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INFRARED AND THERMAL INVESTIGATIONS OF THORIUM(IV) COMPLEXES OF 4-CYANOPYRIDINE *N*-OXIDE

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ABSTRACT

Thorium(IV) complexes of 4-cyanopyridine *N*-oxide (cypyo) of the general composition $ThX_4 \cdot 2cypyo$ (X=Cl, Br, NCS or NO_3), $ThI_4 \cdot 4cypyo$ and $Th(ClO_4)_4 \cdot 6cypyo$ have been synthesised and examined spectroscopically in the solid state and the possible coordination arrangement around the metal atom has been discussed. Thermal studies of some of the representative complexes have also been investigated.

INTRODUCTION

Several investigations have appeared on the infrared spectra and thermal behaviour of the coordination compounds synthesised by thorium(IV) with pyridine *N*-oxide and its ring-substituted derivatives [1–13]. Comparatively less is known about the donor properties of 4-cyanopyridine *N*-oxide with different metal salts [14–16]. We now describe the preparation, IR spectra and thermal behaviour of the coordination compounds formed by the interaction of thorium(IV) salts with 4-cyanopyridine *N*-oxide.

EXPERIMENTAL

Thorium(IV) nitrate (BDH) was used as supplied. Haldies and perchlorate salts were prepared by the reported methods [17,18]. The ligand 4-cyanopyridine *N*-oxide was obtained from Reilly Tar and Chemical Corporation.

The metal complexes were prepared by the following general method. The thorium(IV) salt was dissolved in absolute ethanol and a dehydrating agent (2,2′-dimethoxypropane) and the mixture was warmed on a water bath with

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constant stirring. A warm ethanolic solution of ligand was added dropwise. All the complexes were precipitated after cooling the reaction mixture. The new complexes were filtered, washed with ethanol and finally with ether and dried in vacuo over P_4O_{10}.

The IR, TG and DTA analyses of the complexes were made as reported previously [8].

RESULTS AND DISCUSSION

The stoichiometries of the newly synthesised complexes have been established by elemental analysis. Apart from the iodo complex, all other complexes are white solids; the iodo complex is yellow due to the liberation of iodine.

The IR spectra of 4-cyanopyridine *N*-oxide and its complexes have been recorded in the 4000–200 cm^{-1} region. Shindo [19,20] and Quagliano et al. [21,22] have examined the IR spectra of pyridine *N*-oxide and a number of its derivatives. Their assignments, as well as previous reports [8,9,16], are partially used for the assignment of the IR bands of the ligand and its thorium(IV) complexes. The pertinent IR data are given in Table 1. The N–O stretching vibration appears as a strong band at 1265 cm^{-1} in the free ligand, and suffers a significant negative shift in all the complexes due to coordination of oxygen to the metal ion [23]. Moreover, this shift is of the

TABLE 1

Analytical and partial infrared data (cm^{-1}) of thorium(IV) complexes of 4-cyanopyridine *N*-oxide

Compound	Colour	Metal % found (calcd.)	Nitrogen % found (calcd.)	Carbon % found (calcd.)	Hydrogen % found (calcd.)	Anion % found (calcd.)	ν(N–O)	ν(Th–O)
Cypyo	–	–	–	–	–	–	1265s	–
$ThCl_4\cdot$ 2cypyo	White	37.30 (37.90)	8.68 (9.15)	23.26 (23.52)	1.18 (1.30)	23.42 (23.20)	1210s	410m
$ThBr_4\cdot$ 2cypyo	White	29.62 (29.29)	6.92 (7.07)	17.86 (18.18)	1.20 (1.01)	41.32 (40.40)	1215s	405m
$ThI_4\cdot$ 4cypyo	Yellow	18.60 (19.01)	8.82 (9.18)	23.42 (23.60)	1.20 (1.31)	41.20 (41.63)	1220s	400m
$Th(NCS)_4\cdot$ 2cypyo	White	32.42 (32.95)	15.60 (15.90)	27.10 (27.27)	1.20 (1.13)	31.86 (32.95)	1210s	402m
$Th(NO_3)_4\cdot$ 2cypyo	White	31.96 (32.22)	15.26 (15.55)	19.86 (20.00)	1.19 (1.11)	– –	1205s	405m
$Th(ClO_4)_4\cdot$ 6cypyo	White	17.52 (17.18)	12.11 (12.44)	32.25 (32.00)	1.65 (1.77)	29.13 (29.48)	1220s	395m

order of magnitude expected for complexes in which pyridine *N*-oxide and negatively charged ligands (halogen, NO_3, etc.) constitute the first coordination sphere around the metal ion [21,22]. The N–O bending vibration of the ligand assigned as a strong band at ca. 840 cm^{-1} [8,9] suffers only a small shift in the thorium(IV) complexes studied, which is in agreement with the earlier observations of Quagliano et al. [21,22]. Absorptions associated with C–H out-of-plane deformations assigned at 775 cm^{-1} are supposed to undergo a slight positive shift due to the tightening of the aromatic ring on complexation. A positive shift of ca. 15 cm^{-1} has been observed in this mode of vibration which is in conformity with the observations of earlier workers [21,22]. The bands observed in the ca. 400 cm^{-1} region are assigned as ν(Th–O) [3,8,9].

Infrared spectra of the thorium(IV) nitrate complex studied in the present investigations show the absence of ionic nitrate groups. This is evident from the fact that the ν_3 band of ionic nitrates at ca 1360 cm^{-1} is split into 1520 cm^{-1} (ν_1) and 1290 cm^{-1} (ν_4) in $Th(NO_3)_4 \cdot$2cypyo complex. The nitrate groups seem to be bidentate in this complex, since the IR frequencies due to this group occur in almost the same frequency ranges as in $Th(NO_3)_4 \cdot 5H_2O$ [24], where the bidentate character of the nitrate groups has been established by X-ray analysis [25]. In $Th(NO_3)_4 \cdot$2cypyo the nitrato vibrations occur at 1520 (ν_1), 1290 (ν_4), 1045 (ν_2), 830 (ν_6) and 740 cm^{-1} (ν_3/ν_5), while in $Th(NO_3)_4 \cdot 5H_2O$ the corresponding bands occur at 1520, 1290, 1030, 808, 745 and 715 cm^{-1}, respectively. In the perchlorato complex, the ν_3 and ν_4 bands for the perchlorate ion appear at ca. 1085 and ca. 620 cm^{-1}, respectively, indicating that the tetrahedral symmetry of ClO_4 is maintained and the ClO_4 ions are not bonded to the metal ions [26,27].

The C–N stretching frequency in the thorium(IV) thiocyanate complex appears at 2055 cm^{-1}. This C–N frequency range lies on the borderline for distinguishing between sulphur and nitrogen bonding in the thiocyanate [28]; although the high relative intensity of the band suggests that the thiocyanate groups are nitrogen bonded [29,30]. The ν(C–S) frequency observed at ca. 780 cm^{-1} and δ(NCS) at 480 cm^{-1} further confirm the nitrogen bonding to the metal atom [31]. The ν(Th–Cl) vibration has been assigned at ca. 250 cm^{-1}. ν(Th–Br) and ν(Th–I) could not be assigned because they are out of the region studied here.

Thermal studies

Agarwal et al. [7–12] have reported the thermal results on various thorium(IV) complexes of amine *N*-oxides. The results of the thermal analysis are summarised in Table 2.

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 chloro, bromo, thiocyanato and nitrato complexes decompose endothermi-

TABLE 2

Thermal decomposition data for Th(IV) complexes of 4-cyanopyridine *N*-oxide in air

Complex	Decomp. temp. (°C)		Decomp. product	TG weight loss		DTG temp. (°C) and peak
	Initial	Final		Found (%)	Calcd. (%)	
$Th(cypyo)_2Cl_4$	190	235	$Th(cypyo)Cl_4$	29.83	28.61	290 endo
	250	390	$ThCl_4$	47.32	45.95	450 exo
	410	490	$ThOCl_2$	55.82	53.90	
$Th(cypyo)_2Br_4$	180	220	$Th(cypyo)Br_4$	17.32	15.15	225 endo
	240	380	$ThBr_4$	32.36	30.30	430 exo
	410	490	$ThOBr_2$	51.62	48.48	
$Th(cypyo)_2(NO_3)_4$	205	235	$Th(cypyo)(NO_3)_4$	18.23	16.66	280 endo
	270	430	$Th(NO_3)_4$	35.92	33.33	470 exo
	480	530	ThO_2	65.26	63.33	
$Th(cypyo)_2(NCS)_4$	180	225	$Th(cypyo)(NCS)_4$	19.32	17.04	310 exo
	245	380	$Th(NCS)_4$	37.42	34.09	450 exo
	420	450	$ThO(NCS)_2$	51.61	48.29	
$Th(cypyo)_2(ClO_4)_4$	200	450	ThO_2	78.32	80.44	390 exo

cally while the perchlorate complex decomposes exothermically with slight explosion and evolution of smoke [32]. Apart from the perchlorate complex, all other complexes have two peaks: one endo and other exo; the exo peak at higher temperature is due to complete metal oxidation. TG curves show that halide and nitrato complexes complete their decomposition process in three steps. In the first step, only one ligand molecule is lost, in the second step remaining ligand molecule is lost. Finally in the 450–530°C temperature range, metal oxide is formed. In the case of the perchlorate complex, only one break in the TG curve indicates that no stable intermediate product is formed.

In conclusion, if the minimum TG decomposition temperature is taken as a rough criterion of thermal stability, then the order of stability of the Th(IV) complexes is: $NO_3 > ClO_4 > Cl > Br \approx NCS$.

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