Equilibrium Studies and Mixed Binuclear Complex Formation of Complexes Obtained From Metal-aminopolycarboxylate and Cyano-Complexes

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Summary: The equilibrium constants for mixed binuclear complex formation between certain bivalne transition metal-EDTA complexes and various cyano-complexes in aqueous solution have been obtained from spectrophotometric measurements. The results can be interpreted to obtain the order of strenght of binuclear complex formation with metal (II) which is: $Cu \gg Ni > Co$; with aminocarboxylate complexes,: $NTA > EDDA > HEDTA > EDTA > PDTA > CDTA$; and with cyano-complexes; $Fe(CN)_6^{4-} \sim Ru((CN)_6^{4-} \gg Fe(CN)_6^{3-} > Fe(CN)_5(NO)^{2-}$.

Introduction

Haim and Wilmarth [1] showed the production of binuclear species, $[(CN)_5Co^{III}-NC-Fe^{II}(CN)_5]^{6-}$, in the oxidation of pentacyano complex of Cobalt (II) by $Fe(CN)_6^{3-}$. Similarly, the products of reactions between $[Co^{III}(en)_2(SO_3)(OH_2)]^+$ and different cyanometallates have been characterized as binuclear cyanide-bridged complexes [2]. The formation of mixed Iron-Copper binuear complexes from the reactions of hexacyanoferrate (II), $Fe(CN)_6^{4-}$, with copper-aminopoly-carboxylate complexes, $Cu(EDTA)^{2-}$, and subsequently equilibrium constant for reaction (I) has been reported, in part earlier [3].

$$Cu(EDTA)^{2-} + Fe(CN)_6^{4-} \rightleftharpoons$$

$$[(EDTA)Cu^{II}-NC-Fe(CN)_5]^{6-} \quad (I)$$
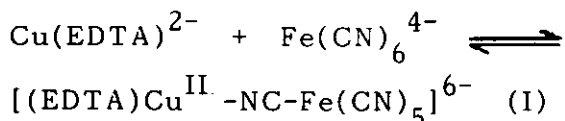
We now report a more detailed equilibrium study of equilibriums of reactions of Cu(II) and other dipositive metals, Co(II) and Ni(II), (complexed with EDTA and its related compounds) with the ligands, cyanometallates,

$Fe(CN)_6^{4-}, Fe(CN)_5(NO)^2, Fe(CN)_6^{3-},$ $Mo(CN)_8^{4-}$ and $Ru(CN)_6^{4-}$
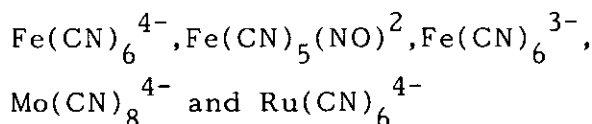
Equilibrium constants for mixed binuclear complex formation were determined spectrophotometrically by observing the change in the absorbance of the reaction mixture in comparison to the reactants at maximum wavelength in the visible region. Spectra of the complexes and reactants were obtained and one or more suitable wavelength were chosen for each determinations. The molar extinction coefficient, ε was determined for the reactants at various concentrations and wavelengths. We define $\varepsilon =OD/C.d.$ where OD is the optical density of a solution whose total concentration is C in an optical cell of path length d, after correction has been made for absorbance by any other species other than C in its various combined forms. The equilibrium constant, K, and molar extinction coefficient, for the reactions under study were determined by deriving equation (2) relating optical densities of K from the equilibrium condition described in equation (1). [Here M, Fe, and Bn, represents the equilibrium concentrations of $M^{11}{}_4{}^-$ (EDTA)$^{2-}$

(metal-complex), $Fe(CN)_6^{4-}$ (second species, cyanometallate), and concentration at equilibrium of $[(EDTA)M^{11}-NC-Fe(CN)_5]^{6-}$, (the binuclear complex)].

$$[M]_o/(OD/d - OD_o/d) - \epsilon_{Fe}.f =$$

$$(\epsilon_{BN} - \epsilon_M) + 1/K (\epsilon_{BN} - \epsilon_M) \times 1/f$$

where $[M_o]$ = initial concentration of metal-complex, f and OD_o are the corrected Fe concentration and absorbance due to unreacted metal complex. A plot of $1/f$ gave a straight line of slope $1/K(\epsilon_{BN} - \epsilon_M)$, intercept $1/\epsilon_{BN} - \epsilon_M)$

However in few cases, this graphical method obtaining the values of K and was not possible because the value of K was either large or the difference in the molar extinction coefficients of the metal-complex and the binuclear species was very small. Under these conditions the use of above equation (2), with two unknowns, ϵ_{BN} and K, leads to large errors, especially in K. Therefore a 'calculation method' was devised by which ϵ_{BN} was determined fairly accurately, since the K was large and from experiments in which high concentrations of Fe was used to convert virtually all M into BN. The BN concentration in solution is determined by equation (3).

$$[BN] = \frac{OD/d - [\epsilon_M - (M_o) + \epsilon_{Fe}(Fe)]}{\epsilon_{BN} - \epsilon_M - \epsilon_{Fe}} \quad (3)$$

Substituting [BN] in equation (4), the equilibrium constant K is determined.

$$K = \frac{[BN]}{([Fe]_o - [BN])([M_o] - [BN])} \quad (4)$$

The values of K obtained were not quite correct since ϵ_{BN} was obtained without allowing for less than 100% conversion. We worked out the proportion of [BN] by assuming the above calculated value of K and hence corrected [M] and [Fe] in the experiments at high Fe concentration. Then we used equation (5) to find an improved.

$$OD/d = \epsilon_{Fe}[Fe]_o + \epsilon_M[M]_o + \epsilon_{BN}.[BN]$$

value of ϵ_{BN} and then repeated the calculations for K. About 3-5 titerations were necessary for a satisfactory value of K.

Results and Discussion

Preliminary results for the systems, $Ni(Y)-Fe(CN)_6^{4-}$, where Y=EDTA, HEDTA, NTA, and EDDA, were studied under the conditions where the concentration of one of the reactants, M^{II} (Y), kept constant and the concentration of the second reactant, $Fe(CN)_6^{4-}$, was varied over a wide range (3-10 times (M^{II}), at ionic strength, I of 1.00 $M(NaClO_4)$, temperature 25°C pH=8.0 (Tris-buffer, tris-hydroxymethyl methyl ammonium chloride), and wavelengths, 650 nm, 670 nm, and 700 nm. The data were used in equation (2) and using the successive aproximation procedure, typical straight line plots giving the values of ϵ and K were obtained (figure 1).

Similarly, in other systems, different sets of combinations of metal-complexes and cyanometallates were studied under the same conditions as described for the $Ni(Y)-Fe(CN)_6^{4-}$ systems (typical plots in Figure 1) at the wavelength where the maximum change in the absorbance for the binuclear complex
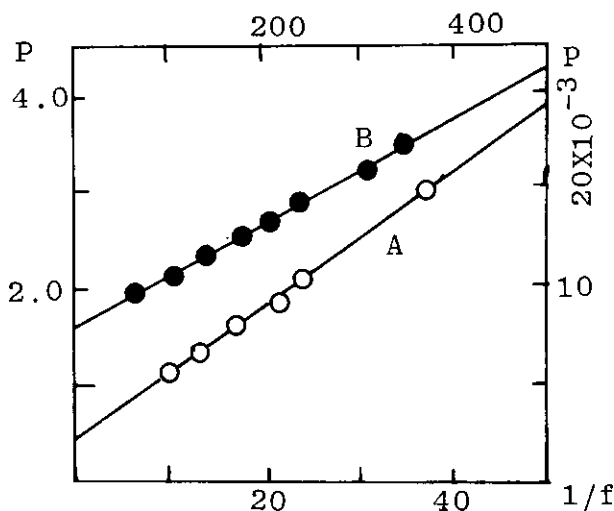
Fig.1 A, plot for obtaining, & K, for the Ni(EDTA)$^{2-}$ -Fe(CN$_6$)$^{4-}$ system at 650 nm; B, Plot for obtaining, ϵ & K for the Co(NTA)$^-$ -Fe(CN)$_6^{4-}$ system at 560 nm. P and 1/f are the values when data were put in the left-hand side and right-hand side of equation 2. The ordinate on R.H.S. and the top abscissa is for the Co(NTA)$^-$ -Fe(CN)$_6^{4-}$ system.

was observed in few systems, Co(CDTA)$^{2-}$ -Fe(CN)$_6^{4-}$, Co(HEDTA)$^-$ -Fe(CN)$^{4-}$ Ni(HEDTA)$^-$,-Fe(CN)$_6^{4-}$, and Ni(NTA)$^-$ -Fe(CN)$_6^{4-}$, the graphical method did not give accurate values of ϵ and K, and therefore, 'calculation method' described above was used, and it gave quite satisfactory values of and K.

The various binuclear complex forma-. tion constants, K are summarized in the table 1(A).

In the system, Cu(Y)-Fe(CN)$^{4-}$ when Cu(II) was replaced by Ni(II) and Co(II), a large drop in the values of K from that for the corresponding value for Cu(II) with EDTA as the lingand was observed. This trend was apparent with all the other chelating ligands, HEDTA, NTA,EDTA, (PDTA and CDTA). Similar types of complexes with Ni(Y)-NH$_3$, where Y=EDTA, HEDTA,

EDDA, and NTA were reported [4] and show the following order, similar to that reported here for binuclear complex formation

NTA > EDDA > HEDTA > EDTA.
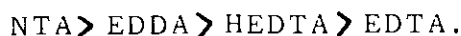
With Ni(II) the combination of small spectral changes on formation of the binuclear complex [table 1(B)] and generally lower K values than for Cu (II) made it impossible to obtain satisfactory K values for binuclear complexes involving PDTA and CDTA. The difference between the K_{HEDTA}-Fe $(CN)_6^{4-}$ and $K_{NTA-Fe(CN)_6}$ or $K_{EDDA-Fe}$ (CN)$_6^{4-}$ for the above two metals Ni(II) and Co(II) was not as great as it was in the corresponding complex with metal [3], Cu(II), [K_{NTA} only four times higher than K_{HEDTA} in the case of Co(II) and Ni(II)]. This small difference suggests that doubly bridged [3] binuclear complexes are not formed with these metals. The general trend of strength of binuclear complex formation was:

Cu(II) $\gg$ Ni(II) > Co(II)
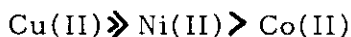
This is the same as the order of complexing tendency of the simple cation [5].

Results with other Cyanometallates

On replacing Fe (CN)$_6^{4-}$ by Fe(CN)$_6^{3-}$, Mo(CN)$_6^{4-}$, Fe(CN)$_5$ (NO)$^{2-}$, and Ru(CN)$_6^{4-}$, and for Cu (EDTA)$^{2-}$ complexes, it was observed that the values of K and molar extinction coefficient dropped very much in the first three cyanometallates and were about the same in the case of Ru(CN)$_6^{4-}$ as for the corresponding experiments with Fe(CN)$_6^{4-}$.The value

Table-1(A):Various binuclear complex formation constants, K^+.

	EDTA=$^{4-}$	PDTA=$^{4-}$	CDTA=$^{4-}$
*Cu(Y)-Fe(II)	35.68 + 1.50	18.03 + 1.0	5.0 + 0.8
Ni(Y)-Fe(II)	6.58 + 0.64		
Co(Y)-Fe(II)	5.52 + 0.22	4.65 + 0.9	2.0 + 0.4

	NTA=Y^{3-}	EDDA=Y^{2-}	HEDTA=Y^{3-}
*Cu(Y)-Fe(II)	3837 + 115	3066 + 160	267.43 + 12.0
Ni(Y)-Fe(II)	414 + 7.0	161.80 + 9.4	107.47 + 11.0
Co(Y)-Fe(II)	305 + 8.2		92.62 + 3.20

	EDTA=Y^{4-}	HEDTA=Y^{3-}	EDDA=Y^{2-}
Cu(Y)-Ru(II)		230.71 + 6.6	3614 + 172
Cu(Y)-Mo(IV)	33.85 + 3.2	66.23 + 6.92	351.5 + 25
Co(Y)-Fe(III)	1.0		

Fe(II)=Fe(CN)$_6^{4-}$; Fe(III)=Fe(CN)$_6^{3-}$; Mo(IV)=Mo(CN)$_8^{4-}$; Ru(II)=Ru(CN)$_6^{2-}$

*Values of K obtained from reference 3.

+K=Equilibrium constant express in $1.mol^{-1}$ units.

of K was very small in the case of $Fe(CN)_5(NO)^{2-}$ and was immeasureable. This trend was also apprent with HEDTA, NTA, and EDDA (PDTA & CDTA). Several combinations of cyanomethallates and aminopolycarboxylate complexes gave no evidence for the formation of binuclear complexes. The values of K and ε were subject to considerable error in the $Mo(CN)_8^{4-}$-$Cu(EDTA)^2$ system and some instability was found in the this system. The values of K in the cases of $Co(Y)^{2-}$-Fe$(CN)_6^{3-}$,where Y=EDTA, PDTA,and CDTA, were small, of the order of K= 1.0 $1.mol^{-1}$ or less. Also some instability with pH was observed in Cu(NTA)-Fe$(CN)_6^{3-}$ system, although there was clear evidence of binuclear complex formation from the change in spectrum. In the systems of Cu(Y)-Ru(CN)$_6^{4-}$, Y=HEDTA and NTA, the values of K were very similar to the corresponding

Table-1 (B): Various molar extinction coefficients, $_{BN}$, for binuclear complexes.

	EDTA=Y^{4-}	PDTA=Y^{4-}	CDTA=Y^{4-}
*Cu(Y)-Fe(II)	235.50 $\pm$ 5.0	217.24 $\pm$ 5.0	79.6 $\pm$ 10.0
at /mn	65,670,500	500	500
Ni(Y)-Fe(II)	6.6,5.4,3.9		
at /mn	650,670,700		
Co(Y)-Fe(II)	62,6,92,0,75.8	52.9,64.0,56.4	23.3,18.8
at /mn	480,520,540	480,500,540	480,500

	NTY=Y^{3-}	EDDA=Y^{2-}	HEDTA=Y^{3-}
*Cu(Y)-Fe(II)	220.05 $\pm$ 3.0	271.27 $\pm$ 4.0	246.44 $\pm$ 10.0
at /nm	520	480	500
Ni(Y)-Fe(II)	3.47,4.3,5.68	8.24,8.55	5.8,11.2,18.1
at /nm	800,825,850	580,600	800,850,900
Co(Y)-Fe(II)	135.2,145.8,8.104		66.3,73.9,66.7
at /nm	560,580,600		500,520,540

	EDTA=Y^{4-}	HEDTA=Y^{3-}	EDDA=Y^{2-}	NTA=Y^{3-}
Cu(Y)-Ru(II)		423,425.0,373		260.0,179.9
at /nm		390,400,420		400,420
Cu(Y)-Mo(IV)	23,55,14.81	60.61,46.87	37.30,62.02	63.3,50.5,39.5
at /nm	520,550	510,530	510,430	530,550,570
Cu(Y)Fe(III)		26.6,25.4,24.1	37.1,38.8,42.6	
at /nm		500,510,520	500,510,520	

Fe(II)=$Fe(CN)_6^{4-}$; Fe(II)=$Fe(CN)_6^{3-}$; Mo(IV)=$Mo(CN)_8^{4-}$; Ru(CN)$_6^{4-}$

*Values of ε_{BN} obtained from reference 3.

ε= molar extinction coefficient expressed in 1 mol^{-1}, cm^{-1} units.

values with $Fe(CN)_6^{4-}$. Consequently no further attempt was made to obtain the stability constants for binuclear complexes formed from $Ru(CN)_6^{4-}$. From the similarity between $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ (reported [7] to form a potassium salt isomorphous with mono-clinic-pseudotetragonal-   from of $K_4Fe(CN)_63H_2O$), in coordinated ligand groups, charge on the complex, and to some extent the size of metal ion, similar values of K for the $Cu(Y)$ $Fe(CN)_6^{4-}$ and $Cu(Y)-Ru(CN)_6^{4-}$ systems were not surprising. Hence it was concluded that the values of K were in increasing order with the increase in charge of cyanometallates of similar structure.

$$Fe(CN)_5(NO)^{2-} < Fe(CN)_6^{3-} \lesssim Ru(CN)_6^{4-} \sim$$
$$Fe(CN)_6^{4-}$$
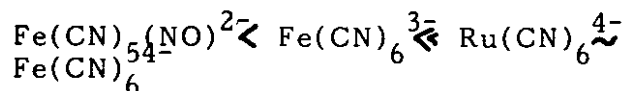
$Mo(CN)_6^{4-}$ although having the same charge as $Fe(CN)_6^{4-}$ is a weaker ligand. This presumably reflects the greater polarizing power of $Mo(IV)$ compared with $Fe (II)$ on the coordinated cyanide groups. A similar charge effect of cyanometallates, $Fe(CN)_5$ $(NO)^{2-}$, $Co(CN)_6$, and $Fe(CN)_6^{4-}$ with the complex, $[Co^{III} (en)_2 (SO_3)$ $(OH_2)]^+$, was observed [2]. The large magnitude of K values $(K=290 \times 10^4$ l. $mol^{-1})$ for the $Fe(CN)_6^{4-}$ with $Co(III)$ complex compared with the aminopoly carboxylate compexes described here could be due to the charge effect of the complex, $[Co(en)(SO_3)(OH_2)]^+$, since no electrostatic repulsion between it and $Fe(CN)_6^{4-}$ occurs and also because cabalt (III) is a much stronger complexing species than cobalt (II),

nickel (II) or copper (II).

To summarize these equilibria studies, there are three factors which should be considered in comparing the values of the stability constants for different binuclear complexes, (i) nature of metal ion, (ii) charge on cyanometallate, and (iii) number of water ligands (if any), attached to metal-amino-polycarboxylate complex.

In the case of metal ions, it was observed that Cu(II) gives bigger K values than Ni(II) and Co(II), and this is in agreement with the general observation that equilibrium constants for the formation of analogous complexes of the divalent-metal ions of Mn through Zn with ligands containing nitrogen as the donor atom fall in the following order of the metal ion:

$$Mn^{2+} < Fe^{2+} < CO^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$
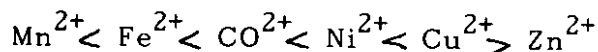
This order is sometimes called Irving-Williams's principle [6].

In the case of charge on cyano-metallate, the high charge species, $Fe(CN)_6^{4-}$, give the largest K values and it seems that charge per cyanide group is an important factor as $Mo(CN)_8^{4-}$ gave smaller K values than $Fe(CN)_6^{4-}$.

In the case of aminopolycarboxylate complexes those which contain water ligand to complete the hexa-coordination with metal ions give bigger K values, e.g. M^{11} (HEDTA) $(H_2O)^-$ gives bigger K values than M^{11} (EDTA)$^{2-}$. Similarly M^{11} (EDDA) $(H_2O)_2^O$ and M^{11}(NTA) $(H_2O)_2^-$ (both are tetradentate ligands) gives bigger K values than M^{11} (HEDTA) $(H_2O)^-$ for the corresponding cyanometallates.

Experimental

All the chemicals used were Analar grade, except HEDTA - N -hydroxy-ethyl-ethylenediamine-NN'N'-triacetate (Koche-high Lab. Ltd.), NTA - nitrilo-triacetate (B.D.H. lab.regent),PDTA - 1,2 diamineopropane-NNN'N-tetra-acetate CDTA - 1,2 diamino-cyclohexane NNN'N'-tetra-acetate, and EDDA - ethylenediaminodiacetate (K & K lab. Inc. N.Y. Calif). Tris-hydroxymethyl-methyl ammonium chloride (B.D.H. regent). Stock solutions of $NaClO_4$ (for maintaining ionic strength) was pre-pared by weight, filtered, and stan-dardized [3,8]. Stock solutions of metalaminopolycarboxylate complex was prepared in solution by mixing solutions of metal(II) sulphate and aminopolycar-boxylate anion with the ligand concen-tration 5% in excess over the metal, and 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. The pH of each solution was measured at 25.0° by using Radiometer PHM 26 pH meter. Stock solutions of hexacyanoferrate (II), hexacyano-ferrate (III), octacyanomolybdate (IV), nitrosopentacyanoferrate (III), and hexacyanoruthenate (II) were prepared by weight. Solid potassium octacyano-molybdate (IV), $K_4Mo(CN)_8$, was pre-pared by Furman and Miller's method [9]. Potassium ions of $K_4Fe(CN)_6$ and $K_4Mo(CN)_8$ were replaced by adding

known concentrations of sodium perchlorate, $NaClO_4$, (also used for adjusting ionic strength). Spectro-photometric measurements were made at 25.0°C by using unicam SP 600, and Uvispek (High and Watts Ltd.). Optical cells of path lengths, 1.0,2.0 or 4.0 cm were used as appropriate.

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