

Instytut Chemii UMCS

Zakład Chemii Nieorganicznej i Ogólnej

Wanda BRZYSKA, Jolanta KOWALEWICZ

### Complexes of Lanthanons and Yttrium with Pyromellitic Acid

Kompleksy lantanowców i itru z kwasem piromelitowym

Комплексы лантанидов и итрия с пиромелитовой кислотой

Benzene-1,2,4,5-tetracarboxylic acid known as pyromellitic acid belongs to crystalline compounds and is a highly insoluble substance in water but very soluble (readily soluble) in spirit [1]. Erdman [2] has received pyromellitates of silver, calcium and lead as 4-substitution salts. Pyromellitate of sodium [3] obtained as basic salt with the formula  $[\text{Sc}(\text{OH})_2]_4 \text{C}_{10}\text{H}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$  has been insoluble in water and spirit. Pyromellitates of rare earths have not been known so far.

### EXPERIMENTAL PART

Reagents:  $\text{La}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$  99.8%, cerous nitrate - Department of Inorganic and General Chemistry of UMCS,  $\text{Gd}_2\text{O}_3$  99.9% - VEB Laborchemie Apolda,  $\text{Er}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$  99.9% - Fluka AG,  $\text{Yb}_2\text{O}_3$  99.9% - Rare Earths Products Limited,  $\text{Eu}_2\text{O}_3$  99.9% - International Enzymes Limited Windsor - Berkshire - England, pyromellitic acid anhydride - Veba Chemia AG.

Apparatus: Pehameter IBS-66 with glass and calomel electrodes, Spectrophotometer UR-20, Diffractometer DRON-2.

The aim of this work was to study the conditions of formation of lanthanons and yttrium complexes with pyromellitic acid, to examine the properties of complexes obtained under existing conditions and to establish their chemical compositions.

On the basis of preliminary tests performed it was found that the pyromellitates of lanthanons were very hard soluble in water, so was pyromellitic acid. On account of it the following method of preparation was applied. Some lanthanons oxides were converted into chlorides (Ce was used as nitrate) and at temperature 70-80°C the solution of 0.2 M ammonium pyromellitate (pH = 4.5) was added dropwise into the solution with constant stirring (ammonium pyromellitate was obtained by dissolving pyromellitic acid with an equivalent amount of ammonia water). During the addition of precipitating agent the precipitate quickly fell down. The forming precipitate had been heated for one hour at temperature 60-70°C and afterwards was filtrated and rinsed until the removal of chloride ions. The salts obtained were dried to the constant mass in air.

Next the experimental coefficient  $a_d$  determining the ratio of salts mass to the oxides formed during roasting was determined and compared with the theoretical one  $a_t$ . The values obtained were given in Table 1.

In this manner the pyromellitates of lanthanons and yttrium were prepared as 4-substitution salts with the general formula  $Ln_4 [C_6H_2(COO)_4]_3 \cdot nH_2O$ , where  $Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Yb, Lu$  and  $Y$ ,  $n = 12, 13, 14, 15, 21, 23, 24$  and with colours characteristic of  $Ln^{+3}$  ions. Pyromellitates of La, Ce, Pr, Nd and Y were received as voluminous precipitates whereas of Sm, Eu, Gd, Er, Yb and Lu were obtained in macrocrystalline form. The precipitates of lanthanons pyromellitates filtrate well and quickly and wash readily. As distinct from pyromellitates of heavy lanthanons, pyromellitates of light lantha-

Table 1. Compositions of lanthanons and yttrium pyromellitates

Formula of complex	$a_t$	$a_d$	$\nu\%$
$\text{La}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 24\text{H}_2\text{O}$	2.741	2.731	0.1
$\text{Ce}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 23\text{H}_2\text{O}$	2.700	2.690	0.1
$\text{Pr}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 21\text{H}_2\text{O}$	2.638	2.648	0.5
$\text{Nd}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 15\text{H}_2\text{O}$	2.445	2.457	0.3
$\text{Sm}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 14\text{H}_2\text{O}$	2.368	2.358	0.1
$\text{Eu}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 15\text{H}_2\text{O}$	2.356	2.353	0.1
$\text{Gd}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 15\text{H}_2\text{O}$	2.341	2.339	0.1
$\text{Er}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 13\text{H}_2\text{O}$	2.224	2.228	0.4
$\text{Yb}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 12\text{H}_2\text{O}$	2.165	2.172	0.4
$\text{Lu}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 12\text{H}_2\text{O}$	2.154	2.154	0.2
$\text{Y}_4(\text{C}_{10}\text{H}_2\text{O}_8)_3 \cdot 13\text{H}_2\text{O}$	3.074	3.083	0.2

nons are far more hydrated. It certainly arises from the contraction of volume effect. Dried pyromellitates lose the crystallization water passing into anhydrous salts. Roasted pyromellitates carbonize forming oxides as products of ultimate decomposition.

Next the IR spectra of pyromellitic acid and the obtained lanthanons and yttrium pyromellitates were registered in the range of  $4000-400\text{ cm}^{-1}$ . The measurements were made using the spectrophotometer UR-20. The samples were prepared in the form of pastilles with KBr. The results are shown in Table 2.

Pyromellitic acid - dihydrate shows sharp absorption bands of unbounded valence vibration of  $-\text{OH}$  groups at  $3520\text{ cm}^{-1}$ , harmonic valence vibrations of  $-\text{C}=\text{O}$  at  $3400\text{ cm}^{-1}$ , bounded  $-\text{OH}$  group at  $2680\text{ cm}^{-1}$ , absorption bands of  $-\text{COOH}$  group at  $1710 -$

Table 2. Frequency of maximum of absorption bands in IR spectra of lanthanons and yttrium pyromellitates ( $\text{cm}^{-1}$ )

La	Ce	Pr	Nd	Sm	Eu	Gd	Er	Yb	Lu	Y	Assignment
3420	3400	3450	3430	3430	3420	3450	3400	3400	3400	3400	stretching vibration of OH group
1620	1620	1630	1620	1630	1630	1630	1620	1630	1630	1620	deformation vibration HOH
1595	1595	1600	1595	1595	1595	1595	1600	1600	1600	1600	symmetrical vibration $\text{COO}^-$
1490	1490	1495	1498	1500	1500	1505	1500	1500	1500	1500	ring vibration
1430	1430	1430	1430	1430	1420	1420	1440	1440	1440	1440	symmetrical vibration $\text{COO}^-$
1390	1395	1395	1395	1395	1390	1400	1400	1390	1400	1400	plane deformation vibration C-H
1180	1185	1185	1180	1170	1150	1170	1150	1150	1150	1150	ring vibration
940	945	950	945	930	930	930	940	945	945	930	valence vibration C-C
880	880	880	880	880	880	880	860	890	860	850	asymmetrical ring vibration
830	830	830	830	820	820	820	820	820	840	820	out-of-plane deformation vibration C-H
780	780	770	775	780	780	780	780	775	780	780	deformation vibrations CH 1, 2, 4, 5 of benzene 4-substitutions
710	710	720	710	680	675	670	680	680	680	680	deformation vibration C-H
550	550	550	550	520	580	540	550	550	550	550	bond of metal - oxygen

-1680  $\text{cm}^{-1}$ , HOH vibrations at 1615  $\text{cm}^{-1}$ , deformation vibration bands OH at 1360  $\text{cm}^{-1}$ , valence vibration -C-OH at 1220 and 1110  $\text{cm}^{-1}$  and bands of ring vibrations at 1080  $\text{cm}^{-1}$  and 965  $\text{cm}^{-1}$ .

When acid converts into salt the spectrum is changed. The absorption band of COOH groups at 1710  $\text{cm}^{-1}$  are missing. The broad absorption band with the maximum of ca 3400  $\text{cm}^{-1}$  confirms the presence of crystallization water in the salt molecules. The appreciable absorption band at 550  $\text{cm}^{-1}$  corresponds to the ionic bond of metal - oxygen.

The solubilities of obtained lanthanons and yttrium pyromellitates in water at temperature 22°C were also determined and their values are given in Table 3.

Table 3. Solubilities of lanthanons and yttrium pyromellitates in water at temp. 22°C

Pyromellitate	Solubility in water		
	g $\text{Ln}_2\text{O}_3/\text{dm}^3$	g anhydrous salt/ $\text{dm}^3$	M/ $\text{dm}^3$
La	0.0082	0.0170	$1.25 \cdot 10^{-5}$
Ce *	0.0058	0.0115	$8.4 \cdot 10^{-6}$
Pr *	0.0087	0.0174	$1.27 \cdot 10^{-5}$
Nd	0.0051	0.0105	$7.6 \cdot 10^{-6}$
Sm	0.0021	0.0042	$3.0 \cdot 10^{-6}$
Eu	0.0017	0.0034	$2.4 \cdot 10^{-6}$
Gd	0.0017	0.0033	$2.3 \cdot 10^{-6}$
Er	0.0040	0.0077	$5.2 \cdot 10^{-6}$
Yb	0.0051	0.0096	$6.4 \cdot 10^{-6}$
Lu	0.0062	0.0117	$7.8 \cdot 10^{-6}$
Y	0.0070	0.0179	$1.54 \cdot 10^{-5}$

\* Solubilities are in term of:  $\text{CeO}_2$  and  $\text{Pr}_6\text{O}_{11}$

Table 4. Date of roentgenographic analysis of light lanthanons pyromellititates

$d$ ( $\text{\AA}$ )	I	$d$ ( $\text{\AA}$ )	I	$d$ ( $\text{\AA}$ )	I	$d$ ( $\text{\AA}$ )	I	$d$ ( $\text{\AA}$ )	I	$d$ ( $\text{\AA}$ )	I
12.63	2	10.40	99	16.07	5	11.79	19	11.5	16	9.02	100
10.40	100	9.82	58	10.40	41	10.05	77	8.84	100	6.51	10
9.02	30	9.12	100	9.51	51	8.84	100	8.42	37	5.54	23
7.31	5	6.76	78	8.93	44	6.61	29	6.92	8	5.12	41
6.71	37	5.54	39	6.71	25	5.44	25	6.49	13	4.93	22
5.57	6	5.10	19	5.50	100	5.07	30	5.50	18	4.44	38
5.12	14	4.87	21	5.21	8	4.90	32	5.06	31	4.23	18
4.90	5	4.44	64	4.87	44	4.82	31	4.82	14	4.09	28
4.69	3	4.09	16	4.74	63	4.44	25	4.74	15	3.78	20
4.39	31	3.77	21	4.35	21	4.35	28	4.42	24	3.63	11
4.08	5	3.51	11	4.21	17	4.23	11	4.17	11	3.51	15
3.80	7	3.47	11	4.04	3	4.06	18	4.04	22	3.23	24
3.62	4	3.40	27	3.74	7	3.77	15	3.77	14	3.03	19
3.53	6	3.35	52	3.56	12	3.65	15	3.62	8	2.88	8
3.40	16	3.29	28	3.31	37	3.49	21	3.49	10	2.73	22
3.36	25	3.07	18	3.12	17	3.29	26	3.33	8	2.45	6
3.17	6	2.87	34	3.06	27	3.23	26	3.28	9	2.38	14
3.08	5	2.79	15	2.97	16	3.04	9	3.22	15	2.25	24
2.87	11	2.75	11	2.85	9	2.88	6	3.03	12	2.17	14
2.79	8	2.72	10	2.71	12	2.83	9	2.97	5	2.10	11
2.69	6	2.68	14	2.67	21	2.73	21	2.88	5	2.03	10
2.60	5	2.61	10	2.40	11	2.56	4	2.71	14		
2.55	8	2.55	16	2.36	10	2.52	7	2.65	6		
2.32	11	2.46	9	2.32	9	2.45	9	2.59	3		
2.27	8	2.31	29	2.23	12	2.39	7	2.45	6		
2.16	5	2.26	24	2.13	14	2.27	26	2.38	11		
2.07	7	2.15	14	2.05	16	2.17	8	2.34	5		
2.03	8	2.07	18	1.91	9	2.10	13	2.25	17		
						2.01	13	2.16	7		
						1.91	10	2.10	7		

Table 5. Date of roentgenographic analysis of heavy lanthanons and yttrium pyromellitates

Gd		Er		Yb		Lu		Y	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
9.31	100	15.24	16	15.50	23	15.78	23	15.24	23
8.51	32	8.84	100	8.84	100	8.84	100	8.84	100
7.08	6	7.25	15	7.31	25	7.37	23	7.14	10
6.56	16	6.46	4	6.56	6	6.51	5	6.51	10
5.61	22	5.54	11	5.61	21	5.57	18	5.50	11
5.12	34	5.29	16	5.37	42	5.34	40	5.21	7
4.87	17	5.02	28	5.10	53	5.04	53	5.01	31
4.77	16	4.84	21	4.87	51	4.85	46	4.82	19
4.46	28	4.39	30	4.41	57	4.39	60	4.40	30
4.19	13	4.15	7	4.31	23	4.19	14	4.15	11
4.06	27	3.71	14	4.19	15	3.69	30	4.02	10
3.80	18	3.62	7	3.71	30	3.62	19	3.71	13
3.66	8	3.43	14	3.61	18	3.53	11	3.56	7
3.52	12	3.20	21	3.55	11	3.41	36	3.44	10
3.45	8	3.02	3	3.43	33	3.21	49	3.16	17
3.22	18	2.92	3	3.21	47	3.14	40	3.13	16
3.19	16	2.75	10	3.17	39	3.02	7	3.07	8
3.04	17	2.71	16	3.02	5	2.92	10	2.83	2
2.98	6	2.47	3	2.90	8	2.74	26	2.71	9
2.88	7	2.43	3	2.85	3	2.70	38	2.66	16
2.73	15	2.39	5	2.75	21	2.67	19	2.63	7
2.66	6	2.37	4	2.71	16	2.51	8	2.34	6
2.59	5	2.22	13	2.52	7	2.47	11	2.22	16
2.47	8	2.18	7	2.48	10	2.42	9	2.13	11
2.38	14	2.13	10	2.43	7	2.38	14	2.08	7
2.34	6	1.07	5	2.39	12	2.29	3	2.01	6
2.26	21	2.00	3	2.23	26	2.22	31	1.89	7
2.20	6	1.94	3	2.18	18	2.18	20		
2.17	10	1.89	3	2.14	23	2.14	26		
2.09	11	1.84	4	2.11	16	2.12	19		
2.04	11			2.06	12	2.06	14		
				2.00	9	2.04	8		
				1.95	5	2.01	10		
				1.91	9	1.96	6		
				1.89	9	1.93	10		
				1.84	10	1.90	10		
				1.79	8	1.85	13		
				1.76	4	1.81	8		
				1.71	8				

On the basis of the data obtained the pyromellitates of lanthanons are found to be highly insoluble in water. Their solubilities are of the order  $10^{-5} - 10^{-6}$  M/dm<sup>3</sup> and decrease from La to Gd and next increase to Lu. Praseodymium pyromellitate is better soluble than pyromellitates of adjacent lanthanons. An analogous change of solubilities is observed in the case of terephthalates and oxalates of light lanthanons. Pyromellitate of yttrium is the best soluble.

The slight solubilities of lanthanons and yttrium pyromellitates are due to the space structure of molecules. Probably the multicentre complexes with space network are formed because of 1, 2, 4, 5 - positions of carboxylic groups.

To find whether these obtained salts are crystalline X-ray radiography measurements were made by means of powder method (Debye - Scherrer method) and CuK<sub>α</sub> radiation and by the use of diffractometer DRON-2 with an appropriate filter. The results determined in the range of 4-60° are given in Tables 4, 5. The maximum intensity I<sub>0</sub> is equal to 100.

On the grounds of diffractodiagrams it can be suggested that the lanthanons and yttrium pyromellitates are characterized by low symmetry because the reflections appear when the angles are small. The first interference reflection occurs when the angle is equal to 5-6° and in this manner it confirms the wide size of unit lattice cell.

\*

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#### REFERENCES

1. Beilsteins Handbuch der Organischen Chemie. Julius von Springer, Berlin 1922.
2. Erdmann O. : Ann. 371, 124 (1911).
3. Crookes W. : Z. anorg. Chem. 61, 373 (1908).



## STRESZCZENIE

Przebadano warunki tworzenia się piromelitanów: La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Yb, Lu i Y, ich skład ilościowy i rozpuszczalność w wodzie w temperaturze pokojowej. Piromelity lantanowców są solami o ogólnym wzorze  $\text{Ln}_4 [\text{C}_6\text{H}_2(\text{COO})_4]_3 \cdot n\text{H}_2\text{O}$ , gdzie  $n = 12-24$ . Rozpuszczalności ich są rzędu  $10^{-5}-10^{-6} \text{ M/dm}^3$ .

Zarejestrowano widma IR i X otrzymanych preparatów i stwierdzono, że piromelity lantanowców i itru są solami krystalicznymi, w których między metalem a tlenem grupy karboksylowej występuje wiązanie jonowe.

## РЕЗЮМЕ

Исследовано условия получения пиromелитатов: La, Ce, Pr, Nd, Sm, Eu, Gd, Er, Yb, Lu и Y, их состав и растворимость в воде при комнатной температуре. Пиromелитаты лантанидов и итрия - это труднорастворимые соли с общей формулой  $\text{Ln}_4 [\text{C}_6\text{H}_2(\text{COO})_4]_3 \cdot n\text{H}_2\text{O}$ , где  $n = 12-24$ . Растворимость их порядка  $10^{-5} - 10^{-6} \text{ M/dm}^3$ . Зарегистрировано спектры IR и X полученных препаратов и констатировано, что пиromелитаты лантанидов это кристаллические соли, у которых между металлом, а кислородом карбоксильной группы выступает ионная связь.

