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New Complexes of Rare Earth Elements with Methylsuccinic Acid

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The rare earth element methylsuccinates were prepared as crystalline solids with general formula $Ln_2(C_5H_8O_4)_3\cdot nH_2O$, where n = 8 for Ce – Nd and Tb, n = 7, for Sm, n = 6 for Y and La, n = 5 for Dy – Tm, n = 4 for Eu,Yb and Lu, n = 3 for Gd. The IR spectra of the complexes prepared were recorded and their solubility in water at 293 K and thermal decomposition in air atmosphere were investigated. During heating the complexes lose crystallization water in one (La, Nd – Gd, Tm – Lu) or two steps (Eu, Dy, Ho, Er) going over to monohydrates (Y, Ce, Tb) or anhydrous compounds (La, Pr – Gd, Dy – Lu) and then the complexes decompose directly to oxides (Ce, Pr, Tb – Er) or with intermediate formation of oxocarbonates $Ln_2O_2CO_3$ (La, Nd – Gd) or $Ln_2O(CO_3)_2$ (Y, Tm – Lu). The carboxylate groups in the complexes prepared act probably as bidentate chelating.

Key words: complexes, methylsuccinic acid, thermal analysis, IR spectra, rare earth elements, synthesis

The methylsuccinic acid, $C_3H_6(COOH)_2$, known as pyrotartaric acid, is a crystalline solid soluble in water, ethanol and ether [1]. Its compounds of NH_4(I), Na, K, Ca, Sr, Ba [1] were isolated as hydrates or anhydrous compounds soluble in water, whereas the complexes of Cu(II), Pb(II), Ni(II), and Mn(II) as solids insoluble in water [1–3]. The methylsuccinic acid was used in preparation of octacalcium phosphate containing this acid with formula $C_8(HPO)_4(2\text{-}z)(H_2L)_z(PO_4)_4\cdot nH_2O$, which was studied by X-ray diffractograms, scanning electron microscope, IR spectrometry, thermogravimetric analysis and chemical analysis. The complexes of rare earth elements with methylsuccinic acid were unknown so far.

The aim of this work was to prepare solid rare earth complexes with methylsuccinic acid and to examine their physico-chemical properties and thermal decomposition in air.

EXPERIMENTAL

Preparation of the complexes. All reagents used for synthesis were reagent grade. Methylsuccinates of Y(III) and lanthanides(III) from La to Lu (without Pm) were prepared by adding stoichiometric quantities of hot (~333 K) 0.2 M solution of ammonium methylsuccinate (pH 4.5–5) to a hot solution of corresponding metal(III) chlorides (Ce was used as its nitrate). The precipitate formed was heated in mother solution for 0.5 hour and then was filtered off, washed with hot water to remove NH_4^+ ions and dried at 303 K to a constant mass. The carbon and hydrogen contents in the complexes prepared were determined by elemental analysis. The metal contents were determined from TG curve and by ignition the complexes to the oxides at 1273 K. The content of crystallization water was determined from TG curves and by heating the samples at a set temperature to a constant mass. The results were in agreement with theoretical data (0.0–0.1%).

The IR spectra of methylsuccinic acid, the sodium salt and the separate rare earth complexes were recorded over the range 4000–400 cm^{-1} using M-80 Carl Zeiss Jena spectrophotometer. The samples were prepared as KBr discs.

The solubility of the complexes in water at 293 K under isothermal conditions was determined spectrophotometrically with Specord M-40 spectrophotometer, using arsenazo III.

The thermal stability of the complexes and the solid products of their decomposition were studied in air. The TG, DTG and DTA curves were recorded by Q 1500 D derivatograph with a Derill converter. Measurements were made at a sensitivity of 100 mg (TG). The sensitivity of DTA and DTG was regulated by the Derill computer programme. The samples (100 mg) were heated in platinum crucibles to 1273 K in static air at a heating rate of 10 K min^{-1} with a full scale. The products of decomposition were verified by registration of their diffractograms.

RESULTS AND DISCUSSION

Methylsuccinates of Y(III) and lanthanide(III) from La to Lu (without Pm) were prepared as crystalline solids with colour characteristic for Ln(III) ions with molar ratio of metal to organic ligand of 2:3 and a general formula $Ln_2(C_3H_6O_4)_3 \cdot nH_2O$, where n = 3–8 (Table 1). The degree of hydration for the light lanthanide complexes has higher values than those determined for the heavy lanthanide ones. The complexes are sparingly soluble in water. Their solubility is of the order of 10^{-4} mole dm^{-3} and increase in the light lanthanide series from La to Gd and change irregularly in the heavy lanthanide series. The Y(III) complex is the least soluble and that of Gd the most in the lanthanide group.

Table 1. Solubilities of rare earth methylsuccinates in water at 293 K.

Complex	Solubility mole $dm^{-3} \times 10^4$	Complex	Solubility mole $dm^{-3} \times 10^4$
$Y_2L_3 \cdot 6H_2O$	0.12	$Tb_2L_3 \cdot 8H_2O$	6.84
$La_2L_3 \cdot 6H_2O$	2.79	$Dy_2L_3 \cdot 5H_2O$	9.15
$Ce_2L_3 \cdot 8H_2O$	2.94	$Ho_2L_3 \cdot 5H_2O$	7.12
$Pr_2L_3 \cdot 8H_2O$	5.06	$Er_2L_3 \cdot 5H_2O$	4.71
$Nd_2L_3 \cdot 8H_2O$	4.51	$Tm_2L_3 \cdot 5H_2O$	7.32
$Sm_2L_3 \cdot 7H_2O$	8.14	$Yb_2L_3 \cdot 4H_2O$	5.42
$Eu_2L_3 \cdot 4H_2O$	0.54	$Lu_2L_3 \cdot 4H_2O$	12.80
$Gd_2L_3 \cdot 3H_2O$	15.90		

L – $C_3H_6(COO)_2^{2-}$.

The methylsuccinates of rare earths are stable in air up to 333–373 K (Table 2). The complexes decompose during heating in many steps in different ways (Tables 2, 3). The hydrated complexes of La, Nd – Gd and Tm – Lu are dehydrated in one step (333–511 K), whereas those of Y, Eu, Dy – Er in two steps (333–676 K) undergoing to anhydrous complexes except of complexes of Y, Ce and Tb, which form monohydrates. The temperature of dehydration is similar for all the complexes. Next dur-

Table 2. Data of dehydration of rare earth methylsuccinates.

Complex	ΔT_2 (K)	Weight loss (%)		Loss of H_2O molecules	T_{endo} (K)	ΔT_2 (K)	Weight loss (%)		Loss of H_2O molecules	T_{endo} (K)
		Calc.	Found				Calc.	Found		
$Y_2L_3{\cdot}6H_2O$	333–403	8.33	8.0	3	393	403–676	14.17	14.0	2	565
$La_2L_3{\cdot}6H_2O$	350–473	13.92	14.0	6	435	–	–		–	–
$CeL_3{\cdot}8H_2O$	342–473	15.47	15.9	7	433	–	–		–	–
$Pr_2L_3{\cdot}8H_2O$	333–411	17.65	17.3	8	405	–	–		–	–
$NdL_3{\cdot}8H_2O$	333–427	17.50	17.0	8	415	–	–		–	–
$SmL_3{\cdot}7H_2O$	333–458	15.43	15.8	7	370	–	–		–	–
$Eu_2L_3{\cdot}4H_2O$	333–373	2.35	2.4	1	350	420–488	9.40	10.0	3	473
$Gd_2L_3{\cdot}3H_2O$	373–511	7.12	6.9	3	485	–	–		–	–
$Tb_2L_3{\cdot}8H_2O$	338–436	14.25	14.7	7	420	436–518	17.58	17.0	1	453
$Dy_2L_3{\cdot}5H_2O$	348–390	7.53	7.0	3	373	390–465	12.11	12.0	2	465
$Ho_2L_3{\cdot}5H_2O$	338–373	5.86	6.0	3	373	373–423	10.86	11.0	2	410
$Er_2L_3{\cdot}5H_2O$	338–383	6.72	6.6	3	373	383–458	10.87	11.0	2	423
$Tm_2L_3{\cdot}5H_2O$	373–503	10.39	10.0	5	463	–	–		–	–
$Yb_2L_3{\cdot}4H_2O$	348–453	9.76	9.0	4	420	–	–		–	–
$Lu_2L_3{\cdot}4H_2O$	373–473	9.17	9.0	4	430	–	–		–	–

Table 3. Data of decomposition of rare earth methylsuccinates.

Complex	ΔT_3 (K)	Weight loss (%)		ΔT_4 (K)	Weight loss (%)		T_k (K)
		Calc.	Found		Calc.	Found	
$Y_2L_3 \cdot H_2O$	595–763	53.33	53.6**	763–903	66.59	66.6	903
La_2L_3	626–1020	42.42	53.0*	1020–1080	57.69	58.0	1080
$Ce_2L_3 \cdot H_2O$	–	–	–	580–905	57.69	58.0	905
Pr_2L_3	–	–	–	584–880	58.27	58.3	880
Nd_2L_3	588–860	53.74	54.0*	860–942	59.09	59.5	942
Sm_2L_3	586–820	51.90	53.0*	820–888	57.31	58.0	888
Eu_2L_3	573–815	51.69	52.0*	815–896	54.05	54.1	896
Gd_2L_3	570–773	46.40	45.6*	773–927	52.21	52.0	927
$Tb_2L_3 \cdot H_2O$	–	–	–	573–928	56.12	56.3	928
Dy_2L_3	–	–	–	588–902	53.67	53.0	902
Ho_2L_3	–	–	–	647–873	53.35	53.5	873
Er_2L_3	–	–	–	623–933	53.05	52.5	933
Tm_2L_3	603–753	42.07	42.8**	753–903	53.83	53.0	903
Yb_2L_3	633–773	40.36	40.0**	773–888	51.25	51.8	888
Lu_2L_3	640–763	40.09	40.0**	763–903	51.04	50.8	905

ΔT_3 – temperature range of decomposition to $Ln_2O_2CO_3$* or $Ln_2O(CO_3)_2$ **.
ΔT_4 – temperature range of decomposition to oxides Ln_2O_3, CeO_2, Pr_6O_{11}, Tb_4O_7.
T_k – temperature of oxide formation.

Table 4. Frequency of the absorption bands in the IR spectra of sodium and rare earth methylsuccinates (cm^{-1}).

Na	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Assignments
3416	3384	3392	3384	3390	3386	3384	3384	3392	3392	3384	3384	3416	3416	3416	3416	ν(OH) from H_2O
3000	2990	3000	2990	3000	3000	3000	3000	3000	2980	2990	2990	2990	2990	2990	2990	ν(C–H)
2980	2980	2980	2970	2980	2980	2980	2980	2980	2960	2980	2980	2970	2970	2970	2970	ν(C–H)
1630	1592	1600	1600	1600	1600	1604	1604	–	1598	1600	1604	1604	1596	1600	1600	δ(H_2O)
1572	1576	1548	1536	1540	1540	1540	1568	1568	1552	1582	1540	1540	1548	1540	1548	ν_{as}(OCO)
1416	1456	1416	1420	1424	1424	1428	1428	1428	1436	1438	1440	1440	1444	1444	1440	ν_s(OCO)
1365	1380	1370	1380	1385	1375	1370	1380	1380	1380	1380	1380	1360	1380	1370	1370	δ(CH_3)
1300	1296	1300	1296	1296	1300	1296	1300	1304	1296	1300	1300	1304	1304	1304	1304	δ(CH_2)
1196	1204	1210	1220	1220	1200	1200	1200	1200	1204	1204	1208	1208	1216	1208	1208	ν(CC) from C(CH_3)
900	890	880	890	890	889	890	890	880	890	888	880	880	880	880	880	ν(C–C)
650	680	680	680	680	680	672	676	676	670	670	672	672	670	672	672	δ(OCO)
–	560	540	570	560	560	550	560	544	570	560	560	560	560	562	560	ν(M–O)

ing heating the anhydrous methylsuccinates of Pr, Dy – Er and monohydrates of Ce and Tb decompose directly to the oxides Ln_2O_3, CeO_2, Pr_6O_{11}. The complexes of light lanthanide of La, Nd – Gd decompose to oxides Ln_2O_3 with intermediate formation oxocarbonates $Ln_2O_2CO_3$, whereas those of Y and heavy lanthanide of Tm – Lu decompose to oxides with intermediate formation of oxocarbonates $Ln_2O(CO_3)_2$. The dehydration process and decomposition of the complexes and oxocarbonates are endothermic and the combustion of the organic ligand and the products of its decomposition are very strong exothermic. The temperature of oxide formation changes irregularly in the lanthanide series from 873 to 942 K, except of La_2O_3, which forms at 1080 K. Very often the temperature of L_2O_3 formation has the highest values in the lanthanide series. The results obtained indicate that the thermal decomposition of rare earth methylsuccinates can be presented as:

$Ln_2L_3{\cdot}nH_2O \rightarrow Ln_2L_3{\cdot}H_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_3$, Ln = Eu, Dy – Er,

$Ln_2L_3{\cdot}nH_2O \rightarrow Ln_2L_3{\cdot}H_2O \rightarrow CeO_2, Tb_4O_7$, Ln = Ce, Tb,

$Ln_2L_3{\cdot}nH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3$, Ln = La, Nd – Gd,

$Ln_2L_3{\cdot}nH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O(CO_3)_2 \rightarrow Ln_2O_3$, Ln = Tm – Lu,

$Y_2L_3{\cdot}6H_2O \rightarrow Y_2L_3{\cdot}H_2O \rightarrow Y_2O(CO_3)_2 \rightarrow Y_2O_3$.

In order to confirm the composition of the complexes and to determine the metal–ligand coordination, the IR spectra of methylsuccinic acid, its complexes with rare earth elements and sodium salt were recorded (Table 4). The IR spectra of the prepared complexes are similar to each other and contain many absorption bands. In the IR spectrum of free methylsuccinic acid there are very strong absorption bands of the COOH group at 1700 cm^{-1}, the bands of vibrations of strongly hydrogen-bonded OH group at 2700–2550 cm^{-1}, the bands of stretching vibrations of CH_2 and CH_3 groups at 2980 and 2920 cm^{-1}, the bands of δ(OH) from COOH group at 1464, 1426 and γ(OH) at 944 cm^{-1}, the band of δ(C–H) in the CH_3 and CH_2 groups at 1380 cm^{-1} and the band of δ(C–O) at 1196 cm^{-1} [5]. In the IR spectra of the methylsuccinates prepared the absorption band of COOH group disappears and the bands of asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the (OCO) group appear at 1536–1548 cm^{-1} and 1420–1440 cm^{-1}, respectively. Only for Y(III) complex the bands of ν_{as}(OCO) and ν_s(OCO) are shifted to higher values 1576 and 1456 cm^{-1}, respectively. The broad absorption band of ν(OH) with maximum at 3384–3416 cm^{-1} and narrow bands at 1592–1604 cm^{-1} confirm the presence of crystallization water molecules. In the IR spectra of the complexes there are also absorption bands of M–O stretching vibrations at 540–570 cm^{-1}. The magnitude of the M–O frequencies and that of the stability constants of the complexes change generally in the same direction [6]. This is to be expected, since an increase in the M–O bond order means a higher stability of the complex. However, in view of the fact that conjugation of the M–O, C–O and C–C bonds may occur in chelate ring of the complex, there will be no pure M–O stretching vibrations and hence the results must be interpreted with great caution. The separation values ($\Delta\nu$) of ν_{as}(OCO) and ν_s(OCO) in the IR spectra of the complexes studied are smaller ($\Delta\nu$ = 100–140 cm^{-1}) compared to the respective bands for the sodium salt ($\Delta\nu$ = 156 cm^{-1}), which indicates the smaller degree of ionic bond in rare earth methylsuccinates, than in the sodium salt. The values of $\Delta\nu$ in the complexes of light lanthanide complexes are greater ($\Delta\nu$ = 120–140 cm^{-1}) than those for heavy lanthanide ones ($\Delta\nu$ = 100–108 cm^{-1}), what is connected with the change of ionic radius of the metal ion, contraction effect and deformation of the ligand in the lanthanide series.

The bands of asymmetrical stretching vibrations, ν_{as}(OCO), of rare earth methylsuccinates are shifted to lower frequencies ($\Delta\nu$ = 24–32 cm^{-1}) or do not change practically their position ($\Delta\nu$ = 4 cm^{-1}) and the symmetric vibrations, $\Delta\nu_s$(OCO), for light lanthanide complexes are shifted insignificantly to higher frequencies ($\Delta\nu$ = 4–8 cm^{-1}) and more stronger for heavy lanthanide complexes ($\Delta\nu$ = 20–36 cm^{-1}). The values of $\Delta\nu$ and the frequency shift of ν_{as}(OCO) and ν_s(OCO) for complexes studied, compared to the sodium salt, suggest according to the spectroscopic criterion [7,8] and our previous works [9,10] that in the hydrated methylsuccinates of rare earth the carboxylate groups act probably as bidentate chelating more or less symmetrical. The stretching vibrations of coordinated carboxyl group are determined by combined effect of the mass, radius, negativity of the central atom and some other factors [5] and hence the results must be explained carefully. Taking into account the high value of coordination number characteristic for Ln(III) ions (CN = 9 for light lanthanide and CN = 8 for heavy ones), it suggests that water molecules are probably in inner and outer sphere of the complexes. In the complexes of rare earths there exist probably hydrogen bonds between hydrogen of the water molecules and oxygen atoms of the carboxylate groups and between the molecules of inner and outer sphere water. The hydrogen bonds stabilize the structure of the complexes prepared. The nature of the metal–ligand bonding can be explained in detail after the determination of crystal and molecular structure of monocrystals.

REFERENCES

1. Beilsteins Handbuch der organischen Chemie, Bd 2, p. 636, Springer Verlag, Berlin 1920.
2. Beilsteins Handbuch der organischen Chemie, Bd 3, p. 1698, Springer Verlag, Berlin 1961.
3. Beilsteins Handbuch der organischen Chemie, Bd 4, p. 198, Springer Verlag, Berlin 1976.
4. Aoki S., Sakamoto K., Yamaguchi S. and Nakahira A., *J. Ceram. Soc. Japan*, **108**, 909 (2000).
5. Bellamy L.J., The Infrared Spectra of Complexes of Molecules , vol. 1, Chapman and Hall, London 1975.
6. Bourger K., Coordination Chemistry. Experimental Methods. Akademiai Kiado, Budapest 1973.
7. Nakamoto K., Infrared Spectra of Inorganic and Coordination Compounds, Willey, NY 1997.
8. Manhas B.S. and Trikha A.K., *J. Indian Chem. Soc*., **59**, 315 (1982).
9. Brzyska W., *J. Thermal Anal. and Cal*., **59**, 799 (2000).
10. Kula A. and Brzyska W., *Polish J. Chem*., **74**, 45 (2000).