Complexes of Heavy Lanthanides and Yttrium with 3,4,5-Trimethoxybenzoic Acid

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3,4,5-Trimethoxybenzoates of yttrium and heavy lanthanides have been obtained as anhydrous salts with a metal to ligand ratio of 1 : 3. They have colours, typical of Ln^{3+} ions. The carboxylate group appears to be a symmetrical, bidentate, chelating ligand. 3,4,5-Trimethoxybenzoates of heavy lanthanides are crystalline compounds characterized by a low symmetry and large size of unit cells. The complexes decompose in one step, forming oxides of the respective metals. The solubilities in water at 293 K for yttrium and heavy lanthanide 3,4,5-trimethoxybenzoates are in the order of 10^{-3} mol dm^{-3}. The magnetic moments for the complexes were determined over the range of 77–298 K. They obey the Curie-Weiss law. The values of μ calculated for all compounds are close to those obtained for Ln^{3+} by Hund and Van Vleck. The results show that there is no influence of the ligand field on the 4f electrons of lanthanide ions.

INTRODUCTION

3,4,5-Trimethoxybenzoic acid of the formula $C_{10}H_{12}O_5$ is a white, crystalline solid, sparingly soluble in water and readily soluble in alcohol, ether and chloroform.[1] Its compounds are comparatively very little known. From the survey of literature it follows that complexes of 3,4,5-trimethoxybenzoic acid have been obtained; however, only with the following cations:[1] K^+, Cu^{2+}, Ag^+, Ca^{2+} and Ba^{2+}. The review of the articles also informs us about the complexes of various isomers of monomethoxy-, dimethoxy-, and trimethoxybenzoic acids with lanthanide series, obtained as solids or investigated only in solution.[3–7] Makusheva[3] and Brzyska[4–6] have obtained, in the solid state, the complexes of rare earth elements with 2-methoxy-, 3-methoxy- and 4-metho-

xybenzoic acids and they have examined some of their physico-chemical properties. Moreover, there is also information on 2-methoxy- and 4- methoxybenzoates of La-Sm, Gd, Dy and Yb, which have been investigated in solution.[7] Also, some physico-chemical properties of the complexes of 2,3-dimethoxy-, 2,4-dimethoxy- and 2,6-dimethoxybenzoic acids with La-Sm, Gd, Dy and Yb and of these elements with 2,4,5-trimethoxy- and 2,4,6-trimethoxybenzoic acids were examined in solution.[7] The complexes of 3,4,5-trimethoxybenzoic acid with yttrium and heavy lanthanides (Tb-Lu), as solids have not been obtained so far. Therefore, the aim of this work was to obtain them in the solid state and to examine some of their properties, such as: thermal stability in air, solubility in water at room temperature, magnetic properties, to estimate their external crystalline form and to present their IR spectra characterization. Methoxybenzoic acids belong to a similar type of acids because they have one carboxylic group and one or more methoxy-groups.

The aim of our investigations was to obtain new complexes of rare earth elements with various methoxybenzoate ligands, to examine some of their physico-chemical properties and to compare them within the series of one isomer or within other methoxy isomers. The comparison enabled us to investigate the influence of the position of substituents in aromatic ring on the properties of the complexes. On the basis of the results of basic investigations, the complexes obtained in the solid state are generally characterized by elemental analysis, IR spectral data, thermogravimetric or magnetic studies, X-ray diffraction measurements and solubilities in water or in various organic solvents. 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 chromatography methods. Thermal stablility investigations enabled us to evaluate the presumed positions of crystallization water molecules in the outer or inner coordination sphere in the complex, to know the mechanism of complex decomposition, to determine the endo- or exo-effects connected with such processes as: dehydration, melting, crystallization, oxidation, reduction and, above all, to estimate the strength of bonding between atoms or groups of atoms and ions. In order to know if 4f electrons of heavy lanthanide ions take part in the formation of metal – ligand bonding and if that bonding is mainly electrostatic in nature, the magnetic susceptibilities were measured.

EXPERIMENTAL

3,4,5-Trimethoxybenzoates of yttrium and heavy lanthanides were prepared by adding the equivalent quantities of 0.1 M ammonium 3,4,5- trimethoxybenzoate (pH ≈ 5) to a hot solution containing rare earth element nitrates, and by crystallization at 293 K. The solids formed were filtered off, washed with hot water to remove ammonium ions and dried at 303 K to constant weight.

Carbon and hydrogen contents were determined by elemental analysis with V_2O_5 as oxidizing agent. Rare earth element contents were established by the oxalic method. From the obtained results (Table I), it follows that 3,4,5-trimethoxybenzoates of rare earth elements are anhydrous salts with a metal to ligand ratio of 1 : 3. They have weak colours, characteristic of Ln^{3+} ions.

In order to confirm the chemical composition of the salts, the IR spectra of the complexes, the 3,4,5-trimethoxybenzoic acid and sodium salt were run in the range of 4000–400 cm^{-1} using KBr discs on an IR M-80 spectrophotometer (Table II).

TABLE I

Analytical data

| Complex	% H		% C		% M	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
YL_3	4.57	4.63	49.93	50.01	13.33	12.40
TbL_3	4.16	4.22	45.45	45.59	20.06	20.16
DyL_3	4.14	4.24	45.25	45.30	20.42	20.56
HoL_3	4.14	4.28	45.16	45.03	20.69	20.72
ErL_3	4.12	4.15	44.98	44.91	20.90	20.84
TmL_3	4.11	4.24	44.86	44.54	21.10	21.20
YbL_3	4.09	4.06	44.66	44.44	21.46	21.58
LuL_3	4.08	4.14	44.55	44.60	21.65	21.62

$L = C_{10}H_{11}O_5$

TABLE II

Frequencies of the absorption bands of COO^- for 3,4,5-trimethoxybenzoates of Y, heavy lanthanides and sodium, and those of CO for 3,4,5-trimethoxybenzoic acid (v/cm^{-1})

In order to study the crystal structure of 3,4,5-trimethoxybenzoates and struc-
tures of the corresponding oxides, obtained upon thermal decomposition of the com-
plexes and ignition of the oxalates, X-ray powder patterns were taken on a DRON-2
diffractometer using Ni-filtered Cu-Kα radiation within the range 2Θ = 5–80°. Ther-
mogravimetric measurements were performed on a Q-1500D derivatograph (10°
min^{-1}). Test samples were heated at the sensitivity of TG-100 mg, DTG-500 µV, DTA-
500 µV (Table III). The solubility of 3,4,5-trimethoxybenzoates of yttrium and heavy
lanthanides in water at 298 K was determined by measuring the concentration of
Ln^{3+} ions in a saturated solution by the oxalic method (Table III).

TABLE III

Decomposition temperature of 3,4,5-trimethoxybenzoates of Y and heavy lanthanides,
their solubilities in water at 293 K, solubility products (I) and densities as solids.

Complex	Temp. range of decompo- sition / K	Loss of mass / %		Temp. of oxide forma- tion / K	Solubility mol dm^{-3}	pI = –log$I$	Density g cm^{-1}
		Calcd.	Found				
YL$_3$	554–1013	85.02	85.71	1013	$0.78 \cdot 10^{-3}$	11.00	1.54
TbL$_3$	573–843	77.80	78.78	843	$0.58 \cdot 10^{-3}$	11.49	2.65
DyL$_3$	563–913	79.59	80.22	913	$0.55 \cdot 10^{-3}$	11.61	2.58
HoL$_3$	558–938	80.61	81.00	938	$0.48 \cdot 10^{-3}$	11.86	2.42
ErL$_3$	573–903	77.24	77.77	903	$0.51 \cdot 10^{-3}$	11.73	2.28
TmL$_3$	553–933	79.22	79.59	933	$0.47 \cdot 10^{-3}$	11.89	2.01
YbL$_3$	563–843	77.42	77.00	843	$0.58 \cdot 10^{-3}$	11.51	1.85
LuL$_3$	563–853	79.34	79.59	853	$0.62 \cdot 10^{-3}$	11.39	1.45

L = C$_{10}$H$_{11}$O$_5$
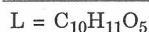
Magnetic susceptibilities of polycrystalline samples of 3,4,5-trimethoxybenzoates
of rare earth elements were measured by the Gouy method using a sensitive Gahn
RM-2 balance. Measurements were made at a magnetic field strength of 9.9 kOe.
The calibrant employed was CoHg(SCN)$_4$, for which the magnetic susceptibility of
16.44×10^{-6} (cm^3 g^{-1}) was taken.[8] Correction for diamagnetism of the constituent at-
oms was calculated by the use of Pascal's constants.[9] The magnetism of the samples
was found to be field independent. The temperature-independent paramagnetism of
rare earth ions was assumed to be zero. Magnetic moments were calculated from
the equations:

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

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

The results are given in Table IV.

TABLE IV

Detailed magnetic data for the heavy lanthanide 3,4,5-trimethoxybenzoates

TbL_3^a $\Theta^b = -7$ K			DyL_3 $\Theta = -4$ K			HoL_3 $\Theta = -8$ K			ErL_3 $\Theta = -3$ K			TmL_3 $\Theta = -6$ K			YbL_3 $\Theta = -42$ K		
T/K	$\chi_M \cdot 10^6$	μ/BM	T/K	$\chi_M \cdot 10^6$	μ/BM	T/K	$\chi_M \cdot 10^6$	μ/BM	T/K	$\chi_M \cdot 10^6$	μ/BM	T/K	$\chi_M \cdot 10^6$	μ/BM	T/K	$\chi_M \cdot 10^6$	μ/BM
77	144336	9.85	77	162207	10.25	77	156737	10.32	77	141276	9.51	77	77073	7.15	77	25274	4.90
122	95237	9.91	132	101407	10.50	122	99353	10.17	128	84570	9.41	128	50248	7.34	120	17698	4.79
130	85734	9.69	136	97407	10.45	135	96644	10.52	137	77779	9.27	137	44096	7.10	130	16489	4.76
142	80190	9.78	144	91107	10.39	147	89471	10.53	151	71151	9.18	151	41946	7.26	141	16166	4.86
150	76231	9.79	156	85407	10.46	157	85007	10.59	158	65996	9.22	158	40650	7.30	148	14716	4.73
168	69895	9.89	172	77807	10.47	169	76320	10.40	168	61741	9.14	168	37943	7.27	162	13748	4.73
176	65144	9.77	176	74407	10.37	182	70343	10.34	176	56340	9.13	176	35482	7.19	172	13184	4.71
183	63560	9.83	190	69007	10.35	189	66358	10.23	201	53231	9.09	201	31380	7.21	180	12942	4.79
192	60392	9.81	198	66407	10.36	196	64764	10.28	215	50040	9.13	215	28099	7.05	194	12459	4.85
218	50889	9.57	206	63207	10.31	206	59185	10.07	223	49139	9.15	223	28919	7.28	203	11492	4.74
230	49306	9.67	218	60207	10.34	222	57592	10.29	230	46194	9.08	230	27279	7.18	214	11089	4.76
234	48514	9.67	225	59407	10.43	234	51215	9.96	242	43903	9.10	242	26458	7.24	222	10686	4.75
242	46138	9.59	234	56407	10.36	248	52809	10.40	250	41939	9.03	250	24818	7.13	235	10202	4.75
253	43762	9.54	244	54907	10.44	265	54403	10.90	263	41530	9.19	263	23991	7.18	244	9880	4.75
264	41386	9.47	256	51007	10.30	278	47230	10.40	271	38502	9.01	271	23177	7.17	258	9477	4.77
275	40594	9.57	265	49407	10.31	298	40057	9.90	272	36947	9.02	275	22111	7.05	270	9074	4.76
286	39803	9.66	276	48207	10.39				280	34738	8.87	298	21372	7.21	282	8993	4.83
294	38219	9.59	290	45607	10.36				298	33838	9.03				295	8671	4.83

(a) L = $C_{10}H_{11}O_5$ (b) Θ = Weiss constant

RESULTS AND DISCUSSION

3,4,5-Trimethoxybenzoates of yttrium and heavy lanthanides were obtained as crystalline products having the weak colours typical of Ln^{3+} ions, a metal to ligand ratio of 1 : 3, and the general formula: $Ln(C_{10}H_{11}O_5)_3$ for Ln = Y, Tb-Lu. The colours of the complexes are those typical of the appropriate trivalent ions. The molecules of 3,4,5-trimethoxybenzoates have probably a planar structure and the OCH_3 group electrons are conjugated with the Π electrons. In these molecules, the f-f electronic transitions of the central ions are those of the lowest energy while absorption occurs at relatively high wave-lengths depending on the nature of the metal ion. The compounds were characterized by elemental analyses (Table I) and IR spectra. Yttrium and all heavy lanthanide trimethoxybenzoates show similar solid-state IR spectra. However, the characteristic frequencies related to the carbonyl group are altered markedly in going from acid to salts. The band of the COOH group at 1700 cm^{-1}, present in the acid spectrum, completely disappears in the spectra of the complexes and two bands arising from asymmetric and symmetric vibrations of COO^- group occur at 1540–1528 cm^{-1} and 1430–1420 cm^{-1}, respectively. The scissoring vibration bands of CH_3 groups are observed in the range of 1475–1455 cm^{-1}. The bands characteristic of $-O-CH_3$ occur at 1330–1315 cm^{-1}, 1250–1240 cm^{-1}, while those also for CH_3 appear at 2960–2945 cm^{-1}, 2855–2845 cm^{-1}. There are numerous bands of the aromatic ring vibrations at 1195–1190 cm^{-1}, 1145–1130 cm^{-1}, 1015–1005 cm^{-1} and 965–955 cm^{-1} and those of CH bond at 3015–3000 cm^{-1}, 885–875 cm^{-1}, 800 cm^{-1}, 780–760 cm^{-1}, 745 cm^{-1} and 695–680 cm^{-1}. These bands are shifted insignificantly (10–5 cm^{-1}) by comparison with the respective bands of 3,4,5-trimethoxybenzoic acid, which indicates that the Ln(III) ions have a weak influence on the benzene ring. Bands due to the metal-oxygen bond appear at 482–476 cm^{-1}. Their regular shifts are not observed in the spectra. Accordingly, it is possible to suggest that 3,4,5-trimethoxybenzoic acid forms complexes with yttrium and heavy lanthanides that have similar stabilities. Their comparison seems possible because they are complexes of the same type. Vibrations of M-O are not pure because of the conjugation of C-O, M-O, and C-C group vibrations.[10] Table II presents the maxima of the frequencies of absorption bands of asymmetric and symmetric vibrations of COO^- for 3,4,5-trimethoxybenzoates of yttrium and heavy lanthanides and sodium. The magnitudes of separation $\Delta\nu$ between frequencies $\nu_{as}(OCO)$ and $\nu_s(OCO)$ in the complexes are lower ($\Delta\nu$ = 120–108 cm^{-1}) than in the sodium salt ($\Delta\nu$ = 170 cm^{-1}), which indicates a smaller degree of ionic bond in the complexes. Having an ionic potential greater than that of a sodium ion, trivalent ions deform the ligand more strongly. In this case, it is not possible to define the degree of the covalent bond because of the changes of the OCO bond angle with the changes of ionic radii in the lanthanide ions.[10] For 3,4,5-trimethoxybenzoates, the shifts of frequencies $\nu_{as}(OCO)$ and $\nu_s(OCO)$ are

lower and higher, respectively, than those for sodium 3,4,5-trimethoxyben-zoate. Accordingly, the carboxylate ion appears to be a symmetrical, biden-tate, chelating ligand.[11–14] In order to estimate the external crystalline form of 3,4,5-trimethoxybenzoates of heavy lanthanides and yttrium, the X-ray powder diffraction measurements were done. The diffractogram analysis shows them to be polycrystalline compounds with various degrees of crys-tallinity and of low symmetry (Figure 1). The appearance of the first inter-ference reflections corresponding to the relatively small angles indicates a large size of unit cells. Based on the results obtained, it is possible to claim that the complexes have different structures but their complete and detailed crystalline structures have not been determined because no single crystals have been obtained.

Structures of all heavy lanthanide and yttrium oxides obtained from ig-nition of the oxalates and 3,4,5-trimethoxybenzoates remain the same irre-spective of the way of their formation. The oxide structures were identified roentgenographically.[15,16]

The thermal stability of 3,4,5-trimethoxybenzoates of yttrium and heavy lanthanides was studied (Table III). All complexes are stable in air and stor-age does not change their mass. Having various stabilities, the anhydrous complexes are decomposed at temperatures of 553–1013 K. The most ther-mally stable complexes are 3,4,5-trimethoxybenzoates of terbium and er-bium, which start to decompose at 573 K while the least thermally stable one is thulium 3,4,5-trimethoxybenzoate whose initial temperature of de-composition is 553 K. Yttrium and heavy lanthanide 3,4,5-trimethoxyben-zoates are decomposed directly to oxides of the respective metals as final products of their decomposition. The oxides are formed at 843–1013 K. The temperature of oxide formation is the highest for Y_2O_3 (1013 K) and the low-est for Yb_2O_3 and Tb_4O_7 (843 K). The derivatogram obtained for dysprosium 3,4,5-trimethoxybenzoate is presented in Figure 2. It shows that the weight loss of complex starts around 563 K. Next, a sudden decrease in weight oc-curs in the temperature range 563–913 K and the TG curve does not proceed horizontally. The weight loss is about 80%. This decrease in weight is as-cribed to oxidation of the organic ligand and formation of the metal oxide: Dy_2O_3. The oxidation process is related to the strong exoeffect observed in the DTA curve. After this, the TG curve is again a horizontal line above 913 K which corresponds to Dy_2O_3 formation.

The density of the complexes as solids was determined (Table III). It de-creases regularly with decreasing the ionic radius of the element and pre-sumably with the changes in the size of the unit cell and its packing.[15]

Solubilities of 3,4,5-trimethoxybenzoates of yttrium and heavy lantha-nides in water were measured at 293 K and their solubility products were determined (Table III). The are in the orders: 10^{-3} mol dm^{-3} and 10^{-12} mol^4 dm^{-12}, respectively. The 3,4,5-trimethoxybenzoate of yttrium is the most sol-
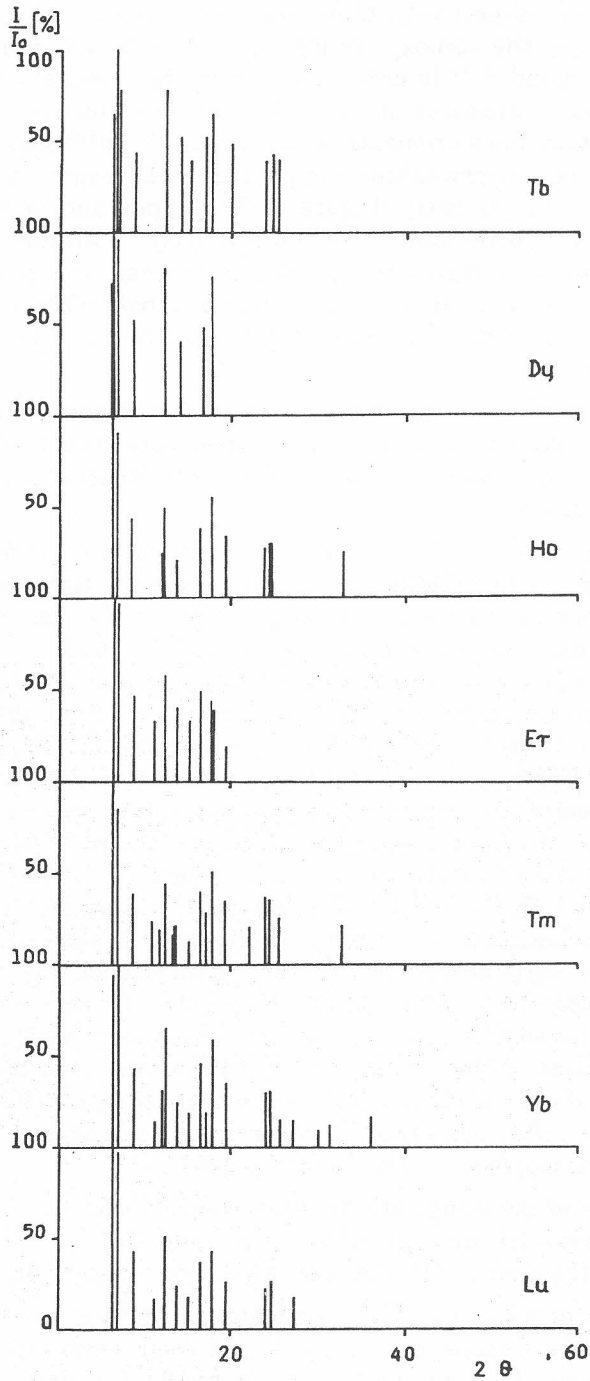
Figure 1. Radiograms of 3,4,5-trimethoxybenzoates of the heavy lanthanides.
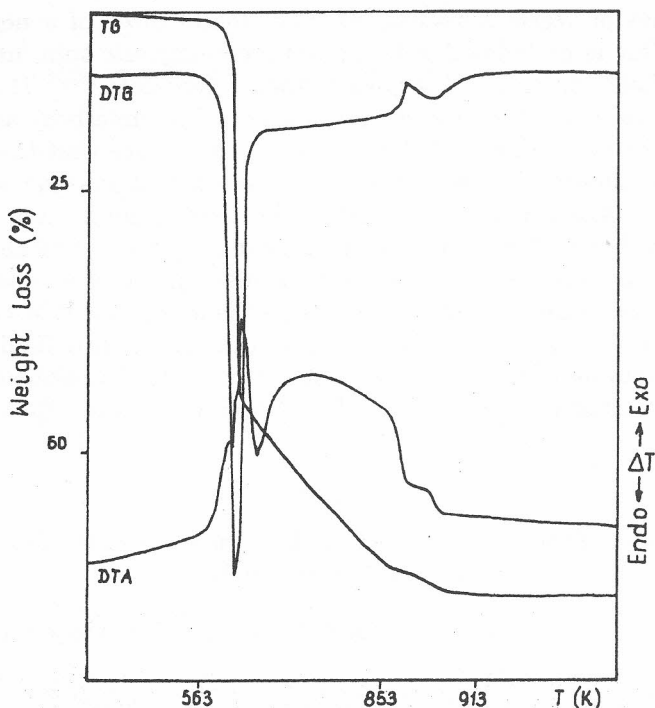
Figure 2. TG, DTG and DTA curves of dysprosium 3,4,5-trimethoxybenzoate.

uble salt while that of thulium is the least soluble one. The order of solubilities of 3,4,5-trimethoxybenzoates of yttrium and heavy lanthanides is in good agreement with those determined for rare earth element benzoates,[17] 3-methoxy- and 4-methoxybenzoates,[4–6] which are also of the orders of 10^{-3} mol dm^{-3}. This is probably connected with the similar ability of benzoates, 3- and 4-methoxybenzoates and 3,4,5-trimethoxybenzoates for dissociation in water which results from the similar electron density in aromatic ring in the complexes, which yields a similar stability of M-O bond in water. The solubility values for the complexes of various isomers of methoxybenzoic acids with heavy lanthanides have the same order irrespective of the position and number of methoxy groups in benzene ring, resulting from a similar electron density in aromatic ring. Moreover, the values suggest that the appropriate methoxybenzoic acids cannot be used as eluent for the separation of heavy lanthanides by the ion-exchange method because their complexes with these elements are not easily soluble.

In order to know if 4f electrons of the heavy lanthanide ions take part in the formation of metal-ligand bonding and if that bond is mainly electrostatic in nature, the magnetic susceptibilities were measured over a temperature range of 77–298 K.

The values of Weiss constants, Θ, were found to be of a negative sign (Table IV). This is probably due to the antiferromagnetic spin interaction or to a crystal field splitting of the paramagnetic spin state.[18–21] The relatively low absolute value of Θ is observed for erbium 3,4,5-trimethoxybenzoate and the highest for ytterbium. It follows from the literature that the small values of Θ are caused by weak interactions between atoms and ions. In the complexes of 3,4,5-trimethoxybenzoates, the paramagnetic central ions remain practically unaffected by the diamagnetic ligands coordinated around them. The f electrons causing their paramagnetism are well separated from outside influencies and do not participate in the formation of M-O bond. The higher values of Θ may suggest interaction of the crystal field of ligands with the central ion. The values of μ determined for all complexes are close to those calculated for Ln^{3+} ions by Hund and Van Vleck (Table IV, V). In

TABLE V

Values of the Hund and Van Vleck μ_{eff} determined for heavy
lathanide ions (μ/BM)

Ln^{3+}	Ground term.	Calcd. Hund μ_{eff}	Van Vleck μ_{eff}
Tb^{3+}	$^7F_6$	9.70	9.70
Dy^{3+}	$^7H_{15/2}$	10.60	10.60
Ho^{3+}	$^5I_8$	10.60	10.60
Er^{3+}	$^4I_{15/2}$	9.60	9.60
Tm^{3+}	$^3H_6$	7.60	7.60
Yb^{3+}	$^2F_{7/2}$	4.50	4.50
Lu^{3+}	$^1S_0$	0.00	0.00

the rare earth element ions, 4f electrons are in an inner shell characterized by a radius of $\sqrt{\langle r^2 \rangle} = 0.35$ Å.[22] This value is very small in comparison with the radius of the $5s^25p^6$ closed shell (≈ 1 Å) and the distance between rare earth ions, which is about 10 times larger. Thus, the 4f electrons interact only weakly with the electrons of the sorrounding atoms. The f electrons are almost unaffected by the chemical environment and the energy levels are the same as in the free ions due to the very effective shielding by the overlapping $5s^25p^6$ shell. For most of the lanthanide ions, the ground state is separated by many hundreds of cm^{-1} from the next higher lying state. Thus, the magnetic properties can be taken as those of the ground state alone, making lanthanide ions in a compound act, in the same way as the free ion as far as the f electrons are concerned. The complexes of 3,4,5-trimethoxybenzoates of heavy lanthanides obey the Curie-Weiss law. A plot of the inverse of the magnetic susceptibility χ_M determined for all compounds yields
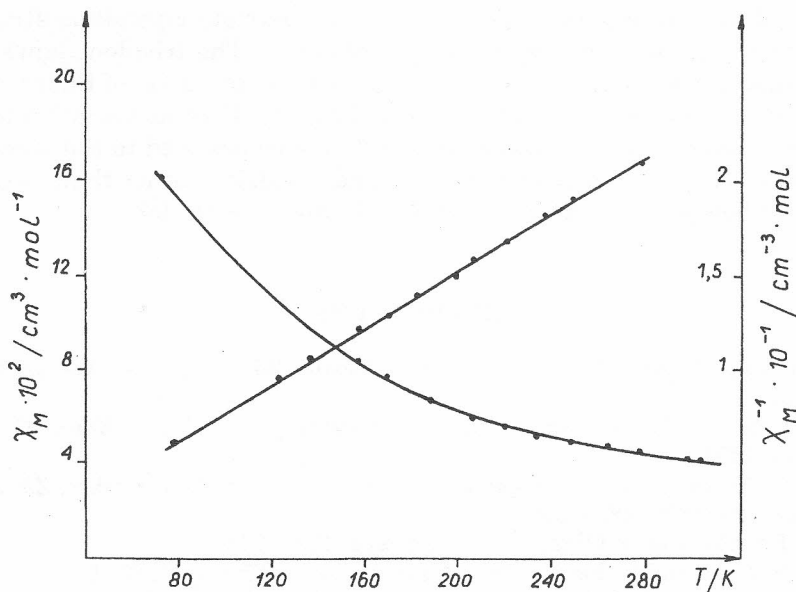
Figure 3. Relationship between χ_M and χ_M^{-1} and T for 3,4,5-trimethoxybenzoate of Ho.

a straight line. In Figure 3, the relationship between χ_M and χ_M^{-1} and T for 3,4,5-trimethoxybenzoate of Ho is presented. Lutetium 3,4,5-trimethoxybenzoate is diamagnetic in nature, as expected. From the obtained results, it is possible to conclude that, in the 3,4,5-trimethoxybenzoates of heavy lanthanides, no influence of ligands on 4f electrons in lanthanide ions occurs and the 4f electrons take no part in the formation of the M-O bond. The values of magnetic moments determined for the complexes may suggest that the 4f electron shells of lanthanide ions are practically not changed. Lanthanide ions in the complexes have similar values of paramagnetism as the free ions have. Lack of 4f electron interactions with atoms or ions around them make the colours of the complexes the same as that of free ions. The f-f electronic transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wave-lengths. It is possible to suppose that the M-O bond in the heavy lanthanide 3,4,5-trimethoxybenzoates is of the same type. One cannot expect the existence of strongly covalent metal ligand interactions in heavy lanthanide complexes since the 4f orbitals of lanthanide ions are effectively shielded by the $5s^2 5p^6$ octet. Hence, the metal ligand bonding in lanthanide complexes is mainly electrostatic in nature.

The analytical, magnetic, thermal and spectral data suggest that, in 3,4,5-trimethoxybenzoates of heavy lanthanides, lanthanide ions presumably exhibit a coordination number of six. The coordination numbers of Ln^{3+}

ions could be determined on the basis of the complete crystalline structure of monocrystals but they have not been obtained. The trivalent lanthanide ions exhibit a wide variety of stereochemistries on the basis of their varying coordination numbers from six to twleve. This coordination variation in lanthanide complexes is well established and may be ascribed to the steric factors and electrostatic force of attraction and repulsion rather than to the direction of bonds by the deep seated 4f orbitals of metal ions.

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SAŽETAK

Kompleksi teških lantanoida i itrija s 3,4,5-trimetoksibenzojevom kiselinom

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Dobiveni su 3,4,5-trimetoksibenzoati itrija i teških lantanoida kao bezvodne soli u omjeru metal : ligand = 1 : 3. Kompleksi su slabo obojeni, što je tipično za ione Ln^{3+}. Karboksilatna skupina javlja se kao simetričan, bidentatni kelatni ligand. 3,4,5-Trimetoksibenzoati teških lantanoida kristalni su spojevi, karakterizirani niskom simetrijom i velikom jediničnom ćelijom. Kompleksi se raspadaju u jednom stupnju, uz nastajanje oksida odgovarajućih metala. Topljivosti u vodi (pri 298 K) 3,4,5-trimetoksibenzoata itrija i teških lantanoida nalaze se oko 10^{-3} mol dm^{-3}. Magnetski momenti, μ, ovih kompleksa, određeni u području od 77 do 298 K, slijede Curie-Weissovo pravilo. Vrijednosti μ izračunane za sve spojeve bliske su onima koje su Hund i Van Vleck dobili za lantanoide. Rezultati pokazuju da ligandno polje ne utječe na 4f-elektrone lantanoidnih iona.