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SYNTHESIS AND THERMAL STABILITY OF THE ADDUCTS OF RARE EARTH ELEMENT β-DIKETONATES WITH MACROCYCLIC POLYETHERS

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Synthesis methods for the adducts of lanthanoid pivaloyltrifluoroacetonates with 1,4,7,10,13,16-hexaoxacyclooctadecane are described. The applicability of thermal analysis at quasi-equilibrium conditions for coordination compounds of this type is demonstrated for the first time. Based on experimental results the effect of the starting reactants on the structure of the adducts, on their volatility and thermal stability is established.

The adducts of rare earth element β-diketonates with additional ligands (tetrakis-chelates) are coordinatively unsaturated compounds and possess therefore many valuable properties as compared to tris-chelates. The tetrakis-chelates rare earth element pivaloyltrifluoroacetonates: $Na[Ln(PTA)_4]$ (where Ln stands for any rare earth element) are thermally stable compounds and pass into the gas phase without decomposition [1], allowing to determine the range of their practical applicability [2]. It appears that tetrakis-chalates with differing ligands, with polydentate additional ligands possess similar properties.

Earlier we succeeded to obtain adducts of $Ln(PTA)_3$ with 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) [3]. In this paper we report on studies that are the continuatoon of the earlier work: different methods for synthetizing the adducts, their structure and thermal stability will be discussed.

The adducts were obtained by different paths. One of these consisted in exchanging water in the coordination sphere of rare earth element tris-chelates for the additional ligand as represented by the following equation:

$$LnL_3 \cdot nH_2O + mQ \xrightarrow{t} LnL_3 \cdot mQ + nH_2O \qquad (1)$$

where L = PTA, Q = 18-crown-6, $n = 1, 2$, m = 1, Ln = a rare earth element.

Such syntheses were carried out both in slightly polar organic solvents and in the absence of solvent by melting the rare earth element tris-chelate with excess

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additional ligand. Utilization of rare earth element trix-chelate as starting material gives rise to certain difficulties connected with purification. Thus, at recrystallization the solvent will also be added, owing to the high coordination number of the central lanthanoid atom. Purification by vacuum sublimation is not feasible owing to thermal decomposition of the complexes resulting in the formation of non-volatile hydroxo compounds.

We presumed that as starting materials in the synthesis of crown ether adducts with rare earth element β-diketonates, rare earth element crown ether complexes and alkali metal salts of β-diketones might be utilized, these being accessible compounds and readily obtained in high yields [4].

In this case the adducts will be formed according to the following equation:

$$LnX_3 \cdot Q + 3\ NaPTA \rightarrow 3NaX + Ln(PTA)_3 \cdot Q \qquad (2)$$

where $X = Cl^-$, NO_3^-.

The adducts synthetized by the above methods were investigated using various physico-chemical techniques. Based on IR spectral data and water percentage obtained by the Fischer method we stated that the substitution of water in the starting materials proceeds completely and the adducts obtained are anhydrous. Data of elemental analysis for C, H, N and F and rare earth element content in per cents indicate that the composition of the adduct is practically independent—within experimental error—of the method of synthesis (Table 1). We also found that the general character of IR and UV spectra of the adducts obtained by the different synthesis methods is identical.

The molecular ion M^+ of the Nd adduct obtained by field mass spectrometry was found to be equal to 993. One may hence confirm that when the substances in question are introduced into the source of the mass spectrometer, the composition of the adduct vapour corresponds to the composition of the initial product.

Table 1 Data of the elemental analysis of the adducts $Ln(PTA)_3 \cdot Q$*

Adduct	Synth. method	C, %		H, %		F, %		Rare earth element, %	
		found.	calcd.	found.	calcd.	found.	calcd.	found.	calcd.
$La(PTA)_3 \cdot Q$	1	43.75	43.75	5.50	5.51	17.5	17.3	14.3	14.1
$La(PTA)_3 \cdot Q$	2	43.68	43.75	5.53	5.51	17.4	17.3	14.2	14.1
$Nd(PTA)_3 \cdot Q$	1	43.26	43.51	5.28	5.48	17.2	17.2	14.6	14.5
$Nd(PTA)_3 \cdot Q$	2	43.40	43.51	5.35	5.48	17.1	17.2	14.4	14.5
$Er(PTA)_3 \cdot Q$	1	42.62	42.53	5.41	5.35	16.6	16.5	16.6	16.4
$Er(PTA)_3 \cdot Q$	2	42.71	42.53	5.47	5.35	16.3	16.5	16.3	16.4

* where Q = 18-crown-6

Table 2 Major ions in the mass spectra of the adducts $Ln(PTA)_3 \cdot Q$

Method 1		
$Er(PTA)_3 \cdot Q$ (I)		
Ions	m/e	I, %
$[Er(PTA)_2Q—C_2H_4]^+$	793	4
$[Er(PTA)_2Q—C_2H_6]^+$	791	3.2
$[Er(PTA)_2Q—C_2H_5O]^+$	776	4
$[Er(PTA)_2Q—C_2H_6O]^+$	775	4
$[Er(PTA)_3—C_4H_8]^+$	696	98
$[Er(PTA)_3—C_4H_9]^+$	695	90
$[Er(PTA)_3—C_4H_{10}]^+$	694	100
$[Er(PTA)_2]^+$	557	78

Method 2					
$Nd(PTA)_3 \cdot Q$ (II)			$La(PTA)_3 \cdot Q$ (III)		
Ions	m/e	I, %	Ions	m/e	I, %
$[Nd(PTA)_2Q—C_2H_4]^+$	770	4	$[La(PTA)_2Q—C_2H_4]^+$	765	0.4
$[Nd(PTA)_2Q—C_2H_6]^+$	769	3	$[La(PTA)_2Q—C_2H_6]^+$	763	2.5
$[Nd(PTA)_2Q—C_2H_4O]^+$	754	80	$[La(PTA)_2Q—C_2H_5O]^+$	748	27.6
$[Nd(PTA)_2Q—C_2H_5O]^+$	753	60	$[La(PTA)_2Q—C_2H_4O]^+$	747	100
$[Nd(PTA)_2Q—C_2H_6O]^+$	752	100	$[La(PTA)_3—C_4H_9]^+$	667	1
$[Nd(PTA)_3—C_4H_9]^+$	672	5.5	$[Ln(PTA)_2]^+$	529	5
$[Nd(PTA)_2]^+$	534	18	$[La(PTA)_2—CF_2]^+$	479	1.2
$[Nd(PTA)_2CF_2]^+$	484	6			

An analysis of the data in Table 2 allows to conclude that significant differences are present in the mass spectra of the adducts obtained by methods 1 and 2, resp. The main fragmentation path of the adducts obtained by method 1 is splitting off of the crown ether and of tert. butyl, according to the reaction

$$M^+ \xrightarrow{e^-} [M—Q—C_4H_{10}]^+$$

The intensity of this ion is equal to 100%, and the intensities of the ions $[M—Q—C_4H_9]^+$ and $[M—Q—C_4H_8]^+$ are 90% and 98%, resp. It is hence evident that the dissociative ionization of these compounds starts with the splitting-off of the molecules of the additional ligand, i.e. the crown ether Q, and continues with the decomposition of the chelate nucleus and the destruction of the β-diketone L.

The fragmentation of the adducts obtained by method 2 proceeds by a fully different mechanism. The major products in this case are the ions formed as follows:

$$M^+ \xrightarrow{e^-} [M—L—C_2H_4O]^+$$

$$M^+ \xrightarrow{e^-} [M—L—C_2H_5O]^+$$

$$M^+ \xrightarrow{e^-} [M—L—C_2H_6O]^+$$

The intensities of the other ions are insignificant. Consequently, the dissociative ionization starts with splitting off β-diketone molecules followed by the destruction of the crown ether molecules.

Thus, taking into account the synthesis methods of the adducts and the experimental results, one may assume that in the case of method 1 the additional ligand, i.e. the crown ether replaces water in the tris-chelate and is located in the external coordination sphere of the complex; in this case the rare earth element does not enter the cavity of the crown ether. In the case of method 2, a mixture of isomers is formed; in one of them the rare earth element is located in the cavity of the crown ether, while the β-diketone molecules occupy the places of the anionic groups NO_3^-.

The structural differences of the adducts should be reflected in their thermal stability. We therefore performed thermal analysis of the substances in the temperature interval of 20 to 500 °C, in helium. The results are presented in Table 3.

Table 3 Thermoanalytical data of the adducts

Adduct	Synth. method	Endotherm. effect	Exotherm. effect	T_{max} of process	Non-volatile residue, %
$Nd(PTA)_3 \cdot$ 18-crown-6	1	140; 180	330	310	22.4
$Nd(PTA)_3 \cdot$ 18-crown-6	2	—	290; 330	315	33
$Pr(PTA)_3 \cdot$ 18-crown-6	2	—	280; 320	315	16.3
$Er(PTA)_3 \cdot$ 18-crown-6	2	—	280; 320	280; 296	11.9

Figure 1 represents the relative TG, DTG and DTA curves of the complexes $Nd(PTA)_3$. 18-crown-6 synthetized by method 1 (substance I) and by method 2 (substance II), resp. On the DTA curve of product I, two endothermic effects not accompanied by mass loss are observable. They may be assigned to the melting process and to polymorphous transformation of the adduct. The presence of a slight exothermic effect after the sublimation of the bulk of the substance may be explained by the decomposition of the non-volatile residue.

No endothermic effects are observed on the DTA curve of product II. Two slight exothermic effects at 290 and 330 °C are present, corresponding to the temperature range where the bulk of the substance sublimates. The percentage of the non-volatile residue is higher than in the case of substance I; it is obvious hence that the sublimation process of adduct II is accompanied by partial decomposition.

However, from the character of the TG curves one cannot conclude on different volatility of the adducts. To determine their relative volatility, we applied—for the first time for volatile coordination compounds—thermogravimetry at quasi-equilibrium conditions [5]. The particular feature of this method consists in the fact

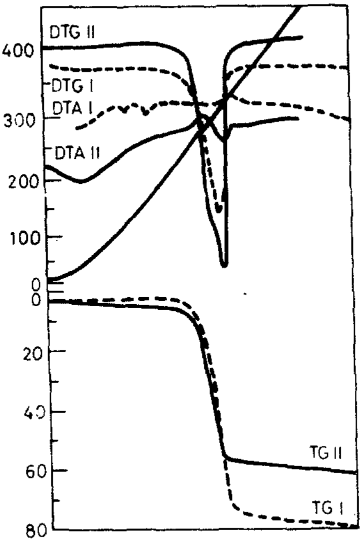

Fig. 1 Thermoanalytical curves of the adducts $Nd(PTA)_3 \cdot$ 18-crown-6 obtained by different synthesis methods

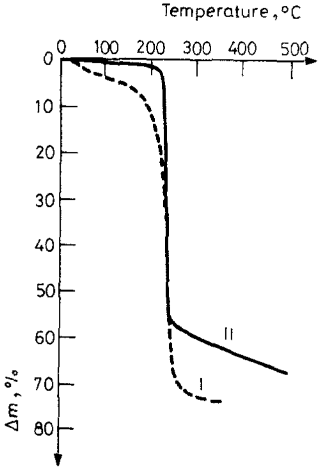

Fig. 2 Sublimation of $Nd(PTA)_3 \cdot$ 18-crown-6 obtained by different synthesis methods at quasi-equilibrium conditions

that by maintaining a low constant mass loss rate (0.16 mg/min) temperature will become stabilized till the end of the process. This temperature is close to equilibrium temperature at the given pressure, defined by the crucible used.

Figure 2 demonstrates that intense mass loss in product II starts at 240...250°. In product I, slow mass loss begins at 50°. The presence of a small step on the Δm *vs.*

T curve in this range, corresponding to 1.5% of total mass loss may be explained by solvent traces being eliminated. Subsequently, in the 60 to 240° range, continuous slight mass loss takes place, obviously related to splitting-off of the crown ether. In the 240–260° range the curve coincides with the curve for substance II.

It is hence more correct to apply the experimental data obtained at quasi-equilibrium conditions for comparing volatility and thermal stability of the adducts than the data obtained at linear heating rate, since the thermal properties observed in the latter experiment are largely defined by the kinetic characteristics of the process and not by its thermodynamics.

The results of the thermoanalytical experiments confirmed that the adducts obtained by different synthesis methods differ both in volatility and thermal stability, by reason of the differences in their structure.

Experimental

Synthesis of $Ln(PTA)_3 \cdot Q$ *adducts by method 1*

To a solution of $Ln(PTA)_3 \cdot 2H_2O$ in chloroform (0.002 mol in 25 ml) 18-crown-6 (0.004 mol) was added during stirring. The reaction mixture was kept at this temperature and stirred for 5–10 min. The product was washed with 25–30 ml water to remove excess crown ether, filtered and dried at ambient temperature. The yield was 95–98%.

Analytical results are listed in Table 1.

Synthesis of $Ln(PTA)_3 \cdot Q$ *adducts by method 2*

To a solution of $Ln(NO_3)_3 \cdot 18\text{-crown-}6 \cdot nH_2O$ (0.002 mol in 80 ml ethanol), where $n = 0$ for La and Nd, $n = 2$ for Eu and Gd, $n = 3$ for Tb and Yb, a solution of 0.006 mol NaPTA in 100 ml chloroform was added during stirring. The reaction mixture was boiled for 2 hours, evaporated to dryness, washed with water to remove $NaNO_3$ and dried in air. Yield: 80–85%.

Analytical results are listed in Table 1.

Water content in the initial and final products has been determined by the Fischer method, establishing the equivalence point by electrometry. The experimental error was equal to ±1%.

Mass spectra were taken using a mass spectrometer MS–902; the sample was introduced at ≈140 °C.

For thermal analysis a Derivatograph ("Paulik, Paulik and Erdey") manufactured by MOM was used; the atmosphere was helium. The standard method of introducing helium directly below the vault of the oven does not allow to maintain the required composition of the inert atmosphere, owing to noticeable amounts of air being sucked in. To obtain a better quality of the inert atmosphere, the following changes were carried out. Both thermocouples were located below a flask fitted with a ground joint to a copper conus placed lower than the base of the oven. In this case, air will be sucked in only through the narrow channel in which the thermocouples are introduced, and the length of the helium column will be increased by a factor of almost two. Helium is introduced into the upper part of the flask and displaces the air in 10 minutes. At such experimental conditions, splitting off of carbon monoxide from both oxalate and carbonyl complexes is accompanied by endothermic effects, while chemisorption of oxygen on the metals Mo and Nb is observable at high temperatures only.

We applied two variants for performing the experiment: linear heating rate and quasi-equilibrium conditions. In the first variant, i.e. in the traditional thermoanalytical experiment we recorded the temperature curve (T), the differential thermal curve (DTA), mass loss (TG) and mass loss rate (DTG). Sample mass was 40. . .80 mg, heating rate was 5 deg/min and 10 deg/min, the sample holder was a conic ceramic crucible.

In the second variant, the sublimation and decomposition process was performed at quasi-equilibrium conditions: a constant mass loss rate of 0.15 mg/min was set; using a plate-shaped sample holder the pressure of the gas being evolved was kept around 0.01 atm. In this case the sublimation temperature was stabilized practically till the end of the process and was close to the equilibrium temperature for the pressure 0.01 atm.

Conclusions

1. Different synthesis methods for the adducts of rare earth element pivaloyltrifluoroacetonates with 18-crown-6 were investigated. It was stated that products can be obtained differing both in structure and in some physico-chemical properties.

2. Mass spectrometry of the adducts obtained demonstrated that their dissociative ionization proceeds along different pathways by reason of the particular features of their structure.

3. The method of thermogravimetry at quasi-equilibrium conditions was applied for the first time to study the volatility and thermal stability of coordination compounds. This method allowed to demonstrate that the adducts obtained by different synthesis methods differ both in volatility and in thermal stability.

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Zusammenfassung — Methoden zur Synthese von Addukten von Lanthanoid-pivaloyltrifluoracetonaten mit 1,4,7,10,13,16-Hexaoxacyclooctadekan werden beschrieben. Die Anwendbarkeit der thermischen Analyse unter Quasi-Gleichgewichtsbedingungen zur Untersuchung von Koordinationsverbindungen wird erstmals aufgezeigt. Basierend auf die Versuchsergebnisse wird die Beziehung zwischen der Natur der Reaktanten und der Struktur, der Flüchtigkeit und der thermischen Stabilität der Addukte aufgezeigt.

Резюме — В работе описаны спобосы синтеза аддуктов пивалоилтрифторацетонатов лантаноидов с 1,4,7,10,13,16-гексаоксациклооктадеканом Впервые показана возможность применения метода термического анализа в квазиравновесных условиях для координационных соединений такого типа. На основании проведенных исследований установлено влияние исходных реагентов на строение аддуктов, их летучесть и термическую устойчивость.