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Preparation and Infrared Spectroscopic Characterization of Some (Oxydiacetato)thorium(IV) Complexes

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A polymeric $[Th(oda)_2]_n$ *(oda = oxydiacetate,* $O_2CCH_2OCH_2CO_2^{2-}$*) complex has been prepared and characterized by I.R. spectroscopy methods.*

The infrared spectrum and assignment of the characteristic frequencies are reported. We suggest for this complex, also on the basis of the analogies with the $[UO_2(oda)]_n$[1] *complex, the chelate structure with decacoordination to the Th atom.*

In the presence of pyridine N-oxide (Opy), the monomeric complex $[Th(oda)_2(Opy)_3]\cdot 3H_2O$ *is obtained. The 1:3 metal/ligand complexes are:* $Na_2[Th(oda)_3]\cdot 2NaNO_3$*, formed from* $[Th(NO_3)_4]\cdot 6H_2O$ *and an excess of* $Na_2(oda)$*, and* $Na_2[Th(oda)_3]\cdot nH_2O$ *(n = 2 or 3), formed from the polymeric complex plus a stoichiometric amount of* $Na_2(oda)$*. Also for these complexes the infrared spectra and assignments are reported.*

The possible structures of these new complexes are discussed.

Introduction

Most of the investigations reported in the literature on the formation of thorium(IV) complexes with various ligands were devoted to the nature and thermodynamic stability of the species formed in aqueous solution[2,3].

Only a few such complexes have been isolated and investigated from a spectroscopic point of view[4]. The aim of our investigation was to study the formation of thorium(IV) complexes with ligands possessing a pronounced tendency to give chelate structures, and to correlate, if possible, the coordination polyhedra in the solid state with the species in solution.

Our attention was thus directed to the oxydiacetate ligand which has two carboxylic groups and an ether oxygen atom in the α position to both of them. This ligand could coordinate a thorium atom through the ether oxygen and the oxygen atoms of the carboxylate groups, as has been ascertained for uranyl(VI) ion by I.R. spectroscopic studies[1] and successively confirmed by X-ray analyses[5–7].

Experimental

Commercial reagent grade chemicals were used without further purification; other chemicals were prepared by standard methods.

Infrared spectra in the region 4000–200 cm^{-1} (KBr pellets) were recorded on a Perkin–Elmer 621 spectrophotometer; spectra in the far I.R. region (Nujol mulls in polythene discs) were recorded on a Beckman I.R. 11 spectrophotometer.

Analyses were performed by the microanalytical laboratory of the University of Padova. Thorium was determined gravimetrically as ThO_2.

Syntheses of Complexes

$[Th(oda)_2]_n$ *(I)*

It was prepared by the addition of a solution of $H_2(oda)$ to a solution of thorium(IV) nitrate (2:1). The white crystals formed after several days were filtered and washed with water and methanol. When the solvent of the reaction mixture was methanol, the complex precipitated immediately and quantitatively as a fine white powder. Also in the presence of a large excess of the acid ligand the same complex was formed. *Anal.* Found: C 19.1, H 1.7, Th 46.0. $Th(oda)_2$ requires: C 19.4, H 1.6, Th 46.7%.

$[Th(oda)_2(Opy)_3]\cdot 3H_2O$ *(II)*

It was prepared by the addition of complex (I) to a ten-fold excess of pyridine N-oxide in methanol. By stirring the mixture at room temperature, complex (I) dissolved rapidly and complex (II) was immediately obtained by addition of ether as a white powder. The precipitate was washed with ether and dried. *Anal.*

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Found: C 32.7, H 3.6, N 4.9, Th 28.0, H_2O 6.6. [Th $(oda)_2(Opy)_3]\cdot 3H_2O$ requires: C 33.0, H 3.5, N 5.0, Th 27.8, H_2O 6.5%.

$Na_2[Th(oda)_3]\cdot 2NaNO_3$ (III)

It was prepared by the addition of a methanolic solution of thorium(IV) nitrate to a solution containing disodium oxydiacetate (1:3) in the same solvent; (ratios of 1:1 and 1:2 gave complex (I)).

Complex (III) precipitated immediately as a white powder and was washed with methanol and then dried. *Anal.* Found: C 17.1, H 1.5, N 3.3, Th 27.9. $Na_2[Th(oda)_3]\cdot 2NaNO_3$ requires: C 17.1, H 1.4, N 3.3, Th 27.5%.

$Na_2[Th(oda)_3]\cdot nH_2O$ ($n = 2$ or 3) (IV)

It was prepared by the addition of $Na_2(oda)$ to a suspension in hydroalcoholic solution (methanol) of complex (I) in stoichiometric amount. By stirring the solution, complex (I) reacted immediately. The reaction is very slow in pure methanol, owing to the insolubility of complex (IV) in this solvent. Complex (IV) was precipitated by the addition of ether, filtered, washed with ether and dried. *Anal.* Found: C 20.0, H 2.5, Th 32.4. $Na_2[Th(oda)_3]\cdot 2H_2O$ requires: C 20.2, H 2.3, Th 32.7%.

Results and Discussion

The reaction of thorium nitrate with oxydiacetic acid in the molar ratio 1:2 or in excess of the ligand in aqueous or methanolic solution gave the same complex, as confirmed by I.R. spectra of stoichiometry $Th(oda)_2$.

The composition, insolubility, high melting point (over 350° C) and absence of coordinated solvent molecules, as shown by I.R. spectra, strongly suggest a polymeric structure for this complex, which is destroyed by a large excess of pyridine N-oxide in methanolic solution to yield complex (II).

The polymeric structure of complex (I) is also destroyed by addition of $Na_2(oda)$ (1:1), resulting in complex (IV).

Complex (III), with the same metal to ligand ratio (1:3) as complex (IV), but containing two molecules of $NaNO_3$, was obtained by reaction of thorium nitrate with an excess of $Na_2(oda)$ in methanolic solution.

Infrared spectra and solubility in water suggest a monomeric structure for complexes (II), (III) and (IV).

Infrared Spectra

The infrared spectra of the thorium(IV) complexes, shown in Figure 1, are compared with that of the disodium salt of the ligand. In Table I the frequencies and assignments for these complexes are given. In order to compare the absorption modes of the characteristic groups, their spectra are analyzed and divided into characteristic regions.

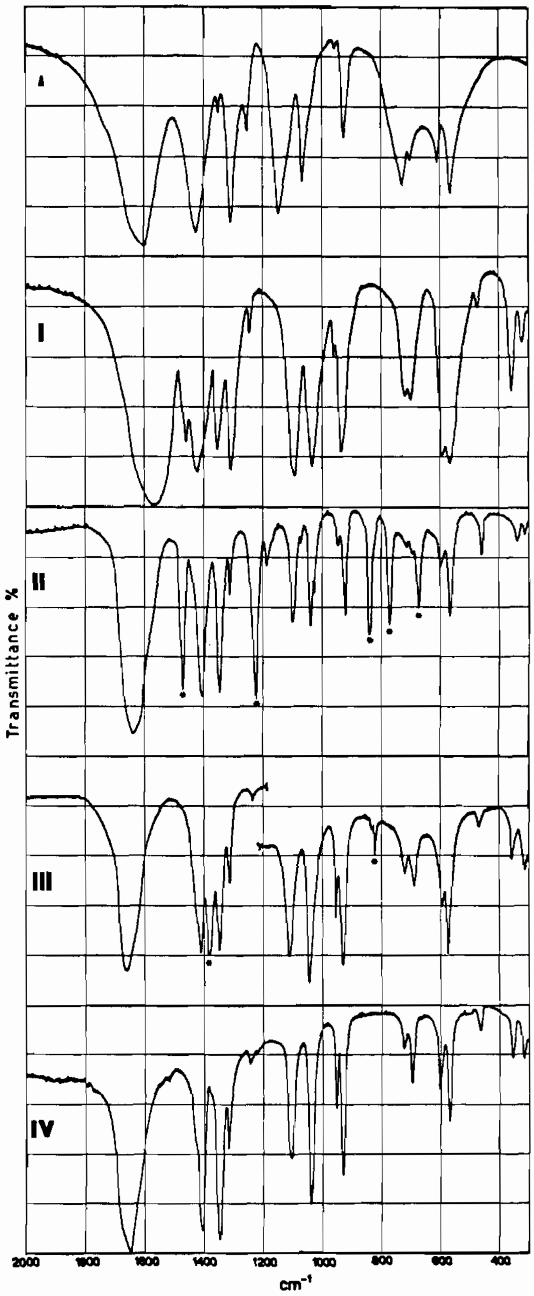

Figure 1. I.R. absorption spectra of disodium oxydiacetate and its Th(IV) complexes: $Na_2(oda)$, A; $[Th(oda)_2]_n$, (I); $[Th(oda)_2(Opy)_3]\cdot 3H_2O$, (II); $Na_2[Th(oda)_3]\cdot 2NaNO_3$, (III); $Na_2[Th(oda)_3]\cdot nH_2O$ ($n = 2$ or 3), (IV). • denotes in complex (II) the absorption bands of the coordinated pyridine N-oxide, and in complex (III) the absorption bands of the ionic nitrato group.

TABLE I. Assignment of the Infrared Frequencies of the Oxydiacetate Ion and Its Th(IV) Complexes in the 2000–100 cm^{-1} Region.

Na_2(oda)	(I)	(II)	(III)	(IV)	Approximate Assignment[a]
1600 vs	1585 vs	1640 vs	1653 vs	1645 vs	ν_a (COO)
–	–	1471 ms	–	–	ν (C=C)
–	1465 m	–	–	–	$\delta(CH_2)$
1418 s	1426 s	1404 s	1409 s	1406 s	ν_s(COO)
–	–	–	1373 s	–	$\nu(NO_3^-)$
1340 w	1351 m	1350 ms	1344 s	1346 s	
1305 ms	1309 ms	1311 mw	1312 mw	1317 mw	$\varrho(CH_2)$
1250 w	1246 w	–	1234 w	1240 w	
–	–	1223 s	–	–	ν(N–O)
1138 s	1118 s	1098 m	1113 m	1107 m	ν_s(C–O–C)$_e$
1053 m	1040 s	1042 m	1042 m	1042 m	ν_a(C–O–C)$_e$
965 w	960 w	945 w	956 w	954 w	ν(C–C)
925 m	934 m	932 m	943 m	942 m	$\varrho(CH_2)$
–	–	840 m	–	–	δ(N–O)
–	–	–	828 w	–	$\delta(NO_3^-)$
–	–	771 m	–	–	π(CH)
726 m	723 m	715 w	722 mw	722 mw	δ(COO) + ring def.
700 w	704 m	694 w	694 mw	694 mw	
–	–	675 m	–	–	
614 mw	680 m	598 mw	598 mw	598 mw	π(COO) + ring def.
558 m	668 m	568 m	570 m	570 m	
–	474 w	462 mw	471 w	471 w	
–	357 mw	337 w	357 w	357 w	ring def. + ν(Th–O)
–	325 w	312 w	314 w	316 w	
	246				
	213				ν(Th–O) + ring def.
	177				

[a] Abbreviations: vs = very strong, s = strong, m = medium, w = weak, mw = medium weak, and as subscripts, a = antisymmetric, s = symmetric. ν, δ and π denote stretching, in-plane and out-of-plane bending modes, respectively; ϱ denotes non assigned wagging, twisting or rocking modes of the CH_2 groups.

4000–2000 cm^{-1} region

All the complexes isolated which contain water molecules show a strong broad absorption at about 3400 cm^{-1}, assigned to the (O–H) stretching. The broadness of this band indicates the presence of hydrogen bonding. The sharp absorption bands of weak intensity at about 3000 cm^{-1} are assigned to the (CH_2) stretching vibrations and to the (C–H) stretching of the pyridine ring in complex (II). This absorption region is not very specific and has been excluded from the spectra in Figure 1 and from the assignments in Table I.

2000–1200 cm^{-1} region

As is well known, the carboxylate ion presents usually a strong band at about 1600 cm^{-1}, due to the antisymmetric stretching vibration and a band at about 1400 cm^{-1} assigned to the symmetric stretching vibration. While for a monodentate carboxylate group the ν_a shifts to higher frequencies with respect to the free anion, for a bidentate carboxylate group the ν_a decreases and the ν_s increases. Particularly a carboxylate group acting as bidentate towards the same metal atom presents two peaks of the same intensity whose separation is smaller than 100 cm^{-1} [8–11].

In the disodium salt of our free ligand (see Figure 1A) ν_a and ν_s occur at 1600 and 1418 cm^{-1} respectively, while in complex (I) the same absorption bands fall at 1585 and 1426 cm^{-1}, and present different intensities.

Therefore, for complex (I), taking into account the geometry of the oxydiacetate anion, a polymeric structure can be formulated, where two carboxylate oxygens and one ether oxygen (see below) of the same ligand are involved in two five-membered rings with a thorium atom; the remaining two carboxylate oxygens coordinate two other thorium atoms. The second ligand coordinates in the same way. Moreover, the features of the I.R. spectra suggest that all the carboxylate groups are equivalent and no evidence for free C–O groups is afforded.

Thus, a coordination number of *ten* around each thorium atom can be suggested (Figure 2). This co-

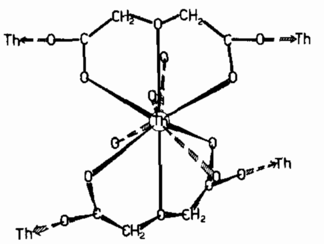

Figure 2. A possible way of decacoordination for complex (I).

ordination number has been found for other Th(IV) complexes[12].

The spectrum of complex (II) shows the characteristic absorption bands of the coordinated pyridine N-oxide: the (C=C) stretching band of the pyridine ring at 1471 cm^{-1} and the (N–O) stretching band at 1223 cm^{-1} significantly shifted with respect to the corresponding band in the free pyridine N-oxide (1243 cm^{-1}), similarly to what was found by Quagliano *et al.*[13,14] In this complex, the (COO) stretching frequencies occur at 1640 and 1404 cm^{-1}, consistent with an increase in double bond character for one of the carbon–oxygen bonds; therefore, we suggest that each oxydiacetate ion is tridentate, with two carboxylic oxygen atoms either free or involved in hydrogen bonds. Hence, the pyridine N-oxide is able to destroy the polymeric structure of complex (I), by breaking the bonds which in the polymer are due to the oxygen atoms *outside* the chelate rings.

In complex (III), having a 1:3 metal/ligand ratio, the (COO) stretching frequencies occur at 1653 and 1409 cm^{-1}. Hence, also in this case we suggest that the carboxylate groups act as monodentate donors, with two free carboxylic oxygen atoms for each anionic ligand. In this region the complex (III) shows also the characteristic stretching band of the ionic nitrato group at 1373 cm^{-1} [15,16]. Complex (IV) shows a spectrum identical with that of complex (III), except for the band at 1373 cm^{-1}. Therefore, the suggestions reported above, concerning the coordination modes of the ligand, are valid in this case also.

The other frequencies in this region are clearly due to the (CH_2) deformation modes (see Table I). This assignment is supported by indicative UBFF force constant calculations for complex (I), carried out by using for the ligand the geometrical data of the analogous $[UO_2(oda)]_n$[6] and confirmed by the full calculations on the latter complex, performed by us.

For the other complexes the (CH_2) deformations are straightforward on the basis of the analogy with complex (I) and are reported in Table I.

1200–1000 cm^{-1} region

The antisymmetric and symmetric stretching frequencies of the ether group which occur in the disodium salt of the ligand at 1138 and 1053 cm^{-1}, respectively, are shifted towards lower wavenumbers: to 1118 and 1040 cm^{-1} in (I), to 1098 and 1042 cm^{-1} in (II), to 1113 and 1042 cm^{-1} in (III), and to 1107 and 1042 cm^{-1} in (IV). These two bands are about equally intense, whereas in the free ligand the band at higher frequency is the most intense. These differences suggest coordination of the ether oxygen atom to the thorium atom[1,17–19].

1000–100 cm^{-1} region

The bands at about 960–950 and 940–930 cm^{-1}, present in all the complexes and in the salt of the ligand without appreciable shift, are assigned to the (C–C) stretching mode and to the (CH_2) rocking mode, respectively, according to Nakamoto[20] and our calculations. The bands at 840 and 771 cm^{-1} in complex (II) are assigned to the (N–O) bending mode and to the (C–H) out-of-plane deformation of the coordinated pyridine ring, respectively, according to Ref. 13. The band at 828 cm^{-1}, present in complex (III) but not in (IV), is assigned to the deformation of the ionic nitrato group[15,16]. The doublets at about 700 and 600 cm^{-1} are assigned to the (COO) in-plane and out-of-plane bending modes, respectively. The corresponding bands in the uranyl(oda) complexes are found at 730–710 and 604–555 cm^{-1}[1].

All the complexes exhibit three bands between 500 and 300 cm^{-1}, which are not present in the disodium salt of the ligand. Therefore, we assign these absorption bands as metal–oxygen stretching modes plus ring deformations. In the polymeric $[UO_2(oda)]_n$ complex three bands are present at 485, 372 and 340 cm^{-1}. In the far I.R. region the complex (I) exhibits three bands at 246, 213 and 177 cm^{-1}, analogous to the ones found for the $[UO_2(oda)]_n$ complex at 261, 217 and 180 cm^{-1}. We assign these bands also as metal–oxygen stretching modes plus ring deformations.

Conclusions

A potentiometric investigation in acid solution shows a strong interaction between Th(IV) and oxydiacetic acid, with formation of a mononuclear complex having the composition $Th(oda)_2$. Indeed, the formation equilibrium

$$Th^{4+} + 2H_2(oda) \rightleftharpoons Th(oda)_2 + 4H^+$$

is completely shifted to the right[21]. This can be adequately explained by admitting that both the ligands behave as tridentate, through the two carboxylic groups and the ether oxygen, so that each ligand forms two five-membered rings with the thorium atom. At the contrary, a chelate structure without the involvement of the ether oxygen, leading to formation of an eight-membered ring, is not particularly stable in aqueous solution[22]. Therefore, when the complex is dissolved in water, the two ligands occupy six coordination sites of the Th^{4+} cation and the molecules of solvent fill the remaining positions. When the complex (I) precipitates the water molecules are replaced by the uncoordinated carboxylato oxygen atoms, thus giving rise to a polymeric structure. The solvent molecules can also be replaced by another ligand (Opy or oda) having higher basicity than water, thus giving complexes (II), (III) and (IV).

The separation between the two (COO) stretching frequencies (see Table I) in the various complexes allows us to clarify the coordination modes of the ligand. In fact, this separation (182 cm^{-1} in the disodium salt of the ligand) decreases to 159 cm^{-1} in the polymeric complex (I) and increases to 236, 244 and 239 cm^{-1} in the monomeric complexes (II), (III) and (IV) respectively.

On this basis we can suggest for complex (I) a decacoordinated structure (Figure 2), where the central thorium atom, besides the two tridentate ligands, coordinates four oxygen atoms from adjacent molecules.

The anionic complexes (III) and (IV) show identical spectra, except for two bands assigned to the ionic nitrato group in (III) (see Figure 1). This finding suggests that the anionic $Th(oda)_3^{2-}$ entity is the same for both complexes, with no changes in symmetry. Hence, the nitrato group, present in complex (III), is not involved in the coordination to the Th atom. In both complexes, each thorium atom should coordinate six carboxylic oxygens and three ether oxygens, so that the anionic entity could be arranged as for $[Yb(oda)_3]^{3-}$ [23].

A comparison between the polymeric complex (I) and the polymeric $[UO_2(oda)]_n$ shows that the (Th–O) frequencies are lower than the corresponding (O_2U–O) ones, suggesting that, once the bonds are formed, the strength of the metal–oxygen bond is weaker in the thorium complex. The higher separation between antisymmetric and symmetric stretching frequencies of the carboxylate groups for the thorium complex supports this suggestion.

The X-ray analyses for complex (I) and the UBFF force constant calculations for the uranyl and thorium oxydiacetate polymeric complexes will be published elsewhere[24].

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