Structure of Ethylenediaminetetra-Acetate Complex of Iron(III) In Aqueous Solution

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Summary: The stability constants for mixed binuclear complex formation in aqueous solution between Iron(III)-EDTA complex and various ligands, thiocyanate and hexacyanoferrate(II), have been obtained from spectrophotometric measurements. The results can be interpreted to obtain the evidence that the Iron(III)-EDTA complex is predominantly six-coordinated and hexadentate in solution.

Introduction

The normal 1:1 complexes of ethylenediaminetetra-acetate (EDTA=Y) with divalent metals have been studied by several workers[1,4]. Schwarzenbach[5] reported the existence of mixed complexes of the type, M^{II}-Y-X, where M is metal, Y=EDTA, and X=SCN$^-$, OH$^-$, NH$_3$. Such mixed[6] complexes in which the substitution of free-donor group of the multidentate ligand (metal-complex) by other ligand, unidentate or multidentate, takes place, were helpful in characterizing the structure of EDTA complexes in aqueous solution. They have been termed as binuclear[7] complexes when the other potential ligand is multidentate (cyanometallate) ligand. In the structural illustration of metal-EDTA complexes an important aspect concerns the number of donor groups of the multidentate ligand (EDTA) which are actually coordinated to metal ion. For most divalent metal ions the proportion of a parent metal-EDTA complex which is sexident (70-76%), the remaining part being aquoquinquedentate[6]. However, in case of trivalent metal ions the information about the structure of EDTA complexes is rare. In terms of coordination of the metal-EDTA complexes, Co(III) appears[8] to be sexidentate in solution. In the solid state, EDTA complexes of manganese(II)[9] and iron(III)[10,11], are known to show sexidentate and possess a ligand water molecule in addition. The structure of Fe(III)EDTA in solution has not yet been well established. In acidic solution [12] a quinquedentate, seven coordinate, bis-aquo complex, Fe(III)(EDTA-H)(H$_2$O)$_2$ with a free CH$_2$COOH group s claimed to be the preferred form of the complex acid. In the crystalline form Hoard[13] and his coworkers have suggested, by X-ray studies, that Fe(III)(OH$_2$)(EDTA)$^-$ is sexidentate and seven coordinate with a water mole-

cule firmly attached to iron(III). We now report here the equilibrium studies of binuclear complex formation between Fe(III)(EDTA)$^-$ and the ligand, hexacyanoferrate(II) (Fe(CN)$_6^{4-}$), and from which it is possible to suggest the coordination of EDTA complex with iron(III) in aqueous solution.

It was essential to make stability constant measurements with such a multidentate ligand which could easily be taken for EDTA and well compared with it. The values of the stability constants for mixed complex formation between thiocyanate and protonated EDTA complexes of divalent metals, Co(II), Ni(II), and Cu(II), are similar to the corresponding values for the HEDTA complexes of these metals[6]. HEDTA represents N-hydroxyethylene-diaminetri-acetate, a ligand identical with a mono-protonated form of EDTA (M(EDTA-H)^{v}H$_2$O, aquoquinquedentate) except that the COOH group of the latter is replaced by CH$_2$OH, and is quinquedentate ligand while EDTA is predominantly sexidentate. Thus we have compared the values of binuclear complex stability constants obtained for EDTA complexes with those found for the corresponding HEDTA complexes. This is equivalent to making the corresponding comparisons between quinquedentate (HEDTA) and sexidentate (EDTA) complexes.

Derivation of expression.

To express things on the quantitative basis, expression was deduced under the equilibrium condition of experiment between the two reactants, Fe(EDTA)$^-$ and the ligand [Fe(CN)$_6^{4-}$]

$$M^{III}(EDTA)^- + Fe(CN)_6^{4-} \rightleftharpoons [(EDTA)Fe(III)\text{-}NC\text{-}Fe(II)(CN)_5]^{5-} \quad (1)$$

$$[M] \qquad\qquad [Fe] \quad \rightleftharpoons \qquad\qquad [BN] \qquad (2)$$

where [M], [Fe], [BN], represents the equilibrium concentrations of $M(EDTA)^-$, $Fe(CN)_6^{4-}$, and the binuclear complex (BN). The derivation relating optical density to equilibrium constant, K, and the molar extinction coefficient, e, was obtained under the condition when the $[Fe]_0 \gg [M]_0$. $[Fe]_0$ and $[M]_0$ represents the initial concentrations of ligand and the metal complex.

$$K = \frac{[BN]}{[M]_0 - [BN] \quad [Fe]_0} \qquad (3)$$

By substituting [BN] and rearranging equation (3), we obtained the final equation which by plotting $[M_0]\,.d/OD$ verses $1/[\text{ligand}]$, gives straight line of slope $1/e.K$, and intercept $1/e$, and so the values of e and K can be calculated. d is the path length of the cell used for the measurement of optical density (OD).

Results and discussions

Visible Spectra

Figure 1 shows the visible spectra of mixture of solution of hexacyanoferrate(II) with solutions of complexes, $(Fe(III) (EDTA)^-$ and $Fe(III)(HEDTA)^0$. An increased absorption in the region 600-900 nm with approximate λ maximum at 800 nm is observed for reaction mixtures. Absorption due to reactants is negligible in this region. From preliminary experiment it is observed that the optical density of reaction mixture was decreased with increasing pH (pH≥5.5), probably due to the formation of hydroxo complexes of ferric-EDTA, and in the acidic medium, at pH≤3.0, a decrease in absorption was observed, probably due to the association of

$$H^+ + Fe(CN)_6^{4-} \rightleftharpoons HFe(CN)_6^{3-}$$
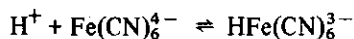
In the pH range 4.5-5.30, the abosorption of the reaction mixture (EDTA complex) was almost constant and pH=5.0 was considered as suitable for measurements. In the case of $Fe(HEDTA)^-$, the pH=3.5 and 4.0 were suitable for measurements and the results at the two pHs were found to be quite consistent. The optical den-
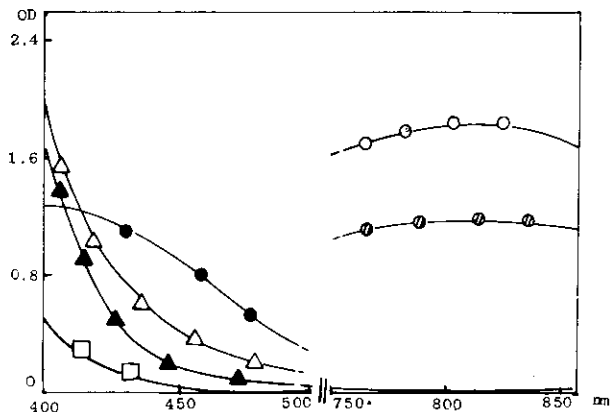

Figure 1 visible absorption spectra of binuclear complexes, $[(EDTA)Fe^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{5-}$ (◯); $[(HEDTA)Fe^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{4-}$ (◯); $(EDTA)Fe^{III}\text{-}NCS^{2-}$ (△); $(HEDTA)Fe^{III}\text{-}NCS$ (●) compared with the parent complexes $(EDTA)Fe^{III}$ (▲) $(HEDTA)^{FeIII}$ (◻), NCS^- (negligible); $Fe(CN)_6^{4-}$ (absorption between 750-850 nm negligible); at $25.0^\circ C$, I=1.0M ($NaClO_4$) cell path length=1.0 cm.

sity measurements were done under a wide range of concentrations of reactants under the condition where hexacyanoferrate(II) was in large excess over Fe(III) (Y), (Y=EDTA or HEDTA). The data were used in equation (3) and the values of e and K were obtained by the least square program. The results are given in the tables 1 and 2.

Considering together the results for $Fe(III)(EDTA)^-$ $Fe(III)(HEDTA)^0$ with $Fe(CN)_6^{4-}$, we observe a very big difference in the magnitude of stability constants, $(K_{HEDTA}/K_{EDTA}=2366)$. This can be compared with the much smaller differences (less than 20 times) found between the HEDTA and EDTA binuclear complexes[14] of divalent metal ions, and even smaller differences[6] found in the value of K (4 times) in the case of $Cu(HEDTA)^-$ with NCS^- than for the corresponding values for EDTA. It is also evident in the log K values for metal formation cconstants for the dipositive[15] and tripositive [16,17] metals, i.e.,

		log K value
$Cu^{2+} + HEDTA \rightleftharpoons Cu(HEDTA)(H_2O)^-$		17.40
$Cu^{2+} + EDTA \rightleftharpoons Cu(EDTA)^{2-} + Cu(EDTA)^Y(H_2O)$		18.30
70% 30%		
$Fe^{3+} + HEDTA \rightleftharpoons Fe^{III}(HEDTA)H_2O^-$		19.06
$Fe_3^+ + EDTA \rightleftharpoons Fe^{III}(EDTA^-$		25.10

On comparing the logK values of Cu(II) and Fe(III) with the same ligand we observe that the latter are

Table 1

Values of K and e for the reaction, $Fe(EDTA)^-$ and $Fe(HEDTA)^O$ with $Fe(CN)_6^{4-}$.

$Fe(EDTA)^-$ + $Fe(CN)_6^{4-}$ system.　　　　　　　　　$Fe(HEDTA)^O$ + $Fe(CN)_6^{4-}$ system.

$\dfrac{Fe}{10^{-2}M}$	$\dfrac{Fe(EDTA)^-}{10^{-2}M}$	$\dfrac{Fe(EDTA)\ d}{OD}/10^{-3}$	$\dfrac{Fe}{10^{-4}M}$	$\dfrac{Fe(HEDTA)^-}{10^{-5}M}$	$\dfrac{Fe(HEDTA)\ d}{OD}/10^{-4}$
0.75	5.00	9.80	1.75	4.0	4.04
0.850	”	9.01	2.00	”	3.85
1.000	”	7.43	2.50	”	3.59
1.225	”	6.33	3.00	”	3.36
1.750	”	4.44	3.50	”	3.23
2.250	”	3.44	4.00	”	3.03
2.500	”	3.09	6.00	”	2.92
2.750	”	3.00	8.00	”	2.74
3.250	”	2.54	10.00	”	2.70
2.750	2.00	2.89	15.00	”	2.60
4.000	”	2.12	17.50	”	2.56
5.500	”	1.54	20.00	”	2.53
6.500	”	1.40	—	—	—
7.500	”	1.19	—	—	—

$K/1.mol^{-1}$　　　　　=3.50 ± 0.60　　　　　　　$K/1.mol^{-1}$　　　　8282 ± 264
$e_{BN}/1.mol^{-1}cm^{-1}$　=3950.50　　　　　　　　$e_{BM}/1.mol.^{-1}cm^{-1}$　4143 ± 33
Fe = $Fe(CN)_6^{4-}$, 800 nm;　　　　　　　　　　error on intercept and gradient is less than 2%.
Cell length = 2.0 cm; pH= 5.0　　　　　　　　　　pH= 3.5 & 4.0

higher by ~1 and 6 log K units. However, although these figures suggest that EDTA is strongly hexadentate with Fe^{3+}, they provide no information about the presence or absence of a coordinated water molecule. The ratio found for the stability constants of the iron(III)-HEDTA and EDTA binuclear complexes with $Fe(CN)_6^{4-}$ was so unexpectedly large that further experiments were done in which the ligand $Fe(CN)_6^{4-}$ was replaced by NCS. This ligand was chosen as a small ion which was not likely to cause steric complications.

The reaction with other ligand (thiocyanate):

The reaction between $Fe^{III}(EDTA)^-$ and $Fe^{III}(HEDTA)^O$ with the ligand NCS^- was studied at pHs=2.0 and 4.0 (in the case of EDTA) and at pHs=2.5 and 3.0 (in the case of HEDTA) at wavelength 440 nm. The value of product, e.K, for the mixed EDTA complex was larger at pH=2.0, probably due to the formation of protonated complex, $Fe(III)(EDTA-H)(H_2O)$, in about 5% which easily replaces the H_2O molecule by NCS^- and hence gives a high constant. One of the difficulties in the case of $Fe(III)(EDTA)-NCS^{2-}$ complex was that the intercept $(1/e_{BN}-e_M)$ was very small of the order of O within experimental error, the absolute value of $(e_{BN}-e_M)$ was uncertain and less than the error upon it. It suggested that the value of $(e_{BN}-e_M)$ was very large. If we assume that the colour in the $Fe(III)$-Y-NCS (Y=EDTA or HEDTA) was due to the part where metal (Fe^{III}) was penta-coordinated with Y and the sixth bond with the ligand, NCS^-, then we can presume that extinction coefficient, e, was likely to be the same or similar in both cases, $Fe^{III}(EDTA)^-$ or $Fe^{III}(HEDTA)^O$. We found the values of $(e_{BN}-e_M)=$ 7180 $1.mol^{-1}cm^{-1}$, and K=12.88 $1.mol^{-1}$ for Fe^{III} (HEDTA)-NCS$^-$ and their product is 92,478 $1.mol^{-1}$

Table 2

Values of K and e and other data for the reaction, $Fe^{III}(EDTA)^-$ and $Fe^{III}(HEDTA)^O$ with NCS^-

Fe(EDTA)$^-$ + NCS$^-$ system.			Fe(HEDTA)^O + NCS$^-$ system.		
NCS$^-$/M	$\dfrac{Fe(EDTA)^-}{10^{-3}M}$	$\dfrac{Fe(EDTA)^-}{*Z}$ d	$\dfrac{NCS^-}{10^{-2}M}$	$\dfrac{Fe(HEDTA)}{10^{-5}M}$	$(\dfrac{Fe(HEDTA)}{OD})/10^{-4}$ d
0.10	5.0	0.1000	1.50	4.0	9.29
0.135	,,	0.0741	2.00	,,	7.20
0.200	,,	0.0617	2.50	,,	5.53
0.400	,,	0.0315	3.00	,,	4.75
0.450	,,	0.0247	4.00	,,	3.97
0.600	,,	0.0198	5.50	,,	3.24
0.700	,,	0.0158	7.00	,,	2.99
0.800	,,	0.0143	12.00	,,	2.29
0.950	,,	0.0124	16.00	,,	2.12
—	—	—	20.00	,,	2.01

$(e_{BN} - e_M)/1.mol^{-1} cm^{-1}$ $= 2182 \pm 4041$	$K/1.mol^{-1}$ $= 12.88 \pm 0.91$
$e.K/1.mol^{-1} cm^{-1}$ $= 86.32 \pm 1.5$	$(e_{BN} - e_M)/1.mol^{-1} cm^{-1}$ $= 7180 \pm 350$
$I=1.0M(NaClO_4)$; Cell length=1.0 cm;	$e_M/1.mol^{-1} cm^{-1}$ $= 0.0$, pH=3.0
pH=4.0	pH=3.0; Cell length=2.0 cm.

cm^{-1}. The product of $(e_{BN} - e_M)$ and K for $Fe^{III}(EDTA)-NCS^{2-}$ at pH=4.0, is 86.32 ± 1.53, this being (1/the gradient of the plot of $1/(OD - OD_O)$ vs 1/ligand). If the molar extinction coefficient are, assumed to be the same for the two systems, then we can find the value of the K for the latter case, i.e.

The product of e.K=86.32 $1.mol^{-1} cm^{-1}$ (for $Fe^{III}(EDTA)-NCS^{2-}$ system).

The value of $e=(e_{BN} - e_M)=7180$ $1.mol^{-1} cm^{-1}$ (for $Fe^{III}(HEDTA)-NCS^-$ system).

Therefore K=0.012 $1.mol^{-1}$ (for $Fe^{III}(EDTA)-NCS^{2-}$ system).

From the results it appears that the stability constants for $Fe^{III}(HEDTA)-NCS^-$, and Fe(III)(EDTA)-NCS^{2-} were in the approximate ratio, $K_{HEDTA}/K_{EDTA}=1000$, thus supporting the results obtained with $Fe(CN)_6^{4-}$ for the corresponding complexes of Fe(III)(EDTA)$^-$and Fe(III)(HEDTA)^O. This suggested that the only satisfactory explanation for the large ratio of K values for the addtion of a ligand (Fe(CN^{4-} or NCS$^-$) to Fe(III)

(HEDTA)^O and Fe(III)(EDTA)$^-$[6] is that whereas the Fe(III)(HEDTA)^O must contain a coordinated water molecule, the Fe(III)(EDTA)$^-$ must contain no coordinated water molecule. Addition of the ligand would therefore involve the displacement of carboxylate group which we know to be difficult from the low pK=0.5 of the acid[18], Fe(III)(EDTA-H). If one water molecule were present in $Fe^{III}(EDTA)^-$ and two in Fe(III)(HEDTA)^O we could expect the latter to give a constant for the addition of a ligand not more than 10 times larger than that with (FeIII)(EDTA)$^-$. This makes some allowances for the lack of charge repulsion in $Fe^{III}(HEDTA)^O$, but this effect is not large as shown[14] in the binuclear complexes with M(II)(NTA)$^-$ and M(II)(EDDA)^O complexes with hexacyanoferrate(II). [NTA is nitrilotriacetate, and EDDA is ehtylenediaminedi-acetate]. Thus, we have come to the interesting conclusion that although there is evidence for seven coordinated $Fe^{III}(EDTA)(H_2O)^-$ in the solid state, in solution the EDTA complex of iron(III) is predominantly six-coordinated and hexadentate.

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