

Heteronuclear complex of *N*-(2-hydroxyethyl)-*N*-carboxymethylaminoaceto-hydroxamic acid with copper(II) and iron(III)

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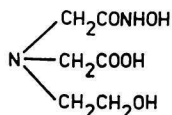
Received 29 July 1982

Paper published on the occasion of the 30th anniversary of the foundation of the Faculty of Pharmacy, Komenský University, Bratislava

The title compound forms in solutions with excess copper(II) ions a binuclear complex $\text{Cu}_2\text{H}_{-1}\text{L}^+$ and in solutions with both copper(II) and iron(III) ions it forms a ternary complex $\text{CuFeH}_{-1}\text{L}^{2+}$. In both cases the complex formation is followed by splitting off two hydrogen ions from one carboxylic functional group. Spectrophotometric characteristics and equilibrium constants of the individual complexes are presented.

Изучаемое вещество образует в растворах, содержащих избыточные ионы двухвалентной меди, двухъядерный комплекс $\text{Cu}_2\text{H}_{-1}\text{L}^+$ и в растворах, в которых содержатся одновременно ионы двухвалентной меди и трехвалентного железа, тройной комплекс $\text{CuFeH}_{-1}\text{L}^{2+}$. При этом в обоих случаях освобождаются два водородных иона из одной карбогидроксамовой функциональной группы. У отдельных комплексов приведены спектрофотометрические характеристики и константы равновесия.

As a part of study of aminopolycarboxylic acids analogues with hydroxamic functional group, *N*-(2-hydroxyethyl)-*N*-carboxymethylaminoaceto-hydroxamic acid (*I*) has been synthesized and its acid-base properties and chelate formation in solutions with excess ligand have been studied [1]. In the present paper the chelates formed by the above-mentioned reagent in solutions with excess copper(II) and iron(III) ions are examined.



I

Experimental

pH of solutions was measured by means of a PHM-64 pH-meter with a combined GK 2321C electrode (Radiometer); the system was calibrated prior to measurement by using standard buffers, pH 1.68 and 4.00. The pH was adjusted by adding 1 M-NaOH or 1 M-HClO₄ by means of an ABU-12 plunger microburette (Radiometer). The analytical concentration [H⁺] for the solutions with pH < 1.5 was calculated according to the added quantity of HClO₄, for other solutions it was calculated from the measured pH value by use of experimentally found value of $\gamma_{H^+} = 0.803$. All the measurements were performed in solutions with addition of NaClO₄, concentration $I = 0.1 \text{ mol dm}^{-3}$.

The spectrophotometric measurements were performed on Unicam SP 1700 recording spectrophotometer equipped with the data printout facility, using 4 cm and special 100 cm³ ($l = 3.48 \text{ cm}$) silica cells for simultaneous absorbance and pH measurements [2].

Fresh solutions of the compound (I) (for $I = 0.1 \text{ mol dm}^{-3}$ NaClO₄ and 20°C, $pK_{a1} = 5.69$, $pK_{a2} = 9.18$ [1]) were prepared daily by dissolving an exactly weighed quantity of the substance in water. Standard solutions of 0.1 mol dm^{-3} Cu(ClO₄)₂ and 0.1 mol dm^{-3} Fe(ClO₄)₃ were prepared from the respective chemicals (Fluka) and their exact concentrations were determined by chelatometry.

For the determination of the composition, charge, and equilibrium constants of the chelates the methods described in the former study [3] were used.

Results and discussion

System copper(II)—N-(2-hydroxyethyl)-N-carboxymethylamino-acetohydroxamic acid

In solutions with excess copper(II) ions two kinds of reaction products come to existence within the examined region of pH 0.8 to 4.8 (Fig. 1, curve 1). Graphical analysis of the ascending part of the A—pH curve proved that at pH 0.8 to 1.8 one hydrogen ion is splitted off during the complex formation and therefore the equilibrium (A) is possible to be assumed. The mole ratios method simultaneously proved that the chelate existing in solutions at pH 1.8 has a stoichiometry Cu:L = 1:1



The obtained molar absorption coefficients and equilibrium constants are referred to in Tables 1 and 2, respectively. These data indicate that the same complex — of the same composition, spectrophotometric properties, and stability — is formed in solutions with excess ligand as well [1].

Analysis of A—pH curves in the region pH 2.4 to 3.4 demonstrated that during a further chelate formation other two hydrogen ions are splitted off without any

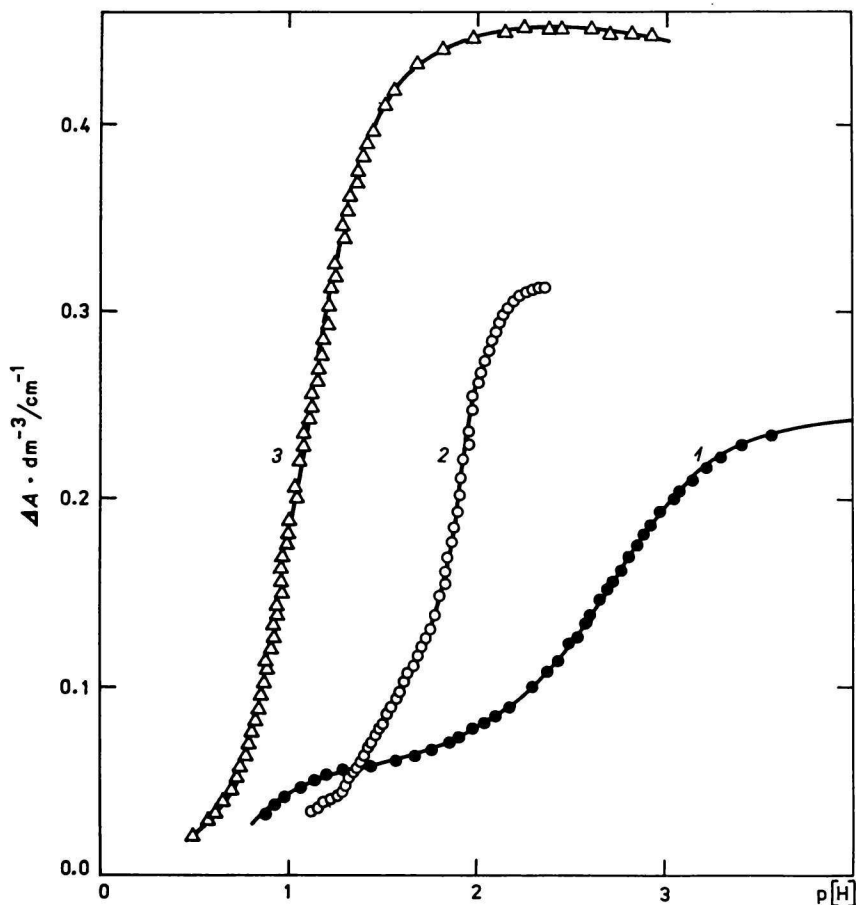


Fig. 1. A—pH curves of complexes.

Curve 1: system Cu(II)—I, $c_M = 20.0 \text{ mmol dm}^{-3}$, $c_L = 2.04 \text{ mmol dm}^{-3}$, 675 nm; curve 2: system Fe(III)—I, $c_M = 2.50 \text{ mmol dm}^{-3}$, $c_L = 0.214 \text{ mmol dm}^{-3}$, 490 nm; curve 3: system Cu(II)—Fe(III)—I, $c_{Cu} = 4.00 \text{ mmol dm}^{-3}$, $c_{Fe} = 3.98 \text{ mmol dm}^{-3}$, $c_L = 0.395 \text{ mmol dm}^{-3}$, 560 nm;
 $\Delta A = A - \epsilon_M \cdot c_M$.

ligand molecule being bound. The obtained electrophoretic mobility curve shows simultaneously that the chelate existing in solutions with excess copper(II) ions with respect to the ligand, and formed in the region pH 3.5 to 4.5 carries a positive charge (relative mobility value $U = +0.60$). In correspondence with these facts is a binuclear chelate $\text{Cu}_2\text{H}_{-1}\text{L}^+$ of theoretical mobility $U = +0.54$, the formation of which can be written as

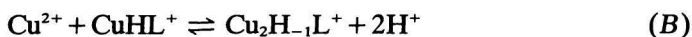


Table 1

Spectrophotometric characteristics of complexes

Complex	pH	λ nm	ϵ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	c_{Cu}	c_{Fe}	c_{L}	Note
				mmol dm^{-3}			
CuHL ⁺	1—2	650	27.3	20.0	—	1.89	a
		675	31.5	20.0	—	1.89	a
Cu ₂ H ₋₁ L ⁺	2—4	650	113.7	20.0	—	2.04	b
			113.9	20.0	—	1.91	c
		675	118.6	20.0	—	1.91	c
			120.4	9.09	—	0.974	d
FeL ⁺	1.2—1.8	490	765	—	2.49	0.294	e
			780	—	2.49	0.214	f
		560	—	2.49	0.214	f	
FeH ₋₁ L ⁰	1.9—2.3	490	1520	—	2.49	0.214	f
			1560	—	2.49	0.294	e
		560	1480	—	3.98	0.396	g
			1142	4.00	3.99	0.385	h
CuFeH ₋₁ L ²⁺	0.9—3	560	1128	4.00	3.99	0.426	i
			1127	2.11	1.97	0.177	k
			1137	4.21	0.494	0.210	l

a—l) Concentration ratios valid for Table 2.

Table 2

 Equilibrium constants of complexes
 $I = 0.1 \text{ mol dm}^{-3} \text{ NaClO}_4, 20^\circ\text{C}$

Equilibrium	Constant	log K
$[\text{CuHL}] \cdot [\text{H}] / [\text{Cu}] \cdot [\text{H}_2\text{L}]$	$*K_{1\text{H}}$	0.69 ^a
$[\text{CuHL}] / [\text{Cu}] \cdot [\text{HL}]$	$\beta_{1\text{H}}$	6.38
$[\text{Cu}_2\text{H}_{-1}\text{L}] \cdot [\text{H}]^2 / [\text{CuHL}] \cdot [\text{Cu}]$	$*K_{21}$	-3.79 ^b , -3.65 ^c
$[\text{FeL}] \cdot [\text{H}]^2 / [\text{Fe}] \cdot [\text{H}_2\text{L}]$	$*K_{12}$	-0.56 ^d , -0.48 ^e
$[\text{FeL}] / [\text{Fe}] \cdot [\text{L}]$	β_1	14.31
$[\text{FeH}_{-1}\text{L}] \cdot [\text{H}]^3 / [\text{Fe}] \cdot [\text{H}_2\text{L}]$	$*K_{13}$	-2.93 ^f , -2.90 ^g
$[\text{CuFeH}_{-1}\text{L}] \cdot [\text{H}]^3 / [\text{Cu}] \cdot [\text{Fe}] \cdot [\text{H}_2\text{L}]$	$*K_{111}$	1.42 ⁱ , 1.47 ^h , 1.40 ^k

For concentration ratios see Table 1.

The total of three detached hydrogen ions was verified also by the difference between the potentiometric acid-base titration of the reagent alone and of the reagent in the presence of excess copper(II) ions.

Thus in solution with excess of copper(II) ions also a hydrogen ion from the carbohydroxamic group nitrogen is splitted off, which cannot happen in aqueous medium in the absence of these ions; quite a different type of chelates is formed compared with solutions with excess ligand (complex CuL^0 , $\lambda_{\text{max}} = 660 \text{ nm}$, $\epsilon = 91.4$ [1]).

System iron(III)—N-(2-hydroxyethyl)-N-carboxymethylamino-acetohydroxamic acid

All the absorption curves of solutions with excess iron(III) ions exhibit in the region pH 1.3 to 2.5 an absorption maximum at 490 nm. Graphical analysis of the A —pH curve (Fig. 1, curve 2) proves the detachment of two hydrogen ions during the formation of a red reaction product in solutions with pH up to 1.9, according to eqn (C). In solutions of $\text{pH} > 1.9$ three protons are splitted off simultaneously during the red complex formation, which can be written as equilibrium (D)



Obviously the third detached hydrogen ion (eqn (D)) originates from the hydroxyethyl group; according to the electrophoretic measurements the complex carries a charge zero. In aqueous medium, however, neither the hydroxo complex formation can be excluded. Spectral properties and equilibrium constants are shown in Tables 1 and 2; a partial hydrolysis of iron(III) ions must have been regarded to in the calculations ($K_{\text{H}} = [\text{Fe}(\text{OH})] \cdot [\text{H}]/[\text{Fe}]$ for $I = 0.1$, $\log K_{\text{H}} = -2.63$ [4]). The properties of mentioned complexes indicate that in solutions with excess iron(III) ions complexes of different structural arrangement and thus also stability are formed than in solutions with excess ligand though in all cases the ratio is $\text{Fe}:\text{L} = 1:1$.

System Cu(II)—Fe(III)—N-(2-hydroxyethyl)-N-carboxymethyl-aminoacetohydroxamic acid

Having studied complexes of the presented reagent we found out that in solutions in which both copper(II) and iron(III) ions are present in excess with respect to the ligand, a qualitatively new complex is formed the properties of which differ essentially from those of Cu(II)—I and Fe(III)—I complexes (Fig. 2). The formation of this violet reaction product was examined in the region of pH 0.6 to 3.1 in solutions with various excess of both metal ions, the $c_{\text{M}}/c_{\text{L}}$ ratio being 1 to 12, and all absorption curves showed maximum lying near 560 nm. Also the course of the evaluated A —pH curve (Fig. 1, curve 3) indicates the formation of a single reaction product.

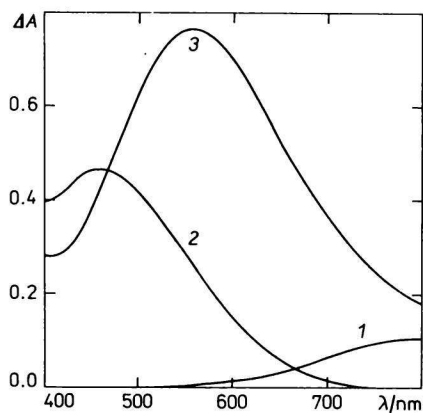


Fig. 2. Absorption curves of complexes.
 $c_{\text{Cu}} = 2.00 \text{ mmol dm}^{-3}$, $c_{\text{Fe}} = 1.97 \text{ mmol dm}^{-3}$,
 $c_{\text{L}} = 0.210 \text{ mmol dm}^{-3}$, pH 1.68, $l = 4.00 \text{ cm}$.
 Curve 1: system Cu(II)—I; curve 2: system
 Fe(III)—I; curve 3: system
 Cu(II)—Fe(III)—I.

The composition of resulting complex was studied using the mole ratios method, adding stepwise iron(III) ions to the solution of the reagent with excess copper(II) ions, the pH being held constant. As curve 1 in Fig. 3 demonstrates, the complex is under these conditions completely formed as early as the iron(III) ions are present in a twofold excess with respect to the reagent (with $c_{\text{Cu}}/c_{\text{L}} = 11.8$), and the iron-to-ligand ratio is Fe:L=1:1. Curves 2 and 3 (Fig. 3) were obtained on measuring a series of solutions with constant concentration of the reagent and

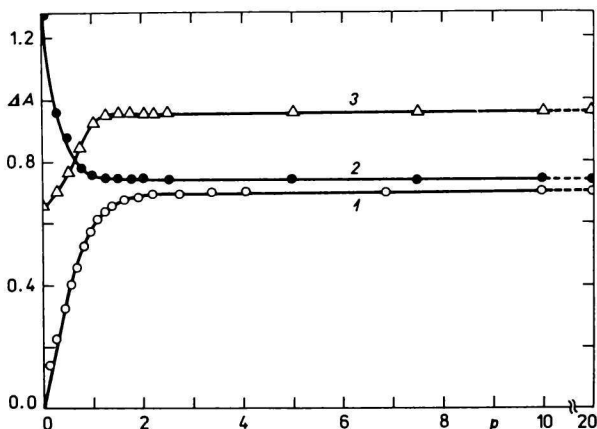


Fig. 3. Mole ratios of the system Cu(II)—Fe(III)—I.

pH 2.80; curve 1: $p = c_{\text{Fe}}/c_{\text{L}}$, $c_{\text{Cu}}/c_{\text{L}} = 11.8$, $c_{\text{Cu}} = 2.11 \text{ mmol dm}^{-3}$, $c_{\text{L}} = 0.178 \text{ mmol dm}^{-3}$, 560 nm, $l = 3.48 \text{ cm}$; curves 2 and 3: $p = c_{\text{Cu}}/c_{\text{L}}$, $c_{\text{Fe}}/c_{\text{L}} = 2.35$, $c_{\text{Fe}} = 0.494 \text{ mmol dm}^{-3}$, $c_{\text{L}} = 0.210 \text{ mmol dm}^{-3}$, $l = 4.00 \text{ cm}$; curve 2: 490 nm, curve 3: 560 nm.

increasing concentration of the copper(II) ions; the pH of these solutions was being held constant and a constant quantity of iron(III) ions was added to them. Also their course confirms that at given conditions ($c_{\text{Fe}}/c_{\text{L}} = 2.35$, pH 2.80), copper can be found in the examined complex in the ratio $M:L = 1:1$. It means that the stoichiometry of the ternary chelate is $\text{Cu:Fe:L} = 1:1:1$.

The results of paper electrophoresis in solutions with excess metal ions unambiguously confirm that the considered ternary complex carries a +2 charge (for $\text{CuFeH}_-1\text{L}^{2+}$ relative mobility: theoretical $U = 1.09$; experimental $U = 1.1$ at pH 2.56).

The supposed equilibrium of the ternary chelate formation according to (E) is confirmed by the graphical analysis of the A —pH curves (Fig. 4) according to the relation (1), which is linear for the equilibrium at the simultaneous detachment of three hydrogen ions

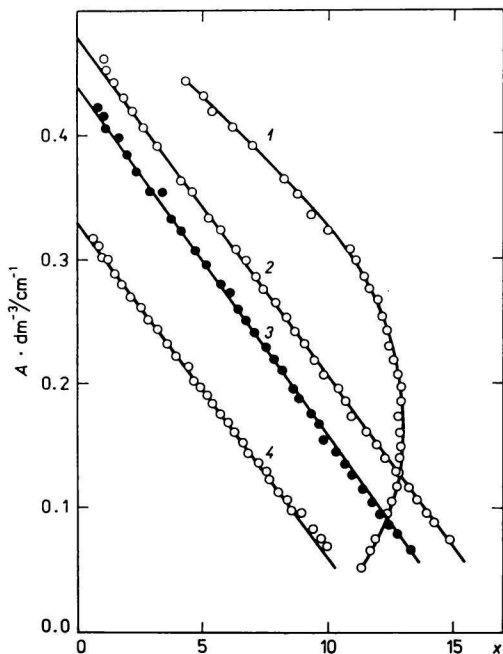


Fig. 4. Graphical analysis of the A —pH curve of the system Cu(II)—Fe(III)—I .

$c_{\text{Cu}} = 4.00 \text{ mmol dm}^{-3}$, $c_{\text{Fe}} = 3.99 \text{ mmol dm}^{-3}$, $c_{\text{L}} = 0.426 \text{ mmol dm}^{-3}$, $\text{p[H]} = 0.84$ to 1.50 .

Curve 1: $x = \Delta A \cdot [\text{H}]^2 \cdot Z_{\text{OH}} \cdot 10^4$, 560 nm; curve 2: $x = \Delta A \cdot [\text{H}]^3 \cdot Z_{\text{OH}} \cdot 10^5$, 560 nm; curve 3:

$x = \Delta A \cdot [\text{H}]^3 \cdot Z_{\text{OH}} \cdot 10^5$, 600 nm; curve 4: $x = \Delta A \cdot [\text{H}]^3 \cdot Z_{\text{OH}} \cdot 10^5$, 650 nm.

$$A = \varepsilon_{111} \cdot c_L - \Delta A \cdot [H]^q \cdot Z_{OH} / K_{111} \cdot c_{Cu} \cdot c_{Fe} \quad (1)$$

$$Z_{OH} = 1 + K_H/[H]$$

Formation of no binary "intermediate" can be noticed, as it happens in the case of the similar *N*-carboxymethylaminoacetohydroxamic acid chelate formation [5]. The dependence (1) is linear in a wide region $p[H]$ 0.84 to 1.50, which means 11–92 % complex formation, and in the measured range from 560 to 650 nm, as the correspondence of the calculated values of the equilibrium constant, referred to in Table 3, well testifies. Also for equimolar solutions ($c_{Cu} = c_{Fe} = c_L$) the

Table 3

Calculation of the equilibrium constant of the equilibrium (E) from individual points of the A—pH curve

$$c_{Cu} = 4.00 \text{ mmol dm}^{-3}, c_{Fe} = 3.99 \text{ mmol dm}^{-3}, c_L = 0.426 \text{ mmol dm}^{-3}, p[H] 0.839 \text{ to } 1.502$$

Value		λ/nm		
		560	600	650
Number of results	<i>n</i>	32	32	31
Mean	$\log * K_{111}$	1.409	1.401	1.422
Standard deviation	<i>s</i>	0.0085	0.0076	0.0126
Relative s. d.	<i>s_r</i> , %	0.060	0.54	0.89
Confidence interval ^a	$L_{1,2} \pm$	0.004	0.004	0.006

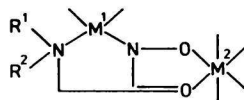
a) For level of significance 0.99.

graphical analysis is, according to the relation (2), linear in its whole range supposing the chelate formation according to eqn (E)

$$A = f \{ \sqrt{(\Delta A \cdot H^q)} \} \quad (2)$$

Thus in solutions containing both copper(II) and iron(III) ions a ternary binuclear chelate with two different central ions is formed. At the same time two hydrogen ions are splitted off from one carbohydroxamic functional group, which reminds of the binuclear copper(II) chelate formation. This hypothesis is confirmed by the fact that an *N*-methylhydroxylamine derivative, the *N*-(2-hydroxyethyl)-*N*-carboxymethylaminoaceto-*N'*-methylhydroxamic acid, results in no violet ternary chelate under similar conditions. Nor the aliphatic and aromatic hydroxamic acids, not derived from amino acids, will detach the two protons from one hydroxamic group during the chelate formation and they will not give similar ternary chelates, as it was observed. Obviously, the ternary chelates formation is conditioned by the

presence of the $>N-CH_2CONH-OH$ functional arrangement. Qualitative reactions proved that the ternary heteronuclear chelates formation runs at presence of other cations too; their structural arrangement can be in general presented as



References

1. Majer, J., Karlíček, R., and Kopecká, B., *Collect. Czech. Chem. Commun.* 35, 1066 (1970).
2. Karlíček, R., *Collect. Czech. Chem. Commun.* 40, 3825 (1975).
3. Karlíček, R. and Jokl, V., *Chem. Zvesti* 35, 65 (1981).
4. Sillén, L. G. and Martell, A. E., *Stability Constants of Metal Complexes*. Chemical Society Monograph, London, 1965.
5. Karlíček, R., Polášek, M., and Jokl, V., *Collect. Czech. Chem. Commun.* 16, 1107 (1981).

Translated by H. Marešová