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Synthesis and characterization of a new 4-pyridone derivative and its complexation of iron(III)

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ABSTRACT

A new complexing and extracting agent, 3-hydroxy-2-methyl-1-(*p*-aminophenyl)-4-pyridone (HZ), was synthesized and its X-ray crystal structure was determined. The protonation constants of free HZ as well as stability constants of ferric mono-, bis- and tris(HZ) complexes in the aqueous solution ($I_c = 0.1 \text{ mol dm}^{-3}$ (NaCl), $t = 25 \,^{\circ}$ C) were determined using spectrophotometry and potentiometry. Distribution of HZ between the chloroform and aqueous phase was explored spectrophotometrically. The ligand investigated was shown to be a promising reagent for the extraction of iron(III) from aqueous solution to organic phase.

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1. Introduction

4-Pyridone derivatives are excellent complexing agents and therefore can be used for extraction and spectrophotometric determination of metal ions [1,2]. There has been a significant interest in these compounds as sequestering agents for various metal ions. A particular attention has been focused on their affinities towards Al(III) and Fe(III) as hydroxypyridones have been shown to be promising ligands for aluminium and iron chelation therapies [3–9]. Furthermore, some pyridone derivatives are inhibitors of bacterial enzymes and are potential antibacterial agents used for bacterial infections [10,11].

Numerous spectrophotometric methods, especially the more sensitive ones, are based on the formation of complexes between the chelating reagents and metal ions. So far we have shown that pyridone derivatives could be used for separation and spectrophotometric determination of different metals, even those with very similar chemical properties. The analytical application of a few 3-hydroxy-4-pyridones has been outlined in the previous papers [12–17].

In the work presented in this paper we have prepared another 4-pyridone derivative, 3-hydroxy-2-methyl-1-(*p*-aminophenyl)-4-pyridone (HZ), and explored its complexing abilities. Introduction of the amino group into the *para* position of the 4-pyridone

molecule can influence not only the protolytic properties of the compound, but also its behaviour as a ligand in complexation reactions with metal ions. Taking that into consideration, we have investigated in detail the structural properties of the new type of pyridone reagent, as well as its coordination reactions with Fe(III) in an aqueous solution. Preliminary investigations of the Fe(III) extraction with HZ in chloroform were also carried out.

2. Experimental

2.1. Synthesis of 3-hydroxy-2-methyl-1-(p-aminophenyl)-4-pyridone (HZ)

Starting compounds, *p*-phenylenediamine and 3-hydroxy-2methyl-4-pyrone (maltol, Sigma Aldrich) were purchased and used as received. All organic solvents were purified using standard procedures. Column chromatography was performed on Merck silica gel 60 (size 70–230 mesh ASTM) and TLC monitoring on Fluka silica gel (60 F 254) plates (0.25 mm). Visualization was effected by the use of UV light at 254 nm. NMR spectra were recorded using Bruker Avance (300 MHz) spectrometer. Melting point was determined with a Büchi B-40 apparatus. Elemental analysis was performed in the Microanalytical laboratory at the Ruđer Bošković Institute, Zagreb, Croatia.

3-Hydroxy-2-methyl-4-pyrone (5 g, 39.6 mmol) and *p*-phenylenediamine (8.5 g, 79.3 mmol) were mixed with water (15 ml) and stirred at 100 °C for 5 days under reflux. The reaction was monitored by TLC (5:2 ethyl acetate/methanol). The mixture was





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then evaporated and column chromatography on silica gel (5:2 ethyl acetate/methanol) gave HZ (3.6 g, 42%). The crude product was recrystallized from ethyl acetate. Colour: pale brown; mp: 202 °C; ¹H NMR (CD₃OD) δ = 2.11 (3H, s), 6.44 (1H, d, *J* = 7.19 Hz), 6.78 (2H, m), 7.03 (2H, m), 7.53 (1H, d, *J* = 7.19 Hz); ¹³C NMR (CD₃OD) δ = 13.78, 112.37, 115.98, 128.34, 132.73, 133.97, 139.89, 146.70, 150.88, 171.18. Elemental analysis: N 13.00%, C 66.60%, H 5.29%, calculated: C₁₂H₁₂N₂O₂, N 12.96%, C 66.68%, H 5.60%.

2.2. Single crystal X-ray diffraction of 3-hydroxy-2-methyl-1-(paminophenyl)-4-pyridone ethyl acetate solvate

The single crystal X-ray diffraction data of HZ-EtOAc (EtOAc = ethyl acetate) were collected by ω -scans on an Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated Mo K_{α} radiation. Data reduction was performed using the CrysAlis software package [18]. Solution, refinement and analysis of the structure was done using the programs integrated in the WinGX system [19]. The structure was solved by the direct method using SHELXS [20]. The refinement procedure was performed by the full-matrix least-squares method based on F^2 against all reflections using SHELXL97 [21]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier maps and refined isotropically. Geometrical calculations were done using PLATON [22]. Drawings of the structures were prepared using PLATON and MERCURY [23] programs. The crystallographic data are summarized in Table 1.

2.3. Reagents and apparatus for spectrophotometric measurements

Solutions of HZ were prepared by dissolving weight amount of the compound in the appropriate solvent. Its stock solution in 96% (v/v) ethanol was used for the spectrophotometric measurements in a water–ethanol mixture. Stock solution of the Fe(III) ion (about

Table 1

Crystallographic data for compound HZ-EtOAc.

Compound	HZ·EtOAc
Chemical formula	$C_{12}H_{12}N_2O_2 \cdot C_4H_8O_2$
M _r	304.34
Crystal colour, habit	Colourless, plate
Crystal size (mm ³)	$0.56 \times 0.30 \times 0.15$
Crystal system	Monoclinic
Space group	C2/c
Unit cell parameters	
a (Å)	12.4976(3)
b (Å)	16.0974(4)
<i>c</i> (Å)	15.6544(4)
α (°)	90
β(°)	99.873(3)
γ (°)	90
V (Å ³)	3102.69(14)
Ζ	8
D_{calc} (g cm ⁻³)	1.303
Temperature (K)	293
Wavelength (Å)	0.71073
$\mu ({\rm mm^{-1}})$	0.094
F(000)	1296
Number of unique data	2716
Number of data $[F_o \ge 4\sigma(F_o)]$	2185
Number of parameters	279
R_1^{a} , $[F_o \ge 4\sigma(F_o)]$	0.0328
wR ₂ ^b	0.0869
Goodness of fit on F^2 , S^c	1.05
Min. and max. electron density (e $Å^{-3}$)	-0.17, 0.23
$a R = \sum F_1 - F_1 / \sum F_1 $	

^a
$$R = \sum ||F_0| - |F_c|| \sum |F_0|.$$

^b $wR = \left[\sum (F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2\right]^{1/2}.$

^c
$$S = \sum_{n=1}^{l} \left[w(F_{o}^{2} - F_{c}^{2})^{2} / (N_{obs} - N_{param}) \right]^{1/2}$$

 $1\times 10^{-2}\ mol\ dm^{-3})$ was prepared by dissolving the required mass of FeCl₃ in 0.1 mol\ dm^{-3} HCl. The iron solution was standardized by titration with 0.05 mol\ dm^{-3} EDTA at pH 2.5 [24]. To prevent the formation of iron(III) hydrolysis species in water, working samples of lower concentrations of iron(III) were prepared daily by diluting aliquots of the stock solutions with water. All the reagents used were of analytical purity. Deionized water was used to prepare all aqueous solutions.



Scheme 1. Synthesis of HZ.



Fig. 1. An ORTEP drawing of HZ-EtOAc with displacement ellipsoids drawn at the 50% probability level.

Tuble 2								
Selected	bond	distances	and	bond	angles	(Å,	°)	for
HZ·EtOA	2.							

Table 2

01-C3	1.3593(15)
O2-C4	1.2719(16)
N1-C7	1.4516(16)
N2-C10	1.3800(18)
C2-C13	1.4951(19)
C2-N1-C7	121.53(10)
01-C3-C2	118.26(11)
02-C4-C3	121.65(12)
N1-C2-C13	118.74(11)
C9-C10-C11	118.13(12)



Fig. 2. Packing arrangement of HZ-EtOAc molecules displayed in the unit cell showing a double layer network of hydrogen bonds.

Geometry of intra- and intermolecular hydrogen bonds (Å, °) for HZ EtOAc.

$D{-}H{\cdot}{\cdot}{\cdot}A$	D–H (Å)	H⊷A (Å)	D· · ·A (Å)	D−H···A(°)
$\begin{array}{c} 01{-}H1{\cdots}02\\ 01{-}H1{\cdots}02^i\\ N2{-}H9{\cdots}02^{ii}\\ N2{-}H9{\cdots}03^{ii}\\ C13{-}H2{\cdots}01\\ C9{-}H6{\cdots}01^{iii}\\ C6{-}H20{\cdots}N2^{iv} \end{array}$	0.90(2) 0.90(2) 0.895(18) 0.870(17) 0.979(17) 0.958(15) 0.934(14)	2.471(19) 1.76(2) 2.108(18) 2.159(17) 2.415(17) 2.520(15) 2.585(14)	2.7747(14) 2.6255(13) 2.9759(17) 3.0172(17) 2.8131(18) 3.2459(16) 3.3529(17)	100.1(14) 159.4(18) 163.0(16) 169.0(15) 103.7(11) 132.6(12) 139.8(11)

 $\frac{1}{1-x}, y, -1/2-z.$

Table 3

^{iv} 1-x, y, 1/2 - z.

For spectrophotometric measurements the solutions of Fe(III)-HZ complexes in the aqueous phase were prepared as follows: to a known volume of the working iron solution a given amount of HZ solution and 96% (v/v) ethanol were added. pH of the solution was adjusted by addition of an appropriate amount of universal buffer solution, and the volume was made up to 5 cm³. Absorbance measurements were made in a wavelength range between 800 and 400 nm on a Varian Cary 3 spectrophotometer with 1.0-cm quartz cells. Acidity was measured with Radiometer PHM 85 Precision pH meter provided with a combined glass-Ag/AgCl electrode. The pH meter was calibrated by standard buffer solutions. A Griffin flask shaker with a time switch served for extraction.

Spectrophotometric–potentiometric titrations of the free HZ ligand and ferric HZ complexes were carried out by means of a Varian Cary 5 spectrometer equipped with a fibre-optic probe (Hellma) of 1 cm path length. In both cases the titrand solution $(V_0 = 50.0 \text{ cm}^3)$ was placed in the thermostated vessel $(t = (25.0 \pm 0.1) \,^{\circ}\text{C})$ and acidified by the addition of standardized HCl solution to the pH slightly below 2. The solution was then titrated by standardized NaOH, and the absorption spectra were recorded after the pH was stabilized. The ionic strength of both titrans and titrand was set to 0.1 mol dm⁻³ by the addition of NaCl. The pH values of the reaction mixtures were measured with a combined glass-Ag/AgCl electrode (Metrohm) and a Metrohm 827 pH lab pH meter. The electrode was calibrated by six standard buffers (Kemika) in the pH range 2–12. The pH-dependent spectral data were processed using the pHab program [25].

Iron concentrations in the aqueous phase after extraction were determined after suitable dilution by flame atomic absorption using a Unicam 919 AA spectrometer. Iron concentrations in the



Fig. 3. (a) UV spectra of aqueous HZ solutions recorded as a function of pH. $c(HZ) = 4.9 \times 10^{-5} \text{ mol dm}^{-3}$; $I_c = 0.1 \text{ mol dm}^{-3}$ (NaCl); l = 1 cm; $t = (25.0 \pm 0.1) \,^{\circ}\text{C}$. Spectra are corrected for dilution. (b) Dependence of absorbance at 313 nm on pH. experimental; --- calculated.

organic phase were calculated from the difference in the iron concentrations in the aqueous phase before and after extraction.

ⁱⁱ -1/2 + x, 1/2 - y, 1/2 + z.

x, -y, 1/2 + z.

Table 4

Successive protonation constants of free HZ and global stability constants of ferric HZ complexes in aqueous solution; $t = (25.0 \pm 0.1)$ °C; $I_c = 0.1$ mol dm⁻³ (NaCl).

Equilibrium ^a	$\log K_i^{ m H} \pm 3\sigma$	$\log\beta\pm3\sigma$
$\begin{array}{l} H^{*} + Z^{-} \rightleftharpoons HZ \\ H^{+} + HZ \rightleftharpoons H_{2}Z^{+} \\ H^{*} + H_{2}Z^{+} \rightleftharpoons H_{3}Z^{2+} \\ Fe^{3+} + H^{*} + Z^{-} \rightleftharpoons FeHZ^{3+} \\ Fe^{3+} + H^{*} + 2Z^{-} \rightleftharpoons FeHZ_{2}^{2+} \\ Fe^{3+} + 2H^{+} + 2Z^{-} \rightleftharpoons FeH_{2}Z_{2}^{3+} \\ Fe^{3+} + 3Z^{-} \rightleftharpoons FeZ_{3} \end{array}$	9.75 ± 0.01 5.60 ± 0.03 2.96 ± 0.01	19.53 ± 0.08 33.2 ± 0.1 37.1 ± 0.1 34.8 ± 0.1

^a Z denotes fully deprotonated HZ.



Fig. 4. Distribution diagram of the protonation species of HZ. $c(HZ) = 4.9 \times 10^{-5} \text{ mol dm}^{-3}$; $I_c = 0.1 \text{ mol dm}^{-3}$ (NaCl); solvent: water; t = 25.0 °C. Z denotes fully deprotonated HZ.

3. Results and discussion

3.1. Synthesis of HZ

The compound was prepared in a one-step synthesis from commercially available maltol and *p*-phenylenediamine as shown in Scheme 1. The mechanism of this reaction is already established and proceeds through the nucleophilic attack by a primary amine, followed by a pyrone ring opening, elimination of water and ring closure to give 4-pyridone [26]. Any factor that effects the electron density on the pyrone ring (especially next to the in-ring oxygen atom at C2 or C6) influences the nucleophilic attack step and therefore the whole conversion reaction [27]. Therefore, electronwithdrawing groups enhance the reactivity of the ring while electron-donating groups, such as a methyl group, have the opposite effect. This explains a rather moderate yield of this reaction.

3.2. Single crystal X-ray diffraction of HZ-EtOAc

The asymmetric unit consists of one HZ molecule and one ethyl acetate solvent molecule (C12H12N2O2·C4H8O2), Fig. 1. Relevant geometric parameters are listed in Table 2. The geometry of the pyridine skeleton is in good agreement with the values observed for N-benzyl-substituted and N-aryl-substituted analogues [28-31]. Different substituents in the para position of the disubstituted benzene molecule induce different deformation in the angular geometry of the benzene ring resulting in deviation of the endocyclic bond angle (σ) from the ideal value of 120°. Such deformation has been discussed by Domenicano et al. [32]. It was of interest to make an analysis using the latest structural data from the Cambridge Structural Database [33]. An analysis gave a mean value of σ of 118.62(3)° for 1111 fragments with the electron-donating -NH₂ substituent, 117.97(1)° for 9874 fragments with the -CH₃ substituent, and 119.75(1)° for 4331 fragments with the -OCH₃ substituent. The σ angle, C9–C10–C11, in the present structure amounts to 118.13(24)° which is close to the found mean value. A similar value of 118.19(19)° was found in a structurally related compound with the -NH₂ substituent [30]. In the structure of HZ the dihedral angle between the benzene and pyridinone rings is 76.74(6)°. An intramolecular hydrogen bond O1-H1...O2 of 2.7752(12) Å is found. In the crystal structure the molecules are linked by a pair of O–H···O hydrogen bonds O1···O2[1–x, y, -1/ 2 - z] of 2.6255(13) Å forming a dimer. This type of dimeric structure is also found in anhydrous and in hydrous 3-hydroxypyridin-4-one [28-31]. In addition, the molecules are linked by N-H--O intermolecular hydrogen bonds N2-H···O2[1-x, y, 1/2 - z] of 2.9759(17) Å and intermolecular hydrogen bonds involving the ethyl acetate molecule N2-H···O3[-1/2 + x, 1/2 - y, 1/2 + z] of 3.0172(17) Å (Fig. 2). Weak C-H···O and C-H···N hydrogen bonds are also found (Table 3).

3.3. Acido-basic properties of HZ in aqueous solution

The pH dependence of the UV absorption spectra of compound HZ is shown in Fig. 3a. By processing these data using pHab program three protonation constants were determined (Table 4). A rather good agreement between experimental and calculated absorbances at 313 nm can be seen in Fig. 3b.



Fig. 5. Determination of the complex composition by Job's method of continuous variation. $c(Fe(III)) + c(HZ) = \mathbf{0} 5 \times 10^{-4} \text{ mol dm}^{-3}; \mathbf{1} \times 10^{-3} \text{ mol dm}^{-3}.$



Fig. 6. (a) Vis spectra of ferric HZ complexes recorded as a function of pH. $c(\text{HZ}) = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$; $c(\text{Fe(III)}) = 1.32 \times 10^{-4} \text{ mol dm}^{-3}$; $l_c = 0.1 \text{ mol dm}^{-3}$ (NaCl); solvent: water; l = 1 cm; $t = (25.0 \pm 0.1) \,^{\circ}\text{C}$. Spectra are corrected for dilution. (b) Dependence of absorbance at 550 nm on pH. \blacksquare experimental; --- calculated.



Fig. 7. Calculated electronic spectra of ferric HZ complexes. Z denotes fully deprotonated HZ.

The protonation constants can be attributed by comparison with analogous compounds. By taking into account the $\log K^{H}$ values of 3-hydroxy-2-methyl-1-phenyl-4-pyridone (9.56 and



Fig. 8. Distribution diagram of ferric HZ complexes. $c(HZ) = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$; $c(Fe(III)) = 1.32 \times 10^{-4} \text{ mol dm}^{-3}$; $I_c = 0.1 \text{ mol dm}^{-3}$ (NaCl); solvent: water; t = 25.0 °C. *Z* denotes fully deprotonated HZ.

Table 5

The distribution of HZ between chloroform and aqueous phase of different content^a.

Composition of aqueous phase	D
(1) H ₂ O; (2) 0.1 M NaCl; (3) 0.1 M NaClO ₄ ; (4) 1 M NaCl; (5) 1 M NaClO ₄	100
(6) 0.09 M NaCl + 0.01 M HCl; (7) 0.09 M NaClO ₄ + 0.01 M HClO ₄ ; (8) 0.01 M HCl; (9) 0.01 M HClO ₄	10.1
(10) 0.9 M NaCl + 0.1 M HCl; (11) 0.9 M NaClO ₄ + 0.1 M HClO ₄	2.8
(12) 0.1 M HCl; (13) 0.1 M HClO ₄	1.9

^a The results are presented as mean values. The relative error is maximum 5%.

3.02) [34] and 3-hydroxy-2-methyl-1-(*p*-methylphenyl)-4-pyridone (9.56 and 3.16) [35], the first $(\log K_1^{\rm H} = 9.75)$ and the third $(\log K_3^{\rm H} = 2.96)$ protonation constants of HZ can be easily assigned to the protonation of hydroxyl oxygen and pyridone nitrogen, respectively. Therefore, the remaining constant, $\log K_2^{\rm H} = 5.60$, corresponds to the protonation of the amino group on the phenyl ring of HZ. Distribution diagram calculated for the experimental conditions used is presented in Fig. 4.

3.4. Iron(III) complexation studies

The chelating ability of HZ towards the Fe(III) ion was estimated by UV–Vis spectrophotometric measurements. When a solution of the reagent in ethanol was gradually added to a moderately acidic solution of FeCl₃, a violet colour appeared, which changed to orange-red and finally to orange-yellow. These observations indicated that in the water–ethanol solution iron(III) and HZ formed different complexes depending on the Fe(III):HZ concentration ratio. The colour changes were also found to be pH dependent.

With the aim of determining the composition of the complexes in the aqueous solution at different pH values, series of isomolar solutions containing FeCl₃ and HZ were prepared and their absorbances were measured at 472, 508 and 560 nm. The results obtained by the Job's method of continuous variation, indicated the existence of three complexes. At pH = 1 only a violet complex with the molar ratio of Fe(III) to HZ 1:1 was formed. Spectrophotometric measurements at pH = 2.5 and 5.0 indicated that the complexes with the Fe(III):HZ stoichiometries 1:2 and 1:3 prevailed in the solution, respectively (Fig. 5).

3.4.1. Stability constants of ferric HZ complexes

The visible absorption spectra recorded in the spectrophotometric-potentiometric titration of aqueous solution of ferric HZ



Fig. 9. (a) Dependence of the absorbance of extracted Fe(III)–HZ complex on pH in the aqueous phase. $c(HZ) = 1 \times 10^{-3} \text{ mol dm}^{-3}$; (b) absorption spectrum of extracted Fe(III)–HZ complex in chloroform at various HZ concentrations. $c(Fe(III)) = 1 \times 10^{-4} \text{ mol dm}^{-3}$.

complexes are shown in Fig. 6a. In the pH range between \approx 6.5 and \approx 5.2 the spectra exhibited bathochromic and hypochromic shifts, accompanied by the occurrence of a well defined isosbestic point at 488 nm. That clearly indicated the existence of an equilibrium between two spectrally distinct species. Another isosbestic point appeared at 520 nm in the 5.3–3.1 pH range. Below pH = 3.1 further decrease of absorbance and bathochromic shift were observed. It should be noted that above $pH\approx7$ a slight and slow precipitation (presumably of the uncharged ferric tris(HZ) complex) occurred which made spectrophotometric observations unreliable. The spectral data were analyzed by the pHab program. Among several chemically reasonable speciations used, the best fit (Fig. 6b) was obtained by assuming the presence of the following species in the reaction mixtures $FeHZ_2^{3+}$, $FeHZ_2^{2+}$, $FeH_2Z_2^{3+}$ and FeZ₃ (Z denotes fully deprotonated HZ). The calculated global stability constants of these complexes are listed in Table 4, and their charge-transfer absorption spectra are shown in Fig. 7.

In the ferric mono(HZ) complex (FeHZ³⁺) the proton is most likely bound to the amino group of the ligand. The same holds for the ferric bis(HZ) complexes FeHZ_2^{2+} and $\text{FeH}_2\text{Z}_2^{2+}$, whereas the coordinated ligands in the FeZ₃ complex are fully deprotonated. Distribution of the complex species as a function of pH is given in Fig. 8, and is qualitatively in agreement with the results obtained by Job's method (Fig. 5).

3.4.2. Studies of the extraction

The distribution of HZ between chloroform and aqueous solutions of different acidity and ionic strength was studied. The concentration of HZ in the aqueous phase was measured spectrophotometrically using standard concentration-absorbance curves established previously. These measurements were made at 288 nm. In the concentration range used the solutions of HZ obeyed Beer's law. The aqueous media were saturated with chloroform and then equilibrated with an equal volume of solutions of HZ in chloroform for 1 h. Three different concentrations of HZ were used and the same results were obtained if the initial concentration in chloroform was 5×10^{-5} , 1×10^{-4} or 1×10^{-3} mol dm⁻³ (Table 5). The distribution coefficient (D) was also independent of the mineral acid used in the aqueous phase as well as of the ionic strength. However, distribution of HZ depended on the acidity of aqueous phase. The increase of acidity resulted in lower distribution coefficient (Table 5) due to the formation of protonated cationic species which were better solvated with water in comparison to chloroform.

3.4.3. The extraction of iron(III) into the organic phase

Preliminary investigations were carried out to explore the possibility of the extraction of Fe(III)–HZ complexes into the organic phase. The results showed that pH about 6 is optimal for the extraction of iron(III) with HZ into chloroform (Fig. 9a). The complex species extracted from the aqueous solution was presumably the uncharged ferric tris(HZ) complex. The absorption spectra of Fe(III)–HZ complex extracted in chloroform with various HZ concentrations are shown in Fig. 9b. The extraction efficiency at optimal pH for the extraction of iron(III) was found to be about 95%.

4. Conclusion

A new 4-pyridone derivative was prepared and explored as iron(III) complexing agent. Its X-ray crystal structure was determined as an ethyl acetate solvate.

The values of protonation constants of free HZ were determined in aqueous solution ($I_c = 0.1 \text{ mol } \text{dm}^{-3}$ (NaCl), $t = 25 \,^{\circ}\text{C}$). The complexation of iron(III) by this ligand was investigated at different pH values and various Fe(III):HZ molar ratios. Global stability constants of ferric mono-, bis- and tris(HZ) complexes in aqueous solution ($I_c = 0.1 \text{ mol } \text{dm}^{-3}$ (NaCl), $t = 25 \,^{\circ}\text{C}$) were determined by means of the spectrophotometric–potentiometric titration.

The extraction of Fe(III)–HZ complexes from aqueous to organic phase was preliminary studied. The pH of aqueous phase optimal for extraction was assessed to be about 6, and the extraction efficiency for iron(III) at this pH was found to be about 95%.

Supplementary material

Supplementary crystallographic data sets for the structure of HZ-EtOAc are available through the Cambridge Structural Data base with deposition number 771960. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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