TERNARY COMPLEXES
OF N-CARBOXYMETHYLAMINOACETOHYDROXAMIC ACID

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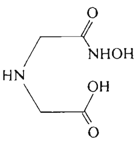
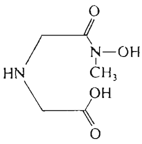
The formation of N-carboxymethylaminoacetohydroxamic acid complexes in solutions with excess copper(II) or iron(III) ions or both of them was studied. In the presence of Cu(II), the binuclear complex $Cu_2H_{-1}L^+$ was identified; in the ternary system, the complex $CuFeH_{-1}L^+$ was found. This complex formation is necessarily associated with the ligand structure $>N—CH_2.$ .CO—NHOH and with a new property of hydroxamic acids of this type — detachment of two hydrogen ions from one carbohydroxamic functional group.

As part of a systematic study of chelones involving a hydroxamic functional group[1], N-carboxymethylaminoacetohydroxamic acid (*I*) has been synthesized and its acid-base and complexing properties have been studied[2]. In solutions containing the ligand in excess with respect to Cu(II) or Fe(III), only complexes with the ratio M : L = 1 : 1 have been identified.

In the present work, the behaviour of the reagent was investigated in solutions in which the metal ions are present in excess, where complexes of other composition and structural arrangement occur. The results are compared with the complexing properties of the N-methylhydroxylamine derivative analogue of the reagent, *viz.* N-carboxymethylaminoaceto-N'-methylhydroxamic acid (*II*), and with those of a compound not involving an amine nitrogen atom, *viz.* N-hydroxyglutaramic acid (*III*).



I



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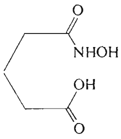


III

EXPERIMENTAL

Apparatus and Chemicals

The spectrophotometric measurements were performed on a Unicam SP 1700 recording spectrophotometer equipped with the data printout facility, using 1 cm and special 100 ml silica cells for simultaneous absorbance and pH measurements[3]. The pH was measured by means of a PHM-64 pH-meter with a combined GK 2321 C electrode (Radiometer, Copenhagen); the system was calibrated prior to use by using standard buffers, pH 1·68, 4·00, 7·43, and 9·22. The pH was adjusted by adding 0·1M or 1M-NaOH or $HClO_4$ by means of an ABU-12 plunger microburette (Radiometer, Copenhagen). All measurements were carried out in solutions with ionic strength $I = 0{\cdot}1$ ($NaClO_4$). For the calculation of the concentration constants, the experimental value of $\gamma_{H^+} = 0{\cdot}803$ was used.

The synthesis and properties of N-carboxymethylaminoacetohydroxamic acid have been described[2]; the experimental values of the dissociation constants at $I = 0{\cdot}1$ ($NaClO_4$) and $t = 20°C$ are $pK_{a0} = 1{\cdot}75$, $pK_{a1} = 6{\cdot}99$, and $pK_{a2} = 9{\cdot}09$.

Fresh solutions of the acid were prepared daily by dissolving a weighed quantity of the chemical in water; solutions of N-carboxymethylaminoaceto-N'-methylhydroxamic acid[4] and of N-hydroxyglutaramic acid[5] were prepared likewise. Standard solutions of 0·1M-$Cu(ClO_4)_2$ and 0·1M-$Fe(ClO_4)_3$ were prepared from the respective chemicals (Fluka, Buchs) and their concentrations were determined chelatometrically.

The composition of the complexes was determined by applying the modified molar ratios method[6] and its graphical analysis. The basic relations and transformations used for the determinations of the molar absorptivities, number of protons detached during the reaction, and equilibrium constants from the spectrophotometric data have been published[1,7]. For the determination of the charge of the complexes, paper electrophoresis was employed[8]; for this, chromatographic paper Whatman 1 was saturated with 0·05M solution of the metal perchlorate whose pH was adjusted as necessary, 2 μl of solution with $c_M = 0{\cdot}1$ mol l^{-1} and $c_L = 0{\cdot}05$ mol . l^{-1} was applied, and the electrophoresis was carried out at 200 V for 2 h.

RESULTS AND DISCUSSION

System Copper(II)–N-*Carboxymethylaminoacetohydroxamic Acid*

The formation of the copper(II) complexes was examined in the region pH 1·96–5·16 in solutions with ten- to fortyfold excess of Cu(II) relative to compound *I*. The absorption curves exhibit a single absorption band with the maximum at 660 nm. As the *A*-pH curves demonstrate (Fig. 1), a green-blue species is produced, its formation being complete at pH 3·5. Graphical analysis of the ascending parts of the *A*-pH curves revealed that at pH 2–2·4, one hydrogen ion is detached during the complex formation wtth the predominantly nonionized reagent; thus the equilibrium (*A*) can be assumed to take place in this region:

$$Cu^{2+} + H_2L \rightleftharpoons CuHL^+ + H^+ . \qquad (A)$$

The values of molar absorptivities and equilibrium constants are given in Tables I and II, respectively.

The data obtained indicate that the same complex – of the same composition, spectrophotometric properties, and stability – is formed in solutions with excess copper(II) ions and in solutions with excess ligand[2].

Graphical analysis of the A-pH curves in the region pH 2·75 – 3·6 evidenced the formation of another complex with simultaneous detachment of two hydrogen

TABLE I

Spectrophotometric Data of Complexes of N-Carboxymethylaminoacetohydroxamic Acid Forming in Solutions with Excess Cu(II) and Fe(III)

Complex	Optimum pH region	λ_{max} nm	$c_{Cu}{}^a$	$c_{Fe}{}^a$	$c_L{}^b$	ε l mol^{-1} cm^{-1}
$CuHL^+$	2·0—2·4	660	19·4		19·9	42·7
			77·8		19·1	43·0
$Cu_2H_{-1}L^+$	2·95—3·6	660	19·4		19·9	125·8
			77·8		19·1	125·9
FeL^+	1·5—2·05	490		2·35	2·46	706
$FeHL^{2+}$	1·5	490	1·94	1·88	2·37	466
$CuFeH_{-1}L^{2+}$	1·75—3·0	560	1·94	1·88	2·37	1 088
			1·94	0·47	1·92	1 085
			5·26	4·94	4·93	1 080

[a] Concentration in 10^{-3} mol l^{-1}; [b] concentration in 10^{-4} mol l^{-1}.

TABLE II

Equilibrium Constants of Complexes of N-Carboxymethylaminoacetohydroxamic Acid $I = 0·1$ ($NaClO_4$), $t = 20°C$.

Equilibrium	Constant	log K
[CuHL] [H]/[Cu] [H_2L]	$^*K_{1H}$	—0·26[a], —0·35[b]
[CuHL]/[Cu] [HL]	β_{1H}	6·69[a]
[$Cu_2H_{-1}L$] $[H]^2$/[Cu] [CuHL]	$^*K_{2H}$	—4·32[a], —4·31[b]
[FeL] $[H]^2$/[Fe] [H_2L]	$^*K_{12}$	—0·03[c]
[FeL] $[H]^3$/[Fe] [H_3L]	$^*K_{13}$	—1·78[c]
[FeL]/[Fe] [L]	β_1	16·05[c]
[FeHL] $[H]^2$/[Fe] [H_3L]	$^*K_{1H}$	0·06[d]
[FeHL]/[Fe] [HL]	β_{1H}	8·80[d]
[$CuFeH_{-1}L$] $[H]^2$/[FeHL] [Cu]	$^*K_{111}$	—1·07[d]

Concentrations (mol l^{-1}): [a] c_{Cu}: 1·94 . 10^{-2}, c_L: 1·99 . 10^{-3}; [b] c_{Cu}: 7·78 . 10^{-2}, c_L: 1·91 . 10^{-3}; c_{Fe}: 2·35 . 10^{-3}, c_L: 2·46 . 10^{-4}; [d] c_{Cu}: 5·26 . 10^{-3}, c_{Fe}: 4·94 . 10^{-3}, c_L: 4·93 . 10^{-4}.

ions; the transformation set up assuming that only one hydrogen ion is released in this region is not rectilinear.

As the relative mobility was found by paper electrophoresis to be $U = +0{\cdot}65$, the complex must carry a positive charge; consistent with this is the binuclear complex $Cu_2H_{-1}L^+$ with the theoretical mobility $U = +0{\cdot}60$. The above formula is to indicate that the complex formation is accompanied by detachment of a hydrogen ion from the nitrogen atom of the hydroxamic functional group. This detachment of two hydrogen ions from one hydroxamic functional group has not been so far reported. The total number of detached hydrogen ions was verified also based on the difference between the potentiometric neutralization titrations of the ligand I alone and of the ligand I in the presence of excess copper(II) ions. The complex formation can be written as

$$CuHL^+ + Cu^{2+} \rightleftharpoons Cu_2H_{-1}L^+ + 2\,H^+ . \qquad (B)$$

Thus in solutions with excess copper ions a quite different type of complex is formed (Table I) than in solutions with excess ligand in the corresponding pH region (the CuL^0 complex, λ_{max} 650 nm, $\varepsilon = 72{\cdot}0\,l\,mol^{-1}\,cm^{-1}$) (ref.[2]). Formation of this binuclear complex with simultaneous detachment of two hydrogen ions from one hydroxamic functional group is conditioned by the occurrence of *a*) an NHOH group;

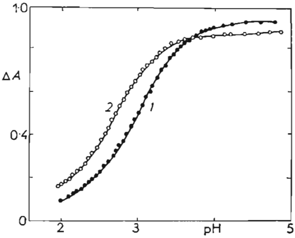


FIG. 1

A-pH Curves of System Cu(II)–N-Carboxymethylaminoacetohydroxamic Acid

λ 660 nm, $l = 3{\cdot}48$ cm; concentrations (mol . l^{-1}): *1* c_{Cu}: $1{\cdot}94 . 10^{-2}$, c_L: $1{\cdot}99 . 10^{-3}$; *2* c_{Cu}: $7{\cdot}78 . 10^{-2}$, c_L: $1{\cdot}91 . 10^{-3}$.

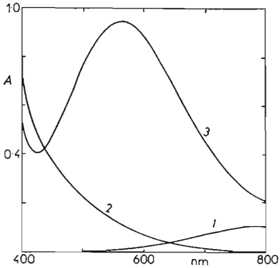


FIG. 2

Absorption Curves of Systems Metal–N-Carboxymethylaminoacetohydroxamic Acid

System: *1* Cu(II)–*I*, *2* Fe(III)–*I*, *3* Cu–Fe–*I*; concentrations (mol l^{-1}): c_{Cu}: $1{\cdot}94 . 10^{-3}$, c_{Fe}: $2{\cdot}04 . 10^{-3}$, c_L: $1{\cdot}98 . 10^{-4}$. pH 2·70, $l = 4$ cm.

with the corresponding N-methylhydroxylamine derivative, *viz.* N-carboxymethylaminoaceto-N'-methylhydroxamic acid (*II*), no formation of an analogous binuclear chelate has been observed[4], and *b*) an additional donor atom (an amine nitrogen atom in this case), capable of closing the chelate ring with copper bonded to the hydroxamic group nitrogen; detachment of two hydrogen atoms of the hydroxamic functional group has not been observed in the case of the reagent not containing an amine type nitrogen, *viz.* N-hydroxyglutaramic acid (*III*) or of other aliphatic or aromatic hydroxamic acids.

System Iron(III)*-Carboxymethylaminoacetohydroxamic Acid*

All the absorption curves of solutions containing iron(III) ions in a tenfold excess with respect to the ligand display in the region pH 1·5 – 2·05 an absorption maximum at 490 nm. Graphical analysis of the *A*-pH curve points to the formation of a red reaction product, associated with the detachment of three or two hydrogen ions according to the equations

$$Fe^{3+} + H_3L^+ \rightleftharpoons FeL^+ + 3\,H^+ \qquad (C)$$

$$Fe^{3+} + H_2L \rightleftharpoons FeL^+ + 2\,H^+ . \qquad (D)$$

The partial hydrolysis of iron ions ($K_H = [Fe(OH)]/[H][Fe]$, $\log K_H = -2{\cdot}63$ for $I = 0{\cdot}1$, ref.[9]) has been taken into account in the calculation. Spectral and stability data of the iron(III) complex indicate unambiguously that in this case the same complex is formed in solutions with excess ligand and in solutions with excess iron(III) ions[2], without detachment of two hydrogen ions from a hydroxamic group.

System Copper(II)*-Iron*(III)*-N-Carboxymethylaminoacetohydroxamic Acid*

The data obtained indicate that in solutions in which both copper(II) and iron(III) ions are in excess with respect to the ligand, a qualitatively new complex is formed whose properties differ essentially from those of the Cu(II)-*I* and Fe(III)-*I* complexes (Fig. 2).

The formation of this complex was examined in the region of pH 1 – 3 in solutions with various c_M/c_L ratios for the two metal ions, ranging from 1 to 10. Some of the absorption curves are shown in Fig. 3. Solutions with pH < 1·5 are red coloured, their absorption maximum lies near 490 nm. This reaction product is formed particularly in solutions with a higher excess of iron(III) ions. As follows from the evaluated *A*-pH curves (Fig. 4), another violet product with the absorption at about 560 nm is formed at pH > 1·5.

The composition of the complex was determined by using the molar ratios method, adding iron(III) ions to a solution of the reagent with a tenfold excess of copper(II) ions, the pH being held constant. As the curve *1* in Fig. 5 demonstrates, the complex is completely formed if iron(III) ions are present in a twofold excess with respect to the reagent (with $c_{Cu}/c_L = 10$), and the iron-to-ligand ratio is 1 : 1. Curve 2 in Fig. 5 was obtained on measuring a series of solutions of constant pH with constant concentration of the reagent I and Fe(III) and with increasing concentration of Cu(II) ions. Since the shape of the dependence does not enable the molar ratio to be red directly, graphical analysis had to be performed; it was linear only for $n = 1$ (curve *3*). Thus the constituents of the ternary chelate are present in the ratio Cu : Fe : L = 1 : 1 : 1. Results of graphical analysis of the *A*-pH curves confirm that at pH $<1{\cdot}5$ the complex is formed with simultaneous detachment of two hydrogen ions. The absorption curves of the ternary system at pH $<1{\cdot}5$ exhibit an absorption maximum at 490 nm, corresponding to the iron(III) chelate. This indicates that in the Cu–Fe–*I* ternary chelate, the equilibrium

$$Fe^{3+} + H_3L^+ \rightleftharpoons FeHL^{2+} + 2\,H^+ \qquad (E)$$

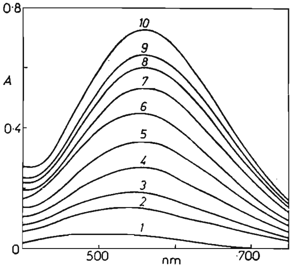


FIG. 3

Absorption Curves of System Cu(II)–Fe(III)–N-Carboxymethylaminoacetohydroxamic Acid

Concentrations (mol l^{-1}): c_{Cu}: $1{\cdot}94 . 10^{-3}$, c_{Fe}: $4{\cdot}70 . 10^{-4}$, c_L: $1{\cdot}92 . 10^{-4}$; $l = 3{\cdot}48$ cm; pH: *1* 1·50, *2* 1·70, *3* 1·80, *4* 1·89, *5* 2·03, *6* 2·11, *7* 2·22, *8* 2·32, *9* 2·39, *10* 2·81.

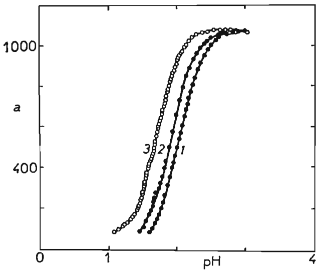


FIG. 4

A-pH Curves of Systems Cu(II)–Fe(III)–N-Carboxymethylaminoacetohydroxamic Acid

λ 560 nm; $a = A/c_L . l$. Concentrations (mol l^{-1}): *1* c_{Cu}: $1{\cdot}94 . 10^{-3}$, c_{Fe}- $4{\cdot}70 . 10^{-4}$, c_L: $1{\cdot}92 . 10^{-4}$; *2* c_{Cu}: $1{\cdot}94 . 10^{-3}$, c_{Fe}: $1{\cdot}88 . 10^{-3}$, c_L: $2{\cdot}37 . 10^{-4}$; *3* c_{Cu}: $5{\cdot}26 . 10^{-3}$, c_{Fe}: $4{\cdot}94 . 10^{-3}$, c_L: $4{\cdot}93 . 10^{-4}$.

is established first. A complex of this composition and these properties has been observed also in solutions with excess ligand with respect to Fe(III) ($FeHL^{2+}$, λ_{max} 490 nm, $\log \beta_{1H} = 8{\cdot}53$, ref.[2]); in solutions in which only iron(III) ions were in excess, however, this "intermediate" of the FeL^+ complex formation could not be traced.

Results of graphical analysis of the A-pH curves for solutions with pH > 1·5 also indicate the detachment of two hydrogen ions during the formation of the complex. At the same time, the results of electrophoresis of solutions with excess metal ions show unequivocally that the ternary complex in question possesses a +2 chargy (for $CuFeH_{-1}L^{2+}$, $U_{theor} = 1{\cdot}2$, $U_{exp} = 1{\cdot}1$). Based on these facts, the ternare complex formation can be represented by the equation

$$FeHL^{2+} + Cu^{2+} \rightleftharpoons CuFeH_{-1}L^{2+} + 2\,H^+ . \qquad (F)$$

This complex is formed in solutions with pH > 1·5 only if the copper(II) ions are added to the ligand solution prior to Fe(III); if the ions are added in the reverse order, the violet reaction product does not appear. This is a consequence of the stability of the "normal" iron(III) complex FeL^+, where the amine nitrogen atom takes part in the coordination; the hydroxamic group acts as a one-donor oxy group only, one hydrogen atom being released from it during the complex formation[2]. Owing to the high stability of this ferric complex, structural rearrangement

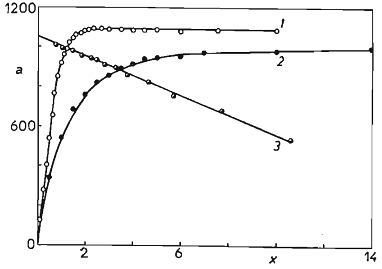


FIG. 5

Molar Ratios in Systems Cu(II)–Fe(III)–N-Carboxymethylaminoacetohydroxamic Acid

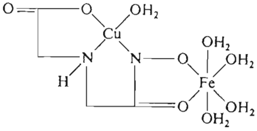
λ 560 nm; $a = \Delta A/c_L \,.\, l$. Curves 1 $x = c_{Fe}/c_L$, pH 2·8, $c_{Cu} = 1{\cdot}94 \,.\, 10^{-3}$ mol . l^{-1}, $c_L = 1{\cdot}87 \,.\, 10^{-4}$ mol l^{-1}; 2 $x = c_{Cu}/c_L$, pH 2·7, $c_{Fe} = 4{\cdot}94 \,.\, 10^{-4}$ mol . l^{-1}, $c_L = 1{\cdot}98 \,.\, 10^{-4}$ mol . l^{-1}; 3 graphical analysis of the dependence 2, $x = \Delta A/(c_{Cu} - \Delta A/\varepsilon_2) \,.\, 10^2$.

and formation of the ternary chelate cannot occur on addition of copper(II) ions even if the latter are present in excess. As only the carbohydroxamic group takes part in the formation of the $FeHL^{2+}$ or $CuHL^{+}$ hydrogen complexes, the non-coordinated amine nitrogen can participate in the coordination of the added Cu(II) ions resulting in the formation of the binuclear complexes.

Thus, in solutions containing simultaneously excess copper(II) and iron(III) ions, a ternary binuclear complex involving two different cations is formed. We suggest that, analogously as in the case of the binuclear copper(II) complex, a hydrogen ion is released from the amide group. This phenomenon has not been so far observed, but it is analogous to the situation with some amide group-containing complexing agents, such as N,N-diglycyl ethylenediamine[10] or diglycyl ethylenediaminetetraacetic acid[11], where a hydrogen atom is detached from the amide group during the coordination of copper(II). The acidity of the hydrogen of the amides as well as of the N-hydroxyamides studied is so low that in aqueous solutions where metal-ions are absent, the hydrogen is not released. As neither N-carboxymethylamino aceto-N'-methylhydroxamic acid (*II*) nor N-hydroxyglutaramic acid (*III*) or the amides mentioned afford the ternary complex in question, this complex formation is obviously conditioned by the occurrence of the functional arrangement

$$>N-CH_2-CONH-OH\ .$$

The structure arrangement in the ternary chelate can be represented as



$(CuFeH_{-1}L^{2+})$

Qualitative reactions confirmed that other hydroxamic acids involving the functional arrangement discussed, such as aminoacetohydroxamic acid or pyridine-2-carbohydroxamic acid, behave likewise, forming a mixed ternary complex with Cu(II) and Fe(III) ions and releasing two protons from one carbohydroxamic group.

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