

AROMATICITY OF SOME METAL BENZOATES

EFFECT OF METAL SALTS ON THE AROMATIC SYSTEM OF BENZOIC ACID USING IR, RAMAN AND UV SPECTROSCOPIC METHODS

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In this paper, the aromaticity of some metal benzoates has been studied using IR, Raman and UV spectroscopic methods. The bond frequencies in IR and Raman spectra of Hg(I), Mg and K benzoates are summarised in table 1. The effects of Cr(III), Fe(III), Cu(II), etc. on the aromatic system of benzoic acid were compared. It is found that Cr(III) iron(III), lanthanides and Al can stabilize this system.

Keywords aromaticity metal benzoate IR, Raman, UV spectroscopy

Introduction

There is an ample literature to study on aromaticity of π -electron compounds. The aromatic properties were studied by the theoretical and experimental methods. The Hückel theory and its modifications belong to methods based on quantum chemistry. The experimental methods are based on thermodynamics, kinetics and molecular spectroscopy. The evaluation of aromatic properties is usually done by determining: (a) delocalization energy (in a theoretical way⁽¹⁾ or experimentally⁽²⁾), (b) magnetic properties of molecules⁽³⁾, (c) degree of averaging the bond lengths⁽⁴⁾, (d) chemical reactivity⁽⁵⁾. Krygowski and Kruszewski⁽⁶⁾ introduced the concept of aromatic stability index as the a quantitative, normal measure of aromaticity. The works mentioned above concern mostly with the aromatic properties of hydrocarbons and their organic derivatives. The literature comprises very few works related to estimation for aromaticity of organo-metallic compounds. There exist still less papers devoted to the effect of various metals on the aromatic system of ligands in complex compounds.

In our previous papers spectroscopic methods were applied to study the effect

of some metals on the aromatic system of benzoic^(7,8) and salicylic^(9,10) acids. The number, frequency and intensity of bands of the aromatic system in IR and Raman spectra as well as frequencies of bands $\pi \rightarrow \pi^*$ and $f \rightarrow f$ in UV/VIS spectra were analysed, respectively. It has been established that lanthanides affect these systems different from alkaline elements and heavy toxic metals. The aim of this paper is to compare the effect of selected metals on the aromatic system of benzoic acid. Another aim is to propose a modified of aromaticity evaluation^(*).

Experimental

1. Reagents

Metal benzoates were prepared as described in the previous papers⁽⁷⁾. The molar ratio of metal to ligand in solid state amounts to 1:1 for Li, K and Hg(I) benzoates; 1:2 for Mg, Ca, Sr, Ba, Zn, Cu(II), Cd, Hg(II) and Pb(II) benzoates; 1:3 for Al, Cr(III), Fe(III) and lanthanide benzoates. The benzoates were anhydrous. In order to remove the crystallization water it must be dried at the temperature of 95°C under reduced pressure.

2. Apparatus and methods

IR spectra range from 4000 to 250 cm^{-1} were recorded by Carl—Zeiss IR 75 and Perkin—Elmer model 580 spectrophotometers with the use of technique of pressing samples into KBr pellets. Raman spectra of solid samples, within the range of 4000 to 100 cm^{-1} were recorded by means of a Coderg spectrometer, model PHO with Spectra Physics He—Ne and Ar^+ lasers (excitation lines 632.8 nm and 488.0 nm, respectively). The UV spectra were recorded on a Varian Techtron 635 spectrophotometer. The benzoates were obtained from an aqueous solution, their concentrations equal exactly to $1.25 \times 10^{-4} \text{ mol/dm}^3$. The accuracy of wavelength of readings recording on an expanded scale (IR: 100 $\text{mm}/100 \text{ cm}^{-1}$; R: 40 $\text{mm}/100 \text{ cm}^{-1}$; UV: 33 $\text{mm}/10 \text{ nm}$) is $\text{IR} \pm 0.5 \text{ cm}^{-1}$, $\text{R} \pm 1 \text{ cm}^{-1}$, $\text{UV} \pm 0.2 \text{ nm}$, respectively.

Results and Discussions

1. Vibrational assignments

Table 1 contains the assignments of vibration bands for Hg(I), Mg and K benzoates. The assignments of spectra were based on the literature data⁽⁹⁾ and

(*) The spectroscopic methods (IR, R and UV) were applied earlier to evaluate the aromaticity of organic compounds. As examples may quote the works by Clar or Badger⁽¹¹⁾. Our method is based on analyses of number, frequency and intensity of those bands of the aromatic system which are active in IR and Raman spectra among thirty feasible bands of normal vibrations of the ring. On the other hand, in electronic spectra analyses are made of frequency of bands derived from transitions between bonding and antibonding orbitals which characterize the magnitude of energy of delocalizing π electrons.

Table 1 Band Frequency in IR and Raman Spectra of Hg(I) Mg and K Benzoate

frequency (cm ⁻¹)						
Hg(I)		Mg		K		assignment
IR	R	IR	R	IR	R	
—	—	—	—	3073vw	—	ν(CH) _{ar}
3053vw	3066w	3060vw	—	—	—	ν(CH) _{ar}
—	—	—	3012w	3027vw	3016w	ν(CH) _{ar}
—	1598s	—	1603s	—	1601s	ν(C...C) _{ar}
1598s	—	1597s	—	1596s	—	ν(C...C) _{ar}
1555vs	—	1552vs	—	1552vs	1562w	ν _{as} (COO)
—	—	1494w	1497w	—	—	ν(C...C) _{ar}
—	—	1446vw	1460w		—	ν(C...C) _{ar}
1413s	—	1423vs	—	1396vs	1410, 1403 ^{sh}	ν(COO)
1307vw	—	1305w	—	1308w	—	ν(C...C) _{ar}
—	—	—	—	1272vw	—	β(CH)
—	—	1180w	1182vw	1178vw	1177w	β(CH)
—	1157vw	1149vw	1157w	—	1157w	β(CH)
—	—	—	—	—	1132w	—
—	—	1097vw	—	1105vw	—	β(CH)
1068w	—	1069m	—	1070m	—	β(CH)
1024w	1025vw	1026m	1025w	1027w	1025w	β(CH)
1006vw	1000vs	1004vw	1003vs	1007vw	1002vs	ring
932vw	—	936vw	—	932vw	—	γ(CH)
836w	850s	842vw	845vw	838m	835m	β _s (COO)
—	846s	—	—	—	—	β _s (COO)
818vw	—	824w	828vw	820w	822vw	γ(CH)
706s	—	718vs	—	706vs	—	γ _s (COO)
685sh	685w	688sh	—	686m	—	φ(CC)
677sh	—	677sh	—	679m	675vw	—
—	615w	—	617m	—	616w	α(CCC)
515vw	—	566vw	—	516w	—	β _{as} (COO)
—	—	470w	—	—	—	—
—	—	—	421vw	437vw	—	M-O

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

g(I) Mg and K Benzoates*

R	assignment	normal vibra- tion of the aromatic ring ⁽¹²⁾
—	$\nu(\text{CH})_{\text{ar}}$	2
—	$\nu(\text{CH})_{\text{ar}}$	7 b
3016 w	$\nu(\text{CH})_{\text{ar}}$	20 b
1601 s	$\nu(\text{C}\cdots\text{C})_{\text{ar}}$	8 a
—	$\nu(\text{C}\cdots\text{C})_{\text{ar}}$	8 b
1562 w	$\nu_{\text{as}}(\text{COO})$	
—	$\nu(\text{C}\cdots\text{C})_{\text{ar}}$	19 a
—	$\nu(\text{C}\cdots\text{C})_{\text{ar}}$	19 b
1410 } sh 1403 }	$\nu(\text{COO})$	
—	$\nu(\text{C}\cdots\text{C})_{\text{ar}}$	14
—	$\beta(\text{CH})$	3
1177 w	$\beta(\text{CH})$	9 a
1157 w	$\beta(\text{CH})$	9 b
1132 w		
—	$\beta(\text{CH})$	7 a
—	$\beta(\text{CH})$	18 b
1025 w	$\beta(\text{CH})$	18 a
1002 vs	ring	12
—	$\gamma(\text{CH})$	17 b
855 m	$\beta_{\text{s}}(\text{COO})$	
—	$\beta_{\text{s}}(\text{COO})$	
822 v w	$\gamma(\text{CH})$	10 a
—	$\gamma_{\text{s}}(\text{COO})$	
—	$\phi(\text{CC})$	4
675 v w		
616 w	$\alpha(\text{CCC})$	6 b
—	$\beta_{\text{as}}(\text{COO})$	
—		
—	M-O	

the symbols were used as suggested in papers, β denotes deformation in-plane vibrations of functional groups, whereas δ represents out-of-plane vibrations; α (CCC) and ϕ (CC) stand for deformation in-plane and out-of-plane vibrations of the aromatic ring, respectively. A good accordance between frequencies of IR and Raman bands follows from Table 1. After a precise analysis, however, it may be observed some regular, though inconsiderable, differences in band frequencies of IR and Raman spectra^(*). In a couple of cases the IR bands are shifted by 3 to 8 cm^{-1} towards lower frequencies in relation to Raman bands. These differences may be explained by the effect of potassium bromide matrix on the bonds in benzoates. Potassium bromide with ionic bonds, interacts with substances under study, thus causing a small increase in the polarity of bonds also in benzoates of metals. The increase in polarity of bonds weakens them. This brings about a diminution of force constants of the bonds and shifting of bands towards lower frequencies simultaneously.

The phenomenon may be compared with the effect of solvents on bonds in the substance dissolved. Like the solvent (as is well known, there are no neutral solvents), potassium bromide must also interact with the sample dispersed in it.

The frequency of a number of respective IR bands recorded by this technique has been shifted by several cm^{-1} . It must be, however, stressed here that these is not to worry about decomposition of samples under the effect of KBr. This is evidenced by the fact that the frequency differences observed (which were possible to be observed owing to a specially extended scale) in Raman and IR spectra and those between IR of KBr pellets and nujol suspension are inconsiderable that they do not exceed 10 cm^{-1} .

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

IR and Raman spectra. Thirty feasible normal vibrations of the aromatic rings in oscillation spectra have been described by Versanyi⁽¹⁴⁾. In order to analyze the effect of metals on the aromatic system of benzoic acid, analyses have been made of; the number of active vibrations of the ring in IR and Raman spectra, as well as of their frequency and intensity. Several bands of the aromatic system (chosen as examples) for metal benzoates under study, have been collected in Table 2. In spectra of transition elements and aluminium benzoates an increase in the number, frequency and intensity of bands of the aromatic system occur, as compared with that of alkaline elements and heavy toxic metals. The most distinct and characteristic changes occur in IR and Raman spectra (No. 19a, 19b and 9a). Therefore, the discussion is going to be confined mainly to analyses of the bands of valence vibrations of the ring bands. The main bands being an evidence of the presence of the aromatic system (bands of stretching vibrations

(*) Similar differences in frequencies have also been observed in the case of IR and Raman spectra of other benzoates and salicylates of metals not mentioned in the present paper.

of the ring No. 19a and 19b) are present in the IR spectra of the following benzoates of, 3d and 4d transition elements (Cr(III), Fe(III), Zn, Cu(I), Cd), lanthanides (III), aluminium and metals belonging to the second main group (Mg, Ca, Sr, Ba). It is to be noted that a particularly high intensity of these bands is displayed by the spectra of Al, Cr(III), Fe(III) and lanthanides benzoates, whereas a very low one by those of Sr, Ba and Cd. These bands are absent in the spectra of Pb(IV), Hg(I), Hg(II) and alkaline elements (Li, Na, K) benzoates (Fig. 1, Table 2). Band 9a of Hg(I), Hg(II), Ba and Na benzoates does not occur in IR spectra, but that of Pb(II), Li and K benzoates have a very low intensity.

Table 2 Comparison of Frequencies and Intensities of Chosen Aromatic Bands in IR and Raman Spectra of Metal Benzoates

benzoate	IR					Raman*				
	normal vibration (cm ⁻¹)									
	19 a	19 b	14	9 a	17 b	19 a	19 b	14	9 a	17 b
Cr	1496m	1450sh	1307 w	1178 w	939vw					
Fe(II)	1492m	1447m	1306 w	1180m	937vw					
Cu(II)	1496 w	1448 w	1318 w	1180 w	933 w					
Zn	1491 w	1448 w	1307 w	1180 w	938vw					
La	1496m	1447 s	1305 w	1178 w	938vw	1497 m	1451m	—	1182vw	—
Nd	1496 s	1448 s	1305 w	1179 w	938vw	1496m	1453 s	—	1183vw	—
Dy	1495 s	1450 s	1305 w	1179 w	938vw	1497 m	1455 s	—	1183vw	—
Yb	1495m	1448m	1305 w	1178 w	938vw	1498m	1458 s	—	1182vw	—
Lu	1495 s	1447 s	1306 w	1178 w	938vw	1499m	1459 s	—	1183vw	—
Li	1490vw	—	1314 }sh 1305 }	1182vw	942 w	1490 w	1435 s	—	1183 w	—
Na	—	—	1306 w	—	919 w	1493 w	1436m	—	1185m	—
K	—	—	1308 w	1178vw	932vw	—	—	—	1177 w	—
Mg	1494 w	1446vw	1305 w	1180 w	936vw	1497 w	1460 w	—	1182vw	—
Ca	1497m	1446m	1306 w	1180 w	936vw	1495 w	1448m	—	1182vw	—
Sr	1492vw	1443vw	1311 w	1182vw	931vw	1494 w	1439m	—	1183 w	—
Ba	1496vw	1441vw	1310 w	—	931vw	1490 w	1432m	—	1183vw	—
Al	1499 s	1452sh	1315vw	1179 w	937vw	1500m	1462m	—	1183vw	—
Cd	1494 w	1447 w	1310 w	1178 w	936vw	1494 w	1450vw	—	—	—
Hg(I)	—	—	1307vw	—	932vw	—	—	—	—	—
Hg(II)	—	—	1301vw	—	934vw	—	—	—	—	—
Pb(II)	—	—	1309vw 1301vw	1177vw	—	1493 w	1449vw	—	1182 w	—

*For Cr(III), Fe(III), Cu(I) and Zn no Raman data. In the Raman spectra of this metal benzoates strong luminescence background appeared which masked other bands.

In Raman spectra the bands of K, Hg(I) and Hg(II) benzoates (No. 19a and 19b) are absent, and these of lead, barium, strontium, sodium and lithium benzoates lie at lower wavenumbers as compared with the spectra of lanthanide, aluminium and magnesium complexes (alkaline elements and heavy toxic metals: 19a 1494-1490 cm^{-1} , 19b 1450-1432 cm^{-1} , while lanthanides, aluminium and magnesium: 19a 1500-1496 cm^{-1} , 19b 1462-1451 cm^{-1}) (Table 2, Fig. 2). The bands 9a of Hg(I), Hg(II) and Cd benzoates does not appear in Raman spectra. The ab-

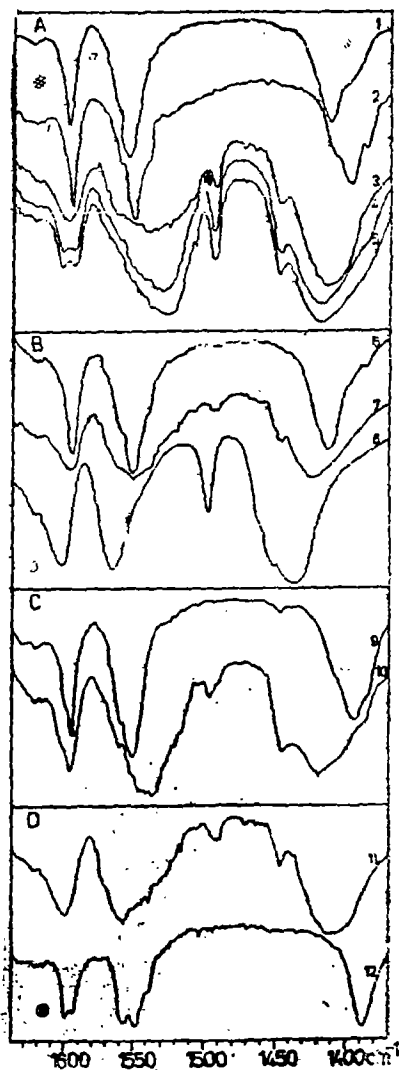


Fig.1 IR spectra of benzoates of:
A: Hg(I) (1); Pb(II) (2); Fe (II) (3); Y(4); Er(III) (5);
B: Na(6); Mg(7); Al(8);
C: K(9); Ca(10); D: Zn(11); Hg(II) (12), in the 1640-1370 cm^{-1} region



Fig.2 Raman spectra of benzoates of: Hg(I) (1); Nd(II) (2); Al(III) (3), in the 1660-1340 cm^{-1} region

sence of the aromatic system bands or their shift towards lower wavenumbers (caused by weakening of the bonds) is an evidence of the perturbation of the aromatic ring. Data of Raman and IR indicate the perturbation of the aromatic system by alkaline elements (Li, Na, K) and by heavy toxic metals (particularly Hg(I), Hg(II) and Pb(II)). A comparison of the number, frequency and intensity of the ring bands in spectra of aluminium and transition (4f and 3d) metal complexes and benzoic acid shows a stabilization for the aromatic system of ligand by these metals^(a).

A question arises: why do the bands of normal vibrations of the aromatic system (No. 19a and 19b) in vibration spectra of metal benzoates change their frequency and intensity to the highest degree, as the metal adjoined, while the changes in other ranges of the ring bands are far less considerable? Versanyi^(1,2) in his monograph analyzed the vibration spectra of 700 benzene derivatives. It is found that in most spectra of derivatives analyzed the vibration bands of carbon-carbon stretching vibrations (among 30 bands of the ring) are the best indicators of the presence of the aromatic system. The range from 1610 to 1450 cm^{-1} in vibration spectra is also often utilized, with good results, by the organic chemists for the purposes of detecting the aromatic system. The existence of bands at about 1500 and 1450 cm^{-1} (bands 10a and 10b) is an unfailing criterion of the ring presence.

It follows from the theory that the IR band intensity depends on the change of dipole moments during the vibrations, while that of Raman bands on polarizability changes. The bands 19a and 19b have a high intensity in IR and Raman spectra of a series of benzene derivatives that do not possess their symmetry center.

The normal vibrations of bands 19a and 19b deform the ring essentially causing changes in the dipole moment. As shown in Fig. 3, particular vibrations may be reduced to two resultants acting in reverse directions.

Moreover, the oscillation frequency of the carboxylate anion (i.e. the anion by the intermediary of which the metal is adjoined to the complex) is similar to that of ring vibrations (No. 19a and 19b). As has been shown in our previous work⁽⁸⁾ there exist correlations between changes in vibration frequency of the ring and of the carboxylate anion. This indicates the mutual interaction of these vibrations. The kind of carboxylate anion structure depends on the metal adjoined. Hence, the considerable differences between spectra of particular metals benzoates occur in parameters of bands 19a and 19b.

By analysis of Raman and IR data a conclusion was drawn that the perturbation of the aromatic system of benzoic acid depends on the position of metals in the periodic table.

In the periods, with an increase in atomic number of the elements, the aromatic bands appear or their intensity increases. In Raman spectra this is to be

(a) IR and Raman spectra of benzoic acid were described earlier.

observed on the example of potassium and calcium, while in IR spectra on the example of sodium, magnesium, aluminium (Fig. 1B), potassium and calcium (Fig. 1C, Table 2). The stabilization of the aromatic system is increased, therefore, with increase in oxidation degree of metals, electronegativity and diminution of the central ion radius, like the series $\text{Na} \rightarrow \text{Mg} \rightarrow \text{Al}$ or $\text{K} \rightarrow \text{Ca}$, and with decrease in the atomic number of the metals (though the changes are not so marked as in the periods). For example, in Raman spectra the number and intensity of bands of the aromatic system increase in the series: $\text{K} \rightarrow \text{Na} \rightarrow \text{Li}$, whereas in IR spectra in the series $\text{K} \rightarrow \text{Na} \rightarrow \text{Li}$, $\text{Hg} \rightarrow \text{Zn}$ (Fig. 1D, Table 2), with decrease in the central ion radius.

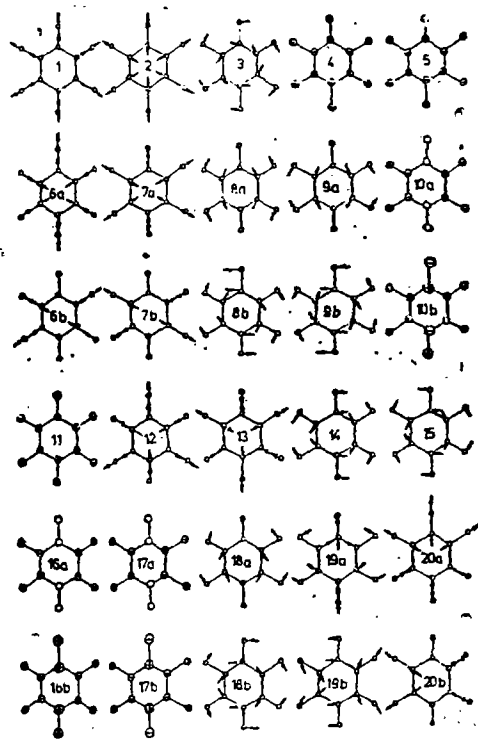


Fig. 3 Normal vibration of the aromatic ring⁽²⁷⁾

The band width in IR and Raman spectra is characteristic. The bands of vibrations of the aromatic ring, and of polar groups, such as COO^- , in the spectra of alkaline metals and toxic metals benzoates are narrow and sharp, while those for transition metals (particularly lanthanides) and aluminium benzoates are diffuse and are characterized by a considerable half-width. The broadening of absorption bands is caused by broadening of the oscillation levels. Formation of delocalized bonds by lanthanides brings about the broadening of energy levels of the complex.

In our previous papers^(7,8) a discussion has been carried out, in what way the metals may affect the aromatic system of benzoic acid. It is found that the perturbation degree of the aromatic system may depend on the structure type of the carboxylate anion^(a). In the case of lanthanide complexes a uniform distribution of the electronic charge in the carboxylic group is favourable for the aromatic properties of the ring. On the other hand, the removal of hydrogen from the carboxylic group by sodium and formation of a ionic bond brings about a perturbation in the electronic charge in the ring, as well.

UV spectra. The bands from 224 to 235 nm were interpreted⁽¹⁵⁾ as a $\pi \rightarrow \pi^*$ transition in the aromatic system^(b). Maxima of wavelengths of this band for metal benzoates lie at: Cr(III) 235.8, Fe(III) 234.7, Zn 228.6, La 230.5, Nd 230.8, Dy 231.5, Yb 231.3, Lu 231.0, Al 233.1, Li 224.0, Ba 228.0, Cd 227.7, Hg(I) 224.4, Hg(II) 227.1 and Pb(II) 227.7 nm. The $\pi \rightarrow \pi^*$ bands of Al, Cr(III) and Fe(III) benzoates are located within the range of 232 to 236 nm, for lanthanides 230 to 232, while those for alkaline elements and heavy toxic metals in the range of 224 to 228 nm. Benzoic acid is absorbed at 227 nm. There are, therefore, a bathochromic shift of $\pi \rightarrow \pi^*$ bands in the spectra of Al, Cr(III), Fe(III) and Ln benzoates in relation to spectra of benzoic acid. This may be explained as follows:

The formation of delocalized, covalent bonds by Ln, Fe(III), Cr(III) and Al stabilizes the uniform distribution of electronic charges in the ring, thus increasing the aromatic properties and delocalization degree of π electrons of the aromatic system. This causes an increase in the delocalization energy of π electrons. A decrease in differences between the energy of π bonding orbitals and

(a) The kind of structure, by means of which the metals are linked to the carboxylic group, was discussed in the papers [7, 8, 13]. It follows from these papers that sodium is bonded with a carboxylate anion by the ionic structure, whereas lanthanides are coordinated either in a mono- or bidentate manner. The structures by means of which a metal ion may be linked a carboxyl group have been suggested by Nakamoto. More recent investigations indicate that, (1) in addition to a bidentate structure, lanthanides may form additional bridges with other carboxylate anions, (2) that bonds of Ln^{3+} ions with particular carboxylate anions may be non-equivalent.⁽¹⁴⁾

The crystallographic structure of some metal benzoates was investigated with the X-ray methods by Chijalov et al. and Gusjeinov et al.

(b) In UV spectra of benzoic acid and its complexes with metals, in addition to the main $\pi \rightarrow \pi^*$ band within the range 225-236 nm (sometimes in the literature⁽¹⁶⁾ under the name of "K band", being derived from a respective band at 202 nm in the benzene spectrum) there also occurs a partly shielded band at about 270 nm, of a very low intensity (derived from the benzene band B lying at about 255 nm).

that of π antibonding orbitals leads to a bathochromic shift in UV spectra. But the alkaline metals and heavy toxic metals perturb the aromatic system of the ligands, thus causing a hypsochromic shift.

The investigations on $f \rightarrow f$ transitions and on the nephelauxetic effect in the spectra of lanthanide complexes with salicylic acid^(1,2) confirm the accepted interpretation, thus indicating that there exists a dependence between the delocalization degree of f electrons in lanthanide ions and π electrons in the aromatic ring.

As mentioned before, there are very few works devoted to the effect of metals on aromatic systems of ligands in complex compounds. Therefore, it is impossible to compare fully with the literature data. It would be purposeful, however, to compare some results studying on aromatic properties of organometallic compounds. Some π -electron systems are stabilized by metals. The compounds belong to this kind are iron with cyclobutadiene^(3,4) or nickel with pentalene^(5,6). Lanthanides and actinides also stabilize a number of π -electron compounds^(7,8). Metallocenes possess marked aromatic properties. At present metallocenes of the majority of transition elements are known^(9,10). The notion of "super-aromaticity" is given owing to the discovery of ferrocene⁽¹¹⁾. The binding between a metal and the ring in ferrocene is mainly the result of a delocalized covalent bond between an iron atom and two cyclopentadienyl radicals⁽¹²⁾. The properties stabilizing a system depend on the kind of metal adjoined. A particular role is played here by transition metals. It is seen from spectroscopic data that transition metals ($4f$ and $3d$) stabilize the aromatic system of benzoic acid, while alkaline elements and heavy toxic metals perturb the system. Our conclusions, concerning the effect of transition metals, are therefore in agreement with the literature.

The conclusions drawn from the IR, Raman and UV spectra indicate that chromium (I), iron (I), lanthanides and aluminum stabilize the aromatic system of benzoic acid. An increase in the number, frequency and intensity of bands of the ring in vibration spectra occurs simultaneously with the bathochromic shift of $\pi \rightarrow \pi^*$ bands in UV spectra. On the other hand, alkaline elements /Li Na and K/ and heavy toxic metals (Hg (I), Hg (II) and Pb(II)) perturb the aromatic system of benzoic acid. The aromaticity of calcium, magnesium, copper (I) and zinc benzoates is similar to that of the ligand.

Acknowledgment: The author is grateful to Associate Professor H. Baranska for her valuable remarks and her help in completing the experimental material.

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