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Hemimelitates of Rare Earths

Hemimelitany pierwiastków ziem rzadkich

Гемимелитаты редкоземельных элементов

Rare earth complexes with benzeno-1,2,3-trimelitic acid (hemimelitic acid) have not been studied so far. Graabe and Leonhardt [1] obtained hemimelitates of potassium as $KH_2C_9H_3O_6$ and $K_3C_9H_3O_6$, highly soluble in water. Hemimelitates of silver and barium were obtained as 3-substitution salts of low solubility in water [1,2]. Yasuda [3] studied constants of stability of Cu^{2+} and Ni^{2+} complexes with hemimelitic acid.

EXPERIMENTAL PART

Reagents

La_2O_3, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Y_2O_3 - 99.9% Department of Inorganic and General Chemistry UMCS, Gd_2O_3 - 99.9% VEB Laborchemie Apolda, cerous nitrate - analar, urea - analar, POCh-Gliwice, hemimelitic acid - pure Fluka AG.

Apparatus: Pehameter N-512 with glass and calomel electrodes. Spectrophotometer UR-20.

The aim of this study was to investigate the conditions under which rare earth complexes with hemimelitic acid are formed and to determine their proper relationships. It was found in the course of preliminary investigations that hemimelitic acid with lanthanons produced hard-soluble complexes. This is why the method of homogenous precipitation from solution was used in obtaining them. The method consisted in adding to the solution of lanthanon chlorides (cer was used as nitrate) an equivalent quantity of 0.5 M solution of hemimelitic acid and urea. The solution was heated to the temperature of 85 to 90°C. Under these conditions urea is hydrolized according to the reaction:

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3$$

and the solution is gradually neutralized by the emission of ammonia. At pH 3.8-4 there appeared in the solution a crystalline precipitate which underwent rapid sedimentation. The precipitate was heated in the original solution for ca 0.5 h to pH 4.5, and after separation it was drained and washed with distilled water until chloride ions were removed. It was then dried in the air to constant mass.

Next, in order to determine the composition of the complexes obtained there was established experimentally coefficient a_d which indicated the ratio of the salt mass to the mass of oxide formed during roasting. This coefficient was compared with coefficient a_t calculated theoretically. The results obtained are presented in Table 1.

This procedure resulted in obtaining hemimelitates of lanthanons as salt with the general formula: $LnC_9H_3O_6 \cdot nH_2O$, where Ln = La, Ce, Pr, Nd, Sm, Gd, Er, Yb and Y, n = 3,4,5,6.

Table 1. Composition of lanthanons and yttrium hemimelitates

Formulae of complexes	a_t	a_d	V %
$LaC_9H_3O_6 \cdot 6H_2O$	2.802	2,848	1.4
$CeC_9H_3O_6 \cdot 6H_2O$	2.644	2.631	0.5
$PrC_9H_3O_6 \cdot 6H_2O$	2.679	2.654	1.0
$NdC_9H_3O_6 \cdot 4H_2O$	2.520	2.540	0.8
$SmC_9H_3O_6 \cdot 3H_2O$	2.358	2.341	0.2
$GdC_9H_3O_6 \cdot 6H_2O$	2,605	2.564	1.5
$ErC_9H_3O_6 \cdot 6H_2O$	2.510	2.526	0.6
$YbC_9H_3O_6 \cdot 5H_2O$	2.386	2.391	0.1
$YC_9H_3O_6 \cdot 6H_2O$	3.578	3.582	0.1

These salts had the colour characteristic of Ln^{3+} ions. Most hemimelitates are crystallized as 6-hydrated salts. Hemimelitates lose crystallization water at the temperature of 180-200°C and become transformed into anhydrous salts. When roasted they become carbonized and are transformed into oxides.

Next the IR spectra of hemimelitic acid and of the obtained lanthanon hemimelitates were registered in the range of 4000 - 400 cm^{-1}. The measurements were made with UR-20 spectrophotometer. Samples were prepared as pastilles with KBr. The results obtained are presented in Table 2.

Hemimelitic acid has sharp absorption bands of bonded group OH at ca. 2680 cm^{-1} and 2560 cm^{-1}, bands of groups COOH at 1780 - 1690 cm^{-1}, bands of deformation vibration - OH at 1385 cm^{-1}, valence vibrations C-OH at 1220 cm^{-1} and 1125 cm^{-1}, bands of ring vibrations at 1080 cm^{-1} and 910 cm^{-1}. When the acid is transformed into the salts, absorption bands disappear at 2680 cm^{-1}, 2560 cm^{-1}, 1730 cm^{-1} and there appear bands of asymmetrical vibration of COO^- at 1590-1540 cm^{-1}, symmetrical bands at ca. 1390 cm^{-1} and absorption bands which are characteristic of hydrates with maximum at 3400 cm^{-1}, the band of HOH vibration

Table 2. Frequency of maximum of absorption bands in IR spectra of lanthanon hemimelitates (cm^{-1})

La	Ce	Pr	Nd	Sm	Gd	Er	Yb	Y	Assignement
3400	3400	3400	3400	3400	3400	3410	3400	3400	stretching vibration of group OH of water
1610	1610	1610	1610	1610	1610	1610	1610	1610	deformation vibration HOH
1560 1540	1560 1550	1560 1540	1560 1540	1590 1540	1590 1550	1570 1560	1590 1560	1570 1560	asymmetrical vibration COO^-
1470	1470	1470	1470	1490	1470	1470	1480	1470	ring vibration
1420	1420	1410	1410	1410	1410	1410	1410	1410	symmetrical vibration COO^-
1380	1390	1390	1380	1380	1390	1390	1380	1390	plane deformation vibration C-H
1190	1190	1190	1190	1170	1190	1190	1180	1180	ring vibration
1080	1080	1080	1080	1080	1080	1080	1080	1080	asymmetrical ring vibration
940	940	940	940	940	940	940	940	940	valence vibration C-C
850	850	860	860	880	860	860	860	860	asymmetrical ring vibration
830	830	840	840	840	840	840	840	840	out-of-plane deformation vibration C-H
780	770	780	780	770	770	770	770	770	deformation vibration C-H 1,2,3 of benzene 3-substitutions
710	715	710	720	720	710	710	710	710	deformation vibration C-H
545	545	545	550	550	545	550	550	550	bond of metal-oxygen

at 1610 cm^{-1}, as well as the absorption band which is characteristic of the bond metal - oxygen at 550 cm^{-1}.

The solubilities of the obtained hemimelitates in water at the temperature of 22°C were also determined. The results are shown in Table 3. The dispersion of results is shown by the coefficient of variance ν % which was calculated with the aid of Student's formula.

According to the data obtained the solubilities of lanthanon hemimelitates are of order 10^{-3}-10^{-4} M/dm^3. Solubilities of lanthanon hemimelitates decrease from La to Sm, and then increase to Er. The solubility of yttrium hemimelitate is of the order 10^{-4} M/dm^3.

The solubilities of lanthanon hemimelitates are smaller than the solubilities of the corresponding izomeric trimezinates [4] and trimelitates [5] of lanthanons. The solubilities of trimelitates are of the order 10^{-5}-10^{-4} M/dm^3. We can see here the influence of the position of carboxylic groups in

Table 3. Solubilites of lanthanons and yttrium hemimelitates in water at temp. 22°C

Hemimelitate	Solubility in water			ν %
	g Ln_2O_3/dm^3	g anhydrous salt/dm^3	M/dm^3	
La	0.2490	0.5279	$1.49 \cdot 10^{-3}$	0.1
Ce	0.0430	0.0867	$2.49 \cdot 10^{-4}$	0.3
Pr	0.0175	0.0358	$1.03 \cdot 10^{-4}$	0.4
Nd	0.0240	0.0501	$1.42 \cdot 10^{-4}$	0.2
Sm	0.0152	0.0360	$1.01 \cdot 10^{-4}$	0.3
Gd	0.0405	0.0814	$2.24 \cdot 10^{-4}$	0.4
Er	0.7450	1.4530	$3.91 \cdot 10^{-3}$	0.2
Yb	0.2190	0.4222	$1.11 \cdot 10^{-3}$	0.4
Y	0.1075	0.2818	$9.52 \cdot 10^{-4}$	0.2

the benzene ring upon the solubility of salts. If the carboxylic groups are in positions 1,3,5 or 1,2,3 multicentre complexes with space network are probably formed which contributes largely to the decrease of solubility.

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STRESZCZENIE

Przebadano warunki powstawania, skład ilościowy i rozpuszczalności w wodzie w temp. 22°C hemimelitanów: La, Ce, Pr, Nd, Sm, Gd, Er, Yb i Y. Metodą homogenicznego wytrącania otrzymano kompleksy o ogólnym wzorze: $LnC_9H_3O_6 \cdot nH_2O$, gdzie n = 3-6. Hemimelitany są solami trudno rozpuszczalnymi w wodzie. Rozpuszczalności badanych kompleksów są rzędu 10^{-3}-10^{-4} M/dm^3.

Zarejestrowano widma IR hemimelitanów lantanowców. Na podstawie analizy widm IR stwierdzono, że wszystkie hemimelitany krystalizują jako sole uwodnione oraz, że wiązanie między metalem a tlenem grupy karboksylowej ma charakter jonowy.

РЕЗЮМЕ

Исследовано условия получения, количественный состав и растворимость в воде при температуре 22°C гемимелитатов: La, Pr, Nd, Sm, Gd, Er, Yb и Y. Методом гомогенического осаждения получено комплексы с общей формулой: $LnC_9H_3O_6 \cdot nH_2O$, где n= 3-6. Гемимелитаты лантанидов являются очень труднорастворимые в воде. Растворимость исследованных комплексов порядка 10^{-3} - 10^{-4} M/dm^3. Зарегистрировано также спектры IR гемимелитатов лантанидов. На основе анализа спектров IR сконстатировано, что все полученные соли кристаллизуют как гидраты, а также, что между металлом, а кислородом карбоксильной группы выступает ионная связь.