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Chloride and pseudohalide complexes of thorium in anhydrous solvents

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Abstract

Interaction of thorium tetrachloride with acetone, methanol and dimethylformamide was studied. It was found that in diluted methanol solutions the metal forms compounds, such as $ThCl_2(OCH_3)_2$. In more concentrated solutions complex $ThCl_4$–$4CH_3OH$ dominates. In DMF solutions, only solvate complex $ThCl_4$–2DMF was found, and the stability of the complex was determined. UV, IR and PMR spectroscopy were used for the investigation of the complexing of thorium with cyanates, thiocyanates and selenocyanates. Stability constants increase from DMF through methanol to acetone. Nitrogen was found as donor atom for all CNO^-, CNS^- and $CNSe^-$ ions. The stability constants were correlated with atomic distance and electron density on nitrogen, obtained from calculations and with spectroscopic data. © 1998 Published by Elsevier Science S.A.

Keywords: Thorium complexes; Anhydrous solvents; Pseudohalides

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1. Introduction

Because of the significant interest in thorium, due to its importance in nuclear power engineering [1–3], the scalene research of its compounds and, initially, pseudohalides (cyanates, thio- and selenocyanates), deserves special attention (wide applications have recently been discovered). The thiocyanates are used in the analysis and extraction separation of metals with similar properties, and for their electrolytic production. The selenocyanate compounds are of practical interest for electronics engineering.

Despite of their importance, until now the complexing reactions of thorium with halide and pseudohalide ligands in anhydrous media have not been investigated enough [4]. The data on thorium tetrachloride behavior in anhydrous solvents are insufficient.

Taking this into account, we have studied thorium tetrachloride reaction in anhydrous media, and also the formation of pseudohalide complexes with thorium.

2. Experimental

The basic techniques in our research were ^{1}H nuclear magnetic resonance, electronic and IR spectroscopy, pH potentiometry, conductometry, elemental chemical analysis and quantum chemical calculations.

Carefully cleaned and dried $ThCl_4$ was used as the initial compound; completely dried acetone, methanol, dimethylformamide (DMF) and also highly purified cyanates, thiocyanates and selenocyanates of potassium, were used as solvents.

3. Results

For the first stage, we investigated the behavior of thorium chloride in acetone, methanol and DMF. With preliminary experiments it was established that acetone does not interact with $ThCl_4$. Therefore in all further experiments it was chosen as an inert solvent.

Introduction of dimethylformamide in a $ThCl_4$–acetone system reflects, in NMR spectra, a new doublet of methyl groups displaced in low magnetic fields. We assign this doublet to DMF that binds thorium tetrachloride. With increase of dimethylformamide concentration, the peak of the methyl groups of DMF in NMR spectra is moved to high magnetic fields, becoming close to free DMF adsorption. Experimental data show that peak displacement in NMR spectra, which are included in the structure of the thorium complex, is proportional to a log of total concentration of this solvent. From the measurements of chemical shifts of coordinated DMF, the composition and dissociation constants of the solvato-complex $ThCl_4(DMF)_n$ are found (Table 1).

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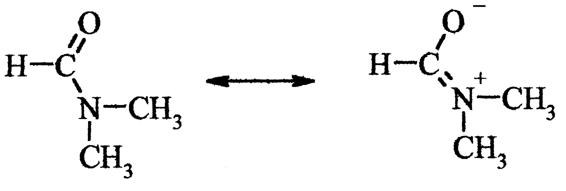
Table 1
Composition and equilibrium constants of a reaction of thorium complexes in non-aqueous solvents

Solvent	Ligand	Composition of complex	Equilibrium constant
Acetone	Cl^-	—	—
Methanol		1:4	5.5×10^{-4}
DMF		1:2	5.0×10^{-4}
Acetone	CNS^-	1:1	3.1×10^{-4}
		1:3	2.7×10^{-10}
		1:4	2.8×10^{-13}
Methanol		1:1	4.3×10^{-4}
		1:2	2.2×10^{-7}
		1:3	1.5×10^{-10}
		1:4	1.3×10^{-13}
DMF		1:1	6.3×10^{-4}
		1:2	5.3×10^{-7}
		1:3	5.5×10^{-10}
		1:4	7.6×10^{-13}
		1:5	1.2×10^{-15}
		1:6	2.0×10^{-18}
Acetone	$CNSe^-$	1:1	5.4×10^{-4}
		1:4	7.5×10^{-13}
DMF		1:1	8.3×10^{-4}
		1:2	1.2×10^{-6}
		1:3	1.6×10^{-9}
		1:4	2.7×10^{-12}
		1:5	4.4×10^{-15}
		1:6	8.6×10^{-18}
DMF	CNO^-	1:1	2.2×10^{-2}
		1:2	7.0×10^{-4}

The NMR method has allowed to establish the dimethylformamide coordination to atoms of thorium. In our experiments, for the $ThCl_4$–DMF–acetone system, two different signals of protons of methyl groups were detected. In the case where the coordination of DMF to thorium was over a nitrogen atom, a single line would be observed instead of the doublet band in an NMR spectrum. In the case of oxygen binding of DMF, the C–N bond should have a double bond character, the rotation around it should be retarded, as in free DMF; and from two dominant resonance structures, preference is given for structure (II):


(I) (II)

In this case, in the NMR spectrum, a doublet band of protons of DMF methyl groups is observed. From the obtained data it is possible to make a conclusion that, in a $ThCl_4$–DMF–acetone system, the interaction goes over the carbonyl oxygen of DMF. This conclusion will be confirmed with data obtained from IR spectra of the above-mentioned and similar systems.

In methanol, for the thorium concentration range from 1.95×10^{-2} to 1.52×10^{-4} mol$\times$l^{-1}, thorium tetrachloride reacts as follows:

$$ThCl_4 + nCH_3OH = ThCl_4 - n(OCH_3)_n + nHCl$$

Up to $ThCl_2(OCH_3)_2$ formation, the low values of solvolysis constants ($K_1 = 3.0\times10^{-5}$, $K_2 = 4.7\times10^{-11}$) reflect that the methanolysis of thorium chloride does not proceed too far. Obviously, for higher dilutions, complexes of thorium with large number methoxy groups can be obtained.

In order to study the properties of more concentrated solutions, in which the main part of thorium tetrachloride remains as solvate, we applied the NMR technique. The $ThCl_4$–H_3OH–acetone system was investigated. From the appearance of an additional peak in the spectrum, the NMR of this system, and the change in its intensity, with increase of methanol concentration, the composition of the solvato complex was found to be $ThCl_4\cdot4CH_3OH$ and the dissociation constant of the complex was determined to be $K_D = 5.5\times10^{-4}$. Confirmation of such a type of complex is also provided by data on conductivity measurements and the pH of investigated solutions. In the case where $ThCl_4$ was exposed to solvolysis, as in the following scheme,

$$ThCl_4 + 4CH_3OH = Th(OCH_3)_4 + 4HCl,$$

HCl produced should increase the acidity of the solutions and their conductivity. In our experiments with increased methanol concentration, the pH and conductivity in the system varied insignificantly. This has allowed to conclude that the solvolysis practically does not take place and, in the concentrated acetone solutions of $ThCl_4$ with methanol, the solvato complex $ThCl_4\cdot4CH_3OH$ is formed.

By comparison of solvation of thorium tetrachloride in acetone by dimethylformamide and methanol it is possible to note that, in both cases, rather strong solvato complexes are formed. However, in the case of methanol, the number of bonded molecules of a solvent is more than in the dimethylformamide solvate, which is probably related to steric factors.

The following stage of work was the investigation of the interaction of thorium tetrachloride with cyanates, thiocyanates and selenocyanates of alkaline metals in the above-mentioned solvents.

Using electronic spectroscopy and conductometry methods, it was established that thiocyanate complexes of thorium in acetone are formed according to the scheme:

$$ThCl_4 + 4mKCNS = K_mTh(CNS)_4Cl_m + (4 - m)KCl$$

where m could be 1, 3 and 4; $K_1 = 3.1\times10^{-4}$, $K_3 = 2.7\times10^{-10}$ and $K_4 = 2.8\times10^{-13}$.

For high concentrations of methanol, thorium tetrachloride forms thiocyanate complexes with compositions of Th^{4+}:CNS^- from 1:1 to 1:4; but, in DMF these compositions range from 1:1 to 1:6. Calculated equilibrium constants for the reaction of complex formation (shown in

Table 1) reflect the increasing stability of thorium thiocyanates in the series: DMF $<$ methanol $<$ acetone.

Using IR spectroscopy, it was established that thiocyanate ions are coordinated to thorium by means of nitrogen atoms (isothiocyanate structure) [5].

The conditions of formation of cyanate and selenocyanate complexes of thorium were investigated using a similar technique; the compositions and equilibrium constants are shown in Table 1. Using IR spectroscopy, the coordination of cyanate and selenocyanate groups to thorium atoms by means of nitrogen was established.

The data obtained allow to trace the properties of some compounds of thorium in anhydrous solutions, and to compare the complexing ability of metal in relation to various pseudohalide ligands: NCO$^-$, NCS$^-$, NCSe$^-$. From Table 1, it follows that the thorium complex compounds in acetone, with cyanate, thiocyanate and selenocyanate ions, are stronger than in methanol and DMF.

Methanol can form coordination bonds with a cation (thorium) by means of free electrons of oxygen atoms, and forms the same bond with an anion (chloride ion) by means of hydrogen atoms. Solvolysis of thorium tetrachloride is evidence of the strong interaction of methanol that was observed in a $ThCl_4$–CH_3OH system. However, methanolysis of $ThCl_4$ only goes up to the second step and, with low solvolysis constants. This is probably related to the fact that the main part of thorium tetrachloride in methanol remains as a solvate, with coordinated methanol molecules. This conclusion is confirmed by the existence of solvato complex $ThCl_4 \cdot 4CH_3OH$, which was found in acetone solution using NMR, and obtained in a crystalline state.

The DMF is dipolar solvent with a high donor number. Thus, it partially reacts with an anion over mobile hydrogen as the electron acceptor. In that case, the main influence on the complexing solvation of ions is rendered. Existence of the tautomeric form of DMF can lead to partial solvolysis in that solution over the oxygen atom. However, this process proceeds extremely slowly, and in DMF solutions it is possible to observe the existence of complicated pseudohalide complexes, such as $Th(NCS)_6^{2-}$, and $Th(NCSe)_6^{2-}$.

The acetone has small donor number. Therefore, the stability of thorium complexes in this media is higher and the complexing process flows easily.

In all solvents studied, the ability of thorium to form pseudohalide complexes decreases in the series: NCS$^-$ $>$ NCSe$^-$ $>$ NCO$^-$.

It is doubtless that the complex compound stability is direct related to charge density on specific atoms of ligands, the character of bonds between atoms, and the distribution of electrons on energy levels.

Quantum chemical calculations (Table 2) have shown that the surplus electronic densities were almost totally concentrated on the nitrogen atom of the pseudohalide ions, and should promote coordination of investigated ions over nitrogen. However, the availability of a small negative charge on X (X = O, S, Se) atoms suggests that coordination is also possible over these atoms, and the highest propensity to this should be exhibited by oxygen ($q = -0.605$). Increase of the negative charge on the oxygen atom, in comparison with sulfur and selenium atoms, and diminution of the charge density on nitrogen atoms should reduce the strength of the M–N bond in compound $M(NCO)_n$ in comparison with the same bond in $M(NCS)_n$ and $M(NCSe)_n$, and decrease the stability of these compounds in the series: NCS$^-$ $>$ NCSe$^-$ $>$ NCO$^-$. This position is in good agreement with the obtained constants for the reaction of thorium with the above-mentioned ions (Table 2). Linear correlation of equilibrium constants with charges on N and X atoms confirms the conclusion.

From the calculated bond orders N–C and C–X in NCS$^-$, NCSe$^-$ and NCO$^-$ ions, it follows that the C–N bond has enhanced multiplicity, which can be described as $3 > C{=}N > 2$, and the C–X bond as $2 > C{-}X > 1$. These calculated data are well in agreement with calculated earlier bond orders for the NCS$^-$ ion and spectral and X-ray data [6,7]. It is also important to note that the CN bond order is increased in the series: S $<$ Se $<$ O (Table 2). This should shift the frequency of the valent band CN in IR spectra to a higher frequency. Indeed, the νCN for thiocyanate, selenocyanate and cyanate complexes of thorium have values of: 2050–2070, 2065–2070 and 2210 cm^{-1} accordingly. On the other hand, the adsorption of the C–X in those complexes is in a higher region than singular C–X bonds, and decreases in the series S $>$ Se $>$ O (800, 675, 637 cm^{-1}) together with a bond order lowering (1.338, 1.319, 1.042).

The electronic spectra of pseudohalide compounds of thorium have absorption maxima at 305, 325 and 275 nm for NCS$^-$, NCSe$^-$ and NCO$^-$ ions. The calculated

Table 2
Effective charges on atoms and bond orders NCS$^-$, NCSe$^-$, NCO$^-$ ions

Ion	Charges on atoms			Orders of bonds		$K_{Th}0$ (NCX)$^{3+}$ in DMF	Ig K
	N	C	X	NC	CX		
NCS$^-$	−1.258	0.419	−0.161	2.295	1.338	6.3×10^{-4}	−3.201
NCSe$^-$	−1.248	0.459	−0.211	2.316	1.319	8.3×10^{-4}	−3.081
NCO$^-$	−1.158	0.759	−0.605	2.498	1.042	1.1×10^{-2}	−1,959

energies of electron transitions from the last filled to the unfilled orbital are in agreement with frequency maxima in electronic spectra of absorption of the indicated ions.

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