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PREPARATION, AND INFRARED AND THERMAL PROPERTIES OF SIX ADDUCTS OF TETRAKIS-(8-HYDROXYQUINOLINATO)THORIUM(IV)

S. Z. Haider, K. M. A. Malik, A. Rahman and *T. Wadsten**

DEPARTMENT OF CHEMISTRY, DHAKA UNIVERSITY, DHAKA-2, BANGLADESH
*ARRHENIUS LABORATORY, DEPARTMENT OF INORGANIC CHEMISTRY,
STOCKHOLM UNIVERSITY, S-106 91 STOCKHOLM, SWEDEN

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Six adducts of the tetrakis(8-hydroxyquinolinato) complex of thorium(IV) with 8-hydroxyquinoline, pyridine, urea, dimethylsulphoxide, dimethylformamide and 1,10-phenanthroline were prepared and characterized, the infrared bands for the room-temperature forms are given and their particular thermal properties are reported. The thermal analyses were performed mostly in the presence of air, but in some cases an argon atmosphere was used for comparison. The adducts were lost from the principal complex at temperatures varying between 110 and 290°. Intermediate oxygenated complexes were formed in each case at about 400°. The thermal data suggest the standardization of a procedure for the formation of $Th(C_9H_6NO)_4$.

The orange-red precipitate formed by thorium(IV) with 8-hydroxyquinoline has been found to be non-stoichiometric [1, 2], mainly due to the formation of adducts with various chemical species present in the medium. In particular, the nature of the linkage of an extra molecule of 8-hydroxyquinoline to the normal tetrakis chelate of thorium, $Th(C_9H_6NO)_4$, has been of interest and the suggestion that one molecule of C_9H_7NO is present as an adduct appears to be conclusive. The adduct molecule has been reported to be removed at temperatures varying from 130° to 300° [3–9], resulting in formation of the tetrakis complex. Moeller and Ramaniah [3] reported the absorption spectrum of the 1 : 5 complex which is actually an adduct and that conversion to a 1 : 4 variety could be achieved by drying at 120–135° for several hours. Corosin et al. [10] reported the i.r. spectrum of the 1 : 5 complex and suggested that the adduct C_9H_7NO molecule is directly coordinated to the thorium through the phenolate oxygen, but the manner in which the proton is hydrogen-bonded could not be clearly established. These workers [10] also used tracer [14] C-8-hydroxyquinoline to determine whether the extra molecule in $Th(C_9H_6NO)_4(C_9H_7NO)$ is a unidentate ligand or a lattice component. It was suggested that the extra molecule may be a coordinated ligand.

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It is assumed that the normal chelate $Th(C_9H_6NO)_4$ is coordinatively unsaturated and hence it can form adducts with suitable Lewis bases such as ammonia, pyridine, urea, water, phenanthroline, sulphoxides, etc. In fact, some of these adducts have been reported [11], but in rather a desultory manner and the nature of the bonding has not been established. Thorium seems to prefer a coordination number of nine in most complexes and this phenomenon appears to have an important bearing on the formation of adducts by chelate complexes such as $Th(C_9H_6NO)_4$.

In the present work the preparation of six adducts of $Th(C_9H_6NO)_4$ is described; these adducts have been characterized by elemental analyses, infrared spectra and thermogravimetric studies. The main objective was to elucidate the nature of the bonding of the additional adduct molecule and thermal analysis techniques have been found to be very useful.

Preparation of the adducts

Most of the following adducts of tetrakis(8-hydroxyquinolinato)thorium(IV) were prepared by simple and straightforward methods, indicating the ease of formation of adducts. Some selected i.r. bands are listed for each compound.

1. Tetrakis(8-hydroxyquinolinato)(8-hydroxyquinoline)thorium(IV) (hydrate), $Th(C_9H_6NO)_4(C_9H_7NO)\cdot(H_2O)$, designated as $Th(OX)_4(HOX)\cdot(H_2O)$. This was prepared by a method similar to that of Moeller et al. [3], with some modifications, starting from thorium nitrate (1.9 g) in 1200 ml water and adding 300 ml 2.5% 8-hydroxyquinoline in acetic acid, followed by the addition of urea (60 g). The mixture was heated on a water-bath and allowed to stand overnight. The precipitate was collected by filtration with suction, washed with water and dried at 85°.

Anal.: Found: Th 23.90, C 55.20, H 3.40, N 7.32.

Calcd. for $Th(C_9H_6NO)_4(C_9H_7NO)\cdot(H_2O)$: Th 24.30, C 55.96, H 3.59, N 7.21.

I.r. bands 482(s), 504(s), 600(m) 728(vs), 1106(vs), 1320(vs), 1338(s), 1635(sh), 3350(wb).

2. Tetrakis(8-hydroxyquinolinato) (pyridine)thorium(IV), designated as $Th(OX)_4(PY)$. This was prepared from $Th(OX)_4(HOX)\cdot(H_2O)$ when 0.7 g was dissolved in warm pyridine (30 ml). The solution, after filtration and treatment with hexane, yielded a greenish-yellow product which was separated by filtration and dried in a desiccator over phosphorus pentoxide.

Anal.: Found: Th 26.7, C 55.50, H 3.39, N 8.03.

Calcd. for $Th(C_9H_6NO)_4(C_5H_5N)$: Th 26.15, C 55.47, H 3.29, N 7.90.

I.r. bands: 482(s), 505(s), 602(m), 728(vs), 1107(vs), 1319(vs), 1600(s).

Table 1

Specimen	Steps involved	Temperature range, °C	Residue observed, %	Residue calculated, %	Remarks
$Th(OX)_4(HOX)(H_2O)$ (air) Fig. 1	I	140–180 (endo)	87.0	84.0	Adducts H_2O and C_9H_7NO lost. The product left is $Th(OX)_4$.
	II	390 (exo)	56.8	56.3	Intermediate $ThO(OX)_2$ formed.
	III	500 (exo)	29.0	28.0	The residue is ThO_2.
$Th(OX)_4(Py)$ (air) Fig. 2	I	630–840 2 J/g (endo)	90.0	91.0	Loss of pyridine involves two distinct processes giving $Th(OX)_4$.
	II	400 (exo)	60.1	60.4	Intermediate $ThO(OX)_2$ formed.
	III	430 (exo)	36.0	35.9	Intermediate $Th_3O_5(OX)_2$ formed.
	IV	500 (exo)	30.0	29.8	Residue ThO_2 formed.
$Th(OX)_4(Urea)$ (air) Fig. 3	I	225–235 122 J/g (endo)	91.0	93.0	Urea exerts vapour pressure starting below 100 °C and is lost giving $Th(OX)_4$.
	II	410 (exo)	70.0	71.5	Intermediate is $ThO(OX)_2$ stable.
	III	450 (exo)	59.0	60.0	Unstable intermediate $Th_3O_2(OX)_8$.
	IV	500 (exo)	30.0	30.2	The residue is ThO_2.
$Th(OX)_4(DMSO)(H_2O)$ (air) Fig. 4a	I	180–220 294 J/g (exo)	89.0	89.4	H_2O and DMSO are lost in several processes producing $Th(OX)_4$.
	II	400 42 J/g (exo) 29 J/g (endo)	61.5	59.3	The intermediate $ThO(OX)_2$ may be formed but the decomposition pathways are rather complex involving both endothermic and exothermic steps.
	III	600 (exo)	29.0	29.2	The formation of residue ThO_2 involves a continuous decomposition of the intermediate with several processes.

Table 1 *continued*

Specimen	Steps involved	Temperature range, °C	Residue observed, %	Residue calculated, %	Remarks
$Th(OX)_4(DMSO)(H_2O)$ (Argon)	I	180–220	89.5	89.4	$Th(OX)_4$ formed as in air. DMSO and H_2O are lost.
Fig. 4b	II	600	44.0	—	No intermediate formed. The solid end product is a black mass, brittle and might contain carbon.
$Th(OXN)_4(DMF)$ (air) Fig. 5	I	220–220 84 J/g (endo)	90.0	91.7	Dimethyl formamide ($HCON(CH_3)_2$) is lost giving $Th(OX)_4$.
	II	400 (exo)	80.0	81.4	Intermediate $Th_3O(OX)_{10}$ is formed.
	III	600 (exo)	29.9	29.9	The end product is ThO_2.
$Th(OX)_4(Phen)(H_2O)_2$	I	110–200 (endo)	95.8	96.5	Two water molecules goes.
(air) Fig. 6a	II	220–270 (endo)	80.0	78.9	(Phen) is lost and $Th(OX)_4$ is remaining. Indication of an unstable intermediate between 420–450 °C.
	III	300–400 (exo)	65.0	65.8	Intermediate $Th_2O(OX)_6$ is formed.
	IV	400–550 (exo)	26.5	25.8	ThO_2 is the residue.
$Th(OX)_4(Phen)(H_2O)_2$	I	110–200	96.2	96.5	Two water molecules goes.
(Argon) Fig. 6b	II	220–270	80.0	78.9	(Phen) is lost and $Th(OX)_4$ is remaining.
	III	300–500	39.0		Residue of indefinite composition formed.

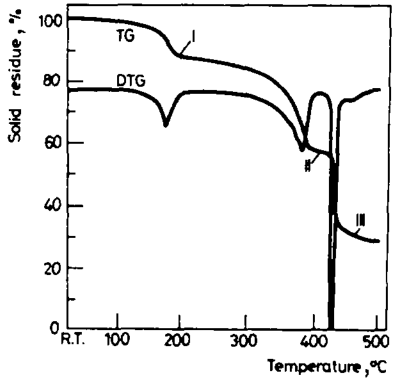

Fig. 1 TG and DTG curves of $Th(C_9H_6NO)_4C_9H_7NO \cdot H_2O$. Sample weight: 2.92 mg; in air atmosphere

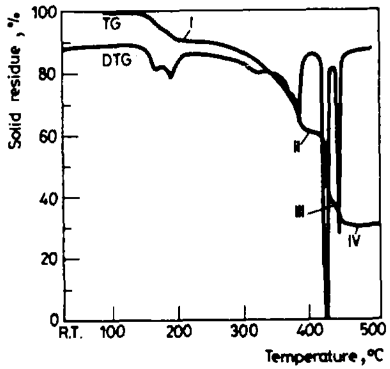

Fig. 2 TG and DTG curves of $Th(C_9H_6NO)_4C_5H_5N$. Sample weight: 3.42 mg, in air atmosphere

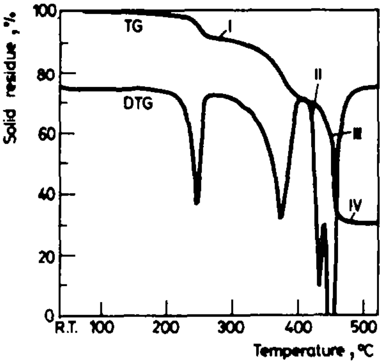

Fig. 3 TG and DTG curves of $Th(C_9H_6NO)_4CON_2H_4$. Sample weight: 3.98 mg; in air atmosphere

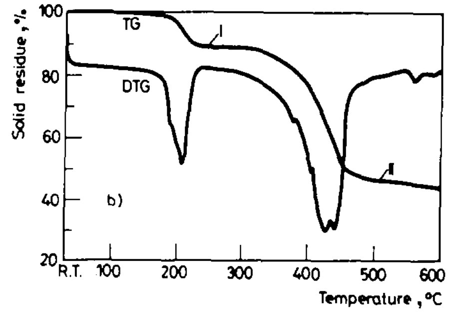

Fig. 4a TG and DTG curves of $Th(C_9H_6NO)_4OS(CH_3)_2 \cdot H_2O$. Sample weight: 2.3 mg; in air atmosphere

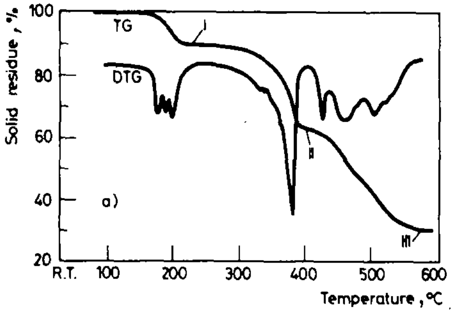

Fig. 4b TG and DTG curves of $Th(C_9H_6NO)_4OS(CH_3)_2 \cdot H_2O$. Sample weight: 3.83 mg; in argon atmosphere

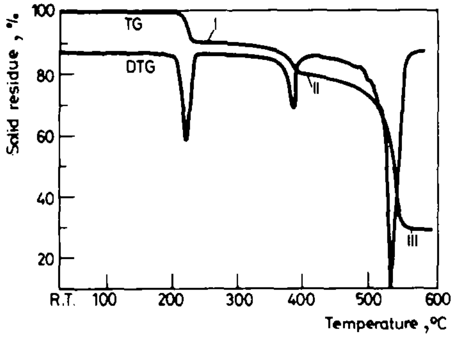

Fig. 5 TG and DTG curves of $Th(C_9H_6NO)_4HCON(CH_3)_2$. Sample weight: 4.20 mg; in air atmosphere

3. Tetrakis(8-hydroxyquinolinato) (urea)thorium(IV), designated as $Th(OX)_4(Urea)$. $Th(OX)_4(HOX) \cdot (H_2O)$ (1.0 g) was suspended in 50 ml methanol in the presence of a large excess of urea. The original orange colour changed to a light greenish-yellow. The precipitate was collected by filtration, washed with methanol and dried at 70°.

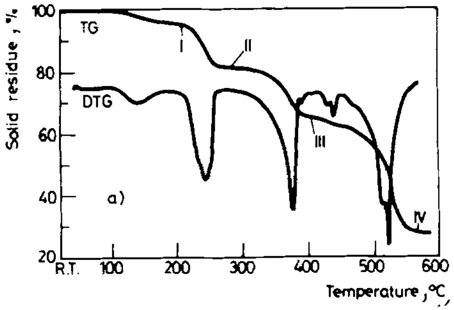

Fig. 6a TG and DTG curves of $Th(C_9H_6NO)_4C_{12}H_8N_2 \cdot 2H_2O$. Sample weight: 3.01 mg; in air atmosphere

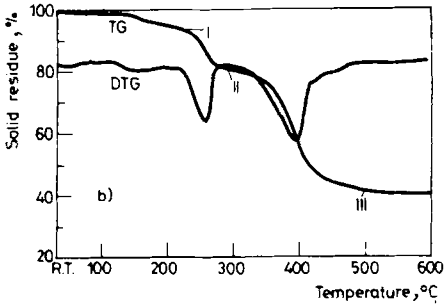

Fig. 6b TG and DTG curves of $Th(C_9H_6NO)_4C_{12}H_8N_2 \cdot 2H_2O$. Sample weight: 1.88 mg; in argon atmosphere

Anal.: Found: Th 27.59, C 49.57, H 3.35, N 9.96.

Calcd. for $Th(C_9H_6NO)_4(CON_2H_4)$: Th 26.71, C 51.15, H 3.22, N 9.67.

I.r. bands: 482(s), 503(s), 602(m), 728(vs), 1108(vs), 1320(vs), 1660(s), 3200–3600(w).

4. Tetrakis(8-hydroxyquinolinato) (dimethylsulphoxide)thorium(IV) (hydrate), designated as $Th(OX)_4(DMSO) \cdot (H_2O)$. $Th(OX)_4(HOX) \cdot (H_2O)$ (1.0 g) was dissolved in 30 ml DMSO and the solution was filtered. On standing, the filtrate yielded light greenish-yellow crystals of $Th(OX)_4(DMSO) \cdot (H_2O)$, which was further recrystallized from dichloromethane and dried over silica gel.

Anal.: Found: Th 26.12, C 49.57, H 3.20, N 5.93.

Calcd. for $Th(C_9H_6NO)_4(OS(CH_3)_2) \cdot (H_2O)$: Th 26.18, C 50.44, H 3.54, N 6.18.

I.r. bands: 485(m), 505(m), 600(w), 725(s), 995(m), 1015(m), 1220(m), 1315(s), 1490(sh), 2700(w), 3400(wb).

5. Tetrakis(8-hydroxyquinolinato) (dimethylformamide)thorium(IV), designated as $Th(OX)_4(DMF)$. $Th(OX)_4(HOX) \cdot (H_2O)$ (1.0 g) was dissolved in 50 ml dimethylformamide (DMF). The solution was filtered and on standing the filtrate yielded light-brown crystals which were collected and dried in a vacuum desiccator over silica gel.

Anal.: Found: Th 26.36, C 52.86, H 3.61, N 8.06.

Calcd. for $Th(C_9H_6NO)_4(HCON(CH_3)_2)$: Th 26.32, C 53.12, H 3.52, N 7.95.

I.r. bands: 485(m), 505(m), 600(w), 645(w), 725(s), 1030(m), 1100(s), 1315(s), 1360(sh), 1630(m).

6. Tetrakis(8-hydroxyquinolinato) (1,10-phenanthroline)thorium(IV) (hydrate), designated as $Th(OX)_4(Phen)(H_2O)_2$. $Th(OX)_4(HOX) \cdot (H_2O)$ (1.0 g) was dissolved in acetone (100 ml) and the solution was stirred with an excess of 1,10-phenanthroline for 1 hour. A light yellow-green crystalline product was separated, washed with acetone and dried in a vacuum desiccator over silica gel.

Anal.: Found: Th 24.16, C 56.93, H 3.25, N 7.91.

Calcd. for $Th(C_9H_6NO)_4(C_{12}H_8N_2)(H_2O)_2$: Th 22.64, C 56.25, H 3.54, N 8.20.

I.r. bands: 485(m), 507(m), 605(m), 732(s), 758(m), 1105(s), 1317(vs), 1491(s), 1600(m), 3380(vw).

Thermal studies

Experimental

Differential scanning calorimeter (DSC) experiments were carried out on a Perkin–Elmer DSC-2 equipped with a Thermal Analysis Data Station (TADS). The thermogravimetric analysis (TG) and recording of the first derivative of the weight loss (DTG) were done simultaneously with a Perkin–Elmer TG 2 instrument under a dynamic gas flow of air or argon at 50 ml/min. The sample sizes were 2–4 mg. A heating rate of 10 deg/min was used throughout the expriments.

Due to the nature of the reactions to be studied, decomposition also involving intermediate oxidation processes, we found it convenient to record and to discuss the reaction steps based on the solid residue formed in the different steps, instead of the weight loss.

As an example of the interpretation of the TG and DTG effects, we can choose $Th(OX)_4(HOX)(H_2O)$ (Fig. 1). There is an indication of a definite vapour pressure starting from just around room temperature and both the adduct water and the 9-hydroxyquinoline molecules are lost within the temperature range 140–180°, $Th(OX)_4$ being formed (step I) in an endothermic reaction. Step II involves the loss of two 8-hydroxyquinoline molecules, with simultaneous oxidation in the presence of air to give the product $ThO(OX)_2$ in an exothermic decomposition at about 390°. The last step III involves complete oxidation of the residue to ThO_2 at about 500°. The gravimetric discrepancy in the first step of thermal analysis might be due to the vapour pressure of the 8-hydroxyquinoline molecule and water vapour initially present, in addition to an infinitesimal part of the ligand molecule, which starts to be lost simultaneously, giving a residue of $ThO(OX)_2$ (and intermediate) at 390–400°. The end-product is ThO_2, as proved by X-ray diffraction.

The thermal decomposition of the other compounds listed in Table 1 could be explained by similar considerations.

Discussion

It seems that tetrakis(8-hydroxyquinolinato)thorium(IV) has a tendency to form adducts with various neutral molecules, including 8-hydroxyquinoline. In fact, the present work describes the formation of adducts of 8-hydroxyquinoline, urea, formamide, dimethylsulphoxide, pyridine and 1,10-phenanthroline with $Th(C_9H_6NO)_4$. Under certain circumstances an additional water molecule is also incorporated, as a second adduct. The factors which govern the formation of adducts are not clearly defined, but coordinative unsaturation, lattice interactions and hydrogen-bonding appear to be operative in most of the adducts.

In the infrared spectra of the adduct species, the characteristic modes of the chelated 8-hydroxyquinoline seem to be unaffected by the adduct molecules and the region of some specific absorption bands remains almost unaltered, indicating structural similarities.

Thermal analysis data show that the temperatures at which the adduct molecules are completely expelled from the principal molecule $Th(OX)_4$ vary considerably, as seen below:

1,10-Phenanthroline	290°
Urea	235°
DMSO	220°
DFA	220°
Pyridine	200°
HOX	180°

It is possible that 1,10-phenanthroline, which is expelled at a considerably higher temperature than for the other adducts, takes part in extensive hydrogen-bonding.

In the presence of air and after the loss of the adducts, decomposition of the principal molecule $Th(C_9H_6NO)_4$ takes place, involving the partial expulsion of 8-hydroxyquinoline anions; oxygenated intermediates are produced, which are ultimately converted to ThO_2. The identity of the end-product, finely dispersed ThO_2, has been confirmed by X-ray powder diffraction. In some cases the degradation process is complex and more than one intermediate is formed. In an argon atmosphere, the initial loss of adduct molecules follows a similar pattern as in air, but the decomposition of $Th(C_9H_6NO)_4$ is quite different, usually involving only one step to produce a mixed end-product which is black and brittle, with no formation of ThO_2, but possibly containing unburnt X-ray-amorphous carbon.

It is interesting to note that for all adducts the oxygenated intermediates in air are formed in a narrow temperature range, i.e. 390–450°, as shown below:

Adduct	Intermediates	Temperature, °C
$Th(XO)_4(C_9H_7NO)(H_2O)$	II. $ThO(OX)_2$	390
$Th(OX)_4(C_9H_5N)$	II. $ThO(OX)_2$	400
	III. $Th_3O_5(OX)_2$	430
$Th(OX)_4(CON_2H_2)$	II. $ThO(OX)_2$	410
	III. $Th_3O_2(OX)_8$	450
$Th(OX)_4(OS(CH_3)_2)(H_2O)$	II. $ThO(OX)_2$	400
$Th(OX)_4(HCON(CH_3)_2)$	II. $Th_3O(OX)_{10}$	400
$Th(OX)_4(C_{12}H_8N_2)(H_2O)_2$	IV. $Th_2O(OX)_6$	400

It is also clear that during the decomposition of the tetrakis complex in air polymerization processes seem to take place, or it could be that the polymerization phenomenon might be a feature of the normal adducts under ordinary conditions.

In view of the fact that the preparation of pure tetrakis(8-hydroxyquinolinato)thorium(IV), $Th(C_9H_6NO)_4$, could not be accomplished under ordinary conditions, the removal of the adducts at a preselected temperature offers a method for isolation of the pure compound, and could be standardized for the purpose of the gravimetric determination of thorium.

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Zusammenfassung — Sechs Addukte des Tetrakis(8-hydroxyquinolinato)-Komplexes von Thorium(IV) mit 8-Hydroxyquinolin, Pyridin, Harnstoff, Dimethylsulphoxid, Dimethylformamid und 1,10-Phenanthrolin wurden dargestellt und charakterisiert. Infrarotbanden und spezielle thermische Eigenschaften der Raumtemperatur-Formen sind angegeben. Die thermischen Analysen wurden meist in Luft ausgeführt, in einigen Fällen zu Vergleichszwecken aber auch in Argonatmosphäre. Die Addukte wurden vom Komplex bei Temperaturen zwischen 110 und 290 °C abgegeben. Intermediäre oxydierte Komplexe wurden in jedem Fall bei etwa 400 °C gebildet. Die thermischen Daten ermöglichen die Standardisierung eines Verfahrens zur Darstellung von $Th(C_9H_6NO)_4$.

Резюме -- Получены и охарактеризованы шесть аддуктов тетракис-(8-оксихинолинато)комплекса тория(IV) с 8-оксихинолином, пиридином, мочевиной, диметилсульфоксидом, диметилформамидом и 1,10-фенантролином. Приведены ИК спектры их комнатно-температурных форм, а также сообщены их подробные термические характеристики. Термический анализ проводился главным образом в атмосфере воздуха, но в некоторых случаях для сравнения использовали данные, полученные в атмосфере аргона. Все исследованные аддукты разлагались в интервале температур 110–290°. В каждом случае при температуре около 400° происходило образование промежуточных кислородсодержащих комплексов. Термические данные позволили провести стандартизацию метода получения комплекса $Th(C_9H_6NO)_4$.