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THERMAL STABILITY OF 2,3,4-, 2,4,5- AND 3,4,5-TRIMETHOXYBENZOATES OF LIGHT LANTHANIDES

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Abstract

The physico-chemical properties and thermal stability in air of light lanthanide 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates were compared and the influence of the position of $–OCH_3$ substituent on their thermal stability was investigated. The complexes of these series are crystalline, hydrated or anhydrous salts with colours typical of Ln^{3+} ions. The carboxylate group is a bidentate, chelating ligand. The thermal stability of 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of rare earth elements was studied in the temperature range 273–1173 K. The positions of methoxy groups in benzene ring influence the thermal properties of the complexes and their decomposition mechanism. The different thermal properties of the complexes are connected with various influence of inductive and mesomeric effects of $–OCH_3$ substituent on the electron density in benzene ring.

Keywords: complexes of rare earth elements, influence of methoxy-substituents, light lanthanide trimethoxybenzoates, properties of trimethoxybenzoates, thermal stability of trimethoxybenzoates, 2,3,4-, 2,4,5 and 3,4,5-trimethoxybenzoates

Introduction

2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoic acids having the formula $C_{10}H_{11}O_5$ are white, crystalline solids, sparingly soluble in cold water. Their solubility in water increases with the rise of temperature [1–3]. The literature survey shows that there is no information about the complexes of 2,3,4-trimethoxybenzoic acid with various cations, but it informs about the complexes of 2,4,5-trimethoxybenzoates with K^+, Na^+, Ca^{2+} which have been obtained and investigated in solid state [2, 4, 5] and those of Cu^{2+}, Be^{2+}, UO_2^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} and Yb^{3+} to have been studied in solution [6]. The salts of 3,4,5-trimethoxybenzoic acid only with the following cations: K^+, Cu^{2+}, Ag^+, Ca^{2+} and Ba^{2+} have been also obtained as solids [3].

In the literature there is no information about these acid complexes with the light lanthanides. Therefore, we decided to obtain them as solids, to examine some of their physico-chemical properties and to compare them. In our previous papers [7–9] we characterized these complexes by elemental analysis, IR spectra data, thermogravimetric studies and X-ray diffraction measurements but now taking into account the presence and positions of three methoxy groups in benzene ring we decided to compare the properties

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of trimethoxybenzoates of light lanthanides in order to investigate the influence of substituent positions on their properties.

Experimental

2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of light lanthanides were prepared by adding the equivalent quantities of 0.1 M ammonium 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates (pH~5) to a hot solution containing the light lanthanide 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 a constant mass. The carbon, and hydrogen contents were determined by elemental analysis with V_2O_5 as oxidizing agent. The rare earth element contents were established by the oxalic acid method. The IR spectra of the complexes, the spectra of 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoic acids and their sodium salts were run in the range 4000–400 cm^{-1} using KBr discs on an M-80 spectrophotometer. Some of the results are presented in Fig. 1. X-ray powder patterns were taken on a DRON-2 diffractometer using Ni-filtered CuK_α radiation within the range $2\Theta=5–80°$ by Debyé-Scherrer-Hull method. The thermal stability of these complexes in air in the range 273–1173 K was studied by the use of TG, DTG and DTA techniques. In the case of 2,3,4- and 2,4,5-trimethoxybenzoates of light lanthanides the measurements

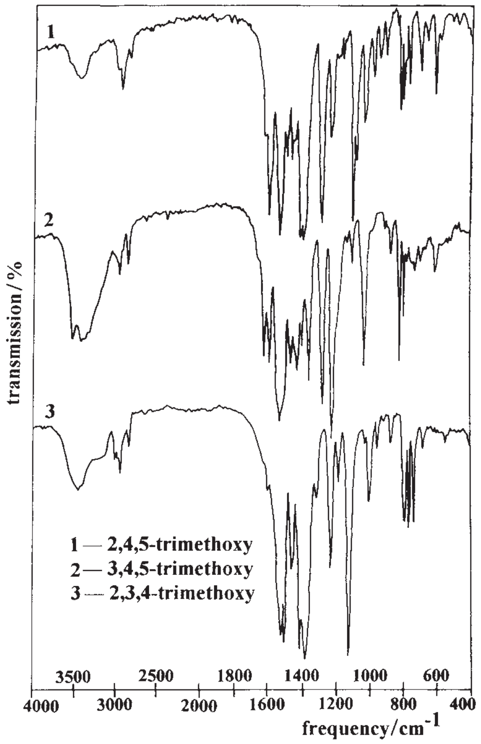

Fig. 1 Infrared spectra of 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of Nd

were made with an OD-102 derivatograph (Firm MOM-Budapest) at a heating rate of 10°C min^{-1}. The test samples were heated at a sensitivity: TG – 100 mg, DTA – 500 μV, DTG – 500 μV [7, 9]. The thermal stability of 3,4,5-trimethoxybenzoates of light lanthanides were made with a Q-1500D derivatograph at a heating rate of 10°C min^{-1}. The test samples were heated at a sensitivity TG – 50 mg, DTA – 500 μV, DTG – 500 μV [8].

Results and discussion

2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of light lanthanides were obtained as crystalline products with a metal to ligand ratio of 1:3. 2,3,4-Trimethoxybenzoates form anhydrous salts of general formula $Ln(C_{10}H_{11}O_5)_3$ for *Ln*=La–Gd [7]. 3,4,5-Trimethoxybenzoates of Ce–Gd were obtained as monohydrates $Ln(C_{10}H_{11}O_5)_3{\cdot}H_2O$ while that of lanthanum forms anhydrous salt [8]. The light lanthanide 2,4,5-trimethoxybenzoates form trihydrates: $Ln(C_{10}H_{11}O_5)_3{\cdot}3H_2O$. In these three series of trimethoxybenzoates being compared the number of crystallization water molecules changes with the change of $-OCH_3$ group positions in benzene ring. The colours of the complexes are typical of the appropriate trivalent lanthanide ions which is connected with the structure of molecules and electron density in benzene ring. In these molecules the f→f electronic transitions of the central ions are those of the lowest energy and absorption occurs at relatively high wavelengths which depends on the nature of metal ion [10, 11]. The compositions of the complexes were established on the basis of elemental analysis and IR spectra data and their external crystalline forms were also estimated [7–9]. From the IR spectra analysis of light lanthanide 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates it appears that the carboxylate ion is a symmetrical, bidentate chelating ligand [7–9, 12–14]. The magnitudes of separation, $\Delta\nu_{OCO^-}$ ($\Delta\nu_{OCO^-}=\nu_{asOCO^-}-\nu_{sOCO^-}$) which characterize the metal– oxygen bond change in the range from 171–160 cm^{-1} for 2,4,5-trimethoxybenzoates to 110–105 cm^{-1} for 3,4,5-trimethoxybenzoates. In the case of 2,3,4-trimethoxybenzoates of light lanthanides the magnitude of separation, $\Delta\nu_{OCO^-}$ is equal to 140 cm^{-1}. In these complexes being compared the participation of M–O ionic bond is presumably the largest in the case of 2,4,5-trimethoxybenzoates while the least one in the case of 3,4,5-trimethoxybenzoates. The bands of metal-oxygen group are being changed depending on the position of $-OCH_3$ substituents in aromatic ring. Accordingly in the case of 3,4,5-trimethoxybenzoates of light lanthanides these bands appear in the range 488–472 cm^{-1} while for 2,3,4- and 2,4,5-trimethoxybenzoates they are shifted to higher frequencies to be equal to 525–520 cm^{-1}. The frequencies of the bands due to ν_{asOCO^-} vibration are changed depending on the position of $-OCH_3$ groups in aromatic ring and they are at 1540 cm^{-1} for 2,3,4-trimethoxybenzoates, at 1540–1530 cm^{-1} for 3,4,5-trimethoxybenzoates and at 1535–1528 cm^{-1} for 2,4,5-trimethoxybenzoates. Similarly, the frequencies of the bands of ν_{sOCO^-} vibrations have various values being equal to: 1400, 1430–1425 and 1370–1364 cm^{-1} for 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of light lanthanides, respectively. The changes in the values of these band frequencies result from the various position of $-OCH_3$ groups in aromatic ring and various influences of inductive and mesomeric effects on electron densities in the molecules of those complexes [15–17]. The X-ray spectra of 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of light lanthanides were recorded. Their analysis suggests that the complexes are polycrystalline compounds with low symmetry, large size of the unit cells and different structures [18].

The thermal stability of these complexes was studied in air in the range 273–1173 K by TG, DTG and DTA techniques. The obtained results are presented in Figs 2–5. When heated at 273–1173 K, the complexes decmpose in various steps. The anhydrous complex of lanthanum 3,4,5-trimethoxybenzoate is decomposed in two steps: first the oxycarbonate is formed which next it is decomposed to La_2O_3. Monohydrates of Pr(III), Nd(III), Sm(III) Eu(III) and Gd(III) are stable up to 336–358 K and then losing one molecule of crystallization water in one step (336–395 K) they form anhydrous complexes (380–395 K) that at 573–903 K are decomposed to the oxides of the respective metals with the intermediate formation of the oxycarbonates. Monohydrate of cerium 3,4,5-trimethoxybenzoate expels one water molecule at 344–392 K to form anhydrous complex which is then directly decomposed to CeO_2 (768 K) which is the final product of decomposition. The oxides of lanthanides to be the final products 3,4,5-trimethoxybenzoate decompositions are formed at 768 (CeO_2)–1008 K (La_2O_3) (Figs 2, 5). Trihydrates of La(III), Pr(III), Nd(III), Eu(III) and Gd(III) 2,4,5-trimethoxybenzoates decompose in three steps while those of Ce(III) and Sm(III) in the two ones. The dehydration process is connected with the endothermic effect in DTA curves. In the range 453–1023 K the anhydrous complexes are decomposed to oxides of the respective metals with the inter-

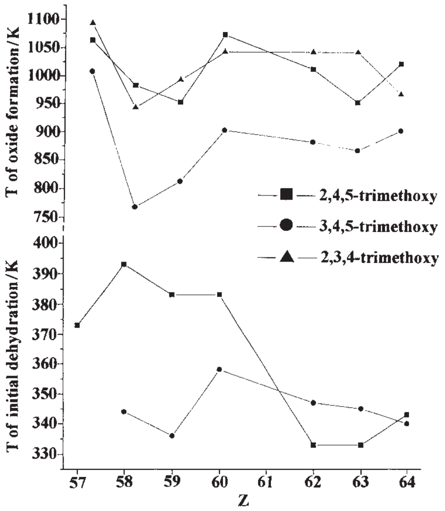

Fig. 2 Dependence of initial dehydration and oxide formation temperatures of 2,4,5- and 3,4,5-trimethoxybenzoates of light lanthanides and Z

mediate formation of the oxycarbonates. 2,4,5-Trimethoxybenzoates of Ce(III) and Sm(III) decompose in two steps. In the first stage at 333–453 K they lose crystallization water and form anhydrous complexes which are next decomposed to oxides (533–973 K). The oxides of the appropriate metals are formed in the range 953 (Pr_6O_{11}, Eu_2O_3)–1073 K (Nd_2O_3) (Figs 2, 4).

The complexes of La(III) and Nd(III) with 2,3,4-trimethoxybenzoic acid decompose in two steps. In the temperature range 533–953 K they are decomposed to oxycarbonates that next decomposes at 893–1093 K forming La_2O_3 and Nd_2O_3 which are the ultimate produts of the decomposition. The complexes of Ce(III), Pr(III), Sm(III) and Eu(III) with 2,3,4-trimethoxybenzoic acid decompose only in one step. The anhydrous salts are directly decomposed to the oxides of respective light lanthanides (523–963 K). The temperatures of the oxide formation change in the series of light lanthanides. The lowest temperature of oxide formation has cerium oxide (943 K) while the highest one has lanthanum (1093 K) (Fig. 3). In the complexes being compared the dehydration process is connected with an endothermic effect in DTA curves whereas the combustion of the organic ligand with an exothermic one. Considering the temperatures at which the dehydration process of the 2,4,5- and 3,4,5-trimethoxybenzoates of the light lanthanides takes place and the way by which it proceeds, it is possible to assume that the molecules of water are differently bound in the outer-sphere of complex coordination. According to Nikolaev *et al.* [19] and Singh *et al.* [20] water eliminated below 413–423 K can be considered as water of crystallization and water eliminated above 423 K may be that coordinated to the central ion [21]. In our complexes water is generally eliminated below 413 K. Therefore, it is assumed to be crystallization water. From the comparison of the mechanism of 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of light lanthanide decompositions it ap-

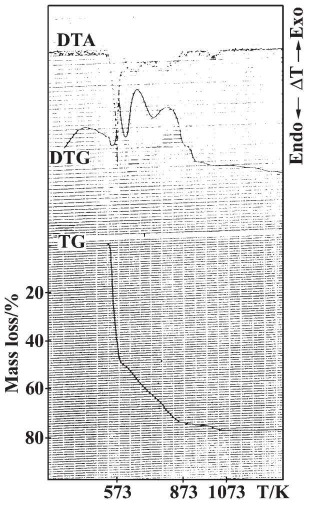

Fig. 3 TG, DTG and DTA curves of 2,3,4-trimethoxybenzoate of Nd

pears that thermal decompositions of 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoic acids with La(III) and Nd(III) proceed through oxycarbonates (Figs 3–5). The anhydrous complex of these acids with Ce(III) are directly decomposed to CeO_2. In the series of trimethoxybenzoates being compared the temperatures of the oxide formations are the highest for La_2O_3 (1008–1093 K) while the lowest ones are for CeO_2 (768–943 K) formed by the cerium 2,3,4- and 3,4,5-trimethoxybenzoate decompositions (Fig. 2). In the series of rare earth element 2,4,5-trimethoxybenzoates the lowest temperature of oxide formation falls to Pr_6O_{11} (Fig. 2).

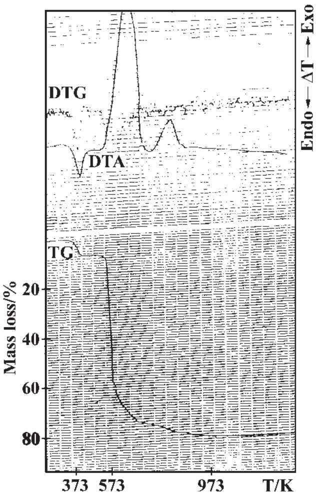

Fig. 4 TG, DTG and DTA curves of 2,4,5-trimethoxybenzoate of Nd

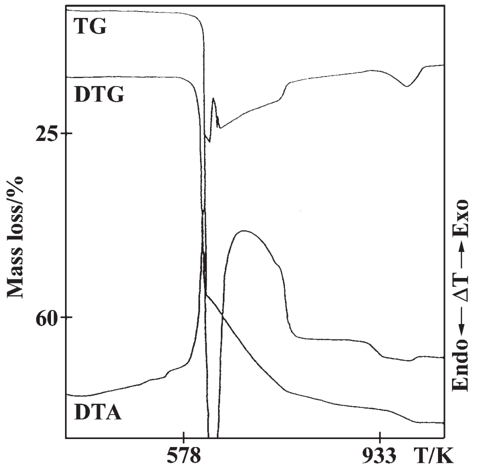

Fig. 5 TG, DTG and DTA curves of 3,4,5-trimethoxybenzoate of La

From the comparison of the decomposition mechanism results for the three series of trimethoxybenzoates of light lanthanides it follows that the various position of $–OCH_3$ substituents in benzene ring influences the decomposition process being strongly connected with the various participations of the inductive and mesomeric effects of methoxy groups in the electron density of the system. The thermal stability of anhydrous trimethoxybenzoates increases in order: 2,4,5-<2,3,4-<3,4,5-. The various position of methoxy groups influence the number of crystallization water molecules in the complexes and the positions of the bands of M–O and asymmetrical vibrations of carboxylate groups in their IR spectra. The number of crystallization water molecules and the positions of asymmetrical vibration bands of carboxylate groups in the IR spectra of trimethoxybenzoates increase in the following sequence: 2,3,4-<3,4,5-< 2,4,5-. The positions of the bands of M–O vibrations change in the order: 3,4,5-<2,3,4-≈2,4,5-. The participation of the ionic bonds in trimethoxybenzoates of light lanthanides decreases in the way: 2,4,5->2,3,4->3,4,5-.

The changes in the values presented above are probably connected with the various influences of inductive and mesomeric effects of methoxy groups on the electron density of the system depending on their position in benzene ring. The inductive effects of each methoxy groups cause the delocalization of the electrons in the molecule and the change of its energy state brought about the conjugation of electrons. It leads to the stabilization of the system. The appearence of the mesomeric effect causes the characteristic changes in the molecule of organic compound. Therefore, the lenghts of some of the σ bonds may be changed. This can be observed in the positions of the bands of the characteristic group vibrations in the IR spectra of complexes and in their various thermal stability in air during heating from 273 to 1173 K.

The obtained results also reveal that irrespective of the methoxy- group positions in benzene ring the ratio of metal: ligand in the complexes, their colours and the dentate of carboxylate group stay the same for all 2,3,4-, 2,4,5- and 3,4,5-trimethoxybenzoates of light lanthanides.

References

1 Beilsteins Handbuch der organischen Chemie, Bd. X, Springer, Berlin 1922.
2 Beilsteins Handbuch der organischen Chemie, Bd. IX, Springer, Berlin 1927.
3 Beilsteins Handbuch der organischen Cehmie, Bd. IX, Springer, Berlin 1922.
4 P. Karrer, Chemia organiczna, PWN, Warszawa 1985.
5 P. V. Laitha and R. Romansovany, Indian Acad. Sci. Chem., 104 (1992) 619.
6 Gmelin Handbook of Inroganic Chemistry, Springer, Berlin 1984.
7 W. Ferenc, B. Bocian and M. Chudziak, J. Therm. Anal. Cal., 58 (1999) 639..
8 W. Ferenc and B. Bocian, Acta Chem. Hung., 133 (1996) 481.
9 W. Ferenc, B. Bocian and M. Ciołek, Indian Journal of Chem., 37A (1998) 176.
10 C. N. R. Rao, Spektroskopia elektronowa związków organicznych, PWN, Warszawa 1982.
11 A. Bartecki, Widma elektronowe związków kompleksowych, WNT, Warszawa 1987.
12 B. S. Manhas and A. K. Trikha, J. Indian Chem. Soc., 59 (1982) 315.
13 R. C. Mehrotra and R. Bohra, Metal Carboxylates, Academic Press, London 1983.

14 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, Toronto 1968.
15 H. A. Staab, Wstęp do teoretycznej chemii organicznej, PWN, Warszawa 1966.
16 J. Shorter, Analiza korelacyjna w chemii organicznej, PWN, Warszawa 1980.
17 G. Kupryszewski, Wstęp do chemii organicznej, PWN, Warszawa 1988.
18 Z. Bojarski and E. Łagiewka, Rentgenowska analiza strukturalna, PWN, Warszawa 1988.
19 A. V. Nikolaev, V. A. Logvienko and L. I. Myachina, Thermal Analysis, Academic Press, New York 1969.
20 B. Singh, B. V. Agarwala, P. L. Mourya and A. K. Dey, J. Indian. Chem. Soc., 59 (1982) 1130.
21 D. N. Todor, Thermal Analysis of Minerals, Abacus Press, Tunbrige Wells, Kent 1976.