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The Infrared Absorption of Crystalline Thorium Tetraformates. I. Characterization of Thorium Tetraformates in the Solid State by Infrared Spectroscopy

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The different thorium tetraformates have been characterized by their infrared spectra, and the totality of the observed absorption bands has been assigned to vibrational modes in the powdered cristalline samples. Discussion of the experimental results has led to the statement that in all the thorium tetraformates the coordination mode of the formate atoms is the same, the corresponding coordination polyhedron of the thorium atoms being a distorted Archimedean antiprism. It has also been established that in the hydrated compounds the crystal water is essentially of the coordinated type, except for one of the three water molecules in the trihydrate, which seems to be distorted lattice water. The infrared spectra of the five polymorphic species of anhydrous thorium tetraformate exhibit residual water bands; these bands disappear completely at 153°C only.

1. Introduction

Carrying on our studies of the several thorium tetraformates isolated in the laboratory (*1–3*), we attempted to characterize these compounds in the solid state by their molecular vibrational spectra. The different tetraformates, which have been isolated and are talked about in the following, are

Tetraformate	Polymorphic species
$Th(HCOO)_4, 3H_2O$	
$Th(HCOO)_4, \frac{2}{3}H_2O$	M and L
$Th(HCOO)_4$	μ, λ, δ, α, and γ

2. Experimental

The formate ion and water fundamental vibrations were investigated by a Perkin–Elmer Model 257, double-beam grating infrared spectrometer. This apparatus covers the spectral range 4000–625 cm^{-1}, and the observed bands were calibrated against the atmospheric water and carbon dioxide bands. For the compounds stable at room temperature, we also used a Perkin–Elmer Model 225, infrared spectrometer. We could thus characterize the absorption bands corresponding to the ν(Th–O) valence vibration along the bond joining the thorium atom to the oxygen atom of a formate group.

The powdered samples were mixed with potassium bromide or cesium iodide and pressed into pellets. Karyakin and Muradova (*4*) have shown that this method is the most suitable for the study of hydrated compounds.

Anhydrous thorium tetraformate has been examined above room temperature in a heating cell built for this purpose (Fig. 1). This cell fits directly into the infrared spectrometer and it has been manufactured in brass. It has been calibrated against a mercury thermometer, and the temperature of the sample is known with an accuracy of ±2°C. We could thus observe the splitting and the shift of

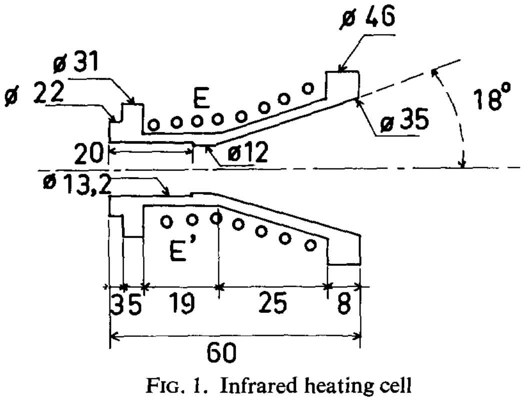
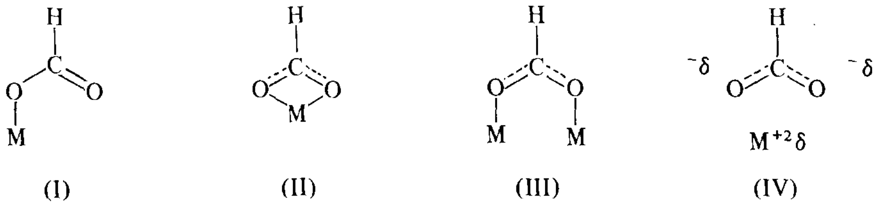


FIG. 1. Infrared heating cell

absorption bands in the temperature range 25–250°C.

3. Vibrational Analysis of the Formate Ion

A formate group is coordinated with a metal in one of the following ways (*5*, *6*):



In thorium tetraformate trihydrate, it has been shown that two thorium atoms are bridged by bidentate formato groups (*7*). This coordination type corresponds to the above model III. Under these conditions, the formate ion is planar and its symmetry belongs to the point group C_{2v}. According to the orientation rules described by Nakamoto (*6*), we can represent on Fig. 2 the structural model of the formate ion. For this ion, the number of normal vibrations is six. Application of group theory to our model leads to the following irreducible representation:

$$\Gamma = 3A_1 + 2B_1 + B_2$$

The internal coordinates describing the formate ion at rest are:

$r_1 = r_2$	valence bond lengths $CO_I = CO_{II}$
d	valence bond length CH
α	valence angle O_ICO_{II}
β_1 and β_2	valence angles $O_ICH = O_{II}CH$
τ	torsion along the CH bond (not represented on Fig. 2).

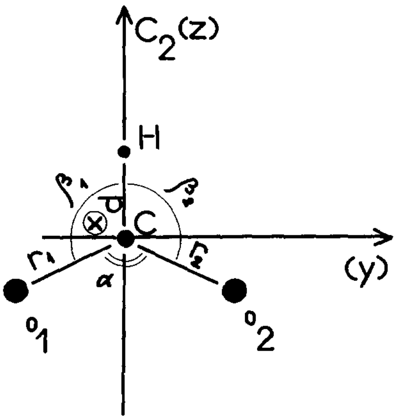


FIG. 2. Structural model for the C_{2v} formate ion.

The results of the vibrational analysis of the formate ion are stated in Table I. In the same table we have also mentioned the observed vibrational bands of α-$Ca(HCOO)_2$ (*8*), which presents the same coordination mode of the formate anion as $Th(HCOO)_4$, $3H_2O$ (*7*).

All the fundamentals of the formate ion are infrared and Raman active. In addition to fundamental vibrations, molecular absorption spectra also exhibit some combinations and overtones of weak intensity. In Table I we mentioned the most commonly observed combinations and overtones of the formate ion spectra.

TABLE I

INFRARED FREQUENCIES AND BAND ASSIGNMENTS FOR THE FORMATE ION OF SYMMETRY C_{2v}[a]

Frequency	Species	Vibration	Observed bands for α-$Ca(HCOO)_2$ (cm^{-1})
ν_2	A_1	$\nu(CH)$	2868, 2890
ν_4	B_2	$\nu_{as}(CO)$	1582, 1618
ν_5	B_2	$\rho_r(COO)$	1386, 1397
ν_1	A_1	$\nu_s(CO)$	1349, 1359
ν_6	B_1	$\pi(CH)$	1060, 1072
ν_3	A_1	$\delta(OCO)$	778, 796
Combinations and overtones			
$2\nu_6$			—
$2\nu_5$			2745, 2775
$\nu_1 + \nu_3$			—
$\nu_1 + \nu_4$			2942
$2\nu_4$			3000
$2\nu_1$			2694

[a] ν, stretching; ν_s, symmetric; ν_{as}, antisymmetric, δ, bending; ρ_r, rocking; π, out-of-plane vibration.

4. Results

4.1. Infrared Spectra of the Solid Phases Issued During the Heating of $Th(HCOO)_4, 3H_2O$

When thorium tetraformate trihydrate is heated at the rate of 0.5°C/day, the following solid phases can be observed:

$$Th(HCOO)_4, 3H_2O \xrightarrow{52°C} Th(HCOO)_4, \tfrac{2}{3}H_2O \text{ “L”} \xrightarrow{62°C} Th(HCOO)_4\lambda \xrightarrow{65°C} Th(HCOO)_4\alpha \xrightarrow{125°C} Th(HCOO)_4\gamma.$$

If we except a weak absorption band at 3420 cm^{-1} and the characteristic bands of water, $Th(HCOO)_4\lambda$ has the same absorption spectrum as the intermediate tetraformate $Th(HCOO)_4, \frac{2}{3}H_2O$ “L”.

Tables II–V describe the infrared bands observed for the above phases.

TABLE II

INFRARED ABSORPTION SPECTRUM OF $Th(HCOO)_4, 3H_2O$

cm^{-1}	Intensity[a]	Band assignments
3590	m_{sd}	$\nu(OH)$
3520	s_{sd}	
3380	vs	
3035	w_{sd}	$\nu_s(CO) + \nu_{as}(CO)$
2940	w_{sd}	
2875	m	$\nu(CH)$
2760	w_{sd}	$2\nu_s(CO)$
1678	s_{sd}	$\delta(HOH)$
1575	vs_b	$\nu_{as}(CO)$
1382	vs	$\rho_r(COO)$
1398	s_{sd}	
1372	vs	$\nu_s(CO)$
1367	vs_{sh}	
1133	vw	$\pi(CH)$
1064	vw	
798	s	$\delta(OCO)$
793	s_{sd}	
781	m_{sh}	
717	vw	$\rho(H_2O)$
553	w_b	
309	w_b	$\nu(Th–O)$
284	m	
262	s	
247	m_{sd}	

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, sharp; b, broad; sd, shoulder.

TABLE III

INFRARED ABSORPTION SPECTRUM OF $Th(HCOO)_4, \frac{2}{3}H_2O$ “L”

cm^{-1}	Intensity	Band assignments
3380	s_{sd}	$\nu_{as}(OH)$
3270	s_b	$\nu_s(OH)$
3200	s_b	$2\nu_{as}(CO)$
2965	m_{sd}	$\nu_s(CO) + \nu_{as}(CO)$
2885	m	$\nu(CH)$
2865	m_{sh}	
2740	w	$2\nu_s(CO)$
2305	w	$\nu_{as}(CO) + \delta(OCO)$
1690	s_{sd}	$\delta(HOH)$
1683	s_{sd}	
1575	ws_b	$\nu_{as}(CO)$
1398	s_{sh}	$\rho_r(COO)$
1390	s_{sd}	
1384	s	
1374	ws_b	$\nu_s(CO)$
1363	ws	
1345	s	
1130	vw_b	$\pi(CH)$
1071	vw_{sh}	
1060	vw	
789	w_{sh}	$\delta(OCO)$
778	s_{sh}	
775	s_{sh}	
770	m_{sd}	
767	m_{sh}	
759	vs_{sh}	
696	vs	$\rho(H_2O)$
552	s_b	
385	w	$\nu(Th–OH_2)$
268	s_b	$\nu_{as}(Th–O)$
259	s_b	$\nu_s(Th–O)$

TABLE IV

INFRARED ABSORPTION SPECTRUM OF $Th(HCOO)_4\alpha$

cm^{-1}	Intensity	Band assignments
3420	m	$\nu(OH)$ of residual water
3030	vw_b	$\nu_s(CO) + \nu_{as}(CO)$
2930	w_b	
2870	m_{sh}	$\nu(CH)$
2750	w	$2\nu_s(CO)$
1570	vs_b	$\nu_{as}(CO)$
1383	vs_{sd}	$\rho_r(COO)$
1374	vs	$\nu_s(CO)$
1128	vw_b	$\pi(CH)$
780	s_{sh}	
771	m_{sh}	$\delta(OCO)$
765	w_{sd}	

TABLE V

INFRARED ABSORPTION SPECTRUM OF Th(HCOO)γ AT 145°C

cm^{-1}	Intensity	Band assignments
3635	w	ν(OH) of residual water
3380	w_b	
2960	w_b	$\nu_s(CO) + \nu_{as}(CO)$
2875	m	ν(CH)
2740	vw	$2\nu_s(CO)$
1570	vs_b	$\nu_{as}(CO)$
1370	vs_b	$\nu_s(CO)$, $\rho_r(COO)$
1065	vw	π(CH)
783	m	δ(OCO)
764	m	

4.2. Infrared Spectra of the Solid Phases Issued during the Heating of $Th(HCOO)_4$, $\frac{2}{3}H_2O$ "M"

In the same conditions as above (Section 4.1), the intermediate tetraformate $Th(HCOO)_4$, $\frac{2}{3}H_2O$ "M", leads to the following solids:

$$Th(HCOO)_4, \tfrac{2}{3}H_2O \text{ “M”} \xrightarrow{93^\circ C} Th(HCOO)_4\mu \xrightarrow{95^\circ C} Th(HCOO)_4\delta \xrightarrow{125^\circ C} Th(HCOO)_4\gamma.$$

Here again, if we except a weak absorption band at 3420 cm^{-1} and the characteristic bands of water, $Th(HCOO)_4\mu$ exhibits the same infrared spectrum as the corresponding intermediate hydrate $Th(HCOO)_4$, $\frac{2}{3}H_2O$ "M".

The observed infrared bands for the two solid phases $Th(HCOO)_4$, $\frac{2}{3}H_2O$ "M", and $Th(HCOO)_4\delta$ are described in Tables VI and VII.

TABLE VI

INFRARED ABSORPTION SPECTRUM OF $Th(HCOO)_4$, $\frac{2}{3}H_2O$ "M"

cm^{-1}	Intensity	Band assignments
3340	m_b	ν(OH)
2922	w_{sd}	$\nu_s(CO) + \nu_{as}(CO)$
2880	w	ν(CH)
2870	w	
2845	w_{sh}	
2755	vw_{sd}	$2\nu_s(CO)$
2730	vw	
2675	vw	
1655	s	δ(HOH)
1560	vs_b	$\nu_{as}(CO)$
1392	vs_{sd}	$\rho_r(COO)$
1384	vs	
1363	s_{sh}	$\nu_s(CO)$
1349	vs	
1340	vs_b	
1132	vw	π(CH)
1078	vw_{sh}	
1064	vw	
791	s_{sh}	δ(OCO)
783	w_{sd}	
770	vw_{sd}	
661	m_b	$\rho(H_2O)$
578	m_b	
307	m_{sd}	ν(Th–O)
285	m_{sd}	
266	s	
232	m_b	
214	m	

5. Discussion

We shall now discuss separately the vibrations of the formate ion, of water, and of the Th–O bond.

5.1. Vibrations of the Formate Ion

For all the solid phases investigated, we can easily assign the six fundamentals of the formate ion, except for $Th(HCOO)_4\gamma$ which presents a coupling effect between the two neighbouring frequencies ν_1 and ν_5. The position of the frequencies, which are the most sensitive to the coordination mode of the formate ion (ν_1 and ν_4), allows us to assert that for all the thorium tetraformates discussed here, the thorium atoms are bridged by bidentate formato groups. For most of the solid formates we can observe the splitting of the ν_1, ν_3, and ν_5 fundamentals. This splitting is due to the crystal field, and this will be discussed further in the next article,[1] in terms of a vibrational analysis under the factor group, applied to the δ(OCO) bending mode.

The experimental spectra exhibit strong and sharp absorption bands corresponding to the δ(OCO) bending mode (Fig. 3), and the profile of these bands are characteristic of the corresponding solid phase.

5.2. Vibrations of Water

Figure 4 compares the infrared absorption spectra of the different thorium tetraformates in the range 4000–3000 cm^{-1}. In crystal hydrates, water is considered to be in the molecular state if its fundamentals are close to those observed for liquid water:

ν_1	$\nu_s(OH)$	3219 cm^{-1},
ν_2	$\delta(HOH)$	1627 cm^{-1},
ν_3	$\nu_{as}(OH)$	3445 cm^{-1}.

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[1] B. F. MENTZEN, *J.S.S.C.*, 3(1), 20 (1971).

TABLE VII

INFRARED ABSORPTION SPECTRUM OF $Th(HCOO)_4\delta$

cm^{-1}	Intensity	Band assignments
3380	w_b	ν(OH) of residual water
3030	vw_b	$\nu_s(CO) + \nu_{as}(CO)$
2960	w_b	
2880	w_{sd}	ν(CH)
2865	w	
2750	vw	$2\nu_s(CO)$
1570	vs_b	$\nu_{as}(CO)$
1386	vs	$\rho_r(COO)$
1374	vs_{sd}	
1362	vs	$\nu_s(CO)$
1343	vs_{sh}	
1124	vw_b	π(CH)
1072	vw	
1066	vw	
791	w_{sd}	δ(OCO)
788	s_{sh}	
770	vs_{sh}	

Crystal water may also enter in inter- and intramolecular hydrogen bonds. In both cases the water molecule presents a particular orientation in the crystal; the ν_1 and ν_3 frequencies shift toward the lower frequencies and the ν_2 shifts towards the higher ones.

In other instances, water can be directly linked to a coordinating atom. In this case, besides the three fundamentals of the free water molecule, coordinated water is expected to show the characteristic wagging, twisting, and rocking modes, due to the metal–water bond; the corresponding absorption bands may be observed in the 800–400 cm^{-1} range. In some cases, it is also possible to observe the metal–water stretching frequency which is situated below 400 cm^{-1}.

Water may also be partially ionized. This kind of water is present in compounds undergoing hydrolysis, and the corresponding ν(OH) frequency may be observed somewhere between the frequency of the free hydroxide ion (3770 cm^{-1}) and the ν_3 frequency in liquid water (3445 cm^{-1}).

$Th(HCOO)_4$, $3H_2O$. The infrared absorption spectrum of this compound presents a complex ν(OH) band, with three distinct maxima at 3590,

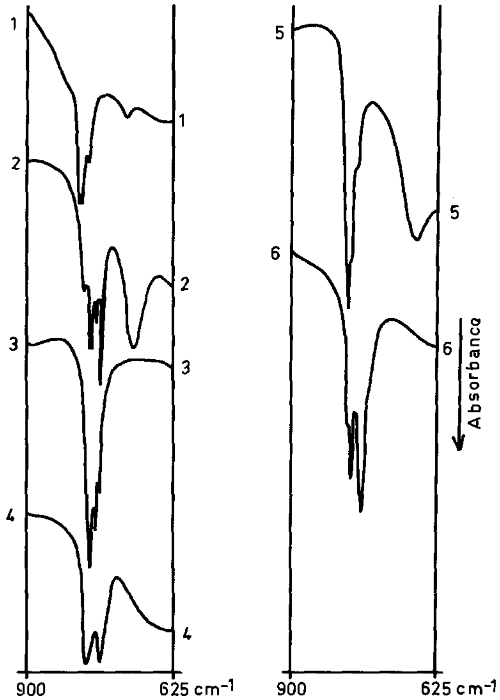

FIG. 3. Splitting of the δ(OCO) band in the thorium tetraformates. 1, $Th(HCOO)_4$, $3H_2O$; 2, Th(HCOO), $\frac{3}{4}H_2O$ "L"; 3, $Th(HCOO)_4\alpha$; 4, $Th(HCOO)_4\gamma$; 5, $Th(HCOO)_4$, $\frac{3}{4}H_2O$ "M"; 6, $Th(HCOO)_4\delta$.

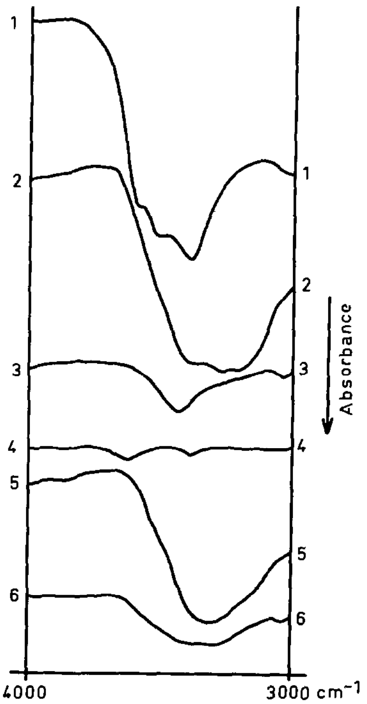

FIG. 4. ν(OH) absorption bands in the thorium tetraformates. 1, $Th(HCOO)_4$, $3H_2O$; 2, $Th(HCOO)_4$, $\frac{3}{4}H_2O$ "L"; 3, $Th(HCOO)_4\alpha$; 4, $Th(HCOO)_4\gamma$; 5, $Th(HCOO)_4$, $\frac{3}{4}H_2O$ 'M"; 6, $Th(HCOO)_4\delta$.

3520, and 3380 cm^{-1} (Fig. 4). The ν_2 frequency of the water at 1678 cm^{-1} forms a shoulder on the intense ν_{as}(CO) band of the formate ion. The frequency of this δ(HOH) band indicates that the crystal water in the trihydrate is partially coordinated to the thorium atom; indeed, we observe two relatively weak absorption bands at 717 and 553 cm^{-1} corresponding to the hindered rotation modes of coordinated water. The relative intensities of these bands show that the Th–OH_2 bonds are weak.

Arutyunyan et al. (*9*) and Molodkin et al. (*10*) have established that the coordination number of the thorium atom in the trihydrate is ten: Each thorium atom is surrounded by eight oxygen atoms from formato groups, located at the vertices of a distorted Archimedean antiprism, and by two oxygen atoms of water molecules above the square bases of this antiprism, at a distance Th–OH_2 = 3.1 Å. It can also be considered that in the crystal structure of the trihydrate each thorium atom is surrounded by eight thorium atoms at the distances 6.5 and 7.1 Å (*9*). This coordination type leaves little space for water molecules in the crystal structure, and we can admit that the third water molecule in the trihydrate is partially distorted, the corresponding infrared ν(OH) bands being observed at 3590 and 3520 cm^{-1}. Thus, we may assert that the trihydrate crystal presents at least two kinds of water: Two of the three water molecules are directly coordinated to the thorium atom, and the third water molecule is distorted lattice water. The presence of two kinds of water in $Th(HCOO)_4$, $3H_2O$ has already been deduced from NMR examination (*11*), but we could not establish in this way, how these water molecules are linked to the crystal structure. Arutyunyan and coworkers' X-ray study suggests that the thorium tetraformate trihydrate may be represented by the following complex structure:

$$[Th(HCOO)_4(H_2O)_2]H_2O.$$

Our infrared spectrophotometry supports this suggestion.

The Th–OH_2 distance being 3.1 Å, the stretching force constant corresponding to the ν(Th–OH_2) bond may be calculated by means of the following Badger-type relation we have recently used (*12*):

$$r_{\mathrm{Th-O}} = \frac{0.49}{k^{1/3}} + 1.246 \text{ Å},$$

where $r_{\mathrm{Th-O}}$ is the length of the Th–O bond and k is the Th–O stretching force constant.

For $r_{\mathrm{Th-O}} = 3.1$ Å we find $k = 0.209 \times 10^5$ dyn/cm. In the harmonic oscillator approximation, and if the coordinated water is assimilated to a sphere having the same mass as the H_2O molecule, the following relation holds:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}},$$

μ being the reduced mass of the Th–OH_2 system. If we introduce in this relation the above calculated value of the stretching force constant, the value of the frequency obtained for the ν(Th–OH_2) vibration is 140 cm^{-1}. Such a low-frequency vibration is beyond the range of the infrared spectrometers used here.

Th(*HCOO*)$_4$, $\frac{2}{3}$*H*$_2$*O* "*L*". The infrared absorption spectrum of this compound exhibits a complex ν(OH) band with three distinct maxima at 3380, 3270, and 3200 cm^{-1}. The ν_2 frequency of the crystal water corresponds to a doublet band with two absorption maxima at 1683 and 1690 cm^{-1}. Two intense absorption bands at 696 and 552 cm^{-1} are assigned to the hindered rotation of strongly coordinated water, and we may reasonably assume that the Th–OH_2 distance in this intermediate hydrate is less than the 3.1 Å found for the trihydrate, the corresponding ν(Th–OH_2) absorption band being observed at 385 cm^{-1}.

The two absorption bands at 3380 and 3270 cm^{-1} are respectively assigned to the antisymmetric (ν_3) and the symmetric (ν_1) vibrations of the coordinated water. The frequency shifts observed with respect to the ν_3 and ν_1 frequencies in liquid water are respectively $\Delta\nu_3 = -65$ cm^{-1} and $\Delta\nu_1 = +51$ cm^{-1}; these shifts may correspond to hydrogen bonds of relatively weak energy. The strong absorption band near 3200 cm^{-1} may be due to a coupling effect between a water fundamental and the $2\nu_4$ overtone of the formate ion.

From the above discussion we conclude that the water in the crystal structure of the intermediate tetraformate $Th(HCOO)_4$, $\frac{2}{3}H_2O$ "L" is totally in the coordinated state.

Th(*HCOO*)$_4\lambda$, α, *and* γ. Throughout the course of the dehydration of the intermediate tetraformate $Th(HCOO)_4$, $\frac{2}{3}H_2O$ "L", the relative intensities of the water absorption bands decrease. At 62°C these bands have disappeared and a new absorption band of relatively weak intensity appears near 3420 cm^{-1}. This new band is assigned to the vibration of residual water. When the temperature reaches 65°C the polymorphic transition,

$$Th(HCOO)_4\lambda \rightarrow Th(HCOO)_4\alpha,$$

is observed. In this tetraformate the weak band near 3420 cm^{-1} still persists. Finally, beyond the temperature of 125°C, a second polymorphic transition is observed:

$$\mathrm{Th(HCOO)_4}\alpha \rightarrow \mathrm{Th(HCOO)_4}\gamma.$$

The infrared spectrum of $\mathrm{Th(HCOO)_4}\gamma$ exhibits two relatively weak absorption bands at 3635 and 3380 $\mathrm{cm^{-1}}$ corresponding to residual water partially in the vapor state, or adsorbed on the solid. This residual water disappears at 153°C.[2]

$Th(HCOO)_4$, $\frac{2}{3}H_2O$ "M". The broad and complex band corresponding to the ν(OH) vibrations presents a single absorption maximum near 3340 $\mathrm{cm^{-1}}$. The ν_2 frequency of the water is observed at 1655 $\mathrm{cm^{-1}}$, and the bands due to the hindered rotation of the water molecules are situated at 661 and 578 $\mathrm{cm^{-1}}$. Consequently, the crystal water in this intermediate tetraformate is entirely in the coordinated state.

Throughout the heating of $\mathrm{Th(HCOO)_4}$, $\frac{2}{3}\mathrm{H_2O}$ "M" the following reactions are observed:

$$\mathrm{Th(HCOO)_4},\ \tfrac{2}{3}\mathrm{H_2O}\ \text{“M”} \xrightarrow{93^\circ\mathrm{C}} \mathrm{Th(HCOO)_4}\mu + \tfrac{2}{3}\mathrm{H_2O},$$

$$\mathrm{Th(HCOO)_4}\mu \xrightarrow{95^\circ\mathrm{C}} \mathrm{Th(HCOO)_4}\delta,$$

$$\mathrm{Th(HCOO)_4}\delta \xrightarrow{125^\circ\mathrm{C}} \mathrm{Th(HCOO)_4}\gamma.$$

The infrared absorption spectra of $\mathrm{Th(HCOO)_4}\mu$ and $\mathrm{Th(HCOO)_4}\delta$ present relatively weak absorption bands of residual water at 3340 and 3380 $\mathrm{cm^{-1}}$, respectively. This residual water disappears during the $\delta \rightarrow \gamma$ transition.

5.3. Vibrations of the Th–O Bond

The infrared absorption spectra of the thorium tetraformates exhibit bands in the 310–200 $\mathrm{cm^{-1}}$ low-frequency range. These bands are split and it will be now demonstrated that they are due to the Th–O stretching vibrations between the thorium atoms and the oxygens of the formato groups.

In the crystal structure of thorium tetraformate trihydrate we may isolate a OThO group of site symmetry C_{2v}. If we assume a generalized force field, we can use the following data (*12*):

$r_{\mathrm{Th-O}}$ is 2.58 Å (average distance);

OThO angle is 90°;

$k_1(\mathrm{ThO}) = 0.76 \times 10^5$ dyn/cm;

$k_2(\mathrm{ThO, ThO'}) = -0.25 \times 10^5$ dyn/cm;

$k\delta/r^2 = k_1/10 = 0.076 \times 10^5$ dyn/cm.

If these data are introduced in the general formulas given by Herzberg (*13*) for a nonlinear triatomic molecule, the following frequencies are calculated for the three fundamentals of the OThO group:

$$\nu_1 = 249\ \mathrm{cm^{-1}} \quad \nu_s(\mathrm{ThO}),$$

$$\nu_2 = 70\ \mathrm{cm^{-1}} \quad \delta(\mathrm{OThO}),$$

$$\nu_3 = 275\ \mathrm{cm^{-1}} \quad \nu_{as}(\mathrm{ThO}).$$

Thus, the complex bands in the 310–200 $\mathrm{cm^{-1}}$ range are assigned to the whole of the symmetric and antisymmetric stretching vibrations of the Th–O (formate) bond.

It is noteworthy that the fundamentals calculated for the OThO triangular group are nearly the same whatever be the force field assumed, and this for any value of the OThO angle between 45 and 135°.

In the infrared spectrum of $\mathrm{Th(HCOO)_4}$, $\frac{2}{3}\mathrm{H_2O}$ "L" the two broad and intense absorption bands observed at 268 and 259 $\mathrm{cm^{-1}}$ are respectively assigned to the ν_{as}(ThO) and ν_s(ThO) modes. The position of these bands indicates that in the investigated compound the average Th–O (formate) distance is nearly the same as in the trihydrate (e.g., 2.58 Å).

At last, the infrared spectrum of $\mathrm{Th(HCOO)_4}$, $\frac{2}{3}\mathrm{H_2O}$ "M" exhibits five absorption bands at 214, 232, 266, 285, and 307 $\mathrm{cm^{-1}}$, corresponding to the ν(ThO) stretching frequencies of the different Th–O (formate) bonds in this crystal.

6. Conclusion

We have seen (Section 5.1) that in the different thorium tetraformates investigated the bidentate formato groups are bridged between two thorium atoms. On the other hand, we have established by X-ray diffraction (*3*) that the different crystal lattices of the thorium tetraformates, which are issued from the trihydrate $\mathrm{Th(HCOO)_4}$, $\mathrm{3H_2O}$, could be derived from a centered-tetragonal cell. We can, therefore, reasonably admit that the coordination polyhedron of the thorium atoms in all the thorium tetraformates is a distorted Archimedean antiprism.

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