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# Synthesis and Study of the Composition and Properties of Chelate Complexes of Benzoyl Acetonates of Rare-Earth Elements and Use of These in Gas Chromatography

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**Abstract**—Chelate complex cerium [Ce(BA)<sub>3</sub>] and europium [Eu(BA)<sub>3</sub>] benzoyl acetonates were synthesized. According to IR spectroscopic data and elemental analyses, the composition of the complexes is described by the empirical formulas M(BA)<sub>3</sub>·2H<sub>2</sub>O. Sorbents based on a mesoporous silica gel modified with cerium and europium benzoyl acetonates were obtained. The nitrogen porosimetry demonstrated that, as the complexes are deposited onto the surface of the starting support, the specific surface area and the pore volume become smaller. The polarity of the sorbents Chromaton N-AW + SiO<sub>2</sub> + M(BA)<sub>3</sub> with respect to all classes of test compounds decreases in the order Ce<sup>III</sup> > Eu<sup>III</sup>. According to the data obtained for the capacity factors, the sorbent modified with cerium benzoyl acetonate selectively separates alcohols, and Chromaton N-AW + SiO<sub>2</sub> with deposited chelates Eu(BA)<sub>3</sub> shows the best separating capacity for alkanes and alcohols. It was shown that the sorbents can be used in practice for separating gaseous mixtures of light hydrocarbons.

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Development of new chromatographic materials distinguished by improved structural-sorption and analytical characteristics is one of the advancement lines of gas chromatography as a method for qualitative and quantitative analyses of objects of natural and anthropogenic origin. Of particular interest in this case are chromatographic materials modified with β-dicarbonyl compounds making it possible to widely vary the physicochemical and chromatographic properties of sorbents [1]. Despite the existence of a large number of reports concerned with the development and application of various kinds of adsorbents, fixed liquid phases, and analytical columns containing β-dicarbonyl complexes, the properties of sorbents modified with benzoyl acetonates of rare-earth elements (REEs) have not been studied, which makes topical the fabrication of these chelate-containing chromatographic materials and examination of their texture and chromatographic properties.

The large ionic radii of REEs and the distinctive features of their complexing capacity, namely the predominantly ionic type of bonding and large variable

coordination numbers, are clearly manifested in the chemistry of β-diketonates of these elements [2, 3]. A CN = 8 is characteristic of Eu and Ce β-diketonates, and their coordination configuration is a square antiprism [4]. Complexes of this structure are hardly applied in gas chromatography, and, consequently, their use is of particular scientific interest.

The goal of our study was to obtain cerium and europium benzoyl acetonates, analyze their physicochemical and structural characteristics, examine the gas-chromatographic properties of sorbents for the example of a mesoporous silica gel modified with chelate complexes Ce(BA)<sub>3</sub> and Eu(BA)<sub>3</sub> (Ba stands for benzoyl acetone), and determine how the nature of a modifying complex affects the chromatographic and sorption properties of the materials obtained.

## EXPERIMENTAL

The benzoyl acetonates were synthesized by the following procedure: 2 g of an REE salt was dissolved in

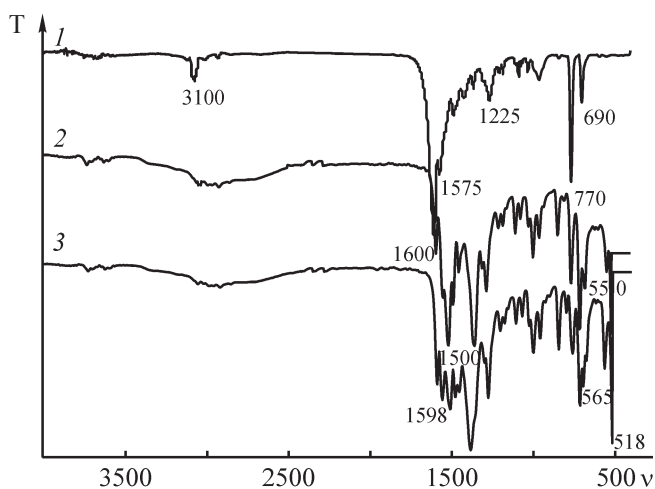
**Table 1.** Elemental composition of the complexes

Compound	Content, wt %				Color of a complex
	C	H	O	M	
Ce(BA) <sub>3</sub> ·2H <sub>2</sub> O	54.6/55.2 <sup>a</sup>	4.7/4.6	14.9/15.4	21.3/21.7	Brown
Eu(BA) <sub>3</sub> ·2H <sub>2</sub> O	53.6/52.7	4.6/4.3	14.6/15.9	22.7/22.7	Yellow

<sup>a</sup> Calculated/found.

5 cm<sup>3</sup> of ethanol and then 3 g of benzoyl acetone dissolved in 20 cm<sup>3</sup> of ethanol was added. NH<sub>4</sub>OH was accurately added dropwise to the resulting solution until a pH value of 7 was reached, at which the M(C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>)<sub>3</sub>·2H<sub>2</sub>O complex precipitates.

To purify the chelate complex to remove impurities, europium benzoyl acetonate was washed with hexane to separate the unreacted benzoyl acetone, and then the precipitate was dissolved in 10 cm<sup>3</sup> of acetone to remove the unreacted salt Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and the solution was filtered. A 50-cm<sup>3</sup> portion of distilled water was added to the light yellow filtrate, the mixture was thoroughly agitated, and the organic layer was separated. The aqueous solution was allowed to stay for a certain time at room temperature. The precipitated crystals of europium benzoyl acetonate were filtered-off and dried in a desiccator. The composition of the thus synthesized chelate complexes of the metals were examined by IR and atomic-emission spectroscopies and subjected to elemental and thermogravimetric analyses.



**Fig. 1.** IR spectra of (1) benzoyl acetone and (2) cerium and (3) europium benzoyl acetonates. (T) Transmission and (v) wave number.

IR spectra were recorded with an Agilent Technologies Cary 630 FTIR spectrometer in the spectral range 400–4000 cm<sup>-1</sup>.

The elemental analysis was made with a Euro EA 3000 elemental composition analyzer; the quantitative content of a metal was determined with an Agilent 4100 atomic-emission spectrophotometer with microwave plasma. The thermogravimetric analysis was made on a Netzsch STA 449 F1 thermal analyzer.

The resulting europium and cerium benzoyl acetonates were deposited by the adsorption method from solution via gradual evaporation of the volatile solvent (CHCl<sub>3</sub>) at room temperature onto the surface of Chromaton N-AW + SiO<sub>2</sub> sorbent synthesized by the procedure described in [5] at the Laboratory of chemical ecology, Research Institute, Tomsk State University.

The specific surface area of the sorbents, their pore volume, and the pore size distribution were characterized by the method of low-temperature adsorption of nitrogen at 77 K on a TriStar II (3020) gas-adsorption analyzer. The relative error of the method is 10%. The chromatographic measurements were made with an Agilent Technologies MAESTRO 7820 gas chromatograph equipped with flame-ionization detector. Metallic packed columns with length of 1 m and inner diameter of 3 mm were used in the study.

## RESULTS AND DISCUSSION

According to the results of an elemental analysis, the chelates are described by the empirical formula M(BA)<sub>3</sub>·2H<sub>2</sub>O. All the chelates are stable in air and can be recrystallized from solvents without any change in their chemical composition (Table 1).

Stretching vibrations of the carbonyl group and vibrations of the benzene ring appear in the IR spectrum of benzoyl acetone at 1600–1575 cm<sup>-1</sup> (Fig. 1, spectrum 1). The vibrations of the carbonyl group are shifted to

**Table 2.** Characteristics of the thermal stability and porous structure of the sorbents under study

Sorbent	Decomposition point of benzoyl acetonates on the SiO <sub>2</sub> surface, °C	Specific surface area, m <sup>2</sup> g <sup>-1</sup>	Pore volume, cm <sup>3</sup> g <sup>-1</sup>	Average pore size, nm
Chromaton N-AW+ SiO <sub>2</sub>	–	133	0.45	13
Chromaton N-AW+ SiO <sub>2</sub> + Ce(BA) <sub>3</sub>	190	104	0.35	14
Chromaton N-AW+ SiO <sub>2</sub> + Eu(BA) <sub>3</sub>	258	117	0.41	14

lower frequencies due to the keto-enol tautomerism of benzoyl acetone [6]. The absorption band  $\nu(\text{C}=\text{O})$ , characteristic of aryl ketones, is observed at 1225 cm<sup>-1</sup>, and vibrations associated with the deformation of the chelate ring and out-of-plane deformation vibrations  $\delta(\text{CH})$  of monosubstituted aromatic compounds, at 770 and 690 cm<sup>-1</sup> [7].

According to [6], the band of stretching vibrations at 1598 cm<sup>-1</sup> in the IR spectra of europium and cerium benzoyl acetonates belongs to the  $\nu(\text{C}=\text{C})$  group. The set of absorption bands at 1555, 1500, and 1483 cm<sup>-1</sup> characterizes the stretching vibrations  $\nu(\text{C}=\text{O})$ , and the absorption at 1382 cm<sup>-1</sup> is associated with stretching  $\nu(\text{C}=\text{O})$  and deformation  $\delta(\text{C}-\text{H})$  vibrations [6, 8]. In the IR spectra of the chelate complexes of  $\beta$ -dicarbonyl compounds, the absorption band  $\nu(\text{C}=\text{O})$  is shifted to the near-IR range of working frequencies, which indicates that the carbonyl group is coordinated with the metal atom via an oxygen atom. Vibrations of M–O bonds appear in the spectra of europium and cerium benzoyl acetonates (Ce–O, 550 and 520 cm<sup>-1</sup>; Eu–O, 565 and 518 cm<sup>-1</sup>).

The thermogravimetric analysis was made to determine the stability of the chelate complexes of REE benzoyl acetonates.

Analysis of the TG and DSC curves shows that the processes of thermal destruction of the complexes occur in the temperature range 176–560°C and are accompanied by burning-out of the organic component. In the case of cerium benzoyl acetate, the full burning-out of ligands occurs at 176–547°C, and that for europium benzoyl acetate, at 225–560°C, with the corresponding metal oxides formed.

When the complexes are deposited on the surface of the Chromaton N-AW+ SiO<sub>2</sub> support, the thermal stability of the chelate somewhat increases, which enables use of the sorbents in chromatographic analyses for separation of various classes of organic compounds at sufficiently high chromatographic column temperatures.

Table 2 presents the texture characteristics of the modified sorbents. Deposition of chelate complexes of the metals onto the surface of the starting support results in that both the specific surface area and the pore volume of the starting silica gel decrease. This is due to the filling of fine pores.

The chromatographic properties of sorbents with fixed phases containing the chelate complexes are largely determined by the amount of the fixed phase on the surface, and also by the composition of a complex compound. The chemical nature of the metals and ligands incorporated into the structure of a modifying chelate makes the most pronounced contribution to the reactivity of the surface due to the increase in the number of its active centers and predetermines its increased capacity for manifestation of intermolecular interactions in the sorbite–sorbent system [9].

The polarity of the modified silica gel was evaluated with the use of the conventional test compounds capable of exhibiting characteristic intermolecular interactions (*n*-alkanes, dispersion interactions; benzene,  $\pi$ – $\pi$  interaction; alcohols, formation of hydrogen bonds; butanone-2 and nitromethane, donor-acceptor and orientation interactions).

The values of the Kovats retention indices *I* of the standard test compounds and the difference of these indexes,  $\Delta I$ , relative to the starting silica gel at 120°C are listed in Table 3.

The results we obtained demonstrate that the polarity of the modified sorbents based on Chromaton N-AW + SiO<sub>2</sub> decreases in the order Ce<sup>III</sup> > Eu<sup>III</sup> with respect to all classes of test compounds. This effect may be due to the electronic structure and properties of the metal ions contained in a chelate and to the structure of the complexes being formed.

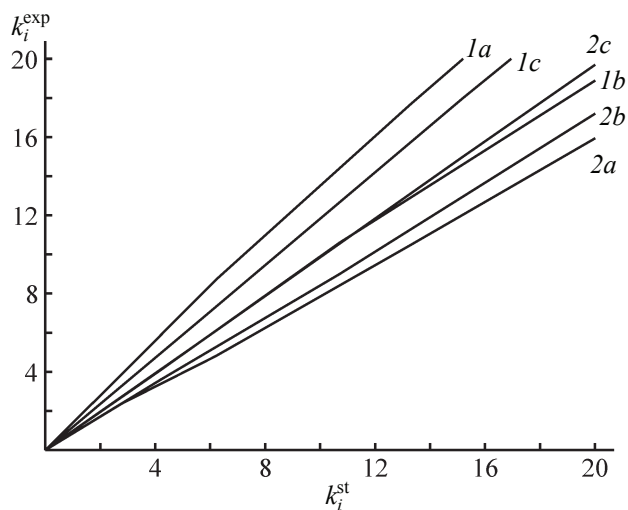
The experimental data suggest that modification of silica gel with the metal benzoyl acetonates leads to a strong change and, in particular, to an increase in the polarity of a sorbent modified with cerium benzoyl

**Table 3.** Kovats retention indices  $I$  of the sorbents and their change relative to the starting Chromaton N-AW + SiO<sub>2</sub>

Sorbent	Benzene		Ethanol		Butanone-2		Nitropropane	
	$I$	$\Delta I$	$I$	$\Delta I$	$I$	$\Delta I$	$I$	$\Delta I$
Chromaton N-AW + SiO <sub>2</sub>	652	–	828	–	1018	–	987	–
Chromaton N-AW + SiO <sub>2</sub> + Ce(BA) <sub>3</sub>	665	13	845	17	1014	–4	989	2
Chromaton N-AW + SiO <sub>2</sub> + Eu(BA) <sub>3</sub>	646	–6	825	–3	969	–49	937	–50

acetate with respect to such test compounds as benzene and ethanol. Chromaton N-AW + SiO<sub>2</sub> and 5% Ce(BA)<sub>3</sub> has an increased capacity toward formation of a hydrogen bond and  $\pi$ -complexation. The significant decrease in the Kovats indices for the Chromaton N-AW + SiO<sub>2</sub> and 5% Eu(BA)<sub>3</sub> sorbent is indicative of a reduced capacity for electrostatic interactions with compounds having an excess electron density: nitromethane and butanone-2.

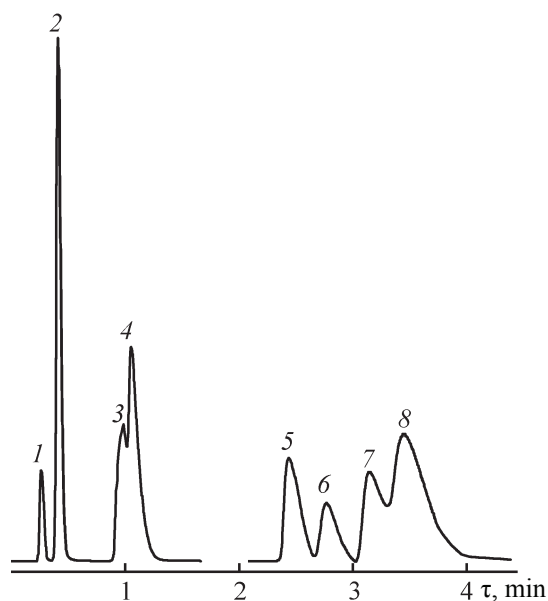
The selectivity of the sorbents with respect to the homologous series of alkanes, arenes, and alcohols was evaluated by the slope ratios of the linear dependences of the column capacity factor  $k_{iexp}$  on the same characteristic of the column for unmodified Chromaton N-AW + SiO<sub>2</sub>, taken as the standard value  $k_{ist}$  (Fig. 2). The highest selectivity of the chromatographic separation between classes of organic substances is reached in columns with the maximum distance between the correlation dependences of the capacity factors [1]. Comparison of the slope ratios suggests that the best separating capac-



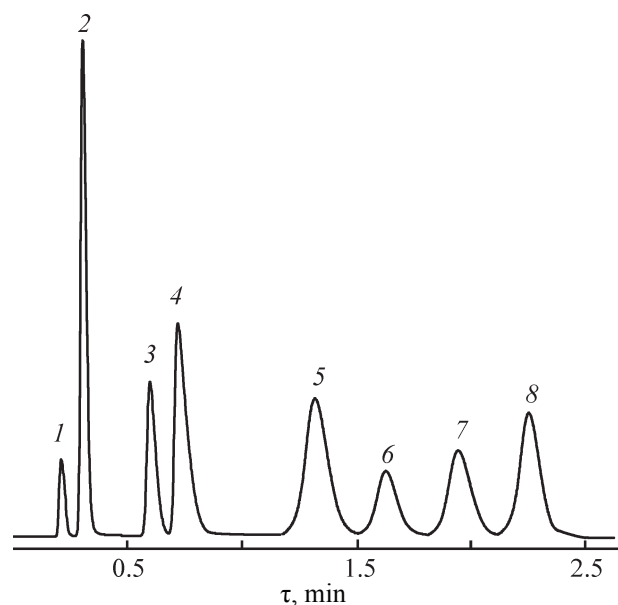
**Fig. 2.** Capacity factors  $k_i$  for (a) alkanes, (b) arenes, and (c) alcohols on the starting Chromaton N-AW + SiO<sub>2</sub> and that modified with (1) europium and (2) cerium benzoyl acetates.

ity for alkanes and alcohols is exhibited by Chromaton N-AW + SiO<sub>2</sub> modified with europium benzoyl acetate. Chromaton N-AW + SiO<sub>2</sub> modified with cerium benzoyl acetate is characterized by the maximum capacity factors for alcohols, which enables a selective separation of these substances.

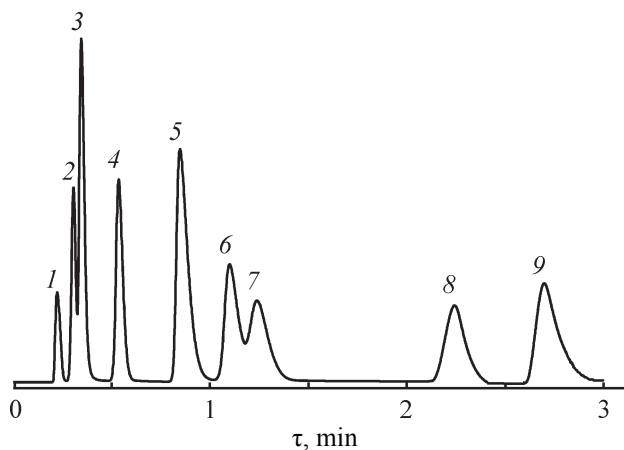
An analysis of mixtures of light saturated and unsaturated hydrocarbons of C<sub>1</sub>–C<sub>4</sub> composition with Chromaton N-AW + SiO<sub>2</sub> modified with 5% Ce(BA)<sub>3</sub> and Eu(BA)<sub>3</sub> demonstrates separation of all the components of the starting model mixture. The mixture components composed of the first representatives of the saturated hydrocarbons are eluted in the order of their increasing boiling points, whereas the unsaturated compounds are eluted in order of their increasing molecular mass. The



**Fig. 3.** Chromatogram of a mixture of light saturated and unsaturated hydrocarbons on Chromaton N-AW + SiO<sub>2</sub> at 25°C. ( $\tau$ ) Time; the same for Figs. 4 and 5. (1) Methane; (2) ethane, ethylene; (3) propylene; (4) propane; (5) isobutene; (6) isobutylene; (7) butane-1; (8) *n*-butane; the same for Fig. 4.



**Fig. 4.** Chromatogram of a mixture of light saturated and unsaturated hydrocarbons on the modified sorbent Chromaton N-AW+ SiO<sub>2</sub> + Ce(BA)<sub>3</sub> at 25°C.



**Fig. 5.** Chromatogram of a mixture of light saturated and unsaturated hydrocarbons on the modified sorbent Chromaton N-AW+ SiO<sub>2</sub> + Eu(BA)<sub>3</sub> at 25°C. (1) Methane, (2) ethane, (3) ethylene, (4) propylene, (5) propane, (6) isobutene, (7) isobutylene, (8) butane-1, (9) *n*-butane.

chromatograms shown in Figs. 3–5 demonstrate that Chromaton N-AW + SiO<sub>2</sub> modified with europium and cerium complexes can be used for their determination in various analytical objects.

## CONCLUSIONS

The modification of the surface of Chromaton N-AW + SiO<sub>2</sub> with europium and cerium benzoyl acetonates improves the thermal stability of the chelate complexes and makes smaller the specific surface area. Chromatographic studies of the sorbents demonstrated that the polarity with respect to all the test compounds decreases in the order Ce<sup>III</sup> > Eu<sup>III</sup>, with significant changes observed with respect to nitropropane and butanone-2. According to the data obtained for the capacity factors of the sorbents, Chromaton N-AW + SiO<sub>2</sub> + Ce(BA)<sub>3</sub> exhibits the best separating capacity for alcohols, and Chromaton N-AW + SiO<sub>2</sub> modified with europium benzoyl acetonates selectively separates alkanes and alcohols.

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