

Complexes of light lanthanides with 2,3-dimethoxybenzoic acid

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The complexes of light lanthanides with 2,3-dimethoxybenzoic acid of the formula: $\text{Ln}(\text{C}_9\text{H}_9\text{O}_4)_3$, where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) have been synthesized and characterized by elemental analysis, IR spectroscopy, thermogravimetric studies, as well as X-ray and magnetic measurements. The complexes have colours typical for Ln^{3+} ions (La, Ce, Eu, Gd—white, Sm—cream, Pr—green, Nd—violet). The carboxylate group in these complexes is a bidentate, chelating ligand or a tridentate chelating and bridging one. They are crystalline compounds characterized by low symmetry. On heating in air to 1173 K, the 2,3-dimethoxybenzoates of the light lanthanides decompose in various ways. The complexes of Ce(III), Pr(III), Sm(III), Eu(III) and Gd(III) decompose directly to oxides of the respective metals while those of La(III) and Nd(III) *via* the intermediate formation of $\text{La}_2\text{O}_2\text{CO}_3$ and $\text{Nd}_2\text{O}_2\text{CO}_3$. The solubilities of the 2,3-dimethoxybenzoates of the light lanthanides in water at 293 K are in the orders of 10^{-3} – 10^{-2} mol dm^{-3} . The magnetic moments were determined in the range 4.2–298 K and the complexes are found to obey the Curie-Weiss law.

Keywords: 2,3-dimethoxybenzoates, light lanthanides, thermal stability, magnetic moments.

INTRODUCTION

A literature survey indicated that the compounds of 2,3-dimethoxybenzoic acid with various cations have been relatively seldom studied. Papers exist on its complexes with such cations as: Cu^{2+} and some of the Ln^{3+} . The compounds were obtained as solids or were investigated in solution.^{1–3} The 2,3-dimethoxybenzoate of Cu(II) was obtained in the solid state and its thermal stability was studied,¹ while those of Ln^{3+} were only investigated in solution and their dissociation constants were established potentiometrically.^{2,3} 2,3-Dimethoxybenzoic acid is a solid sparingly soluble in water^{4–9} and its melting point is 395 K. There is no information about the solid-state properties of the complexes of 2,3-dimethoxybenzoic acid with light lanthanides. Therefore, it was decided to synthesize them in the solid state and to examine some of their

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physicochemical properties, such as their thermal stability in air, solubility in water at room temperature, IR spectral characteristic and crystalline form in order to determine whether they are crystalline or amorphous compounds. The thermal stability investigations enabled the evaluation of the mechanism of the complex decomposition. The determination of the solubility is valuable because it gives information about the practical use of the acid for the separation of rare-earth elements by extraction or ion-exchange chromatographic methods.

EXPERIMENTAL

The 2,3-dimethoxybenzoates of light lanthanides were prepared by the addition of equivalent quantities of 0.1 M ammonium 2,3-dimethoxybenzoate ($\text{pH} \approx 5$) to a hot solution containing the chloride of the light lanthanides followed by crystallization at 293 K. The formed solids were filtered off, washed with water to remove ammonium ions and dried at 303 K to constant weight.

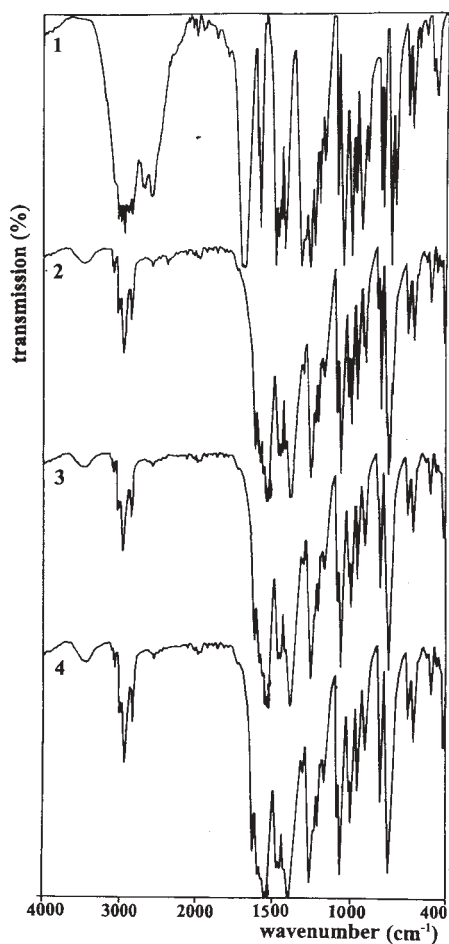


Fig. 1. FTIR spectra of 2,3-dimethoxybenzoic acid (1), 2,3-dimethoxybenzoates of La (2), Pr (3) and Sm (4).

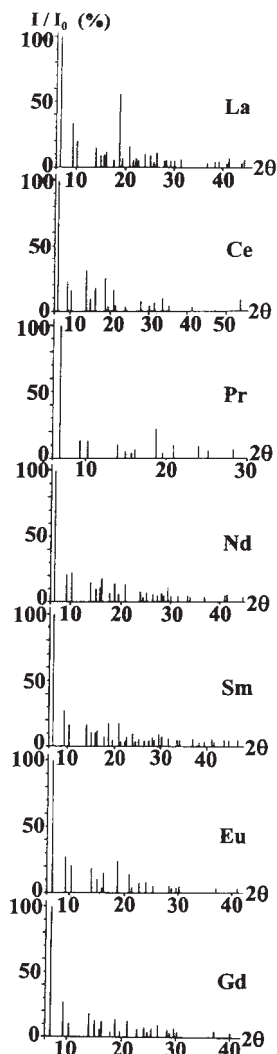


Fig. 2. Diffractograms of light lanthanide 2,3- dimethoxybenzoates.

The contents of carbon and hydrogen were determined by elemental analysis using a CHN 2400 Perkin-Elmer analyser. The contents of metal(III) ions were determined by the oxalic acid method (Table I).

The FTIR spectra of complexes were recorded over the range 4000–400 cm^{-1} using a FTIR 1725X Perkin-Elmer spectrometer. The samples were prepared as KBr discs. Some of the results are presented in Fig. 1 and in Table II.

The X-ray diffraction patterns were taken on a HZG-4 (Carl Zeiss, Jena) diffractometer using Ni filtered $\text{CuK}\alpha$ radiation. The measurements were made within the range $2\theta = 4\text{--}80^\circ$ by means of the Debye-Scherrer-Hull method. The diffractograms of the complexes are presented in Fig. 2.

The thermal stability and decomposition of the prepared complexes were determined using a Paulik-Paulik-Erday Q-1500 D derivatograph with a Derill converter recording TG, DTG and DTA

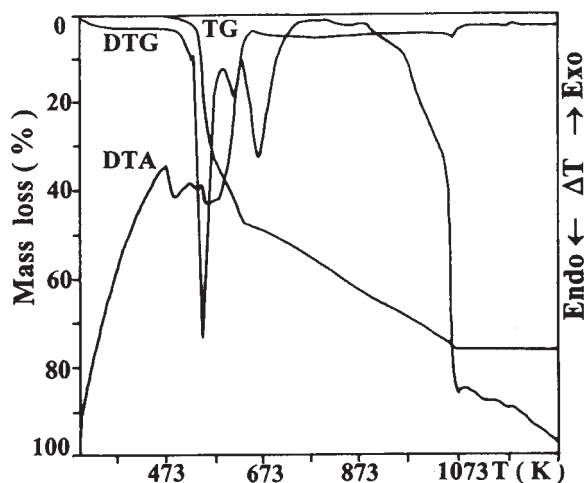


Fig. 3. TG, DTG and DTA curves of neodymium 2,3- dimethoxybenzoate.

curves (Fig. 3). The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The 100 mg samples were heated in platinum crucibles in static air to 1173 K with the sensitivity of the TG, 100 mg (this means that the whole scale in the balance was equal to 100 mg). The DTG and DTA sensitivities were regulated by the Derill computer programme. The paper speed was 2.5 mm min^{-1} and Al_2O_3 was used as the standard. The products of decomposition were calculated from TG curves and verified by the registration of the diffraction pattern.

The solubilities of the 2,3-dimethoxybenzoates of the light lanthanides in water at 293 K were determined by measuring the concentration of Ln^{3+} ions in a saturated solution by the oxalic acid method (Table I).

TABLE I. Analytical data of the light lanthanide 2,3-dimethoxybenzoates and the values of their solubilities in water at 293 K

Complex $\text{L} = \text{C}_9\text{H}_9\text{O}_4$	C/%		H/%		Ln/%		Solubi- lities/mol cm^{-3}
	calcd.	found	calcd.	found	calcd.	found	
LaL_3	47.51	47.67	3.96	3.87	20.36	20.71	2.19×10^{-2}
CeL_3	47.43	47.43	3.95	3.87	20.51	20.67	8.4×10^{-3}
PrL_3	47.37	47.42	3.94	3.87	20.60	20.94	1.74×10^{-2}
NdL_3	47.14	47.07	3.92	3.83	20.98	21.00	1.84×10^{-2}
SmL_3	46.72	47.04	3.89	3.81	21.68	21.56	1.67×10^{-2}
EuL_3	46.62	46.76	3.88	3.84	21.86	21.59	1.93×10^{-2}
GdL_3	46.27	46.42	3.85	3.77	22.56	22.59	2.58×10^{-2}

In order to study the magnetic behaviour of the 2,3-dimethoxybenzoates of light lanthanides at low temperatures, the magnetizations of the samples at 4.3 K were also measured at a magnetic field strength of 0–56 kOe (Fig. 4). On the basis of the obtained results the magnetic susceptibility, χ , was determined according to Eq. (1):

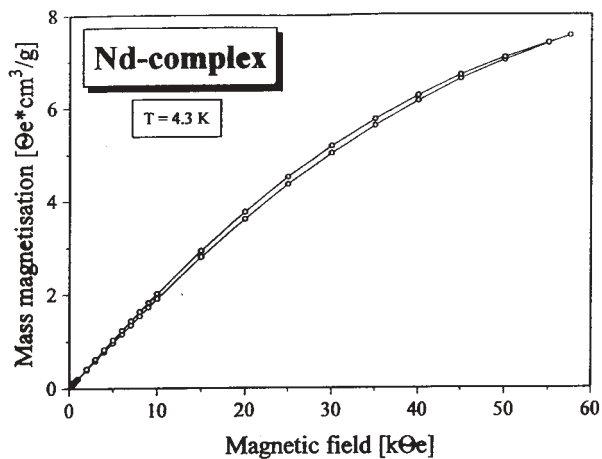


Fig. 4. Dependence between magnetization and magnetic field for the 2,3- dimethoxybenzoate of Nd.

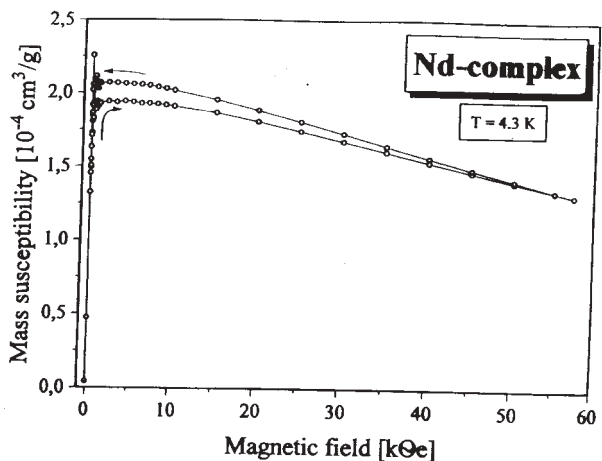


Fig. 5. Relationship between mass susceptibility and magnetic field for the 2,3- dimethoxybenzoate of Nd.

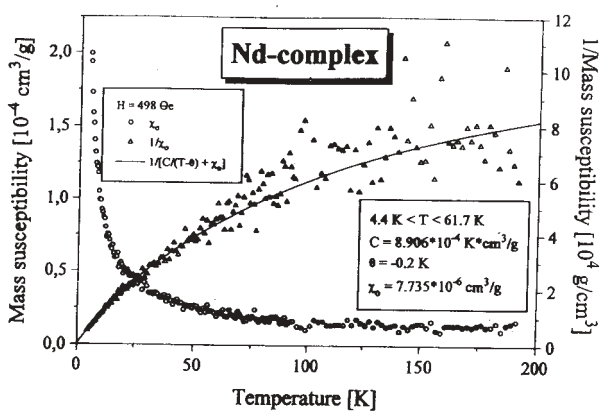


Fig. 6. Mass susceptibility of the 2,3- dimethoxybenzoate of Nd as a function of temperature.

$$\chi = M/H \quad (1)$$

where M is the magnetization and H the applied magnetic field. The dependence between the mass susceptibility values and the field strengths for the Nd complex as an example is presented in Fig. 5. Magnetic susceptibility measurements of the complexes at 4.2–200 K were carried out, as well, using an AC Lake Shore 7225 susceptometer. The parameters of the fitting to the Curie-Weiss law for the 2,3-dimethoxybenzoate of Nd are presented in Fig. 6.

The magnetic susceptibilities of the 2,3-dimethoxybenzoates were also determined by the Gouy method using a sensitive Cahn RG balance. The measurements were carried out at a magnetic field strength of 9.9 kOe. $\text{CoHg}(\text{SCN})_4$ with a magnetic susceptibility¹⁰ of $1.644 \times 10^{-5} \text{ cm}^3/\text{g}$ was employed as the calibrant. The correction for diamagnetism of the constituent atoms was calculated from the Pascal constants.¹¹ The magnetism of the samples was found to be field independent. The temperature-independent magnetism of the lanthanide ions was assumed to be zero.

The magnetic moments were calculated according to Eqs. (2) and (3):

$$\mu_{\text{eff}} = 2.83 (\chi_M \times T)^{1/2} \quad (2)$$

$$\mu_{\text{eff}} = 2.83 [\chi_M (T - \theta)]^{1/2} \quad (3)$$

where θ is the Weiss constant.

The magnetic moment values calculated for the 2,3-dimethoxybenzoates of the light lanthanides at 298 K, μ_{eff} , are presented in Table IV.

RESULTS AND DISCUSSION

The 2,3-dimethoxybenzoates of the light lanthanides were obtained as crystalline anhydrous products with a metal to ligand ratio of 1:3 and general formula: $\text{Ln}(\text{C}_9\text{H}_9\text{O}_4)_3$, where $\text{Ln} = \text{La}(\text{III}), \text{Ce}(\text{III}), \text{Pr}(\text{III}), \text{Nd}(\text{III}), \text{Sm}(\text{III}), \text{Eu}(\text{III})$ and $\text{Gd}(\text{III})$. The colours of the complexes are those typical for the corresponding trivalent Ln^{3+} ions, *i.e.*, white for La, Ce, Eu, Gd, cream for Sm, green for Pr, and violet for Nd and originate from the lowest energy f-f electronic transitions of the central atom.¹²

The complexes were characterized by elemental analysis (Table I) and IR spectroscopy (Fig. 1). All the 2,3-dimethoxybenzoates of the light lanthanides show similar solid state IR spectra. However, the characteristic frequencies related to the carbonyl group are altered markedly in going from the acid to the salts. The band of the COOH group at 1684 cm^{-1} , present in the spectrum of acid, disappears in the spectra of the complexes and two bands arising from the asymmetric and symmetric vibrations of the COO^- group occur at $1549\text{--}1545 \text{ cm}^{-1}$ and $1394\text{--}1388 \text{ cm}^{-1}$, respectively.^{13–19} The bands of the C–H antisymmetric stretching of the CH_3 groups are observed at $2944\text{--}2928 \text{ cm}^{-1}$ and 2850 cm^{-1} , respectively. The bands of the $\nu(\text{C}\text{--}\text{C})$ ring vibrations appear at $1624\text{--}1604 \text{ cm}^{-1}$ and its out of plane deformation modes at 1168 cm^{-1} . The $\nu(\text{C}\text{--}\text{H})$ vibrations are observed at $1396\text{--}1388 \text{ cm}^{-1}$ and $1016\text{--}608 \text{ cm}^{-1}$. The bands typical for the aromatic ring vibrations are shifted insignificantly in the complexes compared to the respective bands in 2,3-dimethoxybenzoic acid, which indicates that the $\text{Ln}(\text{III})$ ions only weakly influence the benzene ring. Bands due to the metal–oxygen bond appear at 520 cm^{-1} for the whole series of complexes.^{14,19} Therefore, it is possible to suppose that 2,3-dimethoxybenzoic acid forms complexes with the light

lanthanides of similar stability.¹⁴ Table II presents the frequency maxima of the absorption bands of the asymmetric and symmetric vibrations of the COO⁻ group for the 2,3-dimethoxybenzoates of light lanthanides and of sodium, as well as of the CO group for 2,3-dimethoxybenzoic acid. The magnitudes of the separation, $\Delta\nu$, between the frequencies $\nu_{\text{as COO}^-}$ and $\nu_{\text{s COO}^-}$ in the complexes are lower ($\Delta\nu_{\text{COO}^-} = 158\text{--}154\text{ cm}^{-1}$) than in the sodium salt ($\Delta\nu_{\text{COO}^-} = 206\text{ cm}^{-1}$), which indicates a lower degree of ionic bonding in the light lanthanide 2,3-dimethoxybenzoates. According to the spectroscopic criteria^{15,19,20} with regard to Nakamoto, the carboxylate ion appears to be a bidentate chelating ligand. However, from a detailed analysis of the bands of the asymmetric and symmetric vibrations of the COO⁻ group it follows that the bands of the $\nu_{\text{as COO}^-}$ vibrations are significantly split. It suggests, on the one hand, that the carboxylate group may be a tridentate chelating and bridging ligand or, on the other, that the carboxylate groups may coordinate in various ways being chelating or bridging ligands. These types of coordination lead to polymerization in these solid compounds making the coordination number of Ln(III) ions equal to 9 in these complexes.

TABLE II. Frequencies of the maxima of the absorption bands of COO⁻ and M–O group vibrations for the 2,3-dimethoxybenzoates of the light lanthanides and Na and for 2,3-dimethoxybenzoic acid (cm⁻¹)

Complex L = C ₉ H ₉ O ₄	$\nu_{\text{C=O}}$	* $\nu_{\text{as COO}^-}$	$\nu_{\text{s COO}^-}$	$\Delta\nu_{\text{COO}^-}$	$\nu_{\text{M-O}}$
LaL ₃	–	1546	1392	154	520
CeL ₃	–	1546	1388	158	520
PrL ₃	–	1545	1391	154	520
NdL ₃	–	1546	1389	157	520
SmL ₃	–	1547	1393	154	520
EuL ₃	–	1547	1392	155	520
CdL ₃	–	1549	1394	155	520
NaL ₃	–	1602	1396	206	540
HL	1684	–	–	–	–

*The strongest intensity of the split band

Analysis of the diffractograms suggests that the light lanthanide 2,3-dimethoxybenzoates are polycrystalline compounds and some of them form independently three isostructural groups of complexes which are the following: Pr with Eu, La with Nd and Gd with Sm. The structures of the complexes have not been determined because single crystals have not been obtained.

On heating to 1173 K, the 2,3-dimethoxybenzoates of the light lanthanides form oxides of the respective metal having the same structures as the oxides obtained by roasting the rare-earth element oxalates.^{21,22} The thermal stabilities of the light lanthanide 2,3-dimethoxybenzoates were studied in air in the temperature range 273–1173 K (Table III). The results obtained from their thermal decomposition showed them to be anhydrous salts. When heated in air they decompose in one or two steps. The

complexes are stable up to 503–520 K and then they decompose (with the exception of the 2,3-dimethoxybenzoates of La and Nd) to the oxides of the respective metal, which are formed at 1098–1178 K. The weight loss calculated from the TG curves are equal to 74.00–76.00 % (the theoretical values are 74.11–76.11 %). The oxides of the light lanthanides were identified by X-ray powder diffraction.²²

TABLE III. Temperatures of decomposition of the 2,3-dimethoxybenzoates of the light lanthanides

Complex L=C ₉ H ₉ O ₄	ΔT_1 /K	Weight loss/%		Product of decomp.	ΔT_2 /K	Weight loss/%		T_K /K	Final prod- uct of decomp.
		calcd.	found			calcd.	found		
LaL ₃	516–655	45.77	46.00	La ₂ O ₂ CO ₃	673–1118	76.11	76.00	1178	La ₂ O ₃
CeL ₃	518–1074	–	–	–	–	74.81	75.00	1148	CeO ₂
PrL ₃	520–1048	–	–	–	–	75.10	75.00	1123	Pr ₆ O ₁₁
NdL ₃	519–645	44.63	44.60	Nd ₂ O ₂ CO ₃	673–1080	75.51	75.00	1148	Nd ₂ O ₃
SmL ₃	503–1073	–	–	–	–	74.85	74.80	1098	Sm ₂ O ₃
EuL ₃	513–1093	–	–	–	–	74.68	74.50	1123	Eu ₂ O ₃
GdL ₃	513–1073	–	–	–	–	74.11	74.00	1163	Gd ₂ O ₃

ΔT_1 , ΔT_2 – Temperature ranges of the decomposition of the anhydrous complex, T_K – temperature of oxide formation

The 2,3-dimethoxybenzoates of La(III) and Nd(III) decompose to La₂O₃ and Nd₂O₃ *via* the intermediate formation of the oxycarbonates of lanthanum La₂O₂CO₃ (516–655 K) and neodymium^{23,24} Nd₂O₂CO₃ (519–645 K). The combustion of the organic ligands is accompanied by strong exo-effects seen in the DTA curves. The large peaks recorded in the curves of the DTG correspond to the gradual weight loss of the complexes during heating.

The derivatogram of neodymium 2,3-dimethoxybenzoate is presented in Fig. 3. The complex decomposes in two steps. The weight loss of the complex starts at 519 K. The decrease in weight occurs in the range 519–645 K and, therefore, the TG curve deviates from the horizontal. The weight loss determined from the TG curve is equal to 44.6 % (the calculated value is 44.63 %) which corresponds to the formation of Nd₂O₂CO₃. Accordingly, the peak ascribed to this loss of weight is also recorded in the DTG curve, which is the first derivative of the weight loss. Next, the oxycarbonate of neodymium is finally decomposed to Nd₂O₃ (673–1080 K). The weight loss determined from the TG curve is equal to 75.00 % (the calculated value is 75.51 %). The oxidation process is associated with a strong exothermic effect reflected in the DTA curve. Subsequently, above 1080 K, the TG curve reaches a plateau, as the formed Nd₂O₃ is thermally stable.

The thermal stability of the series of complexes changes in the order: Sm < Eu = Gd < La < Ce < Nd < Pr. The most thermally stable complex is that with praseodymium which starts to decompose at 520 K, while the least thermally stable is the 2,3-dimethoxybenzoate of Sm (503 K).

The results obtained from the thermal decomposition of the complexes indicate that during heating in air to 1173 K they may decompose in the following ways:

$\text{LnL}_3 \rightarrow \text{Ln}_2\text{O}_2\text{CO}_3 \rightarrow \text{Ln}_2\text{O}_3$; where Ln = La, Nd

$\text{LnL}_3 \rightarrow \text{Ln}_2\text{O}_3$; Pr_6O_{11} , CeO_2 ; where Ln = Ce, Pr, Sm, Eu, Gd

The oxides of the light lanthanide elements formed at 1098–1178 K were identified by X-ray powder diffraction analysis.^{21,22} From the obtained results it can be seen that the oxide of lanthanum has the highest formation temperature while samarium oxide has the lowest one.

The solubilities of the 2,3-dimethoxybenzoates of the light lanthanides in water (at 293 K) were measured. They are in the order of $10^{-2} - 10^{-3} \text{ mol cm}^{-3}$. The gadolinium 2,3-dimethoxybenzoate is the most soluble complex in water, while the least soluble one is the complex of cerium. In view of the values of complex solubilities, it would seem that 2,3-dimethoxybenzoic acid cannot be used for the separation of the light lanthanide elements by ion-exchange chromatography or by extraction methods because the formed complexes are not readily soluble.

TABLE IV. Values of μ_{eff} for the light lanthanides determined by Hund and van Vleck and calculated for the light lanthanide 2,3-dimethoxybenzoates at 298 K*

Ln^{3+}	Ground term.	Calcd. μ_{eff} by Hund	μ_{eff} by van Vleck	μ_{eff} (BM)*
La^{3+}	$^1\text{S}_0$	0.00	0.00	0.00
Ce^{3+}	$^2\text{F}_{5/2}$	2.54	2.56	2.64
Pr^{3+}	$^3\text{H}_4$	3.58	3.62	3.68
Nd^{3+}	$^4\text{I}_{9/2}$	3.62	3.68	3.70
Sm^{3+}	$^6\text{H}_{5/2}$	0.84	1.55–1.65	1.82
Eu^{3+}	$^7\text{F}_0$	0.00	3.40–3.51	6.00
Gd^{3+}	$^8\text{S}_{7/2}$	7.94	7.94	7.90

The magnetic susceptibility of the light lanthanide 2,3-dimethoxybenzoates was determined in the range 4.2–300 K. All the complexes show paramagnetic properties (with the exception of the La complex) and they obey the Curie-Weiss law (Figs. 4–6). A loss compliance caused by a spin-spin interaction is noticed. The values of μ_{eff} determined for all the complexes (except for that with europium) are close to those calculated for Ln(III) ions by Hund and van Vleck (Table IV). The higher value of μ_{eff} for europium 2,3-dimethoxybenzoate compared with that given by Hund may suggest a possible interaction of the ligand field with the central ion or may be associated with the multiplet splitting. The lowest three excited states of the europium ion are sufficiently close in energy to the ground states to be appreciably populated at room temperature.^{25–27} Since the excited states possess higher J values than the ground state, the actual magnetic moment is larger than those calculated by using the J value for the ground state. With the exception of Sm and Eu, the multiplet widths for the lanthanide elements are very large compared with kT ($kT = 200 \text{ cm}^{-1}$) at room temperature, while those for Sm and Eu are not really infinitely large compared to kT . The multiplet intervals in Sm and Eu are not really infinitely large compared to kT . This requires to make a more careful examination of multiplet structures including the J values. For their small values the

interval between two consecutive components $J, J+1$ equals $A(J+1)$. Now, if the multiplicity $2S+1$ is fairly large, and if L and S are nearly equal, so that $J_{\min} = L - S$ is small, the separation between the components with the two lowest values of J may well be small compared to kT , even though the “over-all” multiplet width is considerably greater than kT . For Eu the interval between the lowest multiplet components is only $1/21$ of the overall width and for a 7F term²⁵ applies Eq. (4)

$$\frac{1}{2}[J_{\max}(J_{\max} + 1) - J_{\min}(J_{\min} + 1)] = \frac{1}{2} \times 6 \times 7 - 0 = 21 \quad (4)$$

$$J_{\min} + 1 = 1$$

In the complexes of 2,3-dimethoxybenzoates, the paramagnetic central ions remain virtually unaffected by the surrounding diamagnetic ligands. The 4f electrons, which are responsible for their paramagnetism, are well protected from outside influences and do not participate in the formation of the Ln–O bond. Instead, they interact only weakly with the electrons of the surrounding atoms.²⁸ Their energy levels are the same as in the free ions due to very effective shielding by the overlapping $5s^25p^6$ shell. Hence, the magnetic properties can be considered identical to those of the ground state alone, making the bonded lanthanide ions act in the same way as the free ions.

In conclusion, 2,3-dimethoxybenzoates of the light lanthanides were synthesized as anhydrous complexes. The compounds exhibit colours arising from the relevant Ln(III) ion, *i.e.*, white in the case of La, Ce, Eu, Gd, cream for Sm, green for Pr and violet for Nd, having their origin in the lowest energy f-f electronic transitions of the central atom. The energy levels do not change substantially in bonded and non-bonded lanthanide ions, which means that the colours of the compounds and the free lanthanide ions are similar. The Ln–O bond is predominantly of electrostatic nature, since the 4f orbitals of the lanthanide ions are effectively shielded by the $5s^25p^6$ octet.

The 2,3-dimethoxybenzoates of the light lanthanides are crystalline compounds that decompose in one or two steps on heating in air up to 1173 K forming the oxides of the corresponding metals as the final products of decomposition.

ИЗВОД

КОМПЛЕКСИ ЛАКИХ ЛАНТАНИДА СА 2,3-ДИМЕТОКСИБЕНЗОЕВОМ КИСЕЛИНОМ

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Синтетизовани су комплекси лаких лантанида са 2,3-диметоксибензоевом киселином формуле: $\text{Ln}(\text{C}_9\text{H}_9\text{O}_4)_3$ у којој је $\text{Ln} = \text{La(III)}, \text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}$ и Gd(III) . Комплекси су карактеризовани елементарном анализом, ИР спектроскопијом, термогравиметријом, као и рендгенским и магнетним мерењима. Комплекси имају боје типичне за Ln^{3+} јоне (La, Ce, Eu, Gd – бела, Sm – крем, Pr – зелена, Nd – љубичаста). Карбоксилна група се јавља у овим комплексима или као бидентатни хелатни лиганд или као тридентатни хелатни и премошћујући лиганд. Ово су кристална једињења са ниском симетријом. При загревању на ваздуху до 1173 К 2,3-диметоксибензоати лаких лантанида разлажу се на различите начине. Комплекси Ce(III) , Pr(III) , Sm(III) , Eu(III) и Gd(III) разлажу се директно до одговарајућих

оксида, док се комплекси La(III) и Nd(III) разлажу уз интермедијарно стварање $\text{La}_2\text{O}_2\text{CO}_3$ одн. $\text{Nd}_2\text{O}_2\text{CO}_3$. Реастворљивост 2,3-диметоксибензоата лакних лантанида у води на 293 K је реда величине $10^{-3} - 10^{-2} \text{ mol dm}^{-3}$. Магнетни моменти су одређивани у опсегу 4,2 – 298 K и нађено је да се покоравају Curie-Waiss-овом закону.

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