

Mixed Iron-Copper Binuclear Complexes. Equilibrium Studies of Complexes of Metal-Aminocarboxylate Complexes and Hexacyanoferrate(II).

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Summary: The equilibrium constants for mixed binuclear complex formation between certain metal-EDTA complexes and hexacyanoferrate(II), ligand, $M(II)-EDTA^{2-} + Fe(CN)_6^{4-} \rightleftharpoons [(EDTA)M^{II}-NC-Fe^{II}(CN)_5]^{6-}$ in aqueous solution have obtained by spectrophotometric measurements. The results are interpreted to obtain the reactivity order of chelating agents and the electron-pair donating ability of cyanometallate. The relative magnitudes of equilibrium constants are also discussed.

Recent interest in cyano-bridge binuclear complexes arises,^{1,2} in part, from their importance as intermediates in inner-sphere electron-transfer reactions. Binuclear complexes can be classified either as di-cobalt complexes, where both metal centres are cobalt (III) or as 'mixed' complexes where the second centre is a different metal. The chemistry of the former has been well documented³, detailed studies involving mixed binuclear complexes are rare². A general method has been developed following the demonstration by Schwarzhnbach that cobalt (II)-EDTA complex can form mixed complexes with other ligands such as thiocyanate⁴. Recently, cyanometallates⁵ have been used instead of unidentate ligands to generate the binuclear complexes. We now report the formation of a series of mixed binuclear complexes of metal (II)-EDTA [(EDTA and its related compounds, viz, HEDTA (N-hydroxyethyl) ethylenediamine-NN'-triacetate), NTA (nitrilotriacetate), EDDA (Ethylenediaminediacetate), PDTA (1,2 diaminopropanetetraacetate) and CDTA (1,2, diaminocyclohexanetetra-acetate)] with cyanometallate, $Fe(CN)_6^{4-}$, and their equilibrium constant measurements.

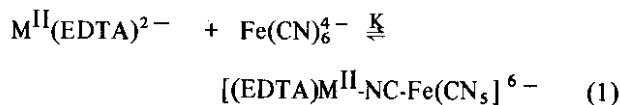
Equilibrium measurement for the binuclear complexes were done spectrophotometrically by observing change in the optical density of the reaction mixture at λ max. Spectra of the binuclears and of the separate reactions were obtained, and one or more suitable wavelengths were chosen for each determination, at which the absorbance due to reactants was relatively less or very small. Spectra for the many of the combinations of chelate and ligand studied have been reported.

Reaction solutions were made in such a way that in one set of experiments the concentration of metal-

aminocarboxylate complex was kept constant (0.001M) and the concentration of second species, cyanometallate, was varied in the range, 0.01-0.1M. The pH of solution was kept constant at 8.00 ± 0.02 by the buffer, tris-HCl (i.e tris(hydroxymethyl)methylammonium chloride) and sodium hydroxide in proportions (0.020M). All Reactions were done at ionic strength, $I=1.0M$ ($NaClO_4$).

Derivation of expression.

1. To determine the equilibrium constant, K, and molar extinction coefficient, e, for the binuclear species, the following expressions were deduced, assuming that there was state of equilibrium under the condition of experiment between the two reactants, metal-aminocarboxylate complex and the second species.



where [M], [Fe] and [BN], represents the equilibrium concentrations of $M^{II}(EDTA)^{2-}$ (metal-complex), $Fe(CN)_6^{4-}$ (second species, ligand), and concentration at equilibrium of $[(EDTA)M^{II}-NC-Fe(CN)_5]^{6-}$ (the binuclear complex).

The derivation of equation relating optical densities to K was much easier under the condition when $[Fe]_0 \gg [M]_0$, so that the change in the concentration of $[Fe]_0$ can be neglected, and absorption due to $[M]_0$ and $[Fe]_0$ was negligible at the wavelength of the measurements, where $[M]_0$ and $[Fe]_0$ represents the initial concentrations of metal complex and the ligand.

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

$$\frac{1}{K [\text{Fe}]_0} = \frac{[\text{M}]_0 - [\text{BN}]}{[\text{BN}]} = \frac{[\text{M}]_0}{[\text{BN}]} - 1 \text{ or}$$

$$1 + 1/K[\text{Fe}]_0 = [\text{M}]_0/[\text{BN}] \quad (4)$$

$$\text{since } OD = c \cdot e \cdot d, \therefore c = [\text{BN}] = OD/e \cdot d \quad (5)$$

substituting $[\text{BN}]$ in equation (4),

$$\frac{[\text{M}]_0 \cdot d \cdot e}{OD} = 1 + \frac{1}{K[\text{Fe}]_0} \quad (6)$$

$$\text{or } \frac{[\text{M}]_0 \cdot d}{OD} = \frac{1}{e} + \frac{1}{\{e K [\text{Fe}]_0\}} \quad (7)$$

Hence a plot of $\frac{[\text{M}]_0 \cdot d}{OD}$ vs $1/[\text{Fe}]_0$ should give a straight line of slope $1/e \cdot K$ and intercept $1/e$. and so the values of e and K can be calculated. [Where OD = optical density; d = cell path length; c = concentration of species].

2. Under the condition of $[\text{Fe}]_0 \gg [\text{M}]_0$, so that the change in the concentration of $[\text{Fe}]_0$ can be neglected, but absorption due to $[\text{M}]_0$ and $[\text{Fe}]_0$ was not negligible. So we can write,

$$OD/d = e_{\text{Fe}} \cdot [\text{Fe}]_0 + e_{\text{M}} \cdot [\text{M}] + e_{\text{BN}} \cdot [\text{BN}]. \quad (8)$$

and by appropriate substitution we can write the final equation as,

$$\frac{[\text{M}]_0}{OD/d - e_{\text{Fe}} \cdot [\text{Fe}]_0 - e_{\text{M}} \cdot [\text{M}]} = \frac{1}{(e_{\text{BN}} - e_{\text{M}})} + \frac{1}{K(e_{\text{BN}} - e_{\text{M}})} \times \frac{1}{[\text{Fe}]_0} \quad (9)$$

Hence a plot of L.H.S vs $1/[\text{Fe}]_0$ will give a straight line of slope $1/K(e_{\text{BN}} - e_{\text{M}})$ and the intercept $1/(e_{\text{BN}} - e_{\text{M}})$.

3. Under the condition when $[\text{Fe}]_0$ was not very large so that change in the concentration of Fe was important, but the absorption by $[\text{Fe}]_0$ and $[\text{M}]_0$ was negligible, the problem can be dealt with by assuming the value of K and solving equation (10) for $[\text{BN}]$,

$$K = \frac{[\text{BN}]}{([\text{Fe}]_0 - [\text{BN}]) \cdot ([\text{M}]_0 - [\text{BN}])} \quad (10)$$

and we can reach a equation, such as,

$$[\text{BN}]^2 - ([\text{M}]_0 + [\text{Fe}]_0 + 1/K) [\text{BN}] + [\text{M}]_0 [\text{Fe}]_0 = 0 \quad (11)$$

Hence we can find the value of $[\text{BN}]$ approx. by assuming a value for K . Now we can write, $f = [\text{Fe}]_0 - [\text{BN}]$ approx. and f is the first approximation to the equilibrium value of $[\text{Fe}]_0$. Equation (7) can now be written as:

$$\frac{[\text{M}]_0 \cdot d}{OD} = \frac{1}{e} + \frac{1}{e \cdot K \cdot f} \quad (12)$$

Hence a plot of L.H.S. against $1/f$ will give a straight line of slope $1/e \cdot K$ and intercept $1/e$. and so the value of K and e can be determined. In practice three to four approximations of value of K were needed until values of K agree.

4. In the case when $[\text{Fe}]_0$ was not very large so that the change in $[\text{Fe}]_0$ was important, and also the absorptions by $[\text{Fe}]_0$ and $[\text{M}]_0$ was not negligible. We can reach to final equation after using equation (10), and value of f from equation (11) and replacing $[\text{Fe}]_0$ by f in equations (3 & 4). Hence,

$$\frac{[\text{M}]_0}{OD/d - e_{\text{Fe}} \cdot f - e_{\text{M}} \cdot [\text{M}]} = \frac{1}{(e_{\text{BN}} - e_{\text{M}})} + \frac{1}{K(e_{\text{BN}} - e_{\text{M}})} \times \frac{1}{f} \quad (13)$$

For a solution of $[\text{M}]_0$ we get $OD/d = e_{\text{M}} [\text{M}]_0$.

$$\therefore \frac{[\text{M}]_0}{(OD/d - OD/d) - e_{\text{Fe}} \cdot f} = \frac{1}{(e_{\text{BN}} - e_{\text{M}})}$$

$$+ \frac{1}{K(e_{BN} - e_M)} \times \frac{1}{f} \quad (14)$$

Hence a plot of L.H.S. against $1/f$ will give straight line of slope $1/K(e_{BN} - e_M)$, and intercept $1/(e_{BN} - e_M)$.

Results and discussions:

Visible Spectra:

Figure 1 shows the visible spectra of $\text{Fe}(\text{CN})_6^{4-}$ and the effect of mixing this solution with solutions of different metal-aminocarboxylate complexes, in which the concentration of hexacyanoferrate (II) was in excess over metal-complex. Solutions of the new complexes were intensely coloured, and their spectra (Fig. 1) show enhanced absorption, except in the case of $\text{Cu}(\text{CDTA})^{2-} - \text{Fe}(\text{CN})_6^{4-}$ system with a large change in the wavelength of maximum absorption (λ_{max} at 500 nm) compared with that of metal complex. This change may be due to charge-transfer absorption. The enormous enhancement in the spectrum at 398 nm, maximum for $\text{Fe}(\text{CN})_6^{4-}$ (ϵ 770 $\text{l mol}^{-1} \text{cm}^{-1}$) accounts for the increased absorption for the binuclear complex at this position.

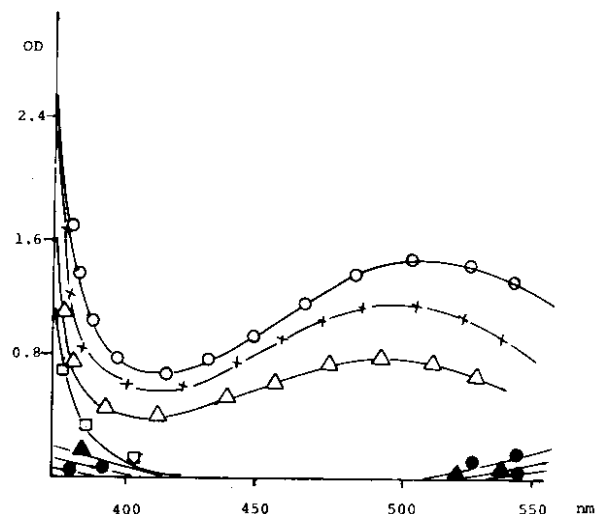


Figure 1 (A)

Visible absorption spectra of binuclears of the complexes, $[(\text{EDTA})\text{Cu-NC-Fe}(\text{CN})_5]^{6-}$ (Δ), $[(\text{HEDTA})\text{Cu-NC-Fe}(\text{CN})_5]^{5-}$ (+), and $[(\text{NTA})\text{Cu-NC-Fe}(\text{CN})_5]^{5-}$ (0), compared with parent complexes, $\text{Cu}(\text{EDTA})^{2-}$ (\blacktriangle), $\text{Cu}(\text{HEDTA})^{-1}$ (\circ), $\text{Cu}(\text{NTA})^{-1}$ (\bullet) and $\text{Fe}(\text{CN})_6^{4-}$ (\square), at 25.0°C , $I=1.0\text{M}(\text{NaClO}_4)$, cell length=1.0cm.

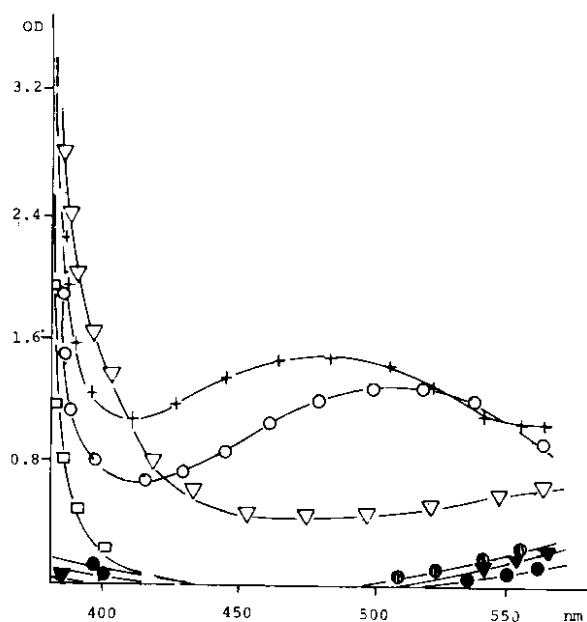
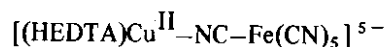
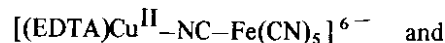


Figure 1(B)

Visible absorption spectra of binuclear complexes, $[(\text{EDDA})\text{Cu-NC-Fe}(\text{CN})_5]^{4-}$ (+), $[(\text{PDTA})\text{Cu-NC-Fe}(\text{CN})_5]^{6-}$ (\circ) and $[(\text{CDTA})\text{Cu-NC-Fe}(\text{CN})_5]^{6-}$ (∇), (cell length 2.0 cm), compared with the parent complexes, $\text{Cu}(\text{EDDA})^0$ (\circ), $\text{Cu}(\text{PDTA})^{2-}$ (\blacktriangledown), $\text{Fe}(\text{CN})_6^{4-}$ (\square) and $\text{Cu}(\text{CDTA})^{2-}$ (\bullet), at 25°C , $I=1.0\text{M}(\text{NaClO}_4)$, cell length=2.0cm, $[\text{Cu}(\text{Y})]=1.25 \times 10^{-2}\text{M}$, $[\text{Fe}(\text{CN})_6^{4-}]=5.0 \times 10^{-2}\text{M}$.

The comparatively low absorption for $\text{Cu}(\text{CDTA})^{2-} - \text{Fe}(\text{CN})_6^{4-}$ binuclear complex with that of $\text{Cu}(\text{EDTA})^{2-} - \text{Fe}(\text{CN})_6^{4-}$ system may be due to the rigidity⁶ and stronger complexing ability of CDTA with metals. With cobalt complexes Haim⁷ and his coworkers studied bridging isocyanides and cyanides on the spectra of amine binuclear complexes. Similarly Murray⁵ and coworkers have identified mixed iron-cobalt complexes of the type, $[(\text{NC})_5\text{Co-CN-Co}(\text{en})_2\text{SO}_3]^{2-}$. On these basis the complexes appear to have the formulae such as:



Preliminary results were obtained under the condition where the concentration of $\text{Cu}(\text{EDTA})^{2-}$ was kept constant and the concentration of $\text{Fe}(\text{CN})_6^{4-}$ was varied over a wide range (5-30 times $[\text{Cu}^{\text{II}}]$). The reaction was studied at $\text{pH}=8.0 \pm 0.20$, $I=1.0\text{M}(\text{NaClO}_4)$, wavelength

500nm, and temperature 25.0°C. The data were used in equation (14), using the successive approximation procedure as described in derivation (3). About three iterations were necessary to find an improved value of K . The values of K and e were obtained by the least square programme with unit weight for each datum point used, and the results are given in the Table 1.

A series of experiments were done in order to check the (i) effects of varying buffers ($\text{HCO}_3^-/\text{CO}_3^{2-}$, and tris buffer, TMAH^+/MAH , at $\text{pH}=8.0$), (ii) varying $\text{pH}=6.60$ and 8.80 , maintained by the above buffers, and (iii) the effect of variation in the sodium ion concentration when the changes were made in the $\text{Na}_4\text{Fe}(\text{CN})_6$ concentration^{8,9}. These experiments gave similar values of K and e to those obtained in Table 1.

The other systems, $\text{Cu}^{\text{II}}(\text{Y})\text{-Fe}(\text{CN})_6^{4-}$, ($\text{Y}=\text{EDTA}$), in which EDTA was replaced by other aminocarboxylate ions, $\text{Y}=\text{HEDTA}$, EDDA , NTA , PDTA , and CDTA , were studied under the same condition and subjected to a series of experiments as described for the above system, $\text{Cu}^{\text{II}}(\text{EDTA})^{2-}\text{-Fe}(\text{CN})_6^{4-}$. The results are given in the Table 2,3,4,5, and 6, respectively.

The various binuclear complex formation constants, K , are summarized in the Table. 7

It is observed that value of K was larger for the binuclear complex $[(\text{HEDTA})\text{Cu}^{\text{II}}\text{-NC-Fe}(\text{CN})_5]^{5-}$ than for $[(\text{EDTA})\text{Cu}^{\text{II}}\text{-NC-Fe}(\text{CN})_5]^{6-}$ (about 8 times). This is understandable because of the decrease in the basicity of HEDTA (N-hydroxyethyl)-ethylenediaminetriacetate) where one COOH group of EDTA has been replaced by weakly acidic group CH_2OH and should correspond to the change in the affinity of the ligand for the metal ions. Samuel and Higginson⁶ reported that much of the metal-EDTA complex (70%) is in the sexadentate form, the remaining portion being in the aquaquinquedentate form. On the other hand metal-HEDTA is considered to be in the aquaquinquedentate form, $\text{M}^{\text{II}}(\text{HEDTA})^{\text{v}}(\text{H}_2\text{O})^-$ (the subscript v indicates the chelation), and there is therefore greater chance for the formation of a binuclear complex with $\text{Fe}(\text{CN})_6^{4-}$. Similarly, high values of K (4 times) in the case of $\text{Cu}^{\text{II}}(\text{HEDTA})^-$ with ligand NCS^- than for the corresponding values for EDTA have been reported.⁶ The ratio of the value of K for $\text{Cu}(\text{YOH})^-\text{-Fe}(\text{CN})_6^{4-}$ and $\text{Cu}(\text{Y})^{2-}\text{-Fe}(\text{CN})_6^{4-}$ where $\text{YOH}=\text{HEDTA}$ and $\text{Y}=\text{EDTA}$, was twice that for the ratio of the corresponding values⁶ of K for NCS^- in place of $\text{Fe}(\text{CN})_6^{4-}$. This may be attributed to the effect of charge repulsions. Similarly, by replacing the ligand NCS^- by $\text{Fe}(\text{CN})_6^{4-}$, the values of K were much higher,

$$(\text{K}_{\text{HEDTA-Fe}(\text{CN})_6^{4-}}) / (\text{K}_{\text{HEDTA-NCS}^-}) = 88$$

$$(\text{K}_{\text{EDTA-Fe}(\text{CN})_6^{4-}}) / (\text{K}_{\text{EDTA-NCS}^-}) = 54.$$

This shows that $\text{Fe}(\text{CN})_6^{4-}$ is a stronger electron-pair donor than NCS^- and this is parallel to the greater basicity of $\text{Fe}(\text{CN})_6^{4-}$ towards proton.

Results with other chelate ligands.

PDTA and CDTA complexes :

Further experiments were done with PDTA (1,2 diaminepropane- NNN^-N^- -tetra-acetate) and CDTA (trans-1,2,diaminecyclohexane- NNN^-N^- -tetra-acetate) as the chelating agents and the stability constants of the binuclear complexes formed were measured. This was done in accordance with great similarity between PDTA or CDTA with EDTA. The absorption due to binuclear complex of metal-CDTA was somewhat lower than for the corresponding absorption for metal-EDTA. The low values of K ($5.01 \cdot \text{mol}^{-1}$) were obtained for the $\text{Cu}(\text{Y})^{2-}\text{-Fe}(\text{CN})_6^{4-}$ system, K with $\text{Y}=\text{PDTA}$ being approximately 1/7 times the corresponding value of K for $\text{Y}=\text{EDTA}$. Similarly lower values of K were obtained⁶ in the $\text{Cu}(\text{Y})^{2-}\text{-NCS}^-$ system, $\text{Y}=\text{CDTA}$ with approximately 1/3 times the corresponding value of K for $\text{Y}=\text{PDTA}$. The behaviour of PDTA is between EDTA and CDTA, the methyl group has a similar but smaller effect than cyclohexane ring. The high pK_1 and pK_2 values^{10,11} of PDTA and CDTA than for EDTA for the two carboxyl protons and the high value of stability constant for $\text{Cu}(\text{CDTA})^{2-}$ ($10^{21.95}$) compared to $\text{Cu}(\text{EDTA})^{2-}$ ($10^{18.8}$) together with the cage-like structure of CDTA, accounts for the stronger metal-chelate complex formation, and so the complexes are difficult to be substituted by other ligands (cyanometalate). This is evident from the observed low values of K for the binuclear complexes of PDTA and CDTA.

EDDA and NTA complexes :

EDDA (ethylenediaminediacetate) and NTA (nitrilotriacetate) behave as tetradentate ligands and consequently, unlike EDTA, they cannot form coordination-saturated complexes of most divalent metal ions. As a result of this, NTA and EDDA complexes have two loosely bound water molecules which may strengthen their tendency to form cyanide bridge complexes. It is apparent from the values of K for EDDA and NTA which are much larger than the corresponding values of K for HEDTA or EDTA. Apart from this the high

Table-1

Values of constants and other data for reaction between
 $\text{Cu}(\text{EDTA})^2 + \text{Fe}(\text{CN})_6^{4-}$.

$[\text{Cu}(\text{EDTA})^2]_0/M$	$[\text{Fe}(\text{CN})_6^{4-}]_0/M$	OD_{obs}	$\frac{1}{[\text{Fe}(\text{CN})_6^{4-}]_f}$	$(P = \frac{[\text{Cu}]}{*Z})/10^{-3}$	Cell length/cm
0.0025	0.030	0.3165	37.79	7.962	1.00
"	0.020	0.2405	52.63	10.519	"
"	0.010	0.1470	106.59	17.103	"
0.00125	0.040	0.3520	25.46	7.190	2.00
"	0.025	0.2770	40.94	9.160	"
"	0.0125	0.1780	82.45	14.103	"
"	0.0075	0.1215	137.95	20.950	"
"	0.0050	0.0885	207.43	28.886	"
0.00075	0.0350	0.2030	28.97	7.491	"
"	0.0250	0.1690	40.56	9.455	"
"	0.0175	0.1364	58.08	11.259	"
"	0.0125	0.1080	81.46	14.179	"
"	0.0075	0.0775	136.11	20.174	"

$K = 35.68 \pm 1.12 \text{ l.mol}^{-1}$; $(e_{\text{BN}} - e_{\text{M}}) = 233.59 \pm 5.23 \text{ l.mol}^{-1}.\text{cm}^{-1}$; $e_{\text{M}} = 0.535 \text{ l.mol}^{-1}.\text{cm}^{-1}$; $e_{\text{Fe}} = 0.1071 \text{ l.mol}^{-1}.\text{cm}^{-1}$;
 $*Z = (\text{OD}/d - \text{OD}/d) - e_{\text{Fe}}.f$. OD_{obs} = Optical density observed. OD_{obs} obtained from the average of four measurements of each experiment, twice with 5% excess of $[\text{EDTA}]_0$ over $[\text{Cu}]_0$, and twice with 100% excess of $[\text{EDTA}]$ over $[\text{Cu}]_0$, and were similar within experimental error. pH=8.00 (Tris-buffer).

Table. 2

Values of constants and other data for the reaction between
 $\text{Cu}(\text{HEDTA})^- + \text{Fe}(\text{CN})_6^{4-}$.

$[\text{Fe}(\text{CN})_6^{4-}]_0/M$	$[\text{Cu}(\text{HEDTA})^-]_0/M$	OD_{obs}	$\frac{1}{[\text{Fe}(\text{CN})_6^{4-}]_f}$	$(P = \frac{[\text{Cu}]}{*Z})/10^{-3}$
0.0010	0.00040	0.0800	1094.18	20.649
0.0020	"	0.1320	538.53	12.424
0.0040	"	0.2225	264.04	7.337
0.0060	"	0.2465	174.01	6.633
0.0080	"	0.2698	129.52	6.073
0.0100	"	0.2940	103.07	5.582
0.0010	0.00060	0.1198	1142.57	20.691
0.0020	"	0.1880	558.55	13.064
0.0040	"	0.2998	271.37	8.149
0.0060	"	0.3605	177.83	6.776
0.0080	"	0.4050	131.83	6.036
0.0100	"	0.4395	104.65	5.563

$K = 267.40 \pm 12 \text{ l.mol}^{-1}$; $(e_{\text{BN}} - e_{\text{M}}) = 247.51 \pm 10 \text{ l.mol}^{-1}.\text{cm}^{-1}$;
 $e_{\text{M}} = 1.393 \text{ l.mol}^{-1}.\text{cm}^{-1}$; $e_{\text{Fe}} = 0.107 \text{ l.mol}^{-1}.\text{cm}^{-1}$; pH=8.0 (Tris-buffer),
 $I = 1.0M$; Cell length-1.0cm; wavelength at $\lambda 500 \text{ nm}$. $*Z = (\text{OD}/d - \text{OD}_0/d) - e_{\text{Fe}}.f$.

Table. 3

Values of constants, K and e, and other data for the reaction between
 $\text{Cu(EDDA)} + \text{Fe(CN)}_6^{4-}$

$[\text{Cu(EDDA)}]_0 / 10^{-4} \text{ M}$	$[\text{Fe(CN)}_6^{4-}]_0 / 10^{-4} \text{ M}$	OD_{obs}	$(P = \frac{[\text{Cu}]}{*Z}) / 10^{-3}$	$\frac{1}{[\text{Fe(CN)}_6^{4-}]_f}$
4.0	6.0	0.2400	6.659	2606.95
"	8.0	0.2825	5.742	1821.89
"	20.0	0.3635	4.456	600.46
"	40.0	0.4095	3.961	275.26
"	60.0	0.4265	3.812	177.88
"	80.0	0.4405	3.699	131.29
3.0	5.0	0.1700	7.178	2894.29
"	7.0	0.1945	6.264	1937.75
"	25.0	0.2725	4.468	446.81
"	40.0	0.3015	4.044	268.52
"	60.0	0.3090	3.959	174.94
"	80.0	0.3270	3.751	129.67

$K = 3066.81 \pm 160 \text{ l.mol}^{-1}$; $(e_{\text{BN}} - e_{\text{M}}) = 271.27 \pm 4.04 \text{ l.mol}^{-1} \text{ cm}^{-1}$;
 $e_{\text{M}} = 2.20 \text{ l.mol}^{-1} \text{ cm}^{-1}$; $e_{\text{Fe}} = 0.41 \text{ l.mol}^{-1} \text{ cm}^{-1}$; Cell length 4.0 cm;
 pH=8.0 (tris-buffer); λ 480 nm; I=1.0M (NaClO₄)*Z=(OD/d) - OD₀/d) - e_{Fe}.f

Table. 4.

Values of constants, K and e, and other data for the reaction between
 $\text{Cu(NTA)}^- + \text{Fe(CN)}_6^{4-}$

$[\text{Cu(NTA)}^-]_0 / 10^{-4} \text{ M}$	$[\text{Fe(CN)}_6^{4-}]_0 / 10^{-4} \text{ M}$	OD_{obs}	$\frac{1}{[\text{Fe(CN)}_6^{4-}]_f}$	$(P = \frac{[\text{Cu}]}{*Z}) / 10^{-3}$
3.0	4.0	0.1308	3997.00	9.257
"	6.0	0.1605	2419.55	7.543
"	8.0	0.1830	1696.24	6.609
"	12.0	0.2120	1039.46	5.701
"	15.0	0.2190	799.92	5.518
"	20.0	0.2290	575.43	5.272
5.0	6.0	0.2560	3127.1	8.196
"	8.0	0.2860	2113.23	7.046
"	10.0	0.3070	1560.86	6.551
"	15.0	0.3670	914.66	5.476
"	20.0	0.3778	637.38	5.345
"	25.0	0.3930	486.76	5.114

$K = 3837 \pm 115 \text{ l.mol}^{-1}$; $(e_{\text{BN}} - e_{\text{M}}) = 219.7 \pm 3.0 \text{ l.mol}^{-1} \text{ cm}^{-1}$;

$e_{\text{M}} = 0.994 \text{ l.mol}^{-1} \text{ cm}^{-1}$; $e_{\text{Fe}} = 0.042 \text{ l.mol}^{-1} \text{ cm}^{-1}$; λ 520 nm,
 cell length=4.0 cm; pH;8.0 (tris-buffer). *Z= (OD/d) - OD₀/d) - e_{Fe}.f.

Table 5

Values of constants, K and e, and other data for the reaction between
 $\text{Cu(PDTA)}^{2-} + \text{Fe(CN)}_6^{4-}$.

$[\text{Cu(PDTA)}^{2-}]_0 / 10^{-3} \text{ M}$	$[\text{Fe(CN)}_6^{4-}]_0 / 10^{-3} \text{ M}$	OD_{obs}	$\frac{1}{[\text{Fe(CN)}_6^{4-}]_f}$	$(P = \frac{[\text{Cu}]}{*Z}) / 10^{-3}$
2.50	15.0	0.118	69.04	22.029
"	20.0	0.140	51.67	18.387
"	25.0	0.166	41.25	15.515
"	30.0	0.196	34.32	13.129
"	50.0	0.258	20.48	9.941
"	60.0	0.289	17.03	8.921
"	80.0	0.334	12.73	7.738
"	95.0	0.357	10.70	7.257
1.25	15.0	0.059	67.85	21.954
"	20.0	0.077	50.83	16.913
"	25.0	0.086	40.62	15.221
"	30.0	0.098	33.82	13.250
"	50.0	0.134	20.788	9.78
"	60.0	0.148	16.85	8.841
"	80.0	0.172	12.62	7.716
"	95.0	0.179	10.61	7.467

$K = 18.03 \pm 1.04 \text{ l.mol}^{-1}$; $(e_{\text{BN}} - e_{\text{M}}) = 217.24 \pm 5.03 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$;
 $e_{\text{M}} = 0.78 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$; $e_{\text{Fe}} = 0.107 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$; cell length = 1.00 cm,
 pH = 8.0 (tris buffer); *Z = (OD/d - OD₀/d) - e_{Fe} · f, λ 500 nm.

Table 6

Values of constants, K and e, and other data for the reaction between
 $\text{Cu(CDTA)}^{2-} + \text{Fe(CN)}_6^{4-}$.

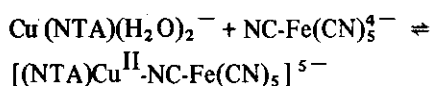
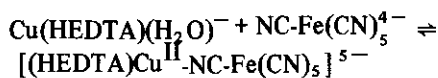
$[\text{Cu(CDTA)}^{2-}]_0 / 10^{-3} \text{ M}$	$[\text{Fe(CN)}_6^{4-}]_0 / 10^{-3} \text{ M}$	OD_{obs}	$\frac{1}{[\text{Fe(CN)}_6^{4-}]_f}$	$(P = \frac{[\text{Cu}]}{*Z}) / 10^{-2}$
2.50	15.0	0.0730	67.58	18.519
"	20.0	0.0910	50.67	14.413
"	25.0	0.1090	40.52	11.798
"	30.0	0.1240	33.76	10.294
"	50.0	0.1835	20.23	6.843
"	60.0	0.2345	16.85	5.214
"	80.0	0.2685	12.63	4.643
"	95.0	0.3160	10.63	3.922
5.00	15.0	0.1400	68.51	18.191
"	20.0	0.1780	51.34	13.759
"	25.0	0.2100	41.05	11.444
"	30.0	0.2455	34.18	9.630
"	50.0	0.3750	20.46	6.139
"	60.0	0.4185	17.04	5.478
"	80.0	0.5155	12.76	4.428
"	95.0	0.6050	10.73	3.750

$K = 5.00 \pm 0.70 \text{ l.mol}^{-1}$; $(e_{\text{BN}} - e_{\text{M}}) = 79.63 \pm 10.0 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$;
 $e_{\text{M}} = 1.12 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$; $e_{\text{Fe}} = 0.107 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$; 4.0 cm cell length;
 λ 500 nm, pH = 8.0 (tris buffer, TMAH/TMA); *z = (OD/d - OD₀/d) - e_{Fe} · f.

Table. 7

	EDTA=Y ⁻⁴	HEDTA=Y ⁻³	PDTA=Y ⁻⁴	CDTA=Y ^{†4}
Cu ^{II} -Y-Fe ^{II}	35.76 ± 1.50	364.43 ± 12.0	18.03 ± 1.0	5.0 ± 0.8
	NTA=Y ⁻³	EDDA=Y ⁻²		
Cu ^{II} -Y-Fe ^{II}	3778 ± 115	3070 ± 160		
Fe ^{II} =Fe(CN) ₆ ⁴⁻ , Cu ^{II} =Cu(Y)				

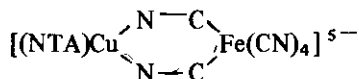
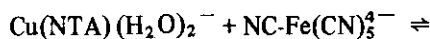
values ^{10/11} of pK₁ and pK₂ and the log K of EDDA than for the corresponding values for HEDTA or EDTA also suggests that metal affinity of NTA and EDDA are less than EDTA, and hence the former make less strong chelate complexes but stronger binuclear complexes. This is evident from the high values of K for EDDA and NTA than the corresponding values of K for HEDTA or EDTA. Another observation was that the values of K for EDDA and NTA for [Cu(EDDA,NTA)-Fe(CN)₆]⁴⁻ system are not much different, although they differ in charge and number of nitrogen atoms of the metal complex, but the value for the K_{NTA} is 14 times higher than the corresponding value for HEDTA. Hence we can assume that charge effect and the number of nitrogen atom of metal complex is not very significantly affecting the K values for binuclear complex formation. It is suggested that in fact the similar values may be due to the resemblance between these two complexes, i.e. with tetradentate ligand and with two replaceable H₂O molecules. Hence we might expect K_{NTA} to be 2 times K_{HEDTA} (Since the later has only one replaceable water molecule).



H₂O

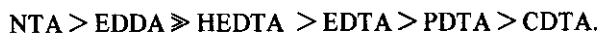
But we observed an unexpectedly large difference between the values of K_{NTA} and K_{HEDTA}. It may be due to (i) steric hinderance, (ii) doubly bridged binuclear

complex formation. However, a model suggests that there is little steric hinderance. If doubly bridged binuclear complexes can be formed they are to be expected with complexes containing two ligand water molecules. In this case the several times bigger value for K_{NTA} than for K_{HEDTA} may be understood, i.e.



Such doubly bridged binuclear complexes have been reported elsewhere.^{1,2}

A general order of affinity for the chelating ligands is found to be:



Experimental

All the chemicals used were Analar grade, except HEDTA (Koch-Light Lab. Ltd, NTA (B.D.H. Lab. Reagent), PDTA, CDTA, and EDDA (K&K Lab. Inc. N.Y. Calif), Potassium hexacyanoferrate (II) (Johnson Matthey Chem. Ltd), Tris (hydroxymethyl)methyl Ammonium chloride (lab. reagent B.D.H.). Doubly distilled water was used for all experiments. Stock solution of NaClO₄ was prepared by weight, filtered, and standardized by passing a diluted solution down an ion exchange resin (Amberlite IR-120(H), acid form), and subsequently titrating the liberated strong acid with standard hydroxide solution. Stock solution of metal-aminocarboxylate complex was prepared in solution by mixing solutions

of metal (II) sulphate and aminocarboxylate anion with the ligand concentration 5% or 100% excess over the metal as is indicated in table 1, experiments in table 2-6 were with solution containing 5% excess of aminocarboxylate. The pH of the solution was brought to 8.0 ± 0.02 by the addition of sodium hydroxide ions and measured on the pH meter. Stock solution of potassium hexacyanoferrate (II) was made by weight. Potassium ions were replaced by adding known concentrations of sodium perchlorate (also used for adjusting ionic strength). The solution was filtered free from potassium perchlorate, washed with distilled water and the volume was made upto mark. A fresh solution of hexacyanoferrate (II) was made (every day) for each set of experiments and was wrapped with aluminium foil to protect from exposure to light. This sodium-hexacyanoferrate(II) solution gave more stable reaction solutions than that obtained directly from the solid sodium salt.

Solutions for measurements of optical density of the metal-complex in the presence or absence of ligand were made at 25.0°C , from the various stock solutions by using standardized pipettes and graduated flasks. Appropriate buffer solutions were used to maintain the pH and the pH of the solution was found to be stable over the period required for spectrophotometric measurements. The ionic strength of all final solutions was made 1.0M by the addition of necessary volume of sodium perchlorate solution, allowance being made for any sodium perchlorate present in the stock solution of the ligand.

Spectrophotometric measurements were made at 25.0°C by using a Unicam SP800 spectrophotometer (for repeated scan spectra) and SP600, and Uvispek H700 (Hilger and Watts Ltd.), each was fitted with a temperature-controlled cell holder. Cells of optical

paths, 1.0, 2.0, and 4.0 cm were used as appropriate. Suitable wavelengths for the measurements of optical density were chosen by comparing the spectra of metal complex in the presence and absence of ligand in the visible and near u.v. region.

The pH of each final solution was measured at 25°C immediately after its optical density had been found, by using a Radiometer PHM26 pH meter.

References

1. A. Haim and W.K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).
2. J.P. Birk, *J. Amer. Chem. Soc.*, **91**, 3189 (1969).
3. A.G. Sykes, and J.A. Weil, *Progr. Inorg. Chem.*, **13**, 1, (1970).
4. G. Schwarzenbach, *Helv. Chim. Acta.*, **32**, 839 (1949).
5. K.L. Scott, R.S. Murray, and W.C.E. Higginson, *J. Chem. Soc. Dalton*, 2335 (1973).
6. B. Samuel and W.C.E. Higginson, *J. Chem. Soc. Dalton*, 1579 (1970).
7. R.A. DeCastello, C.P. MaColt, N.B. Egen and A. Haim, *Inorg. Chem.*, **8**, 699 (1969); **10**, 203 (1971).
8. J.H. Swinehart, *J. Inorg. Nuclear Chem.*, **29**, 2313 (1967).
9. Stability Constants of metal-ion complexes, *Chem. Soc. Special Publ. No. 25*, The Chemical Society, 1971.
10. G. Schwarzenbach, R. Gut and G. Andregg, *Helv. Chim. Acta.*, **37**, 936 (1954).
11. H. Ogino, *Bull. Chem. Soc. Japan.*, **58**, 771 (1965).
12. A.D. James, W.C.E. Higginson, and R.S. Murray, *J. Chem. Res.*, 1084 (1977).