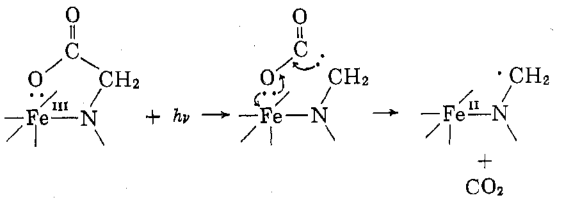
excess of iron(III) hydroxide and the olive-green compound precipitated from hot acetone–water mixture do not contain undissociated carboxylic acid groups, and hence are different in structure from the complex acid described here.

EDTA has been observed to be a pentadentate ligand in chelates of Co(III)[7] and Pb(II).[8] Hoard, Smith, and Lind[9] concluded that the complex acid is sexadentate and seven-coördinate, with a trigonal prism structure having the water molecule bonded to the iron in the square face of the prisms opposite the nitrogen atoms. Hoard, Lind, and Silverton[10] found from X-ray data that $Fe(OH_2)Y^-$ in the salt $RbFe(OH_2)Y\cdot H_2O$ is sexadentate and seven-coördinate, with a configuration "loosely describable" as pentagonal bipyramidal.

The difference in structure apparently is due to the preparation of the complex acid $HFeYH_2O$ with excess H_4Y. The chelate ions of salts resulting from the neutralization of this complex acid probably would assume the configurations described by Hoard and coworkers.

Photolysis of the complex acid is considered to proceed in several steps, *viz.*, the transfer of one of the electrons from an oxygen on a chelated carboxylate group to the iron, followed by rearrangement of the carboxylate group to release carbon dioxide and produce a free radical.



The fate of the free radical is not clear. It probably undergoes one or more of several possible reactions to form stable products. These include reaction with the coördinated water molecule or, if in solution, a solvent water molecule to form hydroxyl free radicals and hydrogen atoms (and eventually oxygen and hydrogen). Reaction of two photochemically produced ligand free radicals to form a dimer also is possible in the solid state. The negative test for oxidizing agents such as Br_2 and H_2O_2 in the potassium bromide pellet after irradiation of the complex acid is understandable, as the strongly-reducing iron(II) complex persists for hours in the presence of the other products.

The coördinating groups of the Y and the H_2O produce a weak-field, high-spin complex, as the magnetic susceptibility measurements indicate. The strong reducing character of the iron(II) complex is due fundamentally to the sixth electron forced on the metal ion, which is not spin-stabilized at all. Whereas iron(III) and cobalt(III) chelates of weak-field ligands having carboxylate donor groups generally are stable but photosensitive, the corresponding manganese(III) chelates undergo spontaneous decomposition, apparently because of the added stability the fifth electron receives when added to the high-spin d^4 complex.

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[7] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).

[8] D. T. Sawyer and P. J. Paulsen, *ibid.*, **81**, 816 (1959).

[9] J. L. Hoard, G. S. Smith, and M. Lind, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 296.

[10] J. L. Hoard, M. Lind, and J. V. Silverton, *J. Am. Chem. Soc.*, **83**, 2770 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES, CALIFORNIA

Reaction of Cobalt(II) Ethylenediaminetetraacetate with Ferricyanide

BY ARTHUR W. ADAMSON AND EMANUEL GONICK

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The oxidation of $Co(EDTA)^{-2}$ by $Fe(CN)_6^{-3}$, while giving $Co(EDTA)^{-1}$ and $Fe(CN)_6^{-4}$ as final products, is found to differ from the usual electron transfer systems in that the reaction occurs in two distinct steps. The first of these is interpreted as a rapid, reversible association to give $[(EDTA_5)Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^{-5}$. The second, slower, process is then the dissociation of this binuclear species to give the final products.

Previous work in this Laboratory has been directed toward the kinetics of electron transfer systems, particularly those involving cobalt and other transition metal complexes of negative charge.[1–3] In particular, during the course of the investigation of the exchange between $Co(EDTA)^{-2}$ and $Co(EDTA)^{-1}$,[3] it was noticed that the former complex reacted with $Fe(CN)_6^{-3}$ at a measurable rate. In undertaking the present investigation of this reaction it was felt that we might have an interesting intermediary situation between the very slow $Co(EDTA)^{-1,-2}$ system and the rapid

[1] A. W. Adamson, *J. Phys. Chem.*, **56**, 858 (1952).

[2] A. W. Adamson, *Rec. trav. chim.*, **75**, 809 (1956).

[3] A. W. Adamson and K. S. Vorres, *J. Inorg. Nucl. Chem.*, **3**, 205 (1960).

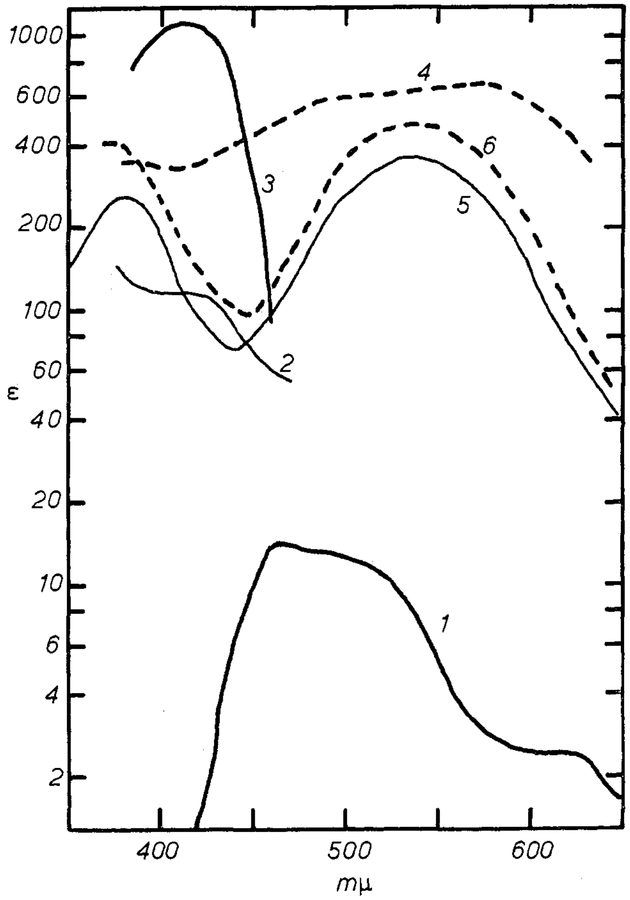

Fig. 1.—Absorption spectra: curve 1, $Co(EDTA)^{-2}$ in pH 5 acetate buffer; curve 2, $Fe(CN)_6^{-4}$ in 0.02 *M* EDTA and buffered to pH 5; curve 3, $Fe(CN)_6^{-3}$ in 0.01 *M* EDTA and buffered to pH 5; curve 4, $(EDTA_5)Co-NC-Fe(CN)_5^{-5}$ (solution initially 10^{-4} *M* in $Fe(CN)_6^{-3}$, 0.005 *M* in $Co(EDTA)^{-2}$, 0.01 *M* in excess EDTA, and buffered to pH 5); curve 5, $Co(EDTA)^{-1}$ in pH 5 buffer; curve 6, final product spectrum (same initial system as for curve 4).

$Fe(CN)_6^{-3,-4}$ one. As an additional point, while there would be a net driving force in the mixed system, it is in fact small and should not provide much of a perturbation over the equilibrium electron transfer situation.[4]

As will be seen, however, the reaction actually takes a more involved course than was anticipated. It appears, in fact, that in this case a bridged binuclear species, similar to those postulated as transition states in so-called atom transfer processes,[5,6] exists here as a relatively stable intermediate.

Experimental

Chemicals used were C.P. or Analyzed grade. Potassium ferricyanide and sodium ferricyanide were purified further by recrystallization from warm (*ca.* 60°) water; the compounds NaCo(EDTA) and $NaCo(EDTA)(H_2O)$ were prepared by methods given in the literature.[7] Cobaltous nitrate solutions were standardized by the method of Cartledge and Nichols.[8]

Reaction mixtures were prepared by diluting 0.01 *M* potassium ferricyanide 100-fold with a solution containing the desired concentration of Co(II) as the nitrate, sufficient disodium ethylenediaminetetraacetate to provide 0.01 *M* excess, and sodium acetate and acetic acid in such amounts as to make the final pH 5.0 and the final total ionic strength 0.66. The reaction was followed spectrophotometrically, either by means of a Beckman Model DU, or a Cary recording instrument. Room temperature runs were at 24–27°, and the low temperature ones at 3–7°; these last were intended only to provide approximate temperature dependence data.

The spectra of the various complexes involved are displayed in Fig. 1. Most of the rate data were obtained by following the optical density changes at the $Fe(CN)_6^{-3}$ maximum at 420 mμ, although some runs using 405 mμ also were made; at 5°, the time sequence of the entire visible spectrum was checked. Except for variations in precision, the results did not depend on the choice of wave length used.

In general, the solutions were not deaerated, but the air oxidation of $Co(EDTA)^{-2}$ was found to be slow relative to the reaction being followed, and, in fact, noticeable only in the case of solutions allowed to stand overnight.

The reaction products were identified as $Co(EDTA)^{-1}$ (and hence $Fe(CN)_6^{-4}$ as the other) from comparisons of the terminal spectra with that of a synthetic mixture in which sodium ferrocyanide and NaCo(EDTA) were added to the buffered $Co(EDTA)^{-2}$ solution. No spectral evidence for any interaction between $Co(EDTA)^{-1}$ (or the pentadentate $Co(EDTA)(H_2O)^{-1}$) and $Fe(CN)_6^{-4}$ was detected, except that with both concentrations about 0.01 *M*, back reaction to form $Co(EDTA)^{-2}$ and $Fe(CN)_6^{-3}$ occurred to about 10%, judging from the increased absorption at 420 mμ. The equilibrium constant is thus about 100 for the reaction

$$Co(EDTA)^{-2} + Fe(CN)_6^{-3} = Co(EDTA)^{-1} + Fe(CN)_6^{-4} \quad (1)$$

Under the usual kinetic conditions of excess $Co(EDTA)^{-2}$, the forward reaction thus went virtually to completion.

Magnetic susceptibility measurements on 0.1 *M* $Co(EDTA)^{-2}$ (0.1*f* in $Co(NO_3)_2$, 0.15*f* in Na_2H_2EDTA, and acetate buffered to pH 5) and on 0.1 *M* $K_3Fe(CN)_6$ showed a paramagnetic component corresponding to the expected three and one unpaired electrons for the two complexes, respectively. Immediately on mixing, either at 20 or at 5°, of equal volumes of the two solutions, the paramagnetic component disappeared completely, and the magnetic susceptibility of the solution remained unchanged after warming (to hasten the second stage reaction, see below) and then cooling to the original temperature.

Several runs were made in a stopped-flow apparatus[9] in which equal volumes of the two reagent solutions were mixed at 5°. The first solution was 0.02 *M* in $Co(EDTA)^{-2}$, 0.01 *M* in excess EDTA, and buffered to pH 5, and the second was 2×10^{-4} *M* in $K_3Fe(CN)_6$. At the point of flow stop a rapid decrease in optical density at 420 mμ could be observed on the monitoring oscilloscope. Although the rate approached the limit that could be handled by the equipment, the half-life could be estimated, fairly reproducibly, to be 0.005 sec.

Results and Discussion

A typical optical density *vs.* time plot is shown by the top curve in Fig. 2, and it is seen that the optical density, D_0, immediately after mixing, was considerably lower than D_0^0, the value computed from the extinc-

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[4] E^0 for the $Fe(CN)_6^{-3,-4}$ couple, while very ionic strength dependent, is about −0.5 v. (W. L. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952), and that for the $Co(EDTA)^{-2,-1}$ couple has been estimated to be about the same as for iodide–iodine (G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 846 (1949)); we estimate *K* (see reaction 1) to be about 100 at 25° and an ionic strength of 0.66.

[5] H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[6] Y. A. Im and D. A. Busch, *J. Am. Chem. Soc.*, **83**, 3357 (1961).

[7] See I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958). These preparations were carried out by Dr. M. A. Bennett.

[8] G. H. Cartledge and P. M. Nichols, *Ind. Eng. Chem., Anal. Ed.*, **13**, 20 (1941).

[9] These were carried out by Dr. R. G. Wilkins, Department of Chemistry, University of Sheffield, Sheffield, England.

tion coefficients of the components as determined separately. The D_0 values, moreover, decreased steadily with increasing $Co(EDTA)^{-2}$ concentration (keeping initial $Fe(CN)_6^{-3}$ constant at 10^{-4} M), as summarized in Table I. Evidently, a $Co(EDTA)^{-2}$ dependent equilibrium was present, and the apparent extinction coefficient of the species formed by the equilibrium is given by curve 4 of Fig. 1. This curve was obtained from the spectrum at 5° immediately after the mixing of a buffer solution 0.005 M in $Co(EDTA)^{-2}$ and 10^{-4} M in $Fe(CN)_6^{-3}$, on the assumption that all of the latter species was consumed, and allowing for substrate absorption.

TABLE I[a]

REACTION OF $Fe(CN)_6^{-3}$ WITH $Co(EDTA)^{-2}$ AT 25°

$Co(EDTA)^{-2}$, M	$D_0^{0\prime}$	D_0'	$(D_0 - D_\infty)$	k_{app}, min.$^{-1}$
0.002	0.525	0.301	0.260	0.228
.005	.525	.226	.187	.312
.010	.525	.195	.153	.340
.020	.525	.157	.124	.383

[a] Other conditions are as specified in the Experimental section; D values are for a cell length of 5 cm., and the primed values are those corrected for absorption due to Co(II) and buffer, all for 420 mμ.

Subsequent to the initial drop in optical density at 420 mμ (or at 405 mμ), there was a slow further decrease to a final value, D_∞. As illustrated in Fig. 2, the data from a representative set of runs at 25° gave linear semi-logarithmic plots of $(D - D_\infty)$ against time, with intercepts, as noted above, and also slopes that were dependent on the concentration of the excess $Co(EDTA)^{-2}$ present. The final spectrum was that of $Co(EDTA)^{-1}$ (after allowing for the absorption of $Co(EDTA)^{-2}$, buffer, etc.), although intensities at the 535 mμ peak were generally somewhat higher than expected. This was traced to some air oxidation of the excess $Co(EDTA)^{-2}$ that occurred on long standing. As illustrated by curve 6 of Fig. 1, the discrepancy was small, and we conclude that reaction 1 does represent the over-all process, and also that it is $Co(EDTA)^{-1}$ and not the pentacoördinated $Co(EDTA)(H_2O)^{-1}$ that is produced. Were it this last species, the visible absorption peak would be at 555 mμ, rather than at 530 mμ.[7]

The reaction, evidently, occurs in two stages, and the most reasonable mechanistic interpretation appears to be the following (ignoring possible protonated species since no investigation was made of the effect of pH)

Rapid equilibrium

$$\underset{A}{Co(EDTA)^{-2}} + \underset{B}{Fe(CN)_6^{-3}} \overset{K}{=} \underset{AB\ (or\ CD)}{[Co(EDTA)\cdot Fe(CN)_6]^{-5}} \qquad (2)$$

Rate determining step

$$\underset{AB\ (or\ CD)}{[Co(EDTA)\cdot Fe(CN)_6]^{-5}} \xrightarrow{k} \underset{C}{Co(EDTA)^{-1}} + \underset{D}{Fe(CN)_6^{-4}} \qquad (3)$$

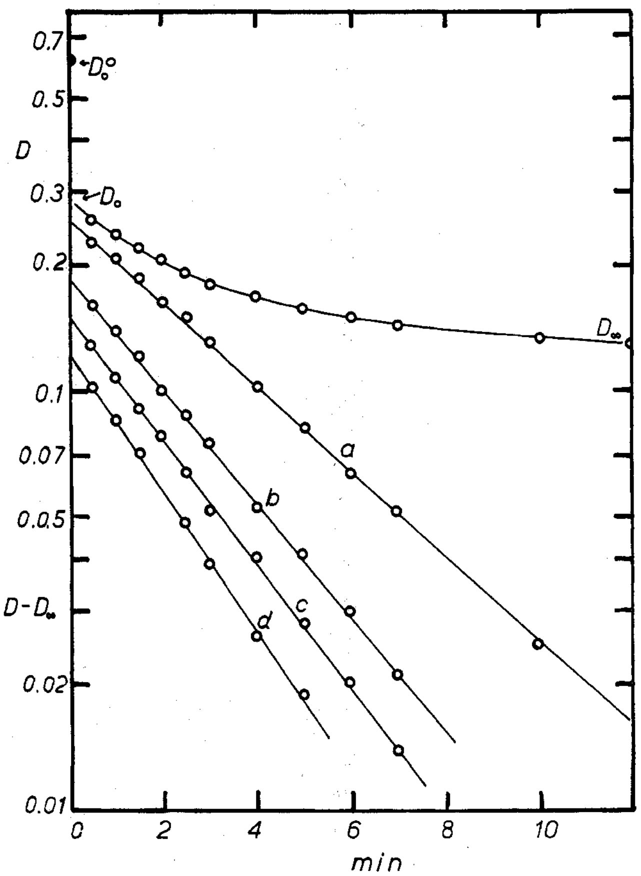

Fig. 2.—Change of optical densities with time (25°, 5-cm. cell length, 420 mμ, pH 5, 0.01 M $Co(EDTA)^{-2}$, 0.01 M excess EDTA, 10^{-4} M initial $Fe(CN)_6^{-3}$): upper curve, variation of total optical density with time; lower curves, variation of $(D - D_\infty)$ with time, for indicated $Co(EDTA)^{-2}$ concentrations: a, 0.02 M; b, 0.01 M; c, 0.005 M; d, 0.002 M.

Under our conditions of large excess of (A) and negligible back reaction, analysis of the above scheme leads to the rate law

$$d(B_{tot})/dt = k\,\frac{K(A)}{1 + K(A)}\,(B_{tot}) = k_{app}(B_{tot}) \qquad (4)$$

where (B_{tot}) denotes the sum of (B) and (AB). Assuming additivity of optical densities, one then concludes that $(D - D_\infty)$ should show a simple exponential decrease with time, as is found, and with a half-life corresponding to k_{app}.

Furthermore, according to (4), a plot of $1/k_{app}$ vs. $1/(A)$ should be linear, with a slope and intercept of $1/kK$ and $1/k$, respectively. As shown in Fig. 3, two independent series of runs, using 5 and 10 cm. cells (as well as other runs using 405 mμ optical densities) do indeed give essentially identical linear plots. Our average k and K values, at 25°, are 0.37 min.$^{-1}$, and 670 M^{-1}, respectively.

Some corroboration of the above mechanism is provided by the independent estimate of K that can be obtained from the optical density changes that occur immediately on mixing. Analysis of the situation shows that

$$1/\Delta D = 1/\alpha + (1/\alpha K)(1/(A)) \qquad (5)$$

where $\Delta D = D_0^0 - D_0 = D_0^{0\prime} - D_0'$ (see Table I),

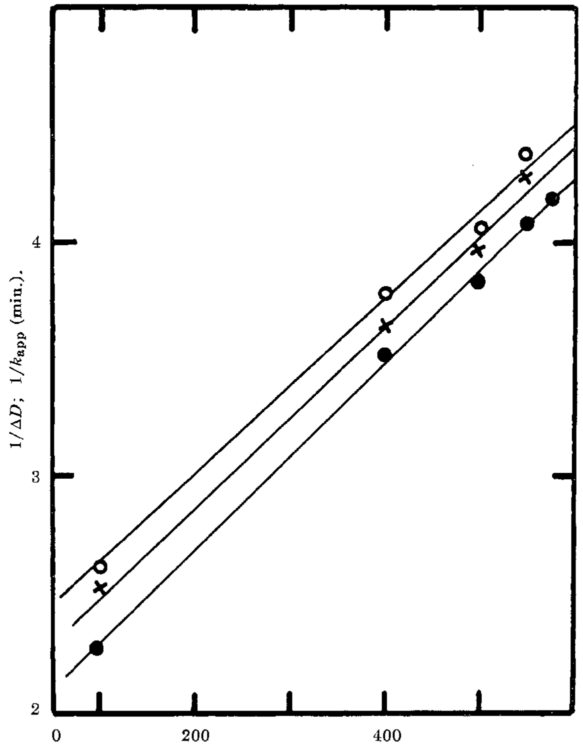

Fig. 3.—Test of eq. 4 and 5 (25°, 420 mμ, other conditions as specified in Experimental section): ○ and ●, $1/k_{app}$ vs. 1/(A) (5 and 10 cm. cells, respectively); ×, $1/\Delta D$ vs. 1/(A) (5 cm. cell).

and $\alpha = l(B_0)(\epsilon_B - \epsilon_{AB})$, l being the cell length. In deriving (5), it again is recognized that $Co(EDTA)^{-2}$ is present in large excess.

As shown in Fig. 3, the plot of $1/\Delta D$ vs. 1/(A) is in fact linear, and gives a K value of 710, in reasonable agreement with the average of 670 from the rate data. The value of α obtained corresponds to $\epsilon_{AB} = 280$ at 420 mμ, as compared with the estimate of 340 from the spectrum obtained at 5° immediately after mixing (and shown in Fig. 1). This last could be a little high because of the difficulty in the 5° runs of completely eliminating moisture condensation on the cell windows.

Some runs were made at 5°, and gave k values of about 0.015 $min.^{-1}$, and thus an activation energy and entropy of 26 kcal./mole and 16 e.u., respectively. Although K appeared to be somewhat larger than at room temperature, the data were not sufficiently accurate to give a firm figure.

It is next of interest to consider the possible nature of the intermediate binuclear species in eq. 2 and 3. Haim and Wilmarth,[10] in studying the oxidation of $Co(CN)_5^{-3}$ by $Fe(CN)_6^{-3}$ reported previously,[11] concluded that the product was

$$[(NC)_5Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{-6} \qquad (6)$$

It is similarly tempting to conclude that our intermediate is

$$[(EDTA_5)Co\text{-}NC\text{-}Fe(CN)_5]^{-5} \qquad (7)$$

Here, the designation $EDTA_5$ denotes ethylenediaminetetraacetate functioning as a pentadentate ligand, as it does with known Co(III) complexes,[12] and very likely does much of the time in the case of the complex with Co(II).

In the case of compound 6 the valency assignments were inferred from its physical properties, and one would in any event expect a rapid electron transfer from Co(II) to Fe(III) in this case, since all of the species involved are spin paired (see ref. 4). In the present case, however, $Co(EDTA)^{-2}$ is a high-spin complex (as confirmed by our magnetic susceptibility measurements), and in view of the general slowness of the electron transfer process

$$Co(II)\ (high\ spin) \longrightarrow Co(III)\ (low\ spin)$$

the reaction sequence can be thought of in terms of three rather than two steps

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CD \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C + D \qquad (8)$$

where the distinction between AB and CD lies in whether the cobalt and iron valences are those of the reactants or of the products. The magnetic susceptibility studies described in the Experimental section show the intermediate to be diamagnetic, and hence to correspond to CD, *i.e.*

$$[(EDTA_5)Co^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^{-5} \qquad (9)$$

The reaction sequence then consists of a rapid association to give AB with concomitant or rapid charge transfer converting it to CD, followed by a slow dissociation into C and D. The 5-msec. half-life observed with the stop-flow apparatus (see Experimental) then corresponds either to k_1 or to k_2 above.

Spectrum 4 of Fig. 1 is then that of species 9 above, and it is perhaps reasonable that it should differ from the sum spectrum of $Co(EDTA)^{-1}$ (or $Co(EDTA)\cdot(H_2O)^{-1}$) and $Fe(CN)_6^{-4}$ in being more intense and shifted somewhat to longer wave lengths, in view of the reduction in symmetry and increase in molecular size on forming the dimer. Finally, the slow breakup of species 9, as compared to the stability of 6, can be rationalized as due to the tendency of $EDTA_5$ to become hexacoördinated.

In summary, we appear to have in the present system an interesting example of catalysis by a bridging group of what is, over-all, a "simple" charge transfer reaction. It may well be that other "simple" charge transfer reactions occur by this type of mechanism and that the binuclear intermediate has simply been too labile to be observed.

Acknowledgment.—A. W. A. is grateful to Professor R. S. Nyholm for the use of the facilities of the Chemistry Department, University College, London, and for many stimulating discussions.

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[10] A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).

[11] A. W. Adamson, *ibid.*, **73**, 5710 (1951).

[12] G. Schwarzenbach, *Helv. Chim. Acta*, **32**, 846 (1949).