro and bromo complexes are non-electrolytes. In the case of iodo complexes, the conductance values indicate that these complexes dissociate in solution and probably behave as 1 : 2 electrolytes.

INFRARED SPECTRA

Infrared absorption frequencies of diagnostic value, namely, NO stretching, NO bending and CH out-of-plane bending modes, which are reported to be affected on complexation [14], are briefly discussed. In the spectra of the aromatic amine *N*-oxides examined a very strong absorption intensity in the range 1265–1228 cm^{-1} has been assigned to the NO stretching vibration mode [9], which undergoes a significant negative shift on complexation. The decrease in the frequency of the NO stretching vibration is attributed to a change in the nature of the nitrogen–oxygen bond as a result of oxygen–metal coordination [14–16]. An absorption of strong intensity in the 900–800 cm^{-1} range has been assigned to the NO bending mode [17], and from the tabulated data it is apparent that only a slight shift of this vibration is observed on complexation which is in agreement with the earlier observations of Quagliano et al. [15,16].

Absorptions associated with CH out-of-plane deformation modes are supposed to undergo a slight positive shift due to tightening of the aromatic ring on complexation. A positive shift of ca. 25–20 cm^{-1} has been observed in this mode of vibration, which is in agreement with the observations of earlier workers [15,16]. If the magnitude of the frequency shift on coordination is any indication of the acceptor strength, then on the basis of shifting in the N–O stretching frequency, the following order emerges: $ThCl_4 > ThBr_4 > ThI_4$.

In the far IR region there is a characteristic medium band in the 400–350 cm^{-1} range which is assigned to the Th–O stretching mode on the basis of reports on amine *N*-oxide complexes of thorium [3,6–10]. The ν(Th–Cl) vibration has been assigned at ca. 250 cm^{-1} [7,8]; ν(Th–Br) and ν(Th–I) could not be assigned because they do not fall within the present range of study. The thorium(IV) atom in these complexes is hexa-coordinated and the

TABLE 2

Thermal decomposition data for Th(IV) complexes of aromatic amine *N*-oxides

Complex	Decompn. temp. (°C)		Decompn. product	TG wt. loss		DTG temp. (°C)
	Initial	Final		Found (%)	Calcd. (%)	
$Th(PyO)_2Cl_4$	190	240	$Th(PyO)Cl_4$	17.23	16.84	290 endo
	250	310	$ThCl_4$	32.20	33.68	410 exo
	350	435	$ThOCl_2$	41.19	43.43	
$Th(PyO)_2Br_4$	180	230	$Th(PyO)Br_4$	12.09	12.80	280 endo
	240	310	$ThBr_4$	24.41	25.60	405 exo
	360	430	$ThOBr_2$	43.17	45.01	
$Th(2MePyO)_2Cl_4$	210	240	$Th(2MePyO)Cl_4$	17.91	18.41	310 endo
	250	320	$ThCl_4$	35.81	36.82	405 exo
	360	420	$ThOCl_2$	43.71	46.11	
$Th(3MePyO)_2Br_4$	205	240	$Th(3MePyO)Br_4$	13.21	14.15	295 endo
	250	310	$ThBr_4$	26.89	28.31	415 exo
	330	430	$ThOBr_2$	43.93	47.01	
$Th(4MePyO)_2Cl_4$	210	240	$Th(4MePyO)Cl_4$	17.26	18.41	295 endo
	240	310	$ThCl_4$	34.91	36.82	425 exo
	340	435	$ThOCl_2$	44.71	46.11	

N=O stretching frequency invariably shows a splitting on complexation, which may be taken as an indication that the ligand molecules occupy *cis*-position in the complexes possessing octahedral symmetry.

THERMAL STUDIES

Thermal investigations of thorium(IV) complexes with some aromatic amine *N*-oxides have already been undertaken by Ramamurthy and Patel [1] and Krishnan and Patel [2] and Agarwal et al. [6–9,19]. In the present work thermal studies with regard to thorium(IV) halide complexes of amine *N*-oxides and their intermediates are reported.

The results of thermal analyses are summarized in Table 2. All the complexes are non-hygroscopic in nature and decompose in three steps which may be shown by

$$Th(L)_2X_4 \rightarrow Th(L)X_4 \rightarrow ThX_4 \rightarrow ThOX_2$$

These changes in the DTG curves are apparent by two peaks; first the endo peak, which indicates the loss of ligand at this temperature, and finally the exo peak which is due to metal oxidation. In general, chloro complexes are more thermally stable than bromo complexes.

ACKNOWLEDGEMENT

The authors are grateful to Dr. A.K. Srivastava, Meerut College, for his keen interest in the work.

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