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Equilibrium Studies on Complexation of Iron(III) by Acet-, Glycinium and Betaine Hydroxamic Acids

Mladen Biruš, Nikola Kujundžić, Marijan Pribanić, and Zvonimir Tabor

Department of Chemistry, Faculty of Pharmacy and Biochemistry,
University of Zagreb, Zagreb, Croatia, Yugoslavia

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Equilibrium studies were performed to investigate the complexation of aqueous high-spin iron(III) by three synthetic monohydroxamic acids: acet-, glycinium, and betaine hydroxamic acids. Under neutral and acidic conditions studied, acethydroxamic acid is neutral (AH), while glycinium (GH₂⁺) and betaine (BH⁺) hydroxamic acids have a positive charge on the nitrogen atom.

The equilibrium quotients for the formation of monoacet-hydroxamatoiron(III) complex $Q_1', A^- = [FeA_2^+]/([Fe^{3+}][A^-])$, bisacethydroxamatoiron(III) complex $Q_2', A^- = [FeA_2^+]/([Fe^{3+}][A^-]^2)$, and trisacethydroxamatoiron(III) complex $Q_3', A^- = [FeA_3]/([Fe^{3+}][A^-]^3)$ were found to be: $\lg Q_1', A^- = 10.38$ (0.01), $\lg Q_2', A^- = 19.16$ (0.14), and $\lg Q_3', A^- = 25.56$ (0.70).

Analogous equilibrium quotients for glycinium-hydroxamic acid with protonated amino group (GH₂⁺) and betaine-hydroxamic acid (BH⁺) ligands are:

$$\begin{aligned}\lg Q_1', GH &= [Fe(GH)^{3+}]/([Fe^{3+}][GH]) = 7.77 \text{ (0.08)}, \\ \lg Q_2', GH &= [Fe(GH)_2^{3+}]/([Fe^{3+}][GH]^2) = 13.71 \text{ (0.08)}, \\ \lg Q_3', GH &= [Fe(GH)_3^{3+}]/([Fe^{3+}][GH]^3) = 17.63 \text{ (0.14)},\end{aligned}$$

$$\begin{aligned}\lg Q_1', B &= [FeB^{3+}]/([Fe^{3+}][B]) = 7.28 \text{ (0.02)}, \\ \lg Q_2', B &= [FeB_2^{3+}]/([Fe^{3+}][B]^2) = 13.41 \text{ (0.05)}, \text{ and} \\ \lg Q_3', B &= [FeB_3^{3+}]/([Fe^{3+}][B]^3) = 16.46 \text{ (0.24)}.\end{aligned}$$

Determinations were made at 1.0 M ionic strength (NaCl) and at 25 °C by spectrophotometric methods.

The synthesis of a new compound betaine hydroxamic acid chloride is described.

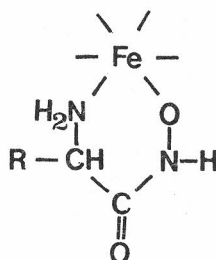
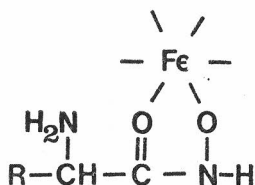
INTRODUCTION

Hydroxamic acids are weak organic acids with a wide variety of applications in industry, pharmacy and chemistry. They serve as commercial flotation reagents in extractive metallurgy, as agents in nuclear fuel processing, inhibitors for copper corrosion, food additives, antifungal agents, therapeutic agents and analytical reagents. Apart from porphyrins, the other major class of naturally occurring iron complexing agents are the hydroxamic acids, which have been noted to exhibit a high affinity for iron(III) relative to other biologically important metal ions. Hydroxamic

acids complex as dihydroxamic acids (forming the mycobactins, mycelianamide, and pulcherrimic acid) and the trihydroxamic acids (forming the ferrichrome and ferrioxamine groups).¹⁻³ Hydroxamates along with thiohydroxamates and catecholates mediate microbial iron transport and are commonly called siderophores. The hydroxamate group $/R_1 C(=O) N(OH R_2/$ is considered to be the most common functional group of siderophores produced by molds, fungi, and yeasts.⁴ The three limiting types among many mechanisms for siderophore-mediated microbial iron transport have been advanced.⁵ Kinetic and thermodynamic information relating to the complexation of iron(III) by various siderophores chelating agents forming five-membered ring (Structure I) continues to be of utmost importance for the understanding of the molecular basis for iron bioavailability.

It is reasonable to assume that the various functionalities besides hydroxamate group may be of importance in the biological rôle of hydroxamatoiron(III) complexes. For example amino group is present in some naturally occurring hydroxamic acids such as desferrioxamine B. It has been suggested that aminohydroxamic acids may be useful in the treatment of iron-overload diseases^{6,7} with emphasis on the surface-active rôle of an uncoordinated amino group.

However, the suggestion has been advanced⁶ that the amino group may be involved in the coordination to iron(III) and cannot be available for other rôles. In that case six-membered ring would be formed by chelation of α -aminohydroxamic acids (Structure II).



FORMULA

STRUCTURE I

STRUCTURE II

Two possible structures of α -aminomonohydroxamatoiron(III) complex.



$R = CH_3-$, acethydroxamic acid (AH)

$R = H_2N-CH_2-$, glycinehydroxamic acid (GH)

$R = H_3N^+-CH_2-$, protonated glycinium hydroxamic acid (GH_2^+) existing under neutral and acidic conditions used in this work

$R = (CH_3)_3N^+-CH_2-$, betaine hydroxamic acid (BH^+)

In this paper we present our results concerning the equilibrium of complexation of iron(III) by three synthetic monohydroxamic acids (see Formula below) acet-, glycinium, and betaine hydroxamic acids containing

no amino group, a protonated amino group and quaternary ammonium ion, respectively. The obtained results may be of help in discriminating between the structures I and II.

EXPERIMENTAL

Materials

A stock solution of iron(III) chloride (0.15 M in 0.1 M HCl) was prepared from iron(III) chloride hexahydrate (Merck), and standardized as described previously.⁸

Acethydroxamic acid was prepared by the procedure described elsewhere⁹ and its reagent solutions were prepared by dissolving the solid immediately before the measurements were done.

Glycinehydroxamic acid was prepared as already described.¹⁰ The crude material was twice recrystallized from ethanol-water (1:1) and stored in a vacuum desiccator over P_4O_{10} .

Synthesis of betaine hydroxamic acid chloride. — Ethyl ester of monochloroacetic acid was converted with trimethylamine in benzene solution to the ethyl ester of *N*-trimethylammonium acetic acid chloride. Saturated solution of the product in cold methanol was mixed with the cold methanol solution of hydroxylamine which was in slight excess over betaine ester chloride. The reaction mixture was left at about 4 °C for three days, and then methanol was removed in a vacuum evaporator. The remaining oily substance began to crystallize in a vacuum desiccator over P_4O_{10} . Recrystallization from methanol gave the pure product, m.p. 176–177 °C.

Anal. $C_5H_{13}N_2O_2Cl$ (168.58) calc'd: C 35.61; H 7.77; N 16.61; Cl 21.02%
found: C 35.33; H 7.85; N 16.43; Cl 21.57%

¹H NMR spectrum (DMSO- d_6): The spectrum shows two peaks at $\delta = 3.25$ ppm and $\delta = 4.16$ ppm with an integral ratio of 9:2, obviously corresponding to the singlets of *N*—(CH₃)₃ and CH₂ protons. Potentiometric titrations gave the following values: $pK_a = 6.64$ (ionic strength 0.15 M NaCl), $pK_a = 6.56$ (ionic strength 1.0 M NaCl), and a molecular weight of 170 ± 1 (calcd. 168.58). All determinations were made in triplicate. All other reagents were of analytical grade and were used without further purification.

Physical Measurements and Computations

All experiments were performed at (25 ± 0.1) °C in an aqueous solution of 1.00 M ionic strength maintained by NaCl. Double-distilled water (from an all-glass apparatus) was used throughout.

The spectrophotometric measurements were performed on a Cary 16 K spectrophotometer equipped with a thermostated cell compartment. A Potentiograph E 436 Metrohm with a combined glass electrode standardized with two buffers was used for potentiometric titration.

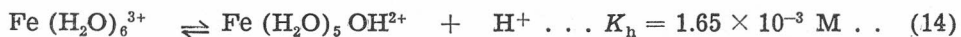
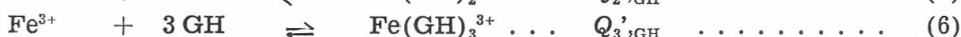
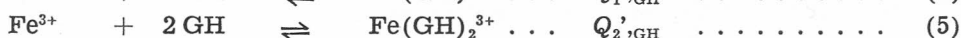
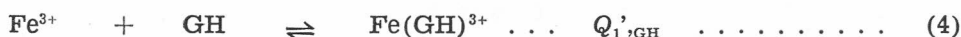
All the computations were performed on a UNIVAC 1100 computer at the University Computing Center, Zagreb. A modified version of the originally published¹¹ CORNEK computer program was used for the refinement of formation quotients from spectrophotometric data, as well as for the refinement of molar absorptivities.

RESULTS

The stepwise formation of the mono-, bis- and tris-hydroxamatoiron(III) complexes by three hydroxamic acids studied, AH, GH_2^+ and BH^+ , are depicted by equations (1) — (9). However, the equations (10) — (14) should also be taken into account for the complete description of the

system studied. Equations (10), (11), and (13) show the proton dissociation with the loss of the OH proton of the hydroxamate group, whereas equation (12) represents the deprotonation of ammonium group which, in contrast to the Brown's results⁶, is not necessarily involved in the coordination. Diprotonic GH_2^+ thus behaves not as an N but rather as an O acid in our model. Since the majority of the data were collected at $\text{pH} < 8$ and on the other hand $\text{p}K_{\text{a, GH}}$ is 9.23⁶, the fraction of glycine-hydroxamate anion (G^-) is low enough to be safely neglected. Coordinated water molecules and chloride ions are omitted for clarity in the presentation of iron species, except in equation (14).

The notation Q' representing the formation quotient for reaction between ferric ions and hydroxamate anion has been adopted here from the Monzyk and Crumbliss paper.¹² For example, in the case of glycinium hydroxamic acid, Q is defined as $Q_n = [\text{Fe}(\text{GH})_n^{3+}] [\text{H}^+]^n / ([\text{Fe}^{3+}] [\text{GH}_2^+]^n)$ and $Q'_n = Q_n / (K_{\text{a, GH}_2^+})^n$, where n means the number of the coordinated hydroxamic acid molecules. The formation quotients are defined in Eqs. (1) — (14), the actual ligand species being additionally specified in the subscript.



Formation of Monohydroxamatoiron(III) Complexes

The first step in the over-all hydroxamatoiron(III) complex formation reaction is the formation of the monohydroxamatoiron(III) complex defined by Q'_1 and equations (1), (4) and (7). The coordination of the second hydroxamic acid could be avoided by keeping the excess of Fe^{III} over the hydroxamic acid in the reaction solution. The higher concentration of Fe^{III} ions requires that the measurements of absorption be performed at

500 nm, where iron(III) ions do not exhibit significant absorption. It is seen from Figure 1. that the absorption bands of monoglyciniumhydroxamatoiron(III) and monobetainehydroxamatoiron(III) complex are located at 492 and 480 nm, respectively. The visible spectrum of monoacethydroxamatoiron(III) complex is not shown, since its characteristics have been already reported.^{8,12,13}

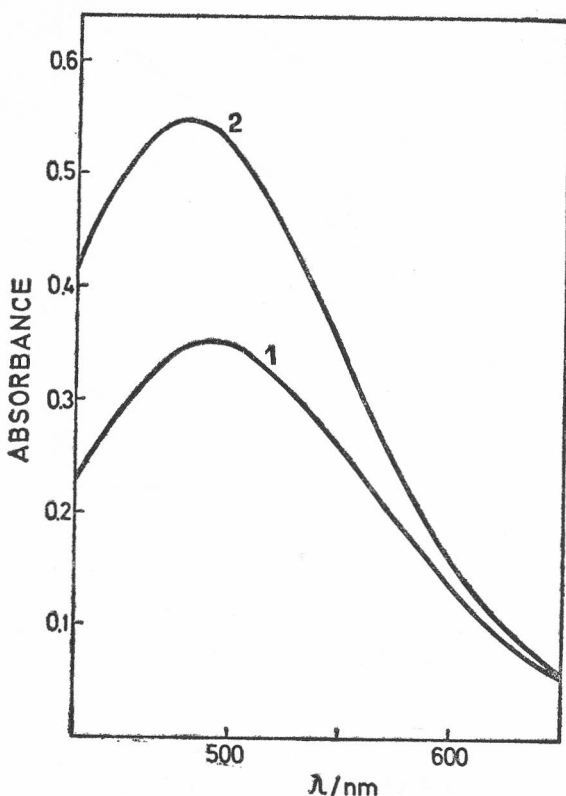


Figure 1. Visible spectrum of monoglyciniumhydroxamatoiron(III) (1) and monobetainehydroxamatoiron(III) (2) complex. Conditions: 0.15 M FeCl_3 , 5×10^{-4} M hydroxamic acid, 0.1 M HCl, 1.0 M ionic strength (NaCl), 25°C. The spectra are taken against 0.15 M FeCl_3 in 0.1 M HCl as a blank.

Figure 2. shows the plot of the ratio of the total iron(III) concentration to the absorbance vs the total iron(III) concentration. The obtained linear relationship indicates the existence of only one complex under these conditions, as it follows from the Benesi-Hildebrand method¹⁴ for calculation of the stability constants (see also e. g. ref. 15). The linear relationship was also obtained in the case of acethydroxamic acid under analogous conditions except that the acidity of the solution was 0.4 M (HCl). The data from Figure 2. and the known values of K_a serve to calculate the particular equilibrium quotient Q' and molar absorptivities of the monohydroxamatoiron(III) complexes.

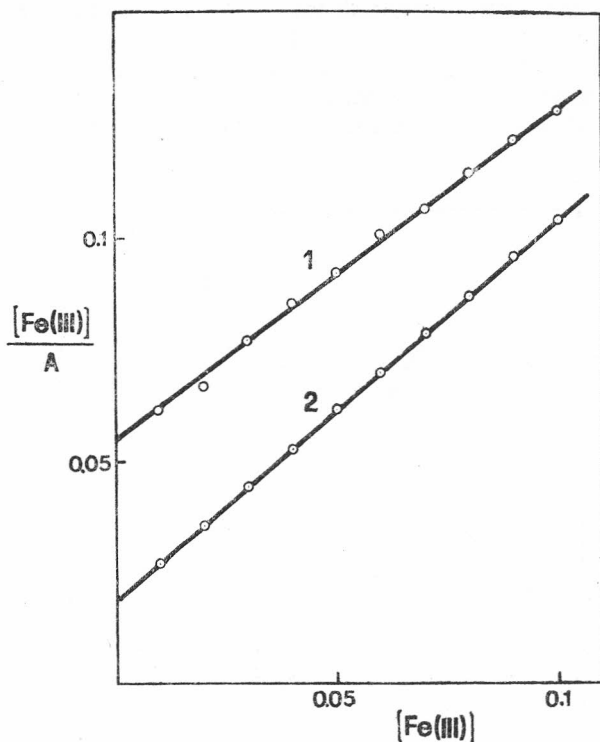


Figure 2. The ratio of the total iron(III) concentration to the absorbance vs the total iron(III) concentration at 500 nm. Conditions: 5×10^{-4} M glycinium hydroxamic acid (1) or betaine hydroxamic acid (2), 1.0 M ionic strength (NaCl), 0.1 M HCl, 25 °C.

The assumption was made that the value of K_{A, GH_2^+} obtained in 0.15 M ionic strength⁶ would not change significantly at 1.0 M ionic strength. This assumption seems reasonable since the values of the analogous K_{A, BH^+} was not appreciably affected by changing the ionic strength (see Experimental Section).

Formation of bis- and tris-hydroxamatoiron(III) Complexes

In an excess of hydroxamic acid over iron(III) the formation of bis- and tris-hydroxamatoiron(III) complexes may take place, depending on the acidity of the reaction solution. Figure 3. shows the increase and then the decrease in the absorption at 500 nm by a steady increase in pH, suggesting the existence of, at least, two absorbing complexes. However, since the obtained maximum value of the absorbance far exceeds that of the monohydroxamatoiron(III) complex at 500 nm it may be concluded that at least three different complexes are present in the solution.

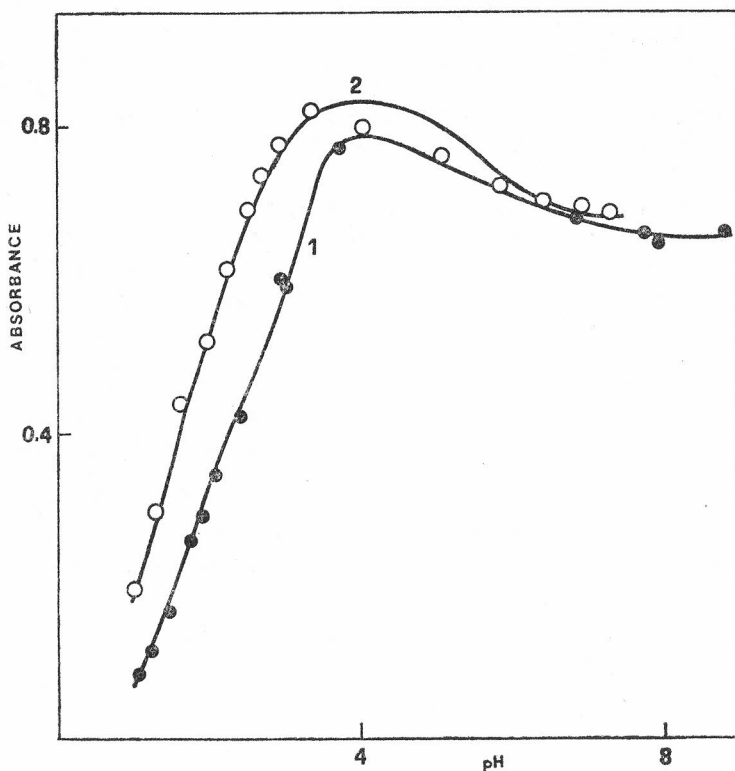


Figure 3. Dependence of the absorbance at 500 nm on pH of solution, Conditions: 5×10^{-4} M FeCl_3 , 1×10^{-2} M glycinium hydroxamic acid (1) or betaine hydroxamic acid (2), 1.0 M ionic strength (NaCl), 25 °C.

TABLE

Spectral and Equilibrium Data for Hydroxamatoiron(III) Complex Formation

		Acethydroxamic Acid	Glycinium Hydroxamic Acid	Betaine Hydroxamic Acid
pK_a		8.92 ^a	7.55 ^b	6.56
$\lg Q'_1$		10.38(0.01) ^c	7.77(0.08)	7.28(0.02)
$\lg Q'_2$		19.16(0.14)	13.71(0.08)	13.41(0.05)
$\lg Q'_3$		25.56(0.70)	17.63(0.14)	16.46(0.24)
$10^{-3}\epsilon(500 \text{ mm})$	mono-	1.06(2) ^d	1.13(3)	1.07(5)
$\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	bis-	1.80(1)	2.1 (5)	1.70(3)
	tris-	1.2 (1)	1.28(3)	1.32(4)
$\epsilon(\lambda_{\text{max}}/\text{nm})$				
$\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	mono-	1060 (500)	1150 (492)	1100 (480)

^a From ref. 8.

^b From ref. 6. referring to the K_{a,GH_2^+}

^c Numbers in parentheses have a meaning of log of single standard deviation.

^d Numbers in parentheses are single standard deviations in units of the last digit given.

The Q_1' and molar absorptivity values obtained as described above have been used in the treatment of these data for the calculation of Q_2' and Q_3' as well as for molar absorptivities of the bis- and tris-hydroxamatoiron(III) complexes. We calculated the curves in Figure 3. by using the Q_n' 's and molar absorptivities given in the Table. The calculated data are in good agreement with experimental data points as it is seen in Figure 3.

The same procedure was followed in obtaining the Q_1' , Q_2' , and Q_3' values for mono-, bis-, and tris-acethydroxamatoiron(III) complexes.

The reliability of the calculated Q_n' values was substantiated by performing the same treatment of data at 450 nm. However, the precision of the results is lower at 450 nm due to the interfering absorption of iron(III) ions. Further support of the obtained results listed in the Table comes from the analysis of spectral changes of the studied solutions as a function of pH. The analysis shows that results compare favourably well with the calculated iron(III) species distribution using the Q_n' values from the Table.

Figure 4. shows the electronic spectra of iron(III) - betaine hydroxamic acid system as a function of pH and the calculated iron(III) species distribution using the equilibrium quotient values from the Table. The

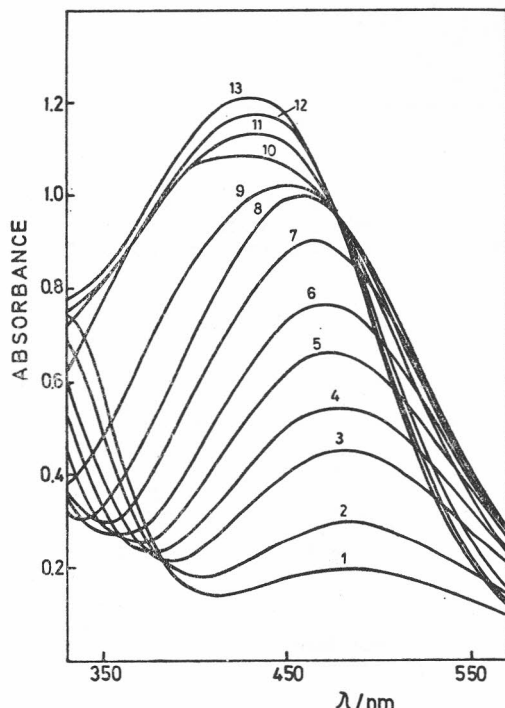


Figure 4. (A) Electronic spectra of betaine hydroxamic acid-iron(III) system at various pH. The curves from 1 to 13 represent the spectra at the following pH: 0.99, 1.27, 1.63, 1.96, 2.23, 2.50, 2.92, 2.35, 4.02, 5.06, 6.38, 6.90, and 7.28.

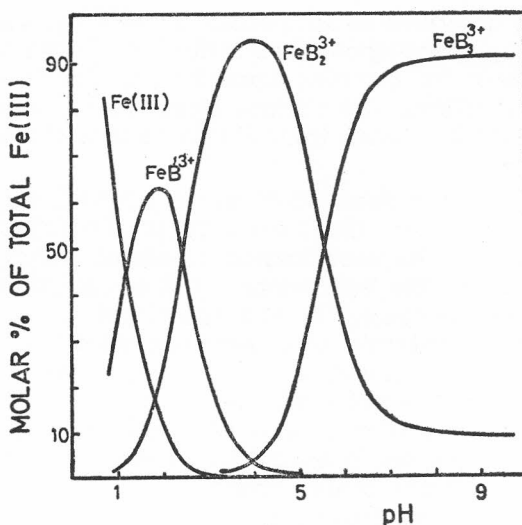


Figure 4. (B) Distribution of different iron(III) species as a function of pH of the solution. Conditions of (A) and (B) : 5×10^{-4} M FeCl_3 , 10^{-2} M betaine hydroxamic acid, 1.0 M ionic strength (NaCl), 25 °C.

inspection of Figure 4. reveals two isosbestic points. One appears at 380 nm, in the pH region 0.99–1.63, and the other at 477 nm, in the pH region 4.02–7.28. The species distribution shown in part B of the Figure 4. predicts in the pH region 0.99–1.63 the existence of Fe(III) ions and monobetainehydroxamatoiron(III) complexes and, in the pH region 4.02–7.28, bis- and tris-betainehydroxamatoiron(III) complexes at the major absorbing species. This analysis is a further substantiation of the reliability of the calculated Q' values.

Analogous analyses have been made for the iron(III) - glyciniunhydroxamic acid system also conforming to the obtained results in the Table.

At pH values as high as 10, some spectral changes occur which are very difficult to explain. Similar ill-defined spectral changes have been reported by other workers.^{6,16,17} One possible explanation might be the deprotonation of the nitrogen atom of the hydroxamate group.

DISCUSSION

There is ample evidence in the literature, including several X-ray structural reports of iron(III) complexes with synthetic and naturally occurring hydroxamic acids, showing that complexation occurs by coordinating both the carbonyl and the hydroxamate OH oxygen atoms to the iron(III) center with concomitant loss of a NOH proton yielding five-membered chelate ring^{12,18–20} (Structure I). In the thorough study¹² the thermodynamic driving force for the monohydroxamatoiron(III) complex

formation has been described as an increase in entropy, with the enthalpy of formation actually opposing complex formation. It has been concluded¹² that the driving force for complex formation is due to entropy change alone which clearly reflects the chelate effect based on the assumption that the hydroxamate ion binds iron(III) to form a five-membered chelate ring.

The presence of other functionalities in hydroxamic acid molecule, such as amino group, offers the possibility of the formation of a six-member ring involving the coordination of amino group nitrogen atom and the oxygen atom of the hydroxamate OH group (Structure II). This explanation has been proposed in the report⁶ of the complexation of iron(III) by glycinehydroxamic acid, seriously questioning the surface-active rôle, of an uncoordinated amino group, proposed earlier, in the chelation therapy of iron.⁷ Involvement of the amino group in the coordination to the iron(III) center is also of importance in the theory of mechanisms of iron transport in biological systems by naturally occurring hydroxamic acids containing amino group.

Our results listed in the Table allow a comparison of the hydroxamatoiron(III) complexes containing as chelating ligands three different synthetic monohydroxamic acids: acethydroxamic acid having no amino group, glycine hydroxamic acid having protonated amino group and betaine hydroxamic acid having a quaternary ammonium ion. It should be noted that the coordination of iron(III) by chloride is neglected in the treatment of data since the used value of $K_h = 1.65 \times 10^{-3}$ M was determined in perchlorate media by Milburn and Vosburgh.²³ However it cannot influence the conclusions made in this paper, because all equilibrium quotients were determined under the same conditions (1 M chloride).

The involvement of amino group in the coordination to iron(III) may be expected only with glycinehydroxamic acid since the quaternary ammonium nitrogen of betaine hydroxamic acid offers no electron pair which could be donated to iron(III). Therefore, acet-, and betaine hydroxamic acids are bonded to iron(III) via the formation of five-membered rings, while the amino group of glycinehydroxamic acid offers the possibility of the formation of a six-membered ring in glycinehydroxamatoiron(III) complex. However, in nearly neutral and acidic solutions we did not find necessary to involve the doubly deprotonated glycinehydroxamate ion (G^-) as a coordinating ligand in order to obtain satisfactory values of Q_n in numerical treatment of our experimental data.

It is reasonable to expect that the shift in the coordination mode from a five-membered ring to the six-membered ring should be reflected in the change of physico-chemical properties of the complexes studied. The data from the Table can be hardly invoked to substantiate the different modes of coordination in the complexes studied. Namely, the data relating to the acet- and betainehydroxamatoiron(III) complexes which are known to follow the same mode of coordination, compare less favourably than the data belonging to the acet- and glycinehydroxamatoiron(III) complexes which might be expected to exhibit five-membered and six-membered rings, respectively.

It seems to us that the obtained differences for acet-, glycine-, and betaine-hydroxamatoiron(III) complexes can be reasonably rationali-

zed in terms of the electronic properties of the carbonyl carbon substituents represented by CH_3 — for acet-, $^+\text{NH}_3\text{CH}_2$ — for glycinium, and $^+\text{N}(\text{CH}_3)_3\text{CH}_2$ — for betaine hydroxamic acids. The influence of these substituents on the affinity of the hydroxamate ion for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ parallels the increasing inductive electron donor strength of the substituents and thereby increasing Q' values as it is seen in the Table. A similar trend is observed in the influence of electron properties of R on the pK_a values. The obtained results are in good agreement with the findings in the extensive studies of the effect of R on the stability of hydroxamatoiron(III) complexes¹² as well as on the pK_a values of hydroxamic acids.²⁴

It has been reported⁶ that the highest limiting λ_{max} value for the $\text{Fe}^{3+}/\text{GH}_2^+$ system is approximately 485 nm whereas for the Fe^{3+}/AH system λ_{max} reaches the value of 500 nm, suggesting that even in the glycinium complex, the mode of coordination of GH_2^+ is different from that of AH. According to our results (see Table) this suggestion is not necessarily valid because the absorption band of betainehydroxamatoiron(III) complex is positioned even at a lower wavelength than the band of glyciniumhydroxamatoiron(III) complex.

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SAŽETAK

Istraživanje ravnoteže pri kompleksiranju željezo(III)-iona s acet-, glicinium i betain-hidroksamatnim kiselinama

M. Biruš, N. Kujundžić, M. Pribanić i Z. Tabor

Kod kompleksacije željezo(III)-iona s acethidroksamatnom kiselinom (AH) dobiveni su slijedeći ravnotežni kvocijenti: $Q'_{1,A-} = [\text{FeA}^{2+}]/([\text{Fe}^{3+}][\text{A}^-] = 10,38$ (0,01) za monoacethidroksamatoželjezo(III)-kompleks; $Q'_{2,A-} = [\text{FeA}_2^+]/([\text{Fe}^{3+}][\text{A}^-]^2) = 19,16$ (0,14) za bisacethidroksamatoželjezo(III)-kompleks i $Q'_{3,A-} = [\text{FeA}_3]/([\text{Fe}^{3+}][\text{A}^-]^3) = 25,56$ (0,70) za trisacethidroksamatoželjezo(III)-kompleks.

Analogni ravnotežni kvocijenti dobiveni su za glicinij ($\text{G}(\text{H}^+)_2$) i betain hidroksamatnu kiselinu (BH^+):

$$\lg Q'_{1,\text{GH}} = [\text{Fe}(\text{GH})^{3+}]/([\text{Fe}^{3+}][\text{GH}]) = 7.77 \text{ (0.08),}$$

$$\lg Q'_{2,\text{GH}} = [\text{Fe}(\text{GH})_2^{3+}]/([\text{Fe}^{3+}][\text{GH}]^2) = 13.71 \text{ (0.08),}$$

$$\lg Q'_{3,\text{GH}} = [\text{Fe}(\text{GH})_3^{3+}]/([\text{Fe}^{3+}][\text{GH}]^3) = 17.63 \text{ (0.14),}$$

$$\lg Q'_{1,\text{B}} = [\text{FeB}^{3+}]/([\text{Fe}^{3+}][\text{B}]) = 7.28 \text{ (0.02),}$$

$$\lg Q'_{2,\text{B}} = [\text{FeB}_2^{3+}]/([\text{Fe}^{3+}][\text{B}]^2) = 13.41 \text{ (0.05), and}$$

$$\lg Q'_{3,\text{B}} = [\text{FeB}_3^{3+}]/([\text{Fe}^{3+}][\text{B}]^3) = 16.46 \text{ (0.24).}$$

Mjerenja su izvršena u otopini ionske jakosti 1,0 M (NaCl) pri 25 °C. Opisana je sinteza novog spoja — klorida betain hidroksamatne kiseline.