Equilibrium Studies of Mixed Binuclear Complexes of Transition Metals

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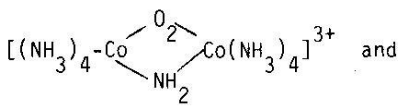
Binuclear cobalt(III) complexes can be classified either as dicobalt complexes, or as 'mixed' complexes. In the former case both metal centres are cobalt(III) and in the latter case the second or both centres are different metals.

A good deal of work was done on binuclear complexes in the late ninteenth century, including, Fremy [1] (1852), Gibbs [2] (1876), Vortmann [3] (1898), Jorgensen [4] (1894), and Mascetti [5] (1900). A number of papers by Werner [6] (1898-1918) greatly expanded the scope of the field. One of these [7] described the properties and preparation of a wide variety of dicobalt complexes. Ligands which make bridged complexes of dicobalt(III) atoms include, NH_2^-, OH^-, O_2^{2-}, O_2H^-, SO_4^{2-}, NO_2^-, $N_2O_2^{2-}$, HPO_4^{2-}, and CH_3COO^-.

Amido Bridged Binuclear Complexes:

The amido-bridged, NH_2^-, are especially common among the dicobalt binuclear complexes, formed by way of 'Vortmann' sulphate [8], containing salts of the ions.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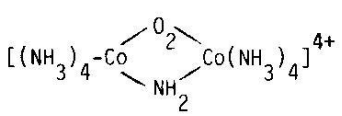
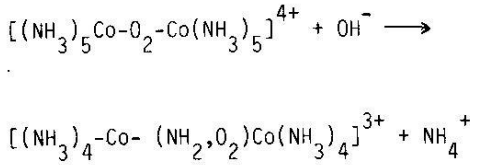
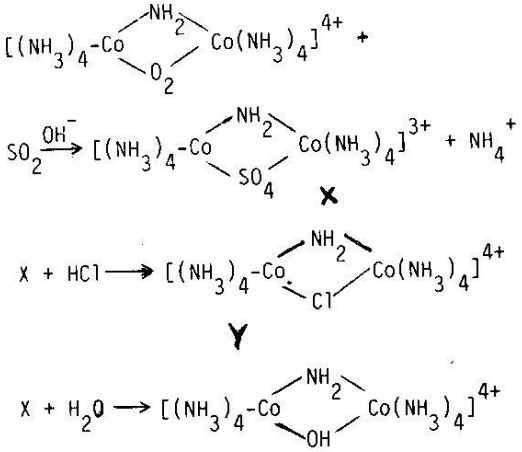


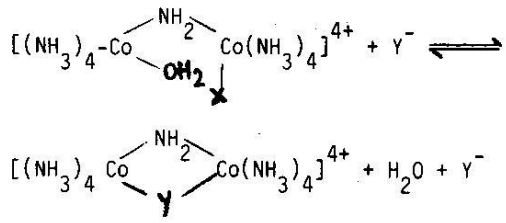
Mori et.al [9] showed that amido complexes are formed by decaammine 4 +ve ion via condensation reactions involving the ammine ligands.



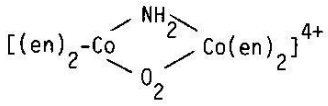
They were found to be very stable, and the O_2 group of the bridge was capable of being replaced by other ligands, like [10,11].



The ion μ-amido-μ-hydroxo-bis(tetraamminecobalt(III) is relatively unreactive with acids (nitrous, acetic, hydrochloric acid), however, aquachloro complexes with a cleaved hydroxo bridge react with these acids to give various dibridged-μ-amido complexes [12].



Binuclear complexes of cobalt, showing optical activity were reported by Werner [13],



and resolved into four different optical active isomers. These were further studied by Susaki [14], who reported the preparation of μ-amido-μ-peroxo-tetrakis-(1-propylene-diamine) dicobalt nitrate trihydrate and resolved [15] optical isomers as had previously been done by Werner [13] with the complex, μ-amido-superoxo-ethylene-diaminedicobalt(III).

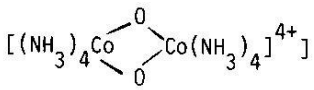
Oxygen Bridged Binuclear Complexes:

Oxygen bridged binuclear complexes are classified into two types, (i) O_2^{2-}, Peroxo linkage and (ii) O_2^{-}, Superoxide linkage, generally referred as "peroxo" and "superoxo", respectively, bridged complexes.

Simplicio and Wilkins [16] studied the kinetics of the reaction of cobalt (II) with molecular oxygen.

$$[(NH_3)_5Co\text{-}H_2O]^{2+} + O_2 \rightleftharpoons [Co(NH_3)_5O_2]^{2+}$$

$$[(Co(NH_3)_5O_2]^{2+} + [Co(NH_3)_5(H_2O)]^{2+} \rightleftharpoons$$

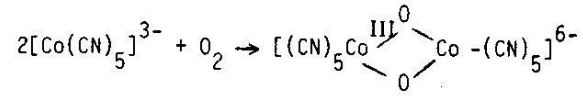


Mori et.al [17] have used cerium(IV) in nitric acid to oxidize the dibridged peroxo complex ion,

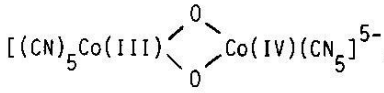
$$[(NH_3)_4Co\text{-}\mu(NH_2.O_2)Co(NH_3)_4]^{3+}.$$

Weil and Kinnaird [18] have also oxidized μ-peroxo-bis(1-histidinato) Co(III) to the μ-superoxo complex with cerium(IV).

Pentacyanocobalt(II) ion is an extremely good reducing agent and reacts with oxygen to give a binuclear μ-peroxo complex in aqueous medium.



This reaction was first studied by Haim and Wilmarth [19], the product undergoes a one-electron oxidation to produce the binuclear complex,



containing cobalt in the formal oxidation states of (III) and (IV). Winfield and coworkers [20] have oxidized the peroxo complex with oxygen.

$$[(CN)_5Co\text{-}O_2\text{-}Co(CN)_5]^{6-} + O_2 \rightarrow$$

$$[(CN)_5Co\text{-}O_2Co(CN)_5]^{5-}$$

Yateman [21] showed that by oxidation of $Co^{II}(EDTA)^{2-}$ with H_2O_2 (pH=6.5-8.5) an intermediate is formed of the type:

$$[(EDTA)Co^{(III)}\text{-}O_2\text{-}Co^{(III)}(EDTA)]^{4-}$$

A number of binuclear complexes of ammonia, ethylenediammine, diethylenetriamine, triethylenetetraamine, and tetra-ethylene-pentaamine, with cobalt(II), containing a μ-peroxo group have been investigated and their analogous μ-superoxo salts. Ammonical solutions of Co(II) absorb molecular oxygen to form μ-superoxo binuclear [22] complexes in two steps such as:

$$[Co(II)(NH_3)_5X]^{2+n} + O_2 \longrightarrow [Co(NH_3)_5(^{\cdot}O_2)]^{2+} + X^{n-}$$

$$[Co(NH_3)_5{}^{\cdot}O_2]^{2+} + [Co(NH_3)_5X]^{2+n} \longrightarrow [(NH_3)_5Co^{(III)}\text{-}O\text{-}Co^{(III)}(NH_3)_5]^{4+} + X^{n-}$$

This diamagnetic complex can react further, by one electron oxidation, and is converted to a paramagnetic form,

$$[(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]\ X_5$$

containing one odd electron equally distributed with respect to the two cobalt nuclei [23]. The μ-superoxo complexes can also form by one electron oxidation of the peroxo complexes [24], for example,

$$[(NH_3)_5Co\text{-}O_2\text{-}CO(NH_3)_5]^{4+} \longrightarrow [(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{5+} + e^-$$

Cyano Bridged Binuclear Complexes:

The formation of a cyano-bridged binuclear complex was first reported by Taube [25] and Myers in 1954. They suggested that the reaction between Cr(II) and $Fe(CN)_6^{3-}$ undergo redox through the cyanide bridged "activated" complex persisting in the insoluble product. Detailed studies of cyanide bridged complexes were reported by Haim and Wilmarth [19], who showed that in the oxidation of pentacyano complex of Co(II) by $Fe(CN)_6^{3-}$, the oxidant was trapped in the coordination sphere of cobalt with the formation of the binuclear ion, $[(CN)\ Co^{(III)}\text{-}NC\text{-}Fe^{(II)}(CN)_5]^{6-}$.

This ion is an inert bridged complex with the same composition and geometry as the bridged 'activated' complex for the reaction, and also shows an instance of an inert binuclear complex containing two different octahedrally substituted metal ions. Haim and coworkers [26] have reported the synthesis of μ-cyanopenta-cyanopenta-aminedicobalt(III,III), $[(NH_3)_5\ Co^{III}\text{-}NC\text{-}Co^{III}(CN)_5]$, on the basis of analytical data, the conductivity, and ion-exchange behaviour of solutions of complex and molecular weight measurements.

Much attention has been given to the reaction between $Fe(CN)_6^{3-}$ and the complex $Co(EDTA)^{2-}$. In the original study, Adamson and Gonick [27] (1963) established that a mixed binuclear complex was formed in the reaction.

$$Co(EDTA)^{2-} + Fe(CN)_6^{3-} \rightleftharpoons [(EDTA)Co^{(III)}\text{-}NC\text{-}Fe^{(III)}(CN)_5]^{5-}$$

involving ring-opening, substitution, and inner-sphere electron transfer. This intermediate was further decomposed to give final product, $Co^{(III)}(EDTA)^-$ and $Fe(CN)_6^{4-}$. Huchital and coworkers have reported the kinetic studies [28] of this reaction and have shown that an analogous [29] reaction occurs with the complexes, $Co(CDTA)2^-$, $Co(PDTA)^{3-}$, $Co^{(II)}(Histidinato)_2$ [30]. Subsequently, Ogino [31] et al. and Eswell [32] have

published similar results with some overlap of the Huchital work. The reaction of $Fe(CN)_6^{3-}$ with $Co(HEDTA)^-$ was different in that though the binuclear complex was formed rapidly as usual, the spectrum then remained unchanged for several hours and only a lower limit could be placed on its rate of disappearance. An explanation for this was given in terms of the quinquedentate nature of the HEDTA ligand where N-hydroxyethyl group has only weak coordinating power. Higginson [33] and coworkers reported the presence of cyano-bridged binuclear complexes by simple substitution reactions involving no electron transfer between the ions:

$$[Fe^{(III)}(CN)_5H_2O]^{2-} + [Co(CN)_6]^{3-} \rightarrow [(CN)_5\,Fe^{(III)}\text{-}NC\text{-}Co^{(III)}(CN)_5]^{5-}$$

They further reported]34] the kinetics of formation and bridge cleavage of binuclear complexes derived from aqua-pentacyanoferrate (II,III) ions in aqueous solution.

$$[Fe^{(II)}(CN)_5(H_2O)]^{3-} + M(CN)_6^{n-} \rightleftharpoons [(NC)_5Fe^{(II)}\text{-}NC\text{-}M(CN)_5]^{(n+3)-} + H_2O$$

X

where $M=Fe^{(II)}$ or $Co^{(III)}$.

They also reported the bridge cleavage reactions of binuclear complexes formed in (X) with pyridine and 4-methyl-pyridine, and substitution [35] and hydrolysis [36] of di-μ-cyano-bis tetracyanoferrate (III) forming singly bridged binuclear complexes.

Higginson [37] further reported the formation of mixed iron-cobalt binuclear complexes by mixing equimolar solutions of [trans-$Co(en)_2(So_3)(H_2O)]^+$ complex and the ions, $Co(CN)_6^{3-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and $[Fe(CN)_5(NO)]^{2-}$, and showed from spectrophotometric measurements that the equilibrium constant increases as the charge on the cyano complexes increases. Comprehensive studies on mixed binuclear complexes was reported by Khan [38] and coworkers involving metal-EDTA and its related compounds, HEDTA, PDTA, CDTA, EDDA, and NTA) complexes and hexacyanoferrate (II), ligand.

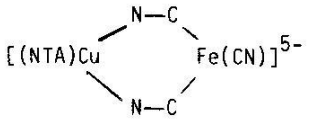
$$M(II) - EDTA^{2-} + Fe(CN)_6^{4-} \overset{K}{\rightleftharpoons} [(EDTA)M^{(II)}\text{-}NC\text{-}Fe^{(II)}(CN)_5]^{5-}$$

From the equilibrium constant measurements [38], it appeared that hexacyanoferrate(II) ion forms intensely coloured complexes with different metal-aminocarboxylate complexes, except in the case of $Cu(CDTA)^{2-}$-$Fe(CN)_6^{4-}$ system, with a large change in the wavelength of maximum absorption compared with that of metal complex. This change may be due to charge-transfer absorption. The comparatively low absorption for $Cu(CDTA)^{2-}$-$Fe(CN)_6^{4-}$ system may be due to the rigidity [39] and stronger complexing ability of CDTA with metals. They found a general order of affinity for the chelating agents to be:

NTA > EDDA ≫ HEDTA > EDTA> PDTA > CDTA

and exceptionally high value of K for the binuclear $Cu(NTA)$-$Fe(CN)_6^{4-}$ system than for $Cu(HEDTA)$-$Fe(CN)_6^{4-}$ suggested a doubly bridged binuclear complex, containing two ligand water molecules:

$Cu(NTA)(H_2O)_2^- + NC\text{-}Fe(CN)_5^{4-} \rightleftharpoons$



Such doubly bridged binuclear complexes have been reported elsewhere [36]. Further work on binuclear complexes was extended [40] to other dipositive metals, such as Ni, and Co, including Cu (complexed with EDTA and its related compounds) and the ligands, cyanometallates, $Fe(CN)_6^{3-}$, $Fe(CN)_5(NO)^{2-}$, $Mo(CN)_8^{4-}$, $Ru(CN)_6^{4-}$, including $Fe(CN)_6^{4-}$. The strength of binuclear complex formation with metal(II) is found:

Cu>> Ni > Co : with cyanometallates,

$Fe(CN)_6^{4-} \sim Ru(CN)_6^{4-} \gg Fe(CN)_6^{3-} > Fe(CN)_5(NO)^{2-}$.

The similar values of K (table 1) for $Cu(Y)\text{-}Ru(CN)_6^{4-}$ and $Cu(Y)Fe(CN)_6^{4-}$ was due to similarities between $Fe(CN)_6^{4-}$ and $Ru(CN)_6^{4-}$ (reported [41] to form a potassium salt isomorphous with mono clinic-pseudotetragonal form of $K_4Fe(CN)_6 3H_2O$), in coordinated ligand group, charge on the complex, and to some extent the size of metal ion. $Mo(CN)_8^{4-}$ 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, $Fe(CN)_5(NO)^{2-}$, $Co(CN)_6^{3-}$, and $Fe(CN)_6^{4-}$ with the complex, $[Co^{III}(en)(SO_3)(H_2O)]^+$ was observed]42].

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 cyanometallates, and (iii) number of water ligands (if any), attached to metal-aminopolycarboxylate 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 order sometimes called Irving William's principle [43].

In the case of charge on cyanometallates, 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 [40] 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. $M^{(II)}(HEDTA)(H_2O)^-$ gives bigger K values than $M^{(II)}(EDTA)^{2-}$. Similarly, $M^{(II)}(EDDA)(H_2O)_2$ and $M^{(II)}(NTA)(H_2O)_2^-$ (both are tetradentate ligands) give bigger K values than $M^{(II)}(HEDTA)(H_2O)^-$ for the corresponding cyanometallates.

In the binuclear studies of $Fe(EDTA)^-$ and Fe(HEDTA) with the ligands, $Fe(CN)_6^{4-}$ and NCS^-, Khan

[44] and coworkers have found large values of K for the addition of a ligand ($Fe(CN)_6^{4-}$ or NCS^-) to Fe(III)(HEDTA) as compared to $Fe(EDTA)^-$ and suggested that the only satisfactory explanation for the large values of K is that whereas the $Fe^{(III)}(HEDTA)$ 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 is known to be difficult from the low pH=0.5 of the acid [45], Fe(III)(EDTA-H). If one water molecule were present in $Fe(EDTA)^-$ and two in Fe(III)(HEDTA), the latter could be expected to give a constant for the addition of a ligand not more than 10 times larger than that with $Fe(III)(EDTA)^-$. This makes some allowance for the lack of charge repulsion in $Fe(III)(HEDTA)^0$, but this effect is not large as shown in the [38] binuclear complexes with $M(II)(NTA)^-$ and M(II)(EDDA) complexes with hexacyanoferrate(II). Thus, an interesting conclusion was put forward [44] that although there is evidence for seven coordinated $Fe(III)(EDTA)(H_2O)^-$ in the solid state [46], in solution the EDTA complex of iron(III) is predominantly six-coordinated and hexadentate.

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