钇对苯甲酸芳香体系的效应

钇在镧系元素中的位置

钇对苯甲酸芳香体系的效应加以研究并与碱和碱土金属以及若干过渡金属和有毒的重金属的效应相比较. 钇与镧系元素相似，具有稳定苯甲酸体系的效应. 芳香体系的微扰作用随着金属离子势的减小而增大. 红外谱带强度的详细分析表示钇的位置是在铒与铥之间. 芳香环谱带的相对强度和频率对于镧系元素原子序数的依赖关系表明双-双效应的存在.

INFLUENCE OF YTTRIUM ON THE

AROMATIC SYSTEM OF BENZOIC ACID

POSITION OF YTTRIUM WITHIN LANTHANIDES

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The effect of yttrium on the aromatic system of benzoic acid was investigated and compared with the effect of selected transition, alkaline and alkaline earth metals, as well as of some heavy toxic metals. Yttrium, like lanthanides, stabilizes the aromatic system of benzoic acid. The perturbation of the aromatic system increases with decreasing ionic potential of the metals. A detailed analysis of intensity of IR bands showed that the position of yttrium is situated between erbium and thulium. The dependence of relative intensity and frequency of bands of aromatic ring on the atomic number of lanthanides indicates the presence of a double—double effect.

Introduction

The effect of some metals on the aromatic system of benzoic (e.g.) [1,2] and salicylic [3] acids was investigated by the methods of molecular spectroscopy.

The aim of the persent paper has been to study the effect of yttrium on the aromatic system of benzoic acid and to compare it with the effect of alkaline and transition metals as well as aluminium and lead. The position of yttrium in relation to lanthanides has been investigated. Yttrium takes various positions among lanthanides and actinides in respect of free energy of

complexation depending on the type of ligands. This is the basis of numerous methods of separating yttrium from lanthanides and actinides. The reasons of migration of yttrium along the series of transition metals have not been, however, elucidated and are at present studied intensively. Works of S. Siekierski et al. [4-7] showed that the position of yttrium among the inner transition elements is dependent on the participation of $4f$ or $5f$ orbitals in bonds in the complexes, on the degree of delocalization of bonds and on electronegativity of metal atoms. In addition, the double–double effect (or tetrad effect) [8-13] has also been studied in IR spectra of lanthanide complexes with benzoic acid. The effect consists in favoring the configurations f^0, f^7, f^{14} as well as $f^{3,4}$ and $f^{10,11}$ of inner transition elements.

Experimental

1. Reagents

Solid yttrium(III) benzoate was obtained by mixing $0.25\text{mole} \times \text{dm}^{-3}$ of yttrium chloride with $0.75\text{mole} \times \text{dm}^{-3}$ of sodium benzoate at volume ratio 1 : 1. The precipitate was crystallized, filtered off, washed with water and dried at room temperature, and then under reduced perssure at 95℃ up to constant mass. Yttrium and other benzoates obtained under the above conditions are anhydrous. The analysis of the composition by C, H elemental analyses and by gravimetric analyses of metal showed the following composition: $Y(C_7H_5O_2)_3$ (C%: calcd. 55.8 found 56.1; H%: calcd. 3.3 found 3.4; Y%: calcd. 19.7 found 19.8). The remaining metal benzoates were prepared as described in the previous papers [14,15].

2. Apparatus and methods

Spectra in the UV region were recorded on a Varian–Techtron 635 spectrophotometer. Concentrations of benzoates amounted exactly to $1.25 \times 10^{-4}\text{mol} / \text{m}^3$. The recording was made 48 hours after perparation of aqueous solutions. Raman spectra (in the $4000-100\text{cm}^{-1}$ region) were recorded with a Coderg spectrometer, model PHO, with Spectra–Physics Ar^+ laser (excitation line 488.0nm). IR absorption spectra were recorded on a CarlZeiss IR–75, or a Perkin–Elmer model 580 spectrophotometer in KBr–pellets.

Results and Discussion

1. Effect of metals on the aromatic system of benzoic acid

Table 1 contains assignments of vibrational bands for yttrium benzoate. The assignments of spectra were based on the literature data [16-21]. The effects of yttrium on the aromatic system of benzoic acid is similar to that of lanthanides (Ln), aluminium and iron(III). The number, frequency and intensity of bands of the aromatic system in IR and Raman spectra of yttrium as well as of Ln, Al and Fe(III) are higher than those in the case of benzoates of other metals under study(Tables 2 and 3). In spectra of benzoates of alkaline elements and of heavy toxic elementas there are no main bands (bands of stretching vibrations of the ring No. 19a and 19b of

Versanyi[21] at 1495 and 1450 cm^{-1}), which evidence the presence of the aromatic system [22,23]. Yttrium, like lanthanides, aluminium and iron stabilize the aromatic ring (in contrast to heavy toxic metals and alkaline elements which destabilize it).

Table 1   Frequencies of Raman and IR Bands of Yttrium Benzoate*

frequency / cm^{-1}		vibration	normal vibration of the aromatic ring [16]
Raman	IR		
3070m	3067vw	$\nu_{(CH)ar}$	2
1603vs	1604 sh	$\nu_{(C\;C)ar}$	8a
—	1595		8b
1535w	1530vs	$\nu_{as(COO)}$	
1498m	1495m	$\nu_{(C\cdots C)ar}$	19a
1455m	1448m	$\nu_{(C\cdots C)ar}$	19b
1408m	1420vs	$\nu_{s(COO)}$	
—	1307vw	$\nu_{(C\cdots C)ar}$	14
1183vw	1179w	$\beta_{(CH)}$	9a
1160m	1157vw	$\beta_{(CH)}$	9b
—	1071w	$\beta_{(CH)}$	18b
1026m	1025w	$\beta_{(CH)}$	18a
1005vs	1003vw	ring	12
—	932vw	$\gamma_{(CH)}$	17b
872 sh 847	863w	$\beta_{s(COO)}$	
820vw	822w	$\gamma_{(CH)}$	10a
—	719vs	$\gamma_{s(COO)}$	
—	687m	$\Phi_{(CC)}$	4
—	670m		1
620m	—	$\alpha_{(OCC)}$	6b
—	565w	$\beta_{as(COO)}$	

* s = strong; m = medium; w = weak; sh = shoulder; v = very
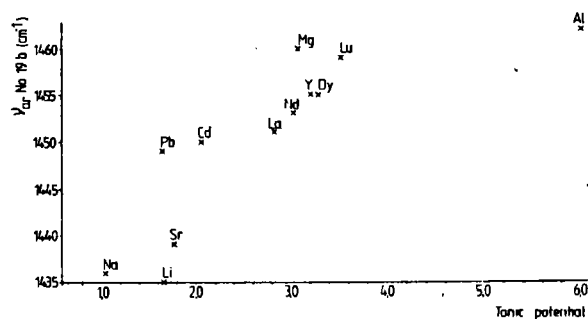

Fig.1 Dependence of the frequency of ν_{ar} No. 19b in Raman

spectra of benzoates on the metal ionic potential

Table 2　Comparison of Frequency and Relative Intensity of Bands

of Aromatic System in IR Spectra of Metal Benzoates

benzoate	frequency of bands of normal vibrations No		rato of intensity bands No 19a to that of bands $v_{as(COO)}$*	references
	19a(cm^{-1})	19b(cm^{-1})		
Li	1490	—	0.02	[15]
Na	—	—	—	[2]
K	—	—	—	[1]
Mg	1494	1446	0.16	[1]
Ca	1497	1446	0.15	[1]
Sr	1492	1443	0.06	[15]
Ba	1497	1441	0.25	[15]
Al	1499	1452	0.38	[1]
Pb(II)	—	—	—	[15]
Fe(III)	1492	1447	0.43	[1]
Cu(II)	1496	1448	0.12	[1]
Zn	1491	1448	0.16	[1]
Cd	1494	1447	0.24	[1]
Hg(I)	—	—	—	[1]
Hg(II)	—	—	—	[1]
Y	1495	1448	0.37	[1]
La	1492	1444	0.21	
Ce	1492	1444	0.22	
Pr	1494	1446	0.26	
Nd	1496	1448	0.28	
Sm	1493	1445	0.32	
Eu	1495	1447	0.37	this
Gd	1494	1447	0.44	work
Tb	1493	1446	0.47	
Dy	1495	1450	0.45	
Ho	1494	1448	0.44	
Er	1494	1448	0.41	
Tm	1494	1448	0.36	
Yb	1494	1448	0.31	
Lu	1495	1447	0.30	

* Relative band intensity was calculated by the method described in ref.14.

Table 3　Frequencies of Chosen Aromatic Bands in Raman Spectra

of Benzoates of Metals under Study

benzoate	normal vibration / cm^{-1}			
	8a	19a	19b	9a
Y	1603vs	1498m	1455m	1183vw
La	1603vs	1497m	1451m	1182vw
Nd	1603vs	1496m	1453s	1183vw
Dy	1603vs	1497m	1455s	1183vw
Na	1605s	1493w	1436m	1185m
K	1601s	—	—	1177w
Mg	1603s	1497w	1460w	1182vw
Al	1611s	1500m	1462m	—
Pb	—	1493w	1449vw	1182w
Cd	1602s	1494w	1450vw	—
Hg(I)	1598s	—	—	—
Hg(II)	1600s	—	—	—

The frequency of band 19b of the aromatic system increases with the rise in ionic potential (measured by the ratio of metal ion charge to its radius) of the metals(Fig.1). Similar relations are observed in other aromatic bands in Raman and IR spectra.With a decrease in ionic potential of the metals, the ring perturbance increases. The metals that are characterized by a low charge and a large radius, such as mercury(I), mercury(II), lead(II), potassium perturb the aromatic system of the ligand to the highest degree. On the other hand metals of a high charge and medium or small radius, such as yttrium, aluminium, iron(III), lanthanides are stabilizers of the system. The mechanism of perturbing the aromatic system by metals of low ionic potentials may be explained as follows: the high ionic potential of metals is propitious for bonds of covalent character [24] . A decrease in the ionic potential increases the polarity of bonds. Covalent bonds between metals and ligands stabilize the aromatic system of benzoic acid [15] ; on the other hand, a rise in polarity of that bond causes perturbances in a uniform distribution of the electron charge in the aromatic ring of the ligand, as well.

In our previous work [14,22] , it was proved that the interaction between the metal and the ring may occur through the carboxylic group. A more uniform distribution of the electron charge in the carboxylate anions stabilizes the aromatic system of the ring.

Maxima of wavelengths of $\pi \rightarrow \pi^*$ bands in UV spectra for metal benzoates amout to: Y 231.5, Li 224.0, Na 225.0, K 226.8, Mg 228.6, Al 233.1, Fe(III) 234.7, Zn 228.6, La 230.5, Nd 230.8, Dy 231.5, Yb 231.3 , Cd 227.7, Hg(I) 224.4, Hg(II) 227.1 and Pb(II) 227.7nm. Benzoic acid absorbs at 227.0nm. The UV data display the similarity of yttrium to lanthanides (the $\pi \rightarrow \pi^*$ absorption band for the enumerated metals lie within the same range). Yttrium stabilizes the aromatic system of benzoic acid. This indicates the presence of a bathochromic shift of $\pi \rightarrow \pi^*$ bands in UV spectra of yttrium benzoate in relation to that band in the spectrum of benzoic acid.

2.Position of yttrium within lanthanides

It follows from IR spectra of lanthanide complexes with benzoic acid that essential differences occur in intensities of the ring bands No. 19a and 19b. The highest intensity of band 19a characterizes the spectra of benzoates of : gadolinium, terbium, dysprosium and holmium (Fig.2). The ratio of relative intensities of bands 19b plotted as function of atomic number displays similar dependence. The relative intensity of band 19a in IR spectra of yttrium benzoate amounts to 0.37 and is similar to that of europium, erbium and thullium (Fig.2).An analysis of intensity of band 19a does not make possible to determine unequivocally the position of yttrium within lanthanides, because the straight line corresponding to yttrium value intersects the curve at two points. Essential differences in the lanthanide group occur also within the range of ca. 700cm^{-1}(normal vibration of the aromatic ring No.1 and 4). The relative intensity of band No.1 vs. Z is plotted in Fig.3. An analysis of intensity of bands in the aromatic system has shown that the properties of yttrium in benzoate, measured by means of IR spectroscopy are most similar to that of erbium. The average result (from the three cruves in Figs 2, 3a and 3b) quoted as the value of atomic number, that defines the position of yttrium in respect to lanthanides, amounts
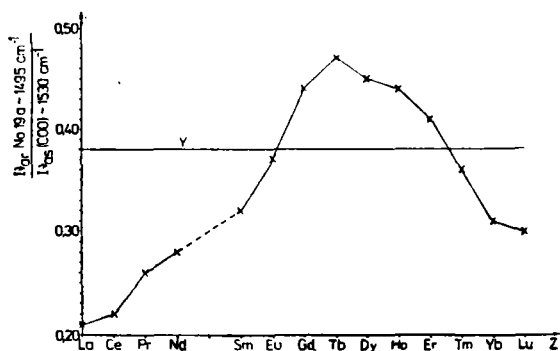
to $Z_y = 68.29$.

Fig.2 Relationships between the intensity ratio of the aromatic bands No. 19 to the $v_{as(COO)}$ bands in the IR spectra of yttrium and lanthanide benzoates and the atomic number of metals (no data for promethium)
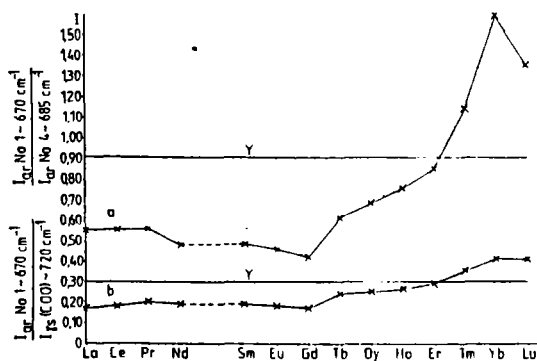

Fig.3 Relationship between the intensity ratio of the aromatic bands: (a) No. 1 to the aromatic bands No. 4 and (b) No.1 to the $\gamma_{s(COO)}$ bands in the IR spectra of yttrium and lanthanide benzoates and the atomic number of metals (no data for promethium)

S. Siekierski discussed the position of yttrium within lanthanides in respect to thermodynamic functions of complex formation [4,6] and to unit cell volumes of isostructural M_mX_n compounds [5] . It has been shown that for most ligands yttrium is a heavier lanthanide in respect to ΔH^0 than to ΔS^0. As a result, yttrium is , in general, a light lanthanide in respect to ΔG. It has also been shown that unit cell volume of yttrium compounds decreases with increasing electronegativity of the X atom from the values characteristic of the respective

isostructural compounds within the range of gadolinium to erbium * . These observations have been explained in terms of covalent bond shortening in the series of lanthanide compounds, due to participation of $4f$ orbitals in bonding [4,5,25,26] .

From our spectroscopic data it follows that yttrium stabilizes the aromatic system of benzoic acid in a degree similar to that of erbium. The number, frequency and intensity of aromatic system bands, that indicate the stability degree of yttrium benzoate, are high.

3. The double—double effect

The function of the relative intensity of the aromatic band No.1 vs. the atomic number of lanthanides (Figs 3a and 3b) show the typical symmetry in the double—double effect. The more pronounced extrema appear for La, Gd and Lu (configurations of trivalent ions f^0, f^7 and f^{14} respectively) and less pronounced ones for Nd, Ho and Er (f^3, f^{10}, f^{11}). On segments that are approximately rectilinear (La—Nd, Sm—Gd and Tb—Lu) in Fig.2 the distribution of points may also suggest the existence of a double—double effect. In this case (Fig.2) the effect is markedly disturbed. The reason thereof is the occurrence of lanthanide benzoates in various crystallographic structures * * . The disturbance brought about by crystallographic differences is revealed more strongly in the case of 19a and 19b vibrations (Fig.2) than 1 and 4 vibrations (Fig.3). It is a result of 19a and 19b vibrations (in contrast to 1 and 4 vibrations) being coupled with vibrations of carboxylic anion $v_{as(COO)} \sim 1530$ and $v_{s(COO)} \sim 1420 cm^{-1}$ [22] . On the other hand, the structure of the carboxylic anion is essentially dependent on the crystallographic system [27] .

However, a detailed analysis points out some differences between the two curves in Fig.3 and those obtained by Fidelis and Siekierski [9,10,28] : a) the double—double effect obtained from our IR data is more pronounced for heavy lanthanides (Gd—Lu) whereas that obtained from chromatographic and thermodynamic data [9,10,28] is for the light lanthanides (La—Gd), b) plots in Figs 3a and 3b differ from those obtained from chromatographic data for Sm—Eu. It is interesting to note that on the plots obtained by Hullet and Thornton [29] for lanthanide complexes with tropolones the species Sm—Eu also differ from those obtained from the chromatographic data and have a similar pattern the plots in Figs 3a and 3b.

A comparison of the present data with previous ones [12,13] leads to a conclusion that the double—double effect in the case of spectra of lanthanide complexes with benzoic acid in weak and is partly disturbed as a result of existing crystallographic differences within the series of lanthanide benzoates. The double—double effect may be observed in its undisturbed form only for isostructural compounds.

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* In some cases the position of yttrium transgresses the position between gadolinium and erbium

* * The benzoate complexes of lanthanides and yttrium may be divided into three isostructural series: (1) La, Ca, Pr, Nd; (2) Sm, Eu, Gd; (3) Tb, Dy, Ho, Er, Yb, Lu and Y [27] .

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