COMPLEXES OF LIGHT LANTHANIDES WITH 3,4-DIMETHOXYBENZOIC ACID

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The complexes of light lanthanides with 3,4-dimethoxybenzoic acid, $Ln(C_9H_9O_4)_3 \cdot 4\ H_2O$, where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III), have been synthesized as polycrystalline solids and characterized by elemental analysis, IR spectroscopy, thermogravimetric and magnetic studies and X-ray diffraction measurements. The complexes possess colours typical of Ln(III) ions (La, Ce, Eu, Gd white, Pr greenish, Nd violet and Sm cream). The carboxylate group in these complexes binds as a symmetrical, bidentate chelating ligand. On heating in air to 1 273 K the 3,4-dimethoxybenzoates of Ce(III), Pr(III), Sm(III), Eu(III) and Gd(III) first dehydrate to anhydrous salts that further decompose to oxides of the respective metals. The 3,4-dimethoxybenzoates of La(III) and Nd(III) decompose in three steps. Firstly, they dehydrate to anhydrous salts that further decompose to the oxides with the intermediate formation of oxycarbonates. The solubilities of the studied complexes in water at 293 K is in the order of 10^{-4}–10^{-3} mol dm^{-3}. Their magnetic moments were determined in the temperature range 77–298 K and found to obey the Curie–Weiss law. The values of μ_{eff} calculated for the all compounds (except that for Eu) are close to those obtained for Ln(III) by Hund and van Vleck. The results show that there is no influence of the ligand field on 4f electrons of the lanthanide ions in these polycrystalline compounds; 4f electrons probably do not participate in the formation of the Ln–O bonds.

Key words: 3,4-Dimethoxybenzoates; Light lanthanides; Thermal stability; Magnetic moments; Rare earth elements; Lanthanoids; IR spectroscopy; Powder X-ray diffraction.

According to literature survey compounds of 3,4-dimethoxybenzoic acid with various metal ions have been studied scarcely. Papers only exist on its complexes with Na(I), Ag(I) and Ba(II) (ref.[1]). The sodium and barium 3,4-dimethoxybenzoates form dihydrate and hexahydrate, respectively, while that of silver is anhydrous[1].

3,4-Dimethoxybenzoic acid, $C_9H_{10}O_4$, is a white crystalline solid sparingly soluble in water and readily soluble in ethanol and diethylether. Its dissociation constant and melting point equal to $3.6 \cdot 10^{-5}$ at 25 and 181 °C, respectively[2]. There is no information about the solid-state proper-

ties of the complexes of 3,4-dimethoxybenzoic acid with light lanthanides. For this reason we decided to synthesize them in the solid state, to examine their thermal stability in air, solubility in water and magnetic properties, and to record their IR spectra and X-ray powder diffractograms.

The aim of the thermal stability investigations was (i) to estimate the position of the crystallization water molecules, *i.e.* in outer or inner coordination spheres, (ii) to resolve the mechanism of complex decomposition and to determine the *endo*- or *exo*-effects associated with processes involved, such as dehydration, melting, crystallization, oxidation, reduction, and (iii) to compare the relative strength of the bonding between the central Ln(III) ions and the surrounding molecules. The determination of the solubility provides valuable information about the practical use of the employed acid for the separation of rare-earth elements by extraction or ion-exchange chromatographic methods.

EXPERIMENTAL

The 3,4-dimethoxybenzoates of the light lanthanides were prepared by adding equivalent amounts of 0.1 M ammonium 3,4-dimethoxybenzoate at pH ≈ 5 to a hot solution containing the nitrate salts of the light lanthanides, followed by crystallization at 293 K. The formed solids were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant weight.

The contents of carbon and hydrogen were determined by elemental analyses using a Perkin–Elmer CHN 2400 analyser. The contents of the Ln(III) ions and crystallization water molecules were determined by the oxalic acid method and from the TG curves, respectively (Table I).

The IR spectra of complexes were recorded in the range 4 000–400 cm^{-1} using an M-80 spectrometer. Samples were prepared as KBr pellets. Some of the results are presented in Table II and in Fig. 1.

The X-ray diffraction patterns were recorded on an HZG-4 difractometer (Zeiss, Jena), using Ni-filtered CuKα radiation. The measurements were made within the range 2 θ = 4–80° by the Debye–Scherrer–Hull method. The radiograms of the complexes are presented in Fig. 2.

The thermal stability and decomposition of the prepared complexes were investigated using a Paulik–Paulik–Erdey Q-1500 D derivatograph connected to a Derill converter recording TG, DTG and DTA curves. The measurements were made at a heating rate of 10 K min^{-1} with a full scale. The samples (100 mg) were heated in platinum crucibles in static air to 1 173 K, with a sensitivity of the TG set to 100 mg. The DTG and DTA sensitivities were regulated by the Derill computer programme. The paper speed was set to 2.5 mm min^{-1}. Al_2O_3 served as a standard. The products of decomposition were calculated from the TG curves and verified by registration of the diffraction patterns (Table III).

The solubilities of the 3,4-dimethoxybenzoates of the light lanthanides in water at 298 K were derived from the concentration of Ln(III) ions in a saturated solution determined by the oxalic acid method (Table II).

TABLE I
Analytical data of the light-lanthanide 3,4-dimethoxybenzoates

Complex $L = C_9H_9O_4$	% H		% C		% Ln	
	Calculated	Found	Calculated	Found	Calculated	Found
$LaL_3 \cdot 4\ H_2O$	5.10	5.00	42.80	42.97	18.34	18.32
$CeL_3 \cdot 4\ H_2O$	5.04	4.98	42.70	42.80	18.47	18.37
$PrL_3 \cdot 4\ H_2O$	4.62	4.58	42.83	42.95	18.62	18.65
$NdL_3 \cdot 4\ H_2O$	5.02	4.92	42.51	42.20	18.91	18.98
$SmL_3 \cdot 4\ H_2O$	4.98	4.90	42.17	42.20	19.56	19.58
$EuL_3 \cdot 4\ H_2O$	4.56	4.46	42.21	42.20	19.79	19.80
$GdL_3 \cdot 4\ H_2O$	4.52	4.49	41.96	41.94	20.34	20.43

TABLE II
Infrared spectral data of the 3,4-dimethoxybenzoates of the light lanthanides and Na, and for 3,4-dimethoxybenzoic acid, their solubilities in water at 293 K and solubility products

Complex $L = C_9H_9O_4$	ν(C=O) cm^{-1}	$\nu_{as}(COO^-)$ cm^{-1}	$\nu_s(COO^-)$ cm^{-1}	$\Delta\nu(COO^-)$ cm^{-1}	Solubility $mol\ l^{-1}$	Solubility product $mol^4\ dm^{-12}$
$LaL_3 \cdot 4\ H_2O$	–	1 520	1 400	120	$1.3 \cdot 10^{-3}$	$2.7 \cdot 10^{-12}$
$CeL_3 \cdot 4\ H_2O$	–	1 520	1 400	120	$1.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-10}$
$PrL_3 \cdot 4\ H_2O$	–	1 520	1 400	120	$7.0 \cdot 10^{-4}$	$7.0 \cdot 10^{-13}$
$NdL_3 \cdot 4\ H_2O$	–	1 530	1 400	130	$7.8 \cdot 10^{-4}$	$1.0 \cdot 10^{-11}$
$SmL_3 \cdot 4\ H_2O$	–	1 530	1 400	130	$5.5 \cdot 10^{-4}$	$2.5 \cdot 10^{-11}$
$EuL_3 \cdot 4\ H_2O$	–	1 520	1 400	120	$7.4 \cdot 10^{-4}$	$9.0 \cdot 10^{-13}$
$GdL_3 \cdot 4\ H_2O$	–	1 520	1 410	110	$7.7 \cdot 10^{-4}$	$1.0 \cdot 10^{-13}$
NaL	–	1 560	1 400	160	–	–
HL	1 700	–	–	–	–	–

Magnetic susceptibilities of polycrystalline samples of the 3,4-dimethoxybenzoates were determined by the Gouy method, using a sensitive Cahn RM-2 balance. Measurements were carried out at a magnetic field strength of 9.9 kOe (Non-SI unit employed: 1 Oe = $10^3 (4\pi)^{-1}$ A m^{-1}). $CoHg(SCN)_4$ with the magnetic susceptibility[3] of $1.644 \cdot 10^{-5}$ cm^3 g^{-1} was employed as calibrant. The correction for diamagnetism of the constituent atoms was calculated by using Pascal's constants[4]. The magnetism of the samples was found to be field independent. The temperature-independent paramagnetism of the lanthanide ions was assumed to be zero. The magnetic moments were calculated according to Eqs (*1*) and (*2*),

$$\mu = 2.83 (\chi_M T)^{1/2} \qquad (1)$$

$$\mu = 2.83 [\chi_M (T - \theta)]^{1/2} , \qquad (2)$$

where θ is the Weiss constant.

The magnetic moment values calculated for the 3,4-dimethoxybenzoates of the light lanthanides at 298 K, μ_{eff}, are presented in Table IV.

RESULTS AND DISCUSSION

The 3,4-dimethoxybenzoates of the light lanthanides were obtained as crystalline hydrated solids of the general formula $Ln(C_9H_9O_4)_3 \cdot 4\ H_2O$, where Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III). The

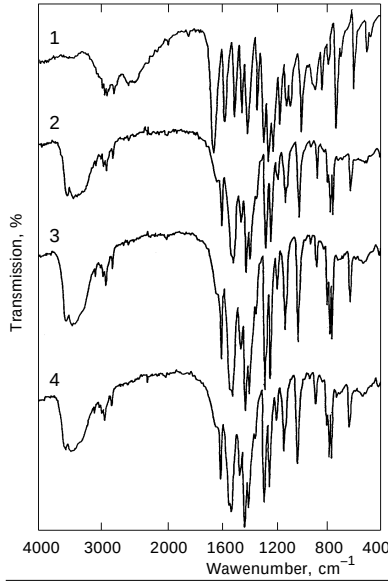

FIG. 1
Infrared spectra of 3,4-dimethoxybenzoic acid (*1*) and 3,4-dimethoxybenzoates of neodymium (*2*), europium (*3*) and gadolinium (*4*)

colours of the complexes are typical of the particular Ln(III) ion, *i.e.* white for La, Ce, Eu and Gd, cream for Sm, greenish for Pr and violet for Nd, having their origin in the lowest-energy f–f electronic transitions of the central ions[5–8].

The complexes were characterized by elemental analyses (Table I) and IR spectroscopy (Table II). All the 3,4-dimethoxybenzoates of the light lanthanides in solid state show similar IR spectra; some of them are presented in Fig. 1. As anticipated the characteristic wavenumbers due to the carbonyl group are altered markedly when going from the acid to the Ln(III) salts. The band due to the COOH group at 1 700 cm^{-1}, present in the IR spectrum of the acid, is replaced in the spectra of the complexes by two bands at 1 550–1 520 and 1 415–1 400 cm^{-1}, due to the asymmetric and symmetric vibration modes of the COO^- group, respectively[9–12]. The bands with maxima at 3 540–3 530 cm^{-1}, characteristic of ν(OH) vibrations, and the narrow $\delta(H_2O)$ band at 1 600 cm^{-1} confirm the presence of crystallization water molecules in the complexes. The bands belonging to asymmetric and symmetric C–H stretching modes of the CH_3 groups are observed at 2 930–2 925 and 2 830–2 825 cm^{-1}, respectively. Bands due to symmetric deformation modes of the CH_3 group appear at 1 325–1 320 cm^{-1}. The presence of the methoxy substituents at the benzene ring is confirmed by the bands at 1 250–1 245 cm^{-1}. The skeletal benzene ring modes are observed at

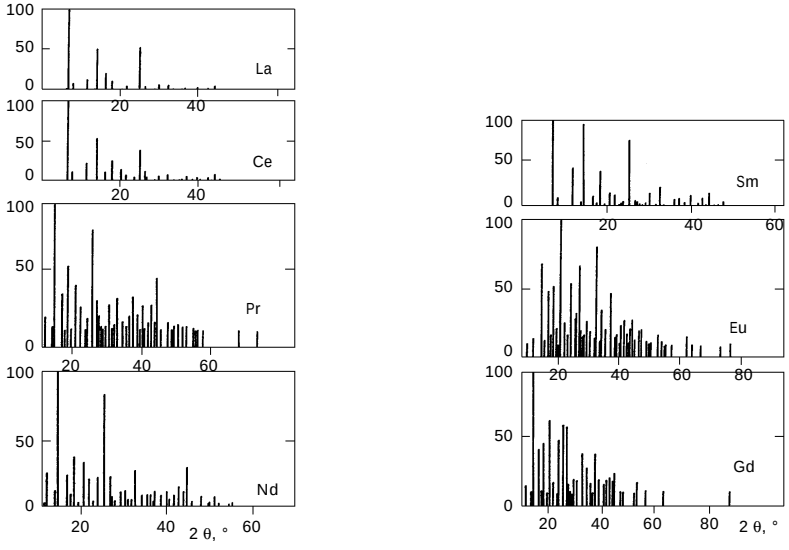

FIG. 2
Diffractograms of the light-lanthanide 3,4-dimethoxybenzoates

TABLE III
Temperature of dehydration and decomposition of the 3,4-dimethoxybenzoates of the light lanthanides

Complex $L = C_9H_9O_4$	ΔT_1[a] K	Weight loss, %		n[b]	ΔT_2[c] K	Weight loss, %		IDP[g]	ΔT_3[d] K	Weight loss, %		T_K[e] K	E_a[f] kJ mol^{-1}
		Calcd.	Found			Calcd.	Found			Calcd.	Found		
$LaL_3 \cdot 4\ H_2O$	333–413	10.50	10.40	4	573–933	75.76	75.56	$La_2O_2CO_3$	953–1 073	80.37	80.27	1 083	22.7
$CeL_3 \cdot 4\ H_2O$	313–393	10.50	10.45	4	533–933	78.00	77.00	–	–	–	–	943	35.0
$PrL_3 \cdot 4\ H_2O$	368–408	9.50	9.24	4	553–893	75.10	75.20	–	–	–	–	923	53.9
$NdL_3 \cdot 4\ H_2O$	353–413	10.40	10.30	4	573–953	75.76	7.76	$Nd_2O_2CO_3$	983–1 053	76.67	76.67	1 073	38.7
$SmL_3 \cdot 4\ H_2O$	343–413	10.40	10.35	4	573–953	78.00	78.00	–	–	–	–	973	24.1
$EuL_3 \cdot 4\ H_2O$	358–393	9.30	9.40	4	553–898	74.98	75.00	–	–	–	–	993	58.7
$GdL_3 \cdot 4\ H_2O$	363–393	9.30	9.20	4	563–943	74.10	74.00	–	–	–	–	1 003	69.5

[a] ΔT_1 = temperature range of dehydration process; [b] n = number of crystallization water molecules lost in one endothermic step; [c] ΔT_2 = temperature range of decomposition of anhydrous complex; [d] ΔT_3 = temperature of decomposition of oxycarbonate of La and Nd; [e] T_K = temperature of the oxide formation; [f] E_a = activation energy of dehydration reaction; [g] IDP = Intermediate decomposition product.

1 610–1 450 cm^{-1}. The =C–H bond stretching appear at 3 015–3 000 cm^{-1} and the out-of-plane C–H bending in the 945–645 cm^{-1} range. The bands typical of the aromatic ring vibrations in the complexes and not shifted significantly compared with the corresponding wavenumbers of the 3,4-dimethoxybenzoic acid, indicating that the influence of the Ln(III) ions on the benzene ring is only weak. The bands due to the metal–oxygen stretch probably appear at 545–540 cm^{-1} for the whole series of the complexes. It is therefore reasonable to suppose that 3,4-dimethoxybenzoic acid and the light lanthanides form complexes of similar stability[11].

Table II presents the wavenumbers of the asymmetric and symmetric COO^- stretching modes for Ln(III) and sodium 3,4-dimethoxybenzoates, as well as of the ν(C=O) mode of the 3,4-dimethoxybenzoic acid[9–14]. The separation between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes of the complexes is smaller ($\Delta\nu$ = 130–110 cm^{-1}) than that for the sodium salt ($\Delta\nu$ = 160 cm^{-1}), indicating a lower degree of ionic bond in the light-lanthanide 3,4-dimethoxybenzoates. Having ionic potentials larger than that of the sodium ion, trivalent ions deform the ligand more strongly. The frequency of the $\nu_{as}(COO^-)$ vibration is lower in the light-lanthanide complexes than that for the sodium 3,4-dimethoxybenzoate. Accordingly, the carboxylate ion is assumed to bind in the complexes as a symmetrical, bidentate chelating ligand[9,11,15].

In order to examine whether the light-lanthanide 3,4-dimethoxybenzoates were prepared as crystalline or amorphous compounds, their X-ray powder diffractograms were recorded. Analyses of the diffractograms point to polycrystalline compounds with variable degree of crystallinity and various symmetries (Fig. 2); only 3,4-dimethoxybenzoates of lanthanum and cerium seem to be isostructural. The crystal structures of the complexes have not been determined, as attempts to obtain single crystals failed.

On heating to 1 273 K, the 3,4-dimethoxybenzoates of the light lanthanides form oxides of the particular metal, having the same structures as the oxides obtained by ignition of rare-earth element oxalates[16,17]. The thermal stabilities of the light-lanthanide 3,4-dimethoxybenzoates were studied in air in the temperature range of 273–1 273 K (Table III). The results obtained from their thermal decomposition support their assignment as tetrahydrates, in agreement with data of elemental analyses (Table I). All the complexes are stable in air at room temperature and do not change their mass on storage. When heated in air, they decompose in two or three steps. Tetrahydrates of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) are stable up to 313–368 K, thereafter losing four water molecules in

one step (313–413 K) and decomposing to the oxides of the particular metal (Eq. (3)). The 3,4-dimethoxybenzoates of La(III) and Nd(III) decompose in three steps with the intermediate formation of oxycarbonates, $Ln_2O_2CO_3$ (Eq. (4)).

$$LnL_3 \cdot 4\,H_2O \rightarrow LnL_3 \rightarrow Ln_2O_3 \qquad Ln = Ce, Pr, Sm, Eu, Gd \qquad (3)$$

$$(+\ CeO_2,\ Pr_6O_{11})$$

$$LnL_3 \cdot 4\,H_2O \rightarrow LnL_3 \rightarrow Ln_2O_2CO_3 \rightarrow Ln_2O_3 \qquad Ln = La, Nd \qquad (4)$$

The oxides of the light lanthanide elements formed at 923–1 083 K were identified by X-ray powder diffraction[16,17].

As example, the derivatogram of neodymium 3,4-dimethoxybenzoate is presented in Fig. 3. The weight loss of the complex starts at 353 K. The decrease in weight occurs in the range of 353–413 K and therefore the TG curve deviates from the horizontal line. The weight loss determined from the TG curve equals to 10.30%, which corresponds to the loss of four water molecules (the theoretical value is 10.40%). Accordingly, a peak ascribed to this weight loss is also recorded in the DTG curve. The dehydration process is associated with an *endo*-effect observed in the DTA curve[18,19]. The anhydrous neodymium 3,4-dimethoxybenzoate decomposes in a second step be-

TABLE IV
Value of μ_{eff} for the light lanthanides determined by Hund and van Vleck, and for the 3,4-dimethoxybenzoates of those elements at 298 K

Ln(III)	Ground term	Hund μ_{eff}	van Vleck μ_{eff}	μ_{eff}(BM)
La(III)	$^1S_0$	0.00	0.00	0.00
Ce(III)	$^2F_{5/2}$	2.54	2.56	2.60
Pr(III)	$^3H_4$	3.58	3.62	3.69
Nd(III)	$^4I_{9/2}$	3.62	3.68	3.70
Sm(III)	$^6H_{5/2}$	0.84	1.55–1.65	1.70
Eu(III)	$^7F_0$	0.00	3.40–3.51	6.18
Gd(III)	$^8S_{7/2}$	7.94	7.94	7.84

tween 573–953 K to the oxycarbonate of neodymium, $Nd_2O_2CO_3$ and then finally to Nd_2O_3 (1 073 K), as confirmed by the overall weight loss of 76.67% determined from the TG curve. The oxidation process is associated with a strong *exo*-effect reflected in the DTA curve. Above 1 053 K the TG curve reaches a plateau, as the ultimate Nd_2O_3 product is thermally stable. In the studied tetrahydrate series, the most thermally stable is the complex of praseodymium that starts to release water at 368 K, while the least thermally stable complex is the 3,4-dimethoxybenzoate of cerium (313 K).

Considering the relatively low temperatures at which the dehydration process takes place (313–413 K), and the fact that the loss of water molecules only occurs in a single step, it is reasonable to assume that in the light-lanthanide 3,4-dimethoxybenzoates the crystallization water molecules bind in the outer coordination sphere[20,21]. Water of crystallization is removed from various compounds in a broad temperature range[18,19]. According to Nikolaev *et al.*[20] and Singh *et al.*[21], water eliminated below 423 K can be considered as crystallization water whereas that eliminated above 423 K may coordinate to the central ion through weak ionic or partially covalent bonds[9]. The exact assignment of the position and bonding interaction of the water molecules in the studied tetrahydrate complexes demands determination of their crystal structures; this has unfortunately been hindered by the lack of suitable single crystals.

From the TG and DTA curves, the activation energies of the dehydration reactions (E_a in Table III) were calculated by the Fotieev and Pletniew method[22] according to Eq. (*5*)

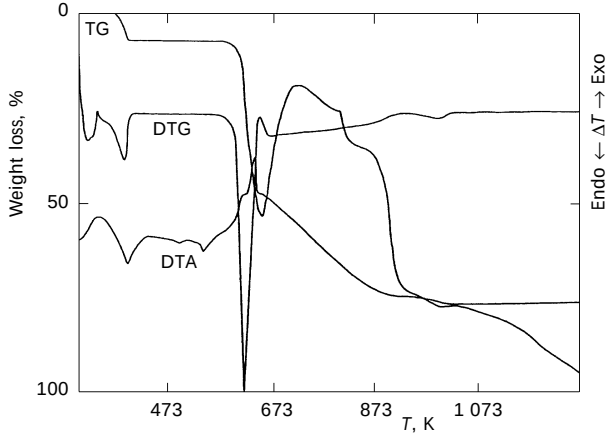

FIG. 3
TG, DTG and DTA curves of neodymium 3,4-dimethoxybenzoate

$$E_a = R T_{max}^2 \Delta m \, m_0^{-1} \Delta T^{-1} \quad , \qquad (5)$$

where R is the gas constant, T_{max} the temperature of maximum of the weight loss, m_0 the weight loss at T_{max}, m the weight loss at T and T the given temperature; $\Delta m = m_0 - m$; $\Delta T = T_{max} - T$.

The different E_a values may suggest that the water molecules in the studied complexes bind with different strength, depending on their positions in the coordination sphere. The smallest E_a value applies for lanthanum 3,4-dimethoxybenzoate whereas the largest one for the gadolinium complex.

The solubilities of the 3,4-dimethoxybenzoates of the light lanthanides in water (at 293 K) and their solubility products are summarized in Table II. They are in the order of 10^{-3}–10^{-4} mol dm^{-3} and 10^{-3}–10^{-11} mol^4 dm^{-12}, respectively. Cerium 3,4-dimethoxybenzoate is the most soluble complex in the series while the least soluble one is the complex of neodymium. The solubilities of 3,4-dimethoxybenzoates of Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) are lower than those determined for benzoates, 3-methoxy- and 4-methoxybenzoates of rare-earth elements[23–26] (10^{-3} mol dm^{-3}); however, the values do not deviate in the case of La(III) and Ce(III). The difference in the solubilities of the former complexes may result from changes in electron density distribution due to the influence of the inductive and mesomeric effects of the methoxy substituents at the benzene ring, causing different ability of the complexes to dissociate in water.

In view of the low values of the complex solubilities, 3,4-dimethoxybenzoic acid appears to be not suitable for the separation of the light-lanthanide elements by ion-exchange chromatography or by extraction methods.

The magnetic susceptibility of the light lanthanide 3,4-dimethoxybenzoates was determined in the temperature range of 77–298 K. The values of the Weiss constant, θ, were found for all the complexes to have a negative sign, which probably arises from the antiferromagnetic spin interaction or from a crystal field splitting of the paramagnetic spin state[27–30]. In the complexes of 3,4-dimethoxybenzoates, the paramagnetic central ions remain virtually unaffected by the surrounding diamagnetic ligands. The 4f electrons causing their paramagnetism are well protected from outside influences and do not participate in the formation of the Ln–O bond. Instead, they only weakly interact with the electrons of the surrounding atoms.

They are spaced in an inner shell characterized by a radius $r \approx 0.35$ Å (ref.[31]). This value is very small in comparison with the radius of the $5s^25p^6$ closed shell (≈1 Å). Therefore their energy levels are the same as in the free ions due to the very effective shielding by the overlapping $5s^25p^6$ shell. For the lanthanide ions the ground state is separated by several hundreds of cm^{-1} from the next higher-lying state. Hence, the magnetic properties can be considered identical to those of the ground state alone, making bonded lanthanide ions act in the same way as the free ions. The 3,4-dimethoxybenzoates of the light lanthanides obey the Curie–Weiss law. The values of μ_{eff} determined for all the complexes (except that for 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 3,4-dimethoxybenzoate compared with that given by Hund, may suggest a possible interaction of the ligand field with central ion or may be associated with the multiplet splitting. The lowest three excited state of the europium ion are sufficiently close in energy to the ground states to be appreciably populated at room temperature[32–34]. Since the excited states possess higher I values than the ground state, the actual magnetic moment is larger than those calculated by using the I 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 cm^{-1}) at room temperature, whereas those for Sm and Eu are not really infinitely large compared to kT. For Eu the interval between the lowest multiplet components is only 1/21 of the overall width, as for a ^7F term[32] it applies:

$$1/2\,[I_{max}\,(I_{max} + 1) - I_{min}\,(I_{min} + 1)] = 1/2 \times 6 \times 7 - 0 = 21, \quad I_{min} + 1 = 1. \quad (6)$$

Concluding, from the obtained results it appears that the Ln–O bond in the light-lanthanide 3,4-dimethoxybenzoates is mainly electrostatic in nature, since the 4f orbitals of the lanthanide ions are effectively shielded by the $5s^25p^6$ octet[31,38].

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