

**New complexanes. XXXIX.**  
**Preparation and study of the solid complexes**  
**of the racemic ethylenediamine-*N,N'*-disuccinic acid with**  
**iron(III), cobalt(III), and bismuth(III) ions**

V. ŠPRINGER, M. KOTOUČEK, and J. MAJER

*Department of Analytical Chemistry, Faculty of Pharmacy,  
Komenský University, 880 34 Bratislava*

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In this paper, attention is paid to the synthesis of the solid complexes of the racemic ethylenediamine-*N,N'*-disuccinic acid with Fe(III), Co(III), and Bi(III). The complexes  $\text{Na}[\text{FeY}] \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}[\text{CoY}] \cdot 3\text{H}_2\text{O}$ , and  $[\text{BiHY}] \cdot \text{H}_2\text{O}$  were prepared. Besides thermogravimetry, the method of infrared spectroscopy was used for the study of these complexes. It has been revealed that the character of oxygen—metal bonds in the five-membered (covalent bond) and in the six-membered (ionic bond) chelate ring is different in all complexes. In the Bi complex, one of the carboxylic functional groups of the racemic EDDS occurs in the protonated form and does not probably take part in chelation.

В работе уделяется внимание синтезу твердых комплексов рацемической этилендиамин-*N,N'*-диянтарной кислоты с Fe(III), Co(III) и Bi(III). Были приготовлены комплексы  $\text{Na}[\text{FeY}] \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}[\text{CoY}] \cdot 3\text{H}_2\text{O}$  и  $[\text{BiHY}] \cdot \text{H}_2\text{O}$ . Для изучения комплексов была использована кроме термогравиметрии ИК спектроскопия. Было найдено, что характер связи кислород—металл отличается в 5-членном (ковалентная связь) и 6-членном (ионная связь) хелатных циклах. В случае комплекса Bi одна из карбоксильных функциональных групп рацемической EDDS выступает в протонизированной форме и, вероятно, не участвует в образовании хелатной связи.

The racemic ethylenediamine-*N,N'*-disuccinic acid which is a substance isomeric with EDTA was synthesized as the first from the group of complexanes exhibiting the character of tetracarboxylic acids with secondary aminic functional group [1]. The formation of the EDDS complexes with a great number of cations in solution [1—6] as well as the problems of structure of the Co(III) and Ni(II) complexes studied from the view-point of stereochemistry by the methods of nuclear magnetic

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*Abbreviations:*

EDDS racemic ethylenediamine-*N,N'*-disuccinic acid.

resonance, circular dichroism, and infrared spectroscopy [7, 8] was already given great attention. The solid Co(III) complexes were investigated by X-ray diffraction analysis in our laboratory [9, 10] and there the crystal structure of the  $\text{Li}[\text{CoY}] \cdot 3\text{H}_2\text{O}$  complex was determined. It has been established that the complex  $[\text{CoY}]^-$  anion has an octahedral structure with the six-membered equatorially oriented  $\beta$ -alanine rings and the five-membered glycine rings in axial positions. The anions are linked in the orthorhombic crystal through the lithium cations by the hydrogen bonds of the  $\text{NH}\dots\text{O}$  type and by the van der Waals forces.

In this study, we were engaged in the preparation of the solid EDDS chelates with Fe(III) and Bi(III). Besides, we also paid attention to the Co(III) chelate. After elemental analysis, the chelates were investigated by infrared spectroscopy in order to find out the participation of individual donors in chelation and elucidate the character of the arising bonds. The results of the study of the solid EDDS chelates with Cu(II) were published in our preceding paper [11].

### Experimental

EDDS and  $\text{Na}_4\text{EDDS}$  were prepared according to the procedures published [1, 10]. The infrared spectra were measured on a spectrophotometer Perkin—Elmer 377 in the form of KBr discs. The elemental analysis (C, H, N) was performed with an analyzer Carlo Erba, Milan, Model 1102. The content of metal in the isolated products was determined by complexometric titration after preceding mineralization with  $\text{HClO}_4$  and  $\text{HNO}_3$ . The content of water in the chelates was estimated with a derivatograph OD-102. The results of elemental analysis of the investigated substances are given in Table 1.

Table 1

Results of elemental analysis of the investigated substances

Substance	M	Calculated/found				
		% H <sub>2</sub> O	% C	% H	% N	% M(III)
Na <sub>4</sub> Y	380.17	0.00	31.59	3.18	7.37	
		0.5	30.87	3.39	7.13	
Na[FeY]·2H <sub>2</sub> O	421.10	12.83	28.52	4.31	6.65	13.26
		13.0	28.32	4.08	6.75	13.51
Na[CoY]·3H <sub>2</sub> O	424.22	12.74	29.57	3.80	6.60	13.89
		12.5	29.28	3.56	6.44	13.56
[BiHY]·H <sub>2</sub> O	516.21	3.49	23.27	2.93	5.43	40.48
		3.6	22.82	2.68	5.23	40.85

## Synthesis of the EDDS complexes

### *Preparation of the Na[FeY]·2H<sub>2</sub>O complex*

3.8 g (10 mmol) of EDDS in the form of pentahydrate were dissolved in 50 ml of the aqueous solution containing 0.4 g (10 mmol) of NaOH. The solution was mixed with 1.07 g (10 mmol) of the freshly precipitated Fe(OH)<sub>3</sub> and afterwards it was stirred under mild heating until the substance dissolved. Subsequently, the solution was concentrated nearly to dry state on a water bath. The substance was isolated by adding the sirupy residue into acetone. The brown powdered product was sucked and after drying in air it was analyzed.

### *Preparation of the Na[CoY]·3H<sub>2</sub>O complex*

3.8 g (10 mmol) of EDDS were dissolved in 50 ml of water containing 0.4 g of NaOH. The solution was mixed with the product of alkaline hydrolysis of 1.8 g (10 mmol) of cobalt(II) nitrate. The reaction mixture was stirred under mild heating as long as the precipitate dissolved. Afterwards, 1 ml of 30% H<sub>2</sub>O<sub>2</sub> was added into the solution. After short boiling, the violet product was isolated from the solution in the same way as the Fe(III) chelate and analyzed.

### *Preparation of the [BiHY]·H<sub>2</sub>O complex*

3.8 g (10 mmol) of EDDS were dissolved in 50 ml of water containing 0.4 g of NaOH and 20 ml of 0.5 M-Bi(NO<sub>3</sub>)<sub>3</sub> solution were slowly added under constant stirring. When the solution was adjusted to pH 2.0, the white powdered product separated. It was washed with ethanol and ether and analyzed.

## Results and discussion

For the preparation of complexes, we used the method according to which the EDTA complexes had been prepared [12]. In this case, the nitrate of metal is allowed to react with monosodium or disodium salt of the agent and the corresponding complex separates after concentrating the solution or it is precipitated with alcohol or acetone. In our case, this method was successful only in case of the Bi(III) complex which immediately separated from the aqueous solution. Our attempt to prepare the other two complexes of necessary purity by this method failed. The Co(III) and Fe(III) complexes were prepared by reaction of the particular hydroxide with the monosodium salt of EDDS.

The content of water in the complexes prepared was investigated thermogravimetrically. As for the Fe(III) complex, the first molecule of water is released in the temperature range 60—110°C, which gives evidence that it is bonded outside the coordination sphere of iron. The second molecule of water is liberated in the

temperature range 150—210°C, which allows to assume a coordination to the central atom of chelate. This result is in agreement with the results presented in paper [13] dealing with the X-ray diffraction analysis of the EDTA chelate with Fe(III).

As for the Co(III) complex, the loss of weight in the interval 50—120°C corresponds to liberation of three water molecules, which indicates that the water is outside the coordination sphere of cobalt. Equal result was also obtained with the Bi(III) complex.

In Table 2, the values of frequencies of the absorption bands of the three investigated complexes as well as of EDDS and its tetrasodium salt are given. Attention is focused on the bands of the stretching and bending vibrations of the bonds of the —NH— and —COO<sup>-</sup> groups which directly take part in chelation. The evaluation of the infrared spectra was aimed at appreciating the character of the ligand—metal bond. In this sense, the position of the absorption bands was compared with the corresponding values of Na<sub>4</sub>EDDS in which the ligand—metal bond exhibits ionic character [10].

Table 2

Frequencies of the bands of particular vibrations of the investigated substances in KBr discs (cm <sup>-1</sup> )					
Substance	$\nu(\text{C}=\text{O})$	$\delta(\text{NH}_2^+)$	$\delta(\text{NH})$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$
H <sub>4</sub> Y·5H <sub>2</sub> O	1715 s	1630 s		1565 m	1420 m
Na <sub>4</sub> Y			1630 m	1580 s	1405 m
Na[FeY]·2H <sub>2</sub> O			1640—1600* s	1640—1600* s	1365 m
Na[CoY]·3H <sub>2</sub> O			1650—1600* s	1650—1600* s	1380 m
[BiHY]·H <sub>2</sub> O	1710 m		1630 sh	1570 s	1400 m

s — strong, m — medium, sh — shoulder.

\* See Discussion.

As for the Na[CoY]·3H<sub>2</sub>O complex measured in KBr disc, only one broad band at 1650—1600 cm<sup>-1</sup> was observed in the region of occurrence of  $\nu_{\text{as}}(\text{COO}^-)$  and  $\delta(\text{NH})$ . For the purpose of differentiation of this band, the complex was also measured in a solution of D<sub>2</sub>O (cells Irtran-2). The shift in band position of N—H bending vibration owing to a deuteration caused that two bands (Fig. 1) appeared in the region of antisymmetric stretching vibration of COO<sup>-</sup>. The band at 1645 cm<sup>-1</sup> may be assigned to the covalent bond of COO<sup>-</sup> on Co(III) in the five-membered chelate ring while the band at 1590 cm<sup>-1</sup> identifies the ionic character of this bond in the six-membered chelate ring (Fig. 2). This result confirms the assumption put forward by Neal and Rose [7].

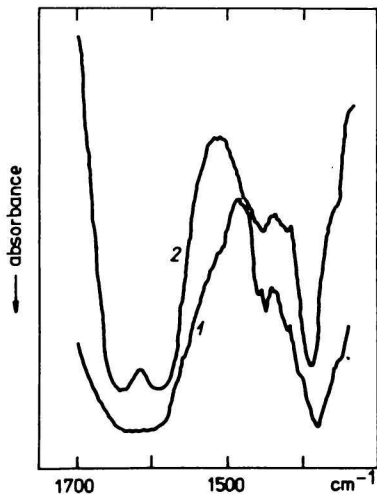


Fig. 1. Infrared spectra of the  $\text{Na}[\text{CoY}] \cdot 3\text{H}_2\text{O}$  complex.

1. In KBr disc; 2. in  $\text{D}_2\text{O}$  (cell Irtran-2).

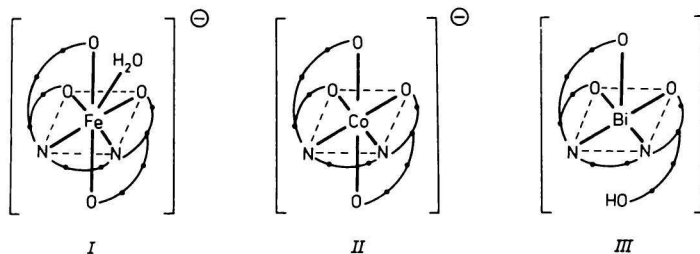


Fig. 2. Suggested structures of the EDDS complexes with the ions of  $\text{Fe}(\text{III})$ ,  $\text{Co}(\text{III})$ , and  $\text{Bi}(\text{III})$ .

The infrared spectrum of the  $\text{Na}[\text{FeY}] \cdot 2\text{H}_2\text{O}$  complex is also of a similar character as stated in the preceding case. The ascertained positions of the absorption bands of carboxyl, too, allow to expect a different character of the oxygen—metal bond in the five-membered and six-membered chelate ring. The results ensuing from the study of the infrared spectra and thermogravimetric evaluations enable us to suggest the structures represented in Fig. 2 for the  $\text{Co}(\text{III})$  and  $\text{Fe}(\text{III})$  complexes.

As for the  $\text{Bi}(\text{III})$  complex, the absorption maximum of  $\nu_{\text{as}}(\text{COO}^-)$  occurs at  $1570 \text{ cm}^{-1}$ , which indicates the ionic character of the oxygen—Bi bond. Besides, a band appears at  $1710 \text{ cm}^{-1}$  which confirms that one of the carboxylic functional groups occurs in the protonated form. We may deduce from this fact that the coordination number of bismuth in this complex is equal to five. The suggested structure of the complex is represented in Fig. 2.

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