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Preparation and Examination of Properties of Lanthanide Chloride Salts with Hexamethylenetetramine

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Summary. New complex salts of lanthanide chlorides with hexamethylenetramine of the general formula $LnCl_3 \cdot 2HMTA \cdot nH_2O$ [Ln = La, Pr, Nd, Sm, Dy, Er; *HMTA*-hexamethylenetetramine $N_4(CH_2)_6$; $n = 8, 10, 12$] have been obtained. On the basis of IR spectra (4000–200 cm^{-1}) and Raman spectra (3000–300 cm^{-1}), changes in the coordination sphere structure of the salts occurring in the course of thermal dehydration have been determined.

Keywords. Complex salts; Preparation; IR spectra; Raman spectra.

Darstellung und Untersuchung der Eigenschaften von Komplexsalzen der Lanthanidchloride mit Hexamethylentetramin

Zusammenfassung. Neue Komplexsalze der Lanthanidchloride mit Hexamethylentetramin mit der allgemeinen Formel $LnCl_3 \cdot 2HMTA \cdot nH_2O$ [Ln = La, Pr, Nd, Sm, Dy, Er; *HMTA* – Hexamethylentetramin $N_4(CH_2)_6$; $n = 8, 10, 12$] wurden dargestellt. Die Änderungen in der Struktur der Koordinationssphäre während der thermischen Dehydration der Salze wurden mittels Infrarot- (4000–200 cm^{-1}) und Ramanspektroskopie (3000–300 cm^{-1}) bestimmt.

Introduction

First works on coordination combinations of hexamethylenetetramine with metals referred to Mg (II), Zn (II), Hg (II), Au (III) chlorides, Hg (II), Bi (III) iodides, silver carbonate and silver nitrate [1]. The work by Santis and Kovacs [2] which presented X-ray structural analysis of the $CaBr_2 \cdot 2HMTA \cdot 10H_2O$ salt marked a progress in studies on *HMTA* coordination salts. Allan et al. [3] examined $MX_2\,(HMTA)_{1-2}$ salts where M = Mn (II), Ni (II); $X = Cl^-, Br^-, I^-, SCN^-$. They determined the composition of coordination sphere and coordination number of metals in the examined salts. Łodzinska and Grodzicki [4] analyzed vibrational specra of halide salts of Co (II) with *HMTA* and studied the thermal stability of these salts. Their work gave a start to a series of investigations upon the relation between hydration state of *HMTA* coordination salts and their structure. Łodzinska, Grodzicki et al. [5–8] studied changes occurring in dehydration process of halide salts of Ni (II) with *HMTA* on the basis of electronic and IR spectra.

In this work, preparation of chloride complex salts of lanthanides with hexamethylenetramine of different hydration state is described. The quantitative composition of these salts has been determined and thermal decomposition studies have been carried out. The obtained IR and Raman spectra are discussed in this paper and the changes which occur in the coordination sphere when the hydration state of the saltsy is changed as a result of thermal dehydration are presented.

Experimental Part

Apparatus and Reagents

A MOM derivatograph (Hungary) type OD-102 was used. Thermal curves were obtained in the temperature range 20–1 000°C at a heating rate of 2.5°/min. TG sensitivity was 100 mg, DTA and DTG sensitivity was 1/10. IR spectra were obtained by means of Carl-Zeiss Jena spectrophotometer in the range 700–4 000 cm^{-1} and 400–700 cm^{-1}, whereas in the range 200–400 cm^{-1} Perkin Elmer spectrophotometer Mode 577 was applied. In the range of far infrared, the technique os suspension and nujol was used. The suspensio was placed in polyethylene foil between CsI plates. Dry nitrogen was blown through the spectrophotometer chamber. Raman spectra were obtained in Coderg PHO apparatus in the range 300–3 000 cm^{-1}. An argon laser $\lambda = 488$ nm was used as the source of radiation. Salt samples were placed in a capillary which rotated at a rate of approx. 2 700 rev./min.

Analytically pure hexamethylenetetramine produced by P.O.Ch. Gliwice, lanthanide oxides and hydrochloric acid (1 + 1) were used fro synthesis.

Preparation Method

Lanthanide salts with hexamethylenetetramine and Cl^- were obtained in three ways: from water solutions, by thermal dehydration, and by dehydration with anhydrous ethanol and rectified alcohol. Salts with different hydration states and anhydrous salts were obtained. Lanthanide solutions were obtained by solving weighed samples of lanthanide oxides at high temperatures: La_2O_3 – 1.62 g; Pr_6O_{11} – 1.70 g; Nd_2O_3 – 1.68 g; Gd_2O_3 – 1.81 g; Dy_2O_3 – 1.86 g; Er_2O_3 – 1.91 g at high temperatures

Table 1. Results of analyses of salts of the general formula $Ln\mathrm{Cl}_3 \cdot 2HMTA \cdot 12\mathrm{H_2O}$

Ln	% Metal Calcd. Detd.	% Cl Calcd. Detd.	% C Calcd. Detd.	% N Calcd. Detd.	% H Calcd. Detd.
La	18.74 18.96	14.35 14.49	19.42 19.35	15.11 15.05	6.47 6.82
Pr	18.96 19.09	14.31 14.42	19.47 19.34	15.07 14.95	6.46 6.81
Nd	19.32 19.49	14.24 14.37	19.28 19.20	15.00 14.90	6.43 6.67
GD	20.07 20.05	14.00 14.26	18.96 18.90	14.74 14.45	6.32 6.60
Dy	21.25 20.50	13.90 14.25	18.83 18.65	14.64 14.70	6.27 6.55
Er	21.73 21.00	13.82 14.05	18.71 18.55	14.55 14.45	6.24 6.35

Ln La, Pr, Nd, Gd, Dy, Er

Table 2. Results of analyses of salts of the general formula $LnCl_3 \cdot 2HMTA \cdot 10H_2O$

Ln	% Metal Calcd. Detd.	% Cl Calcd. Detd.	% C Calcd. Detd.	% N Calcd. Detd.	% H Calcd. Detd.
La	19.96	15.08	20.42	15.88	6.24
	20.10	15.20	19.98	15.80	6.20
Pr	19.92	15.04	20.36	15.83	6.22
	20.15	14.91	19.61	15.11	6.20
Nd	20.29	14.96	20.26	15.76	6.19
	20.42	14.80	19.86	15.73	6.15
Gd	21.73	14.70	19.90	15.48	6.08
	21.85	14.65	19.80	15.40	6.05
Dy	22.30	14.59	19.76	15.37	6.04
	23.00	14.85	18.85	15.30	6.00
Er	22.80	14.49	19.63	15.27	5.99
	23.05	14.70	19.55	15.30	6.00

Ln La, Pr, Nd, Gd, Dy, Er

Table 3. Results of analyses of salts of the general formula $LnCl_3 \cdot 2HMTA \cdot 8H_2O$

Ln	% Metal Calcd. Detd.	% Cl Calcd. Detd.	% C Calcd. Detd.	% N Calcd. Detd.	% H Calcd. Detd.
La	20.75	15.89	21.52	16.73	5.97
	20.70	15.98	21.00	16.50	6.00
Pr	20.99	15.84	21.45	16.68	5.96
	21.05	15.92	21.00	16.45	5.95
Nd	21.38	15.76	21.34	16.60	5.93
	21.49	15.86	20.95	16.50	5.65
Gd	22.87	15.47	20.94	16.29	5.82
	22.55	15.60	20.90	16.40	5.70
Dy	23.45	15.35	20.78	16.16	5.77
	22.80	15.55	20.70	16.20	5.65
Er	23.98	15.24	20.64	16.05	5.73
	23.05	15.20	20.55	16.00	5.50

Ln La, Pr, Nd, Gd, Dy, Er

in hydrochloric acid (1 + 1). The HCl solution was added at a slow rate so that after the solution of lanthanide oxides *pH* equaled 7. Solutions of lanthanide chlorides were poured together with saturated water solutions of *HMTA* (molar ratio 1 : 2). The joining of the solutions was accompanied by an exothermic effect. After cooling in a stream of cold water a precipitate appeared. The obtained precipitates were filtered and dried in air at room temperature.

Table 4. Salts of different hydration stage obtained as a result of thermal dehydration

Initial Compound	Heating Temp. (°C)	Compound Obtained
$LaCl_3 \cdot 2HMTA \cdot 12H_2O$	65	$LaCl_3 \cdot 2HMTA \cdot 2H_2O$
	130	$LaCl_3 \cdot 2HMTA$
$PrCl_3 \cdot 2HMTA \cdot 12H_2O$	50	$PrCl_3 \cdot 2HMTA \cdot 8H_2O$
	85	$PrCl_3 \cdot 2HMTA \cdot 2H_2O$
	135	$PrCl_3 \cdot 2HMTA$
$NdCl_3 \cdot 2HMTA \cdot 12H_2O$	60	$NdCl_3 \cdot 2HMTA \cdot 8H_2O$
	90	$NdCl_3 \cdot 2HMTA \cdot 2H_2O$
	100	$NdCl_3 \cdot 2HMTA$
$GdCl_3 \cdot 2HMTA \cdot 12H_2O$	65	$GdCl_3 \cdot 2HMTA \cdot 8H_2O$
	100	$GdCl_3 \cdot 2HMTA \cdot 2H_2O$
	140	$GdCl_3 \cdot 2HMTA$
$DyCl_3 \cdot 2HMTA \cdot 12H_2O$	60	$DyCl_3 \cdot 2HMTA \cdot 8H_2O$
	105	$DyCl_3 \cdot 2HMTA \cdot 2H_2O$
	140	$DyCl_3 \cdot 2HMTA$
$ErCl_3 \cdot 2HMTA \cdot 12H_2O$	60	$ErCl_3 \cdot 2HMTA \cdot 8H_2O$
	100	$ErCl_3 \cdot 2HMTA \cdot 2H_2O$
	135	$ErCl_3 \cdot 2HMTA$

Table 5. Salts of different hydration stage obtained as a result of thermal dehydration

Initial Compound	Heating Temp. (°C)	Compound Obtained
$LaCl_3 \cdot 2HMTA \cdot 10H_2O$	90	$LaCl_3 \cdot 2HMTA$
$PrCl_3 \cdot 2HMTA \cdot 10H_2O$	85	$PrCl_3 \cdot 2HMTA \cdot 5H_2O$
	175	$PrCl_3 \cdot 2HMTA \cdot 1.5H_2O$
$NdCl_3 \cdot 2HMTA \cdot 10H_2O$	85	$NdCl_3 \cdot 2HMTA \cdot 3H_2O$
	105	$NdCl_3 \cdot 2HMTA \cdot H_2O$
$LaCl_3 \cdot 2HMTA \cdot 8H_2O$	80	$LaCl_3 \cdot 2HMTA \cdot 3H_2O$
	180	$LaCl_3 \cdot 2HMTA$
$PrCl_3 \cdot 2HMTA \cdot 8H_2O$	80	$PrCl_3 \cdot 2HMTA \cdot 2H_2O$
	175	$PrCl_3 \cdot 2HMTA$
$NdCl_3 \cdot 2HMTA \cdot 8H_2O$	50	$NdCl_3 \cdot 2HMTA \cdot 6H_2O$
	145	$NdCl_3 \cdot 2HMTA \cdot H_2O$

The results of quantitative analysis permitted to determine the stoichiometric composition of the obtained salts presented in Table 1.

10-hydrous salts were obtained by crystallization from alcoholic solution of hexamethylenetetramine (2.8 g of hexamethylenetetramine were dissolved in a solution containing 16 ml of rectified alcohol and 4 ml of water). Lanthanide chlorides were obtained in the way described above.

Lanthanide chloride solutions were mixed with alcoholic *HMTA* solutions (ratio 1 : 2). While they were cooled in a stream of cold water and stirred vigorously the salts were precipitated. Their composition is presented in Table 2.

Using an alcoholic solution containing 2.8 g of hexamethylenetetramine dissolved in a mixture of 16 ml of anhydrous alcohol and 4 ml of water, we obtained salts of a composition presented in Table 3.

The compounds obtained were heated in a derivatograph at a rate of 2.5°/min.

The salts undergo thermal dehydration and, as a consequence, compounds of different hydration stage are obtained. The composition of the compounds and temperatures at which they are formed are listed in Tables 4 and 5.

The details of the thermal analysis of the compounds under discussion are presented in a separate paper [17].

Analysis

Lanthanides were determined by complexometry [9], chlorides were determined by Volhard's method, whereas nitrogen, carbon and hydrogen were determined by elementary analysis. The content of water was determined on the basis of the thermal curves and on the basis of hydrogen determination. The result of analyses of the obtained lanthanide salts with hexamethylenetetramine and Cl^- are presented in Tables 1, 2 and 3.

Results

IR Spectroscopic Analysis

To interprete the IR spectra of the complex salts under investigation it is necessary to consider free vibrations of *HMTA* [10], water [11, 12] and valence vibrations $M-X$ where $X =$ Cl, Br, I [13–16].

Figure 1 presents as examples the IR spectra of salts $LaCl_3 \cdot 2HMTA \cdot 12H_2O$ and $LaCl_3 \cdot 2HMTA \cdot 8H_2O$ obtained in the range 700–4000 cm^{-1}. Figure 2 presents the IR spectrum in the range 400–700 cm^{-1} of $LaCl_3 \cdot 2HMTA \cdot 12H_2O$ and $LaCl_3 \cdot 2HMTA$.

In Figs. 1 and 2 unsplit bands originating from CN valence vibrations and CN deformation vibrations for $LaCl_3 \cdot 2HMTA \cdot 12H_2O$ are marked. The same – but

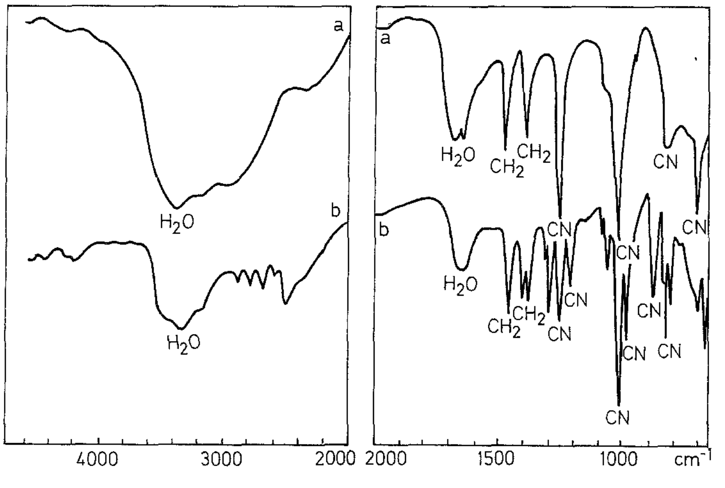

Fig. 1. IR spectra (4000–700 cm^{-1}): *a* $LaCl_3 \cdot 2HMTA \cdot 12H_2O$; *b* $LaCl_3 \cdot 2HMTA \cdot 8H_2O$

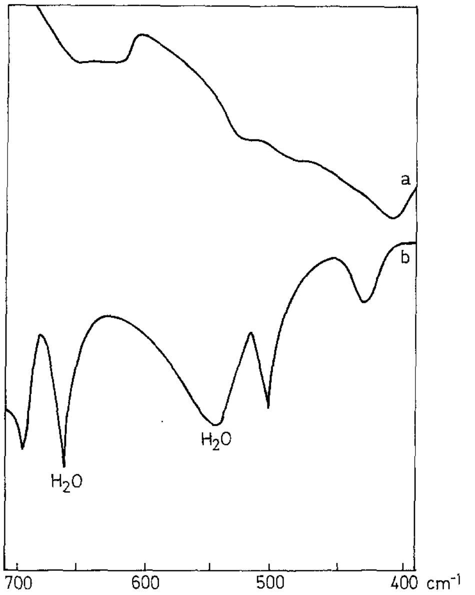

Fig. 2. IR spectra (700–400 cm^{-1}: *a* $LaCl_3 \cdot 2HMTA$; *b* $LaCl_3 \cdot 2HMTA \cdot 12H_2O$

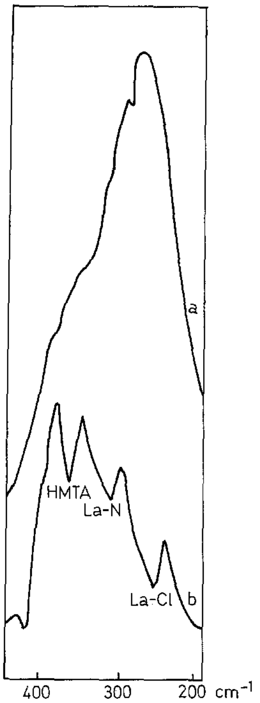

Fig. 3. IR spectra (400–200 cm^{-1}): *a* $LaCl_3 \cdot 2HMTA \cdot 12H_2O$; *b* $LaCl_3 \cdot 2HMTA$

split—vibrations are shown for salts with lower hydration state. In 12-, 10-, and 8-hydrous salts there are double bands (in the range 1 630–1 680 cm^{-1}) which indicate that bonds with water molecules are not of equal value. In compounds with lower hydration state obtained in the reaction of thermal dehydration, a wide

Table 6. Frequencies of Raman spectra vibrations of $LaCl_3 \cdot 2$*HMTA*$\cdot 12H_2O$, $LaCl_3 \cdot 2$*HMTA*, $ErCl_3 \cdot 2$*HMTA*$\cdot 12H_2O$ and $ErCl_3 \cdot 2$*HMTA*

$LaCl_3 \cdot 2$*HMTA*$\cdot 12H_2O$ [cm^{-1}]	$LaCl_3 \cdot 2$*HMTA* [cm^{-1}]	$ErCl_3 \cdot 2$*HMTA*$\cdot 12H_2O$ [cm^{-1}]	$ErCl_3 \cdot 2$*HMTA* [cm^{-1}]	Attributed vibration
		340		
435	446			
456	456	460	460	valence CN
	501		500	
511	511	515	514	
691	691			
	716		720	
791	791	790	791	valence CN
1 016	1 016		1 015	
	1 021	1 020	1 020	$-CH_2-$
1 056	1 056	1 065	1 056	
	1 091		1 090	$-CH_2-$
	1 206			
1 241	1 236	1 240	1 238	$-CH_2-$
	1 311			
1 351	1 351	1 355	1 355	$-CH_2-$
	1 360	1 370		
1 381	1 381			
	1 446			
1 456	1 456	1 465	1 465	deformation CN
2 901				
2 921		2 921		
2 956		2 956		
3 001		3 001		
				$-CH_2-$
				$-CH_2-$
				$-CH_2-$

bands appears in the range 1 610–1 650 cm^{-1}. In all spectra a band occurs at 550 cm^{-1} which can be attributed to libration vibrations of water molecules. The spectra of 12-hydrous and anhydrous salts obtained at 200–400 cm^{-1} differ considerably from each other (Fig. 3). In the spectrum of the anhydrous salt a band appears at 250 cm^{-1} bent at 255 cm^{-1} (from the La-N bond with *HMTA*), another one at 310 cm^{-1} (from the La-Cl bond) and the third at 370 cm^{-1} attributed to *HMTA* free vibrations.

Raman Spectra

IR absorption symmetry and Raman spectrometry provide full information about the vibrational/rotational spectrum of a molecule. They are complementary methods, so apart from IR spectra, Raman spectra of some of the obtained salts were examined. The *HMTA* molecule has 16 active vibrations in Raman spectrum. Table 6 presents vibration frequencies of the obtained Raman spectra for $LaCl_3 \cdot 2HMTA \cdot 12H_2O$, $LaCl_3 \cdot 2HMTA$, $ErCl_3 \cdot 2HMTA \cdot 12H_2O$ and $ErCl_3 \cdot 2HMTA$.

The analysis of specra of hydrated and anhydrous compounds reveals definite differences in their vibration frequencies. In anhydrous salts there are clearly split bands resulting from valence and deformation vibrations of the *HMTA* ring, which indicates a reduced symmetry of the *HMTA* molecule.

Discussion and Conclusions

If *HMTA* induced deformation and valence vibrations of the CN-ring in the spectrum of the salt are respresented by single bands at 510, 690, 1 010 and 1 240 cm^{-1}, it can be assumed that the *HMTA* molecules retained the symmetry of the space group and they do not directly form bonds with metals. Salts which bind *HMTA* molecules tong-wise should contain double valence and deformation vibration bands of the CN (*HMTA*)-ring. In the case of chelate bonds by two N atoms with one metal ion or a bridge bond of *M-N*(*HMTA*)*N-M* type, a triple valence and deformation vibration bands of the *C-N* (*HMTA*)-ring are obtained.

In the case of 12-, 10- and 8-hydrous chloride salts of the examined lanthanides with *HMTA*, single valence and deformation vibration bands are observed in the IR spectra.

In the case of salts of lower hydration state obtained as a result of thermal dehydration, the valence and deformation vibration bands in the IR spectra are split, which indicates a different bond between *HMTA* and metal. For further interpreation of IR spectra of the salts the maximum values corresponding with free vibrations of H_2O should be investigated.

In the IR spectra of the examined 12-, 10- and 8-hydrous salts, double bands occur in the range 1 630–1 680 cm^{-1}, corresponding with deformation vibrations of water, which indicates that bonds with water molecules are not of equal value.

The band located at lower frequencies corresponds with deformation vibrations of water molecules which are not directly bound with metal, whereas that located at higher frequencies corresponds with deformation vibrations of coordinated water molecules.

Libration vibration bands of water molecules are also observed in the IR spectra indicating the presence of coordinated water molecules. The O-H valence vibration frequency of crystallization water is in the range of 3 600–2 700 cm^{-1}. In the salts under study a wide band with a number of weak peaks appears in this range. It is hard to attribute them explicity to particular vibrations of water molecules.

The shape and location of the bands corresponding with the vibrations of water molecules in the examined 12-, 10- 8-hydrous salts confirm the presence of water molecules coordinated with metal and water molecules in hydrogen bond with remaining ligands.

In the case of salts with lower hydration state being obtained in thermal dehydration reaction, a wide band in the wavelength range 1 610–1 650 cm^{-1} is observed. The presence of a single band of water deformation vibrations indicates that only one kind of water, i.e. coordination water, is present in these salts.

Therefore, it can be assumed that the coordination sphere of the examined salts consists of water molecules, whereas *HMTA*, Cl^- and the remaining water molecules are outside the closest neighbourhood of the metal and are bound by hydrogen bonds.

In the process of dehydration certain changes occur in the inner coordination sphere of the metal. Water molecules are replaced by *HMTA* molecules. As a *HMTA* molecule has a big volume, it is more likely that *HMTA* behaves like a bridging group, and not like a chelating one.

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