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Structure and Properties of 2,2-Dihydroxymalonates of Trivalent Y, Lanthanides, Pu and Am[1]

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Abstract—The M–O bond lengths in the lanthanide series show a well-known behaviour due to lanthanide contraction, including so-called "gadolinium break". All three bond lengths show a good linear correlation with Shannon ionic radii for Y^{3+} and Ln^{3+} ions with coordination number 9. Nevertheless, the slopes of these dependences are different (0.957(16) for OH-groups, 0.85(2) for carboxylate groups and 1.080(17) for water molecules) and differ from unity due to a layer nature of the structures. The ionic radii for Pu^{3+} and Am^{3+} with coordination number 9 are absent in the Shannon system of ionic radii. From our data, we can propose the values 1.172 and 1.156 Å for Pu^{3+}, and Am^{3+}, respectively. In all crystals the structure is stabilized through extensive hydrogen bonding involving carboxylic and hydroxyl groups and water molecules.

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INTRODUCTION

The interaction of metal ions and dicarboxylic acid family has been investigated in details in view of the importance of their application. Particularly the study of the interactions of actinide and lanthanide ions with oxalic acid has been carried out because the precipitation of *f*-element oxalates is widely used in industrial scale in technology of these metals and laboratory practice [1]. The coordination of trivalent *f*-elements ions with homologues of oxalic acid is less studied. The relatively many works have been done in respect of the rare earth malonates. Malonic acid is the next higher homologue of oxalic acid with methylene group between the two carboxylic groups. It is known that the malonate is dicarboxylic ligand with a singular behaviour different from the other dicarboxylic ligands [2]. This difference was shown for 3*d*-elements but there is some possibility of the same behaviour for ions of *f*-elements. It is not clear if the derivatives of malonic acid have these atypical properties or not. The most unusual derivative of malonic acid is dihydroxymalonic acid (mesoxalic acid, $C_3O_6H_4$) because the keto group is hydrated in aqueous solutions as well as in the solid due to the inductive and mesomeric effects of the two carboxylate groups. There are very few known examples of structurally characterized crystals containing anions of dihydroxymalonic acid. Structural data on complexes of actinides with anions of polyhydroxypolycarboxylic acids are rather sparse generally due to difficulties in preparing of crystals suitable for X-ray studies. The crystal structures of one-dimensional chain complex $\{Na[MnL(H_2O)_2]\}_n$ and analogous compound of zinc are known where trivalent 2-hydroxyl-2-hydroxylate-malonate-ion is a bridging ligand [3]. In addition the structures of mixed ligand complexes of copper and palladium containing 2,2-dihydroxymalonate-anions were reported [4–6]. Also there is the example of crystal structure, where three types of species (dihydroxymalonate, dihydroxyhydrogenmalonate and dihydroxymalonic acid) exist simultaneously [7]. 2,2-Dihydroxymalonic acid is a promising ligand for investigation of coordination mode of bifunctional ligand. The occurrence of two carboxylate groups in 1,3 position allows to use dihydroxymalonic acid as classic bridging ligand. The ability of acidic dissociation of hydroxyl groups is responsible for larger number of possible structures.

Various synthetic approaches have been used to isolate highly crystalline samples suitable for structural characterization using X-ray diffraction, in particular that of single crystals. Among the various ligands, multidentate O-donor ligands, such as aliphatic dicarboxylate family, have drawn extensive attention in the construction of metal-organic coordination polymers. Furthermore, the high affinity of *f*-elements for oxygen donor atoms makes carboxylates excellent candidates as bridging ligands for preparing stable coordination polymers. The coordination polymers constructed from dihydroxymalonic acid and trivalent *f*-elements are possible during the retreatment of radioactive wastes [8, 9]. The possibility of the formation of slightly soluble crystals with general formula $Ln_2(C_3H_2O_6)_3 \cdot 7H_2O$, where Ln = Ce, Nd and Sm, was shown in a brief communication [10]. These compounds were obtained by mixing of solutions of sodium 2,2-dihydroxymalonate and REE chlorides. The crystallographic data for

[1] The article is published in the original.

$La_2(C_3H_2O_6)_3 \cdot 6H_2O$ and $Gd_2(C_3H_2O_6)_3 \cdot 7H_2O$ were published [11].

The range of trivalent lanthanides (Ln), in which cationic radii change in wide limits, presents the optimal ability for comparative investigation. For instance, it is known that the structural type is changed in the range of oxalates of lanthanides. The trivalent ions of transuranium elements have very similar properties to rare earth elements cations, especially trivalent plutonium and americium. X-ray structural data on compounds, containing 2,2-dihydroxymalonic acid anions and cations of trivalent *f*-elements were reported breafly [12]. In our work we describe the synthesis and X-ray crystal structure characterization of 17 new isostructural metal-organic coordination polymers using a series of trivalent 4*f*-elements and trivalent plutonium and americium with 2,2-dihydroxymalonic acid.

EXPERIMENTAL

Materials and methods. The nitrate and chloride salts of lanthanides were used to prepare the aqueous stock solutions. The REE solutions were prepared by dissolution of commercially available REE chlorides and nitrates. Aqueous solutions of plutonium-239 and americium-243 were prepared by standard procedure. The initial Am solutions were purified and standardized by known procedures. We performed extraction-chromatographic purification followed by precipitation of Am(III) oxalate and its dissolution in concentrated HNO_3 on heating. Aliquots of the initial nitric acid solution of Am were evaporated to dryness with concentrated $HClO_4$ and the residue was dissolved in water to obtained $Am(ClO_4)_3$ solution. The Am(III) concentration in the stock solution was determined by spectrophotometric titration with EDTA and $K_{10}P_2W_{17}O_{61}$. A sample of ^{239}Pu containing minor amounts of other Pu isotopes was purified by anion-exchange procedure. To a nitric acid solution of Pu(IV) eluted from the ion-exchange column, we added $HClO_4$. The solution was evaporated in a quartz beaker until a thick white fume appeared. The resulting $PuO_2(ClO_4)_2 \cdot nH_2O$ was dissolved in 0.01 M $HClO_4$. The Pu(VI) concentration was determined with spectrophotometry. The 2,2'-dihydroxymalonic acid were used without special purification.

The infrared and visible spectra of the lanthanides and actinides 2,2-dihydroxymalonates were registrated at room temperature using Specord M80 or Shimadzu 3100 spectrophotometer, respectively. Samples were prepared as NaCl discs.

The thermal gravimetric analysis was carried out for crystals of prepared neodymium complexes by using Q 1500D derivatograph. The TG and DTA curves were recorded. Samples were heated in platinum crucibles to 800 K in static air at heating rate 5 K/min. The thermal analysis results confirm the chemical formula as $Nd_2(DHM)_3 \cdot 7H_2O$ for neodymium compound.

Synthesis of $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$. Equimolar mixtures of Ln or Am(III) nitrates (in some cases chlorides or perchlorates) and dihydroxymalonic acid in water were kept at room temperature during 6–7 h. The mother liquors exhibited acidic reaction due to significant acidic properties of dihydroxymalonic acid. The single crystals suitable for X-ray diffraction analysis were formed. Aliquot of stock solution 0.02 M $Am(NO_3)_3$ in dilute nitric acid was evaporated up to dryness at the temperature of about 120°C and dissolved in water after cooling for obtaining ~0.05 M solution to which 0.1 M $C_3O_6H_4$ was added. After some hours well shaped yellow-rose crystals were formed. In the case of Pu(III) the ~1 mL of Pu amalgam with Pu content of about 20–30 mg was placed in solution of 0.1 M $C_3O_6H_4$ for some hours. Very quickly fine crystalline precipitate becomes to form, what suppose that the oxidation of $C_3O_6H_4$ into oxalic acid takes place and this fine precipitate is oxalate of Pu(III). Nevertheless some large blue-violet crystals in the form of trigonal antiprism were found.

The color of crystals corresponds to the color of metal cations. The crystals kept in mother liquor without visible transformations for a period of two weeks.

X-ray structure determination. Diffraction experiments were carried out on a Bruker KAPPA APEX II autodiffractometer (MoK_α radiation, graphite monochromator) at 100 K. The crystals were sealed in glass capillaries. For Am compound, first 20 frames were remeasured at the end of the experiment to check for possible self-radiolysis. Average loss of diffraction intensities was less than 2%. Data reduction was made using SAINT-Plus program [13]. Absorption correction was made using SADABS program [14]. The structures were solved by direct method (SHELXS-97) and refined on F^2 with the full-matrix least-squares procedure (SHELXL-97) [15] using all reflections.

Supplementary material for $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$ structures have been deposited with the Cambridge Crystallographic Data Centre (nos. 851627–851643; http://www.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The H atoms of coordinated water molecules and OH-groups were located from difference Fourier maps and refined with restrained O–H distances, for water molecule the H–O–H angle was also restrained. All the compounds are isostructural and crystallize in a chiral space group *R*32. The values of Flack parameter [16] *x* are in the range from –0.10(15) for Ce to 0.027(10) for Gd compound showing the correctness of the determination of the absolute structures. Crystal

Table 1. Crystal data for $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$ (M = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) compounds

Parameter	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
a, Å	9.5993(1)	9.7612(2)	9.7336(2)	9.7313(2)	9.7054(3)	9.6757(2)	9.6458(3)	9.6450(3)	9.6493(9)
c, Å	20.4611(4)	21.2994(7)	21.1384(6)	21.0345(8)	20.9040(12)	20.7397(8)	20.6369(8)	20.6028(14)	20.500(4)
V, Å^3	1632.82(4)	1757.54(8)	1734.40(7)	1725.06(8)	1705.24(12)	1681.50(8)	1662.84(10)	1659.82(13)	1653.0(4)
n	0.37	0.00	0.17	0.27	0.45	0.57	0.39	0.38	0.44
ρ_{calcd}, g/cm^3	2.120	2.234	2.279	2.302	2.357	2.433	2.460	2.495	2.519
R_1 ($I > 2\sigma(I)$)	0.0158	0.0179	0.0159	0.0128	0.0123	0.0172	0.0132	0.0129	0.0165

Table 2. Crystal data for $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$ (M = Dy, Ho, Er, Tm, Yb, Lu, Pu, Am) compounds

Parameter	Dy	Ho	Er	Tm	Yb	Lu	Pu	Am
a, Å	9.6138(1)	9.5955(1)	9.5837(1)	9.5540(5)	9.5576(1)	9.5506(2)	9.7043(2)	9.6950(2)
c, Å	20.4885(6)	20.4457(3)	20.4083(4)	20.3242(12)	20.3233(4)	20.2948(8)	21.0053(8)	20.8234(6)
V, Å^3	1639.95(5)	1630.30(3)	1623.32(4)	1606.62(15)	1607.76(4)	1603.16(8)	1713.12(8)	1695.03(7)
n	0.45	0.52	0.27	0.35	0.53	0.27	0.28	0.44
ρ_{calcd}, g/cm^3	2.562	2.596	2.607	2.649	2.683	2.688	2.887	2.951
R_1 ($I > 2\sigma(I)$)	0.0085	0.0108	0.0137	0.0129	0.0119	0.0180	0.0111	0.0091

data are given in Tables 1, 2. A description of the structure will be given for the Am compound.

Am atom occupies a special position on a threefold axis. Dihydroxidomalonate anion (its central C atom) occupies a special position on a twofold axis. The coordination polyhedron of Am atom (coordination number 9) is a distorted tricapped trigonal prism, one base of the prism is formed by O atoms of coordinated water molecules, the other base is formed by O atoms of OH-groups of dihydroximalonate anions. The "caps" are O atoms of carboxylate groups. Each Am atom is linked with three dihydroxymalonate anions, each anion is linked with two Am atoms (Fig. 1).

A bridging function of dihydroxymalonate anions results in a formation of electroneutral layers parallel to the (001) plane (Fig. 2). The layers contain cavities

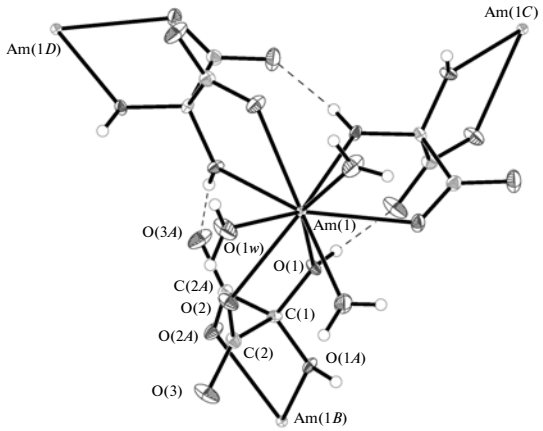

Fig. 1. A fragment of the structure of $[Am_2(DHM)_3(H_2O)_6] \cdot nH_2O$. Dashed lines show H-bonding interactions. Symmetry transformations: (*A*) 1.333 − *x*, 0.667 − *x* + *y*, 1.667 − *z*; (*B*) 0.333 + *y*, 0.667 + *x*, 1.333 −*z*; (*C*) −0.667 + *y*, 0.667 + *x*, 1.333 − *z*; (*D*) −0.667 + *y*, −0.333 + *x*, 1.333 − *z*.

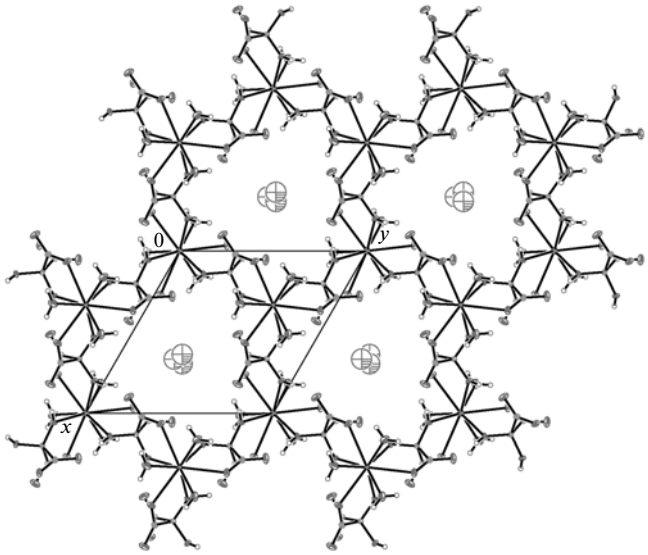

Fig. 2. Electroneutral layer in the structure of $[Am_2(DHM)_3(H_2O)_6] \cdot nH_2O$.

Table 3. Selected bond lengths (Å) in $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$ (M = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) compounds

Bond	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
M–O(1)	2.4370(7)	2.5763(14)	2.5573(12)	2.5393(10)	2.5207(10)	2.4920(15)	2.4736(16)	2.4715(11)	2.4546(16)
M–O(2)	2.3932(8)	2.5227(16)	2.5024(14)	2.4889(10)	2.4653(11)	2.4462(16)	2.4312(17)	2.4231(12)	2.4204(17)
M–O(1*w*)	2.3425(9)	2.5042(18)	2.4705(14)	2.4557(12)	2.4417(13)	2.4083(17)	2.3899(18)	2.3852(14)	2.3663(18)

Table 4. Selected bond lengths (Å) in $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$ (M = Dy, Ho, Er, Tm, Yb, Lu, Pu, Am) compounds

Bond	Dy	Ho	Er	Tm	Yb	Lu	Pu	Am
M–O(1)	2.4487(8)	2.4353(10)	2.4277(13)	2.4143(13)	2.4370(7)	2.4008(19)	2.5305(13)	2.5125(14)
M–O(2)	2.4034(9)	2.3916(11)	2.3857(15)	2.3776(14)	2.3932(8)	2.3693(19)	2.4779(15)	2.4642(15)
M–O(1*w*)	2.3562(9)	2.3438(12)	2.3326(15)	2.3145(14)	2.3425(8)	2.300(2)	2.4529(16)	2.4395(17)

partially occupied by disordered zeolite-like water molecules. At rhombohedral packing, Am atoms of the next layer are over the centres of the cavities of the previous layer. Thus, the cavities are closed. The number of crystallization water molecules per formula unit (***n***, Tables 1, 2) differs and is, possibly, dependent on details of synthesis procedure.

The M–O bond lengths (Tables 3, 4; Fig. 3) in the lanthanide series show a well-known behaviour due to lanthanide contraction, including so-called "gadolinium break". All three bond lengths show a good linear correlation (Fig. 4) with Shannon ionic radii for Y^{3+} and Ln^{3+} ions with coordination number 9 [17]. Nevertheless, the slopes of these dependences are different (0.957(16) for OH-groups, 0.85(2) for carboxylate groups and 1.080(17) for water molecules) and differ from unity due to a layer nature of the structures. The ionic radii for Pu^{3+} and Am^{3+} with coordination number 9 are absent in the Shannon system of ionic radii. From our data, we can propose the values 1.172 and 1.156 Å for Pu^{3+} and Am^{3+}, respectively.

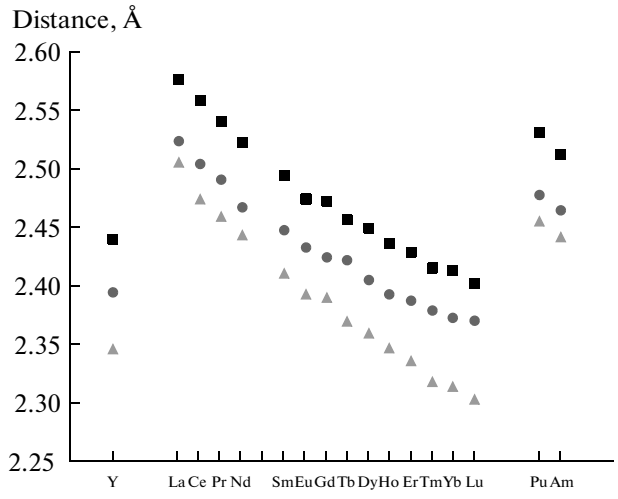

Fig. 3. Bond lengths M–O in the structures of $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$ compounds: (■)—OH, (●)—OOC, (▲)—H_2O.

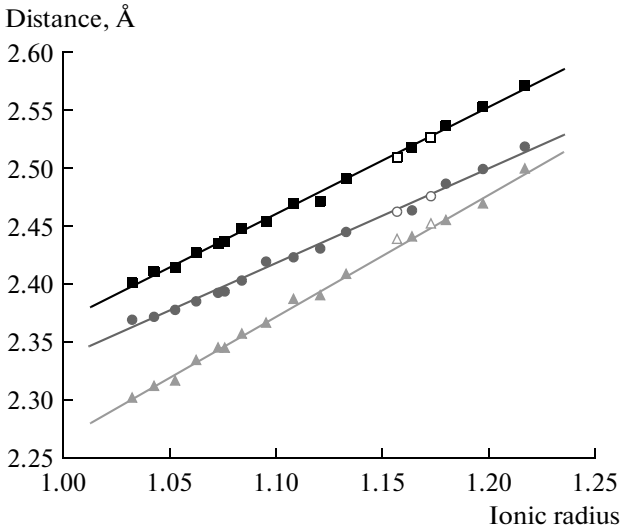

Fig. 4. Bond lengths M–O in the structures of $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$ compounds versus ionic radii. The symbols are the same as in Fig. 3. Open symbols represent Pu and Am compounds with calculated here (see text) ionic radii.

Table 5. Geometric parameters of hydrogen bonds of complexes $[M_2(DHM)_3(H_2O)_6] \cdot nH_2O$

Contact D–H···A	Distance, Å			Angle DHA, deg	Symmetry for A
	D–H	H···A	D···A		
O(1)–H(1)···O(3)	0.809(17)	1.796(18)	2.591(2)	167(3)	$x-y+0.333, -y+1.667, -z+1.667$
O(1*w*)–H(1*A*)···O(3)	0.834(17)	1.873(18)	2.699(2)	171(3)	$x-y, -y+1, -z+2$
O(1*w*)–H(1*B*)···O(2)	0.823(17)	2.109(17)	2.917(2)	167(3)	$y, x, -z+2$

A number of H-bonds can be located in the structures (an example is given for Am compound, Table 5). The proton donors are OH-groups and coordinated water molecules, the acceptors being O atoms of carboxylate groups. The OH-groups participate in H-bonds in the same electroneutral layer (Fig. 1). The coordinated water molecules form the H-bonds between neighbouring layers. The compounds reported in [11] are isomorphous and isostructural with the compounds obtained in this work.

Dihydroxymalonates of trivalent *f*-elements were prepared as crystal hydrates with molar ratio M : DHM = 2 : 3 and general formula $M_2(DHM)_3(H_2O)_6 \cdot nH_2O$, where $n = 0–1$.

A typical TG plot is shown on Fig. 5. The loss of water molecules in the first stage is accompanied by the ligand decomposition. In this temperature range, endothermic peak takes place. The loss of weight relates to formation of $Nd_2(C_2O_4)_3$. In the next stage, the decomposition of neodymium oxalate leads to formation of stable Nd_2O_3. The exothermic peak corresponds to this decomposition. The thermal analysis results confirmed the chemical formula $M_2(DHM)_3 \cdot 7H_2O$ of neodymium dihydroxymalonate.

All measured infrared spectra of polycrystalline compounds are similar.

In the high frequencies region 4000–2000 cm^{-1}, all spectra exhibit the broad intense bands centered around 3470, 3340, 3200, 2960, and 2650 cm^{-1} . This frequencies can be assigned to various combination of the stretching modes ν(HOH) of hydrogen-bonded water molecules in compounds of crystal structure [18, 19]. The effect of hydrogen bonding is that the ν(OH) stretching frequencies varies slightly from one complex to the next.

In the low frequencies region, infrared spectra of all studied compounds contain very strong combination bands in 1670–1605 cm^{-1} region, assigned to asymmetric modes $\nu_{as}(CO)$ and in-plane bending modes $\delta(H_2O)$. Symmetric modes $\nu_s(CO)$ of carboxylate-groups appears at 1460–1440 cm^{-1}. The undissociated OH-group gives the deformation vibration bands at 1154, 1120 cm^{-1} and out-of-plane bending modes

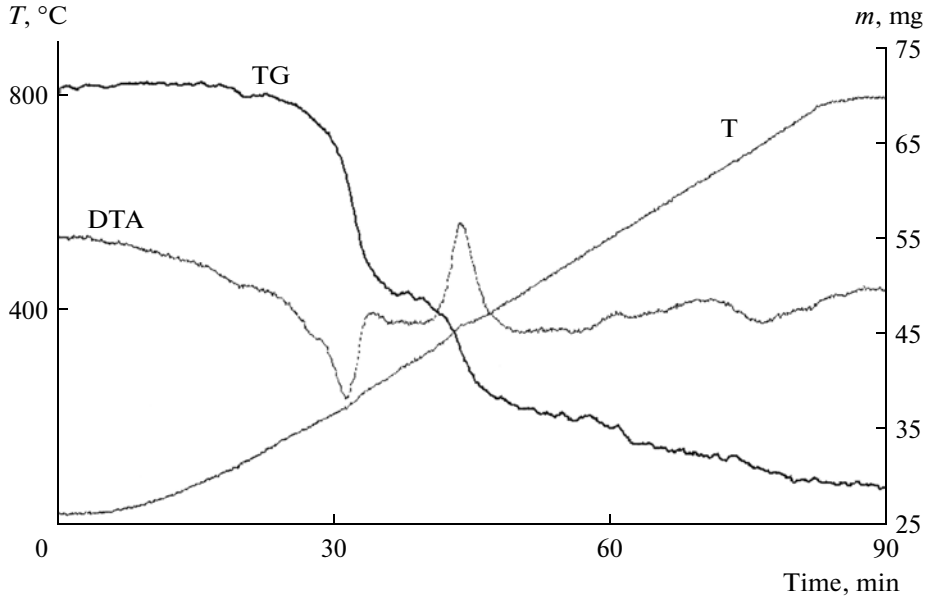

Fig. 5. TG and DTA curves of $Nd_2(C_3O_6H_4)_3 \cdot 7H_2O$.

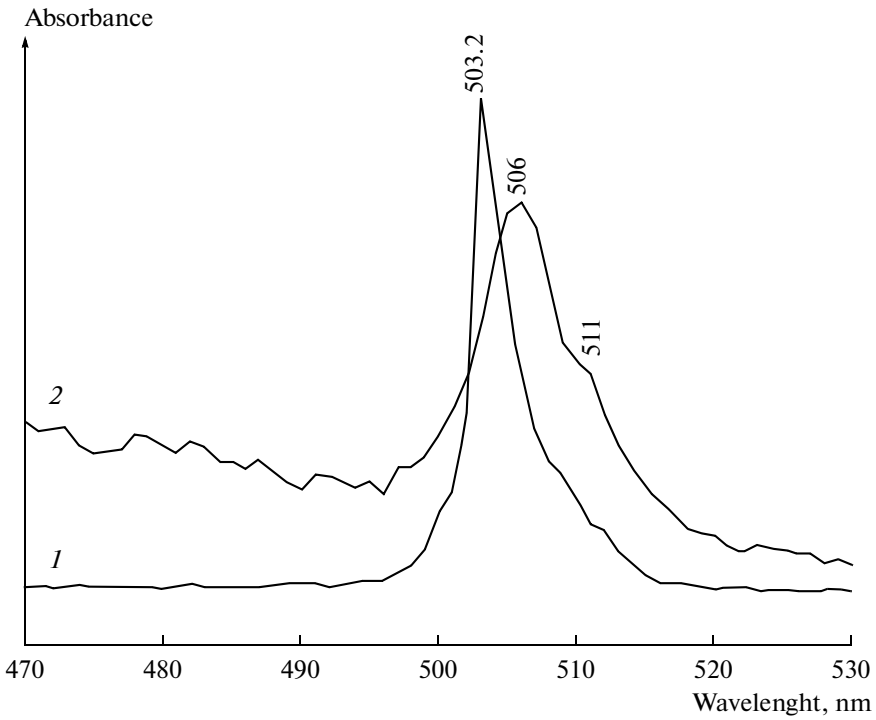

Fig. 6. The red shift of the main absorption band in the spectrum of Am(III) ions: Am(III) in 1 M $HClO_4$ solution (*1*), Am(III) in solid compound $\{Am_2[C(OH)_2(COO)_2]_3(H_2O)_6\}$ (*2*).

γ(C–OH) at 860 cm^{-1}. The librational bands of water molecules ρ(H_2O) are found appearing in 660–450 cm^{-1} range.

The visible spectra of the hydroxymalonates, exhibits the *ff* electron transitions bands, similar to solution spectra. However, while the Ln- and An-ions coordinated with O-donor atoms of the 2,2-dihydroxymalonic acid some bands were split into two or three components. The spectral characteristics of some investigated compounds are presented in Table 6. The electron absorption spectra of solid $\{Am_2[C(OH)_2(COO)_2]_3(H_2O)_6\}$ and its water solution are shown in Fig. 6. As can be seen the $^7F_0 \rightarrow {}^5L_6$ electronic transition of Am(III), which appears around 504 nm, is shifted towards lower energies when the complex is formed.

Table 6. The maxima of absorption bands (nm) in the spectra of some solid complexes

Complex (color)					
Nd	Pr	Ho	Am(III)	Pu(III)	Sm(III)
Lila-ceous	Light green	Pink	Pink	Blue violet	Color-less
573.8 579.1 581.2	444.7 470	473.5 475.8 484.7	506.7 511 sh	612.8	459.2 464.1

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