

The Redox Reaction between Hexachloroiridate(IV) and Pentacyanocobaltate(II). Evidence for the Binuclear Intermediate μ -Chloro-pentacyanocobaltate(III) Pentachloroiridate(III)¹

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Abstract: The reaction between hexachloroiridate(IV) and pentacyanocobaltate(II) to produce hexachloroiridate(III) and hydroxypentacyanocobaltate(III) proceeds in two stages. The first stage, too fast to be measured ($k_1 > 10^7 M^{-1} \text{sec}^{-1}$), is attributed to the inner-sphere redox reaction of IrCl_6^{2-} with $\text{Co}(\text{CN})_5^{3-}$ to produce the metastable intermediate $\text{Cl}_5\text{IrClCo}(\text{CN})_5^{5-}$. The second stage is attributed to the dissociation of the intermediate *via* Co-Cl bond rupture, and yields the final products. The dissociation of the intermediate is a first-order process with $k_d = 4.0 \text{ sec}^{-1}$ at 25° and ionic strength $0.10 M$, $\Delta H^\ddagger = 15.4 \text{ kcal/mol}$, and $\Delta S^\ddagger = -4.2 \text{ eu}$. The mechanism of this and related reactions is discussed.

Since the discovery of the bridged activated complex in oxidation-reduction reactions,² there has been considerable interest in the binuclear complexes formed as the primary products of the electron transfer step.³ The direct detection and characterization of such bridged, binuclear products, either as long-lived species or as transient intermediates, is possible only under very favorable circumstances.³ The first example of a chloride-bridged binuclear complex, namely $\text{Cl}_5\text{IrClCr}(\text{H}_2\text{O})_5$, was found in the reaction between hexachloroiridate(IV) and chromium(II), originally studied by Taube and Myers,⁴ and recently reexamined in detail by Thorneley and Sykes.⁵ Additional oxidation-reduction systems that feature chloride-bridged binuclear intermediates have been recently found in the reactions of various chlororuthenium(III) complexes with chromium(II).⁶⁻⁸ In the present study, we are concerned with the binuclear, chloride-bridged intermediate $\text{Cl}_5\text{IrClCo}(\text{CN})_5^{5-}$ produced in the oxidation of $\text{Co}(\text{CN})_5^{3-}$ by IrCl_6^{2-} . The question of whether the bridging chloride is transferred to the reductant or retained by the oxidant is examined in considerable detail.

Experimental Section

Materials. All solutions were prepared with triply distilled water. Ionic strength was maintained with sodium perchlorate prepared from 70% perchloric acid and anhydrous sodium carbonate. Manipulations involving oxygen-sensitive solutions were carried out in an atmosphere of argon. The argon was purified by passing it over a BTS catalyst (B.A.S.F. Colors and Chemicals, Inc.). Sodium hexachloroiridate(IV) hexahydrate was tested for the presence of iridium(III) species by comparing the spectra of solutions in 2.36 *M* perchloric acid before and after saturation with chlorine.⁹ No reduced species were detected. Sodium cy-

anide was standardized by titration with silver(I) in the presence of iodide ion as an indicator.¹⁰ Solutions of cobalt(II) perchlorate were standardized against $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ using murexide as an indicator.¹¹ Solutions containing $\text{Co}(\text{CN})_5^{3-}$ were prepared by adding the appropriate amount of the deoxygenated cobalt(II) perchlorate stock solution to a deoxygenated solution containing the desired quantities of sodium cyanide, sodium hydroxide, and sodium perchlorate.

Kinetic Measurements. The rates of reaction were measured spectrophotometrically in a rapid flow apparatus constructed following the design of Dulz and Sutin.¹² The disappearance of the intermediate produced in the reaction of IrCl_6^{2-} with an excess (usually 10%) of $\text{Co}(\text{CN})_5^{3-}$ was followed at 420 nm, near an absorption maximum for the intermediate, and at 487 nm, an absorption maximum for IrCl_6^{2-} . Plots of $\log(A_t - A_\infty)$ vs. time were linear over three-four half-lives, and the slopes of such plots were used to calculate the first-order rate coefficient for the disappearance of the intermediate.

Stoichiometry of the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ Reaction. Considerable difficulty was experienced in determining the concentrations of IrCl_6^{2-} and $\text{Ir}(\text{OH})_2\text{Cl}_5^{2-}$ produced in the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ reaction. Briefly, the procedure consisted of mixing the IrCl_6^{2-} with a slight excess of $\text{Co}(\text{CN})_5^{3-}$, allowing the reaction to proceed to completion, adding perchloric acid to decompose the excess $\text{Co}(\text{CN})_5^{3-}$, oxidizing the IrCl_6^{2-} and $\text{Ir}(\text{OH})_2\text{Cl}_5^{2-}$ produced in the reaction to IrCl_6^{2-} and $\text{Ir}(\text{OH})_2\text{Cl}_5^{2-}$, respectively, by means of chlorine,⁹ sweeping out the chlorine, and finally examining the resulting solution spectrophotometrically in the 700-300-nm region. It was found that the absorbances at 487 nm of samples of the product solution taken in succession and subjected to the above procedure decreased as the time elapsed between the completion of the reaction and the acidification increased.¹³ There was also a slight decrease in absorbance for successive oxidations of a given acidified product solution,¹⁴ but oxidized solutions were quite stable. In order to minimize the above changes, the following procedure was adopted. The reaction was carried out in a 100-ml volumetric flask fitted with a serum cap. Manipulations were

(1) This work was supported by Grants GP-6528 and GP-9669 from the National Science Foundation.

(2) H. Taube, H. Myers, and R. Rich, *J. Amer. Chem. Soc.*, **75**, 4118 (1953).

(3) For a review, see A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 183 (1967).

(4) H. Taube and H. Meyers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

(5) R. N. F. Thorneley and A. G. Sykes, *J. Chem. Soc.*, 232 (1970).

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(8) D. Seewald, N. Sutin, and K. O. Watkins, *J. Amer. Chem. Soc.*, **91**, 7307 (1969).

(9) I. A. Poulsen and C. S. Garner, *ibid.*, **84**, 2032 (1962).

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," Macmillan, New York, N. Y., 1952, p 546.

(11) G. Schwarzenbach, "Complexometric Titrations," Interscience, New York, N. Y., 1957, p 68.

(12) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(13) It was also observed that product solutions (basic medium) developed a slight turbidity after 1 hr. Possibly, colation phenomena are responsible for this effect.

(14) The rate of decrease in absorbance was somewhat faster than that expected on the basis of the early⁹ kinetic measurements on the aequation of IrCl_6^{2-} , but appears to be compatible with the recent measurements of A. J. P. Domingos, A. M. T. S. Domingos, and J. M. P. Cabrial, *J. Inorg. Nucl. Chem.*, **31**, 2563 (1969).

Table I. Kinetics of the Dissociation of $(\text{CN})_5\text{CoClIrCl}_6^{5-}$ ^a

Expt	$[\text{IrCl}_6^{2-}]_0 \times 10^4$, <i>M</i>	$[\text{Co}(\text{CN})_5^{3-}]_0 \times 10^4$, <i>M</i>	$[\text{CN}^-]_0 \times 10^4$, <i>M</i>	Temp, °C	k_d , sec^{-1} ^b
1	8.0	8.4	2.0	10	1.08
2	2.0	20	2.0	10	1.00, 0.90, 0.98 ^c
3	2.0	4.0	2.0	10	0.96, 0.99
4	2.0	2.1	2.0	10	0.86, 0.82
5	0.20	0.21	2.0 ^d	10	0.94, 0.93 ^e
6	2.0	20	2.0	20	2.35
7	2.0	4.0	2.0	20	2.43, 2.38
8	2.0	2.1	2.0	20	2.35, 2.40
9	2.0	2.1	10 ^f	20	2.61, 2.74
10	2.0	2.1	200	20	2.67, 2.57
11	2.0	2.1	1000	20	2.53, 2.50
12	2.0	2.1	2.0	30	5.85, 5.90
13	2.0	4.0	2.0	30	6.22, 5.87

^a Ionic strength 0.10 *M* maintained with sodium perchlorate. $[\text{OH}^-] = 5.0 \times 10^{-3}$ *M* unless otherwise indicated. ^b Unless indicated otherwise, first entry from measurement at 420 nm and second entry from measurement at 487 nm. Each figure represents the average of duplicate experiments with the same pair of solutions. ^c Measurement at 390 nm. ^d $[\text{OH}^-] = 1.0 \times 10^{-3}$ *M*. ^e Measurement at 260 nm. ^f $[\text{OH}^-] = 5.0 \times 10^{-2}$ *M*.

performed in the absence of oxygen by means of syringe techniques. The desired amount of a stock cobalt(II) perchlorate solution was added to ca. 40 ml of a solution containing the appropriate amounts of sodium cyanide, sodium hydroxide, and sodium perchlorate. The required amount of IrCl_6^{2-} solution was then added, followed immediately (ca. 15 sec at 0° and 2–3 sec at room temperature) by the addition of 10 ml of chilled 1 *M* perchloric acid (**CAUTION:** HCN). The flask was placed in a 0° bath, the serum cap was removed, and then 20 ml of 11.8 *M* perchloric acid at –15° was rapidly added. After dilution to volume, the solution (hereafter called the product solution) contained ca. 2×10^{-4} *M* Co(III), ca. 2×10^{-4} *M* Ir(III), and ca. 2.4 *M* perchloric acid. A 10-ml aliquot of the product solution was added to a chilled solution containing 18 ml of 11.8 *M* perchloric acid and 60 ml of water. After dilution to 100 ml, the solution was treated with chlorine for 1 min followed by a vigorous stream of nitrogen for 10 min. The spectrum of the resulting solution in a 10-cm cell was recorded in the 600–300-nm region. A total of three aliquots was taken from the chilled product solution over a period of about 45 min and treated as described above. The concentrations of IrCl_6^{2-} and $\text{Ir}(\text{OH})_2\text{Cl}_5^-$ were calculated from the measured absorbances at 487 and 450 nm and the known extinction coefficients.^{9,15} In order to identify the cobalt(III) products formed, the spectrum of the product solution in a 10-cm cell was also recorded in the 600–300-nm region.¹⁶

Spectroscopy. Routine spectra were measured with a Cary 14 recording spectrophotometer. The spectrum of the $\text{Cl}_5\text{IrClCo}(\text{CN})_5^{5-}$ intermediate was determined in the rapid flow apparatus. As will be seen, at reactant concentrations larger than 10^{-5} *M*, the redox reaction between $\text{Co}(\text{CN})_5^{3-}$ and IrCl_6^{2-} is complete in the mixing time of the flow apparatus (2–3 msec); therefore, all that is seen in the oscilloscope is the decay of the intermediate. The decrease in absorbance, ΔA , accompanying the dissociation of the intermediate was measured at 5-nm intervals from 605 to 250 nm in a series of stop-flow measurements.

Results

Kinetics of the IrCl_6^{2-} – $\text{Co}(\text{CN})_5^{3-}$ Reaction. The reaction between IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ was found to proceed in two stages. At 487 nm, an absorption maximum for IrCl_6^{2-} , both stages are accompanied by absorbance decreases. The first stage corresponds to the rapid disappearance of IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ with the formation, at least in part, of an intermediate which disappears in the subsequent, slower second stage. At 10^{-4} *M* reactant concentrations, the first stage (attributed to the redox reaction of IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$) was too fast to be followed in the flow apparatus. At

10^{-5} *M* concentrations, however, the last portion of the redox stage could be detected as a slight initial curvature in the $\ln(A_t - A_\infty)$ vs. time plots (487 nm) for the decay of the intermediate. Assuming the redox stage to be a second-order reaction between IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$, it is estimated that k_r , the second-order rate constant, is larger than 10^7 $\text{M}^{-1} \text{sec}^{-1}$. The second stage could be readily followed by measuring the absorbance decrease accompanying the decay of the intermediate. The observed first-order absorbance decrease defines a rate coefficient k_d which is identified as the first-order rate constant for the disappearance of the intermediate.

$$\frac{d \ln(A_t - A_\infty)}{dt} = -\frac{d \ln[\text{Int}]}{dt} = k_d \quad (1)$$

The values of k_d obtained in the present work are presented in the last column of Table I. It will be seen that all the measurements were carried out in the presence of an excess of $\text{Co}(\text{CN})_5^{3-}$. When the IrCl_6^{2-} was in excess, following the disappearance of the intermediate, a subsequent slower (by a factor of ca. 10 under usual concentration conditions) absorbance decrease was observed. Blank experiments in which IrCl_6^{2-} was mixed with alkaline cyanide solutions (no cobalt(II) added) indicated that the slower absorbance decrease was caused by a reaction of IrCl_6^{2-} with cyanide, and, consequently, all measurements were restricted to the conditions $[\text{Co}(\text{II})]_0/[\text{Ir}(\text{IV})]_0 > 1$. An examination of the data presented in Table I will show that k_d is independent of wavelength and of the initial concentrations of IrCl_6^{2-} (40-fold change), $\text{Co}(\text{CN})_5^{3-}$ (100-fold change), cyanide (500-fold change), and hydroxide (10-fold change). The average value of k_d at 20° is $2.49 \pm 0.14 \text{ sec}^{-1}$, and the associated activation parameters, calculated by using a nonlinear least-squares program, are $\Delta H^\ddagger = 15.2 \pm 0.2 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -4.2 \pm 0.7 \text{ eu}$.

The Yield of the Intermediate. Although it is not possible to obtain an absolute value of the yield of the intermediate, the changes in absorbance, ΔA , accompanying the decay of the intermediate provide a relative measure of the amount of intermediate produced under various conditions. The measurements were performed at a series of selected wavelengths in the

(15) At these wavelengths the absorbances of cobalt(III) are negligible compared to the absorbances of iridium(IV).

(16) In this wavelength region the extinction coefficients of the chloroiridium(III) complexes and the pentacyanocobalt(III) complexes are comparable.

Table II. Yield of Intermediate in the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ Reaction^a

$[\text{IrCl}_6^{2-}]_0 \times 10^4, M$	$[\text{Co}(\text{CN})_5^{3-}]_0 \times 10^4, M$	$[\text{CN}^-]_0 \times 10^4, M$	$10^3 \Delta A / l [\text{IrCl}_6^{2-}]_0, M^{-1} \text{ cm}^{-1} \text{ }^b$				
			$\lambda, \text{ nm}$				
			489	420	315	300	260
0.20	0.21	2.0		1.12 ^e			7.8
1.0	1.05	2.0					7.8
2.0	2.1	2.0	0.39 ^{d,e}	1.05 ^f	1.45 ^e	1.17	
2.0	4.0	2.0	0.32	1.00	1.44	1.13	
2.0	4.0	1000	0.31	1.02	1.50		8.0
8.0	8.4	2.0	0.30	1.13	1.32	1.09	8.2

^a Ionic strength maintained at 0.10 M with sodium perchlorate. $[\text{OH}^-] = 5.0 \times 10^{-3} M$. ^b ΔA is the change in absorbance accompanying the decay of the intermediate. l is the path length of the observation tube of the flow apparatus, 0.2 cm. Average of duplicate measurements. ^c Corrected for the last portion of the first stage of the reaction. See text. ^d At 490 nm. ^e Single measurement. ^f Average of three independent measurements.

500–250-nm region, and the results are presented in Table II.

It will be seen that the yield of the intermediate, as measured by the quantity $\Delta A / l [\text{IrCl}_6^{2-}]_0$, is unaffected by a 40-fold change in the initial concentrations of IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$. Of particular importance is the independence of the yield of the intermediate on the concentration of excess cyanide (500-fold change), and the significance of this observation will be discussed below.

Final Products of the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ Reaction.

The nature and concentration of the iridium(III) and cobalt(III) products formed in the overall reaction between IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ (e.g., upon completion of the two stages described above) were determined by spectrophotometric techniques. The spectra of IrCl_6^{3-} and $\text{IrCl}_5\text{OH}_2^{2-}$, the anticipated iridium(III) mononuclear products, are quite similar, and spectral measurements are not useful in the quantitative determination of mixtures of these two complexes.⁹ However, the quantitative oxidation of these species to IrCl_6^{2-} and $\text{IrCl}_5\text{OH}_2^-$, respectively, provides a sensitive spectral method for such a determination.⁹ As indicated in the Experimental Section, within a particular experiment there was a decrease in absorbance for successive oxidations of the product solution. For example, the absorbances at 487 nm (10-cm cell) of oxidized solutions from the reaction of $2.05 \times 10^{-4} M$ IrCl_6^{2-} with $2.1 \times 10^{-4} M$ $\text{Co}(\text{CN})_5^{3-}$ decreased from 0.800 to 0.789 over a sampling time of 60 min. This corresponds to a decrease from 97.1 to 93.4% in the yield of IrCl_6^{3-} . The absorbance decrease is small and slow, and, therefore, the absorbances of the first sample in each experiment are considered to represent, as far as can be ascertained, an accurate measurement of the amount of IrCl_6^{3-} produced. The results of the measurements are presented in Table III, and it will be seen that the yield of IrCl_6^{3-} is independent of temperature and has an average value of 98.5%. As an additional check of the reaction stoichiometry, the absorption spectra of the product solutions in each experiment listed in Table III were recorded and compared with the spectrum calculated on the basis of quantitative formation of IrCl_6^{3-} and $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$.¹⁷ The results are included in Table III, and the agreement between experimental and calculated values is considered satisfactory.

(17) Since the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ reaction is carried out in alkaline solution, the pentacyanocobalt(III) species present at the end of the reaction is $\text{Co}(\text{CN})_5\text{OH}^{2-}$. In the calculated extinction coefficients presented in Table III, the cobalt species is $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$ since product solutions are acidic.

Table III. Final Products of the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ Reaction^a

$[\text{IrCl}_6^{2-}]_0 \times 10^4, M$	% IrCl_6^{3-} formed ^b	$10^2 A / l [\text{IrCl}_6^{2-}]_0, M^{-1} \text{ cm}^{-1} \text{ }^c$						
		$\lambda, \text{ nm}$						
		450	420	400	380	360	340	
1.94 ^d	101	0.56	1.75	2.74	3.15	2.64	1.59	
2.03 ^d	97	0.56	1.87	2.95	3.45	2.74	1.71	
2.08 ^d	97	0.47	1.61	2.58	3.09	2.57	1.55	
2.00 ^e	101	0.59	1.76	2.71	3.10	2.70	1.65	
2.02 ^e	98	0.48	1.66	2.62	3.08	2.59	1.45	
2.05 ^e	97	0.45	1.58	2.53	3.00	2.50	1.47	
Av	98.5	0.52	1.71	2.69	3.14	2.62	1.57	
Calcd ^f		0.50	1.73	2.87	3.33	2.73	1.63	

^a Ionic strength maintained at 0.10 M with sodium perchlorate. $[\text{Co}(\text{CN})_5^{3-}]_0 = 2.1 \times 10^{-4} M$; $[\text{CN}^-]_0 = 2.0 \times 10^{-4} M$; $[\text{OH}^-] = 5.0 \times 10^{-3} M$. ^b Defined as 100 \times mol of IrCl_6^{3-} produced in the reaction/mol of IrCl_6^{2-} initially present. ^c A is the absorbance of the product solution; l is path length of the cell. ^d Measurements at 0°. ^e Measurements at $22 \pm 2^\circ$. ^f Values calculated assuming quantitative formation of IrCl_6^{3-} and $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$.

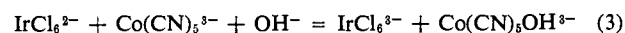
The Spectrum of the Intermediate. As already indicated, it is not possible to obtain an absolute value of the yield of the intermediate formed in the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ reaction. Consequently, unless an assumption is made about the yield of the intermediate, it is not possible to calculate absolute values of the extinction coefficients of the intermediate. However, an apparent extinction coefficient, ϵ_{app} , can be defined by the expression

$$\epsilon_{\text{app}} = \frac{\Delta A}{l [\text{IrCl}_6^{2-}]_0} + \epsilon_{\text{Ir}} + \epsilon_{\text{Co}} \quad (2)$$

where ΔA is the change in absorbance accompanying the decay of the intermediate, l is the path length of the observation tube in the flow apparatus, $[\text{IrCl}_6^{2-}]_0$ is the initial concentration of IrCl_6^{2-} , the limiting reagent, and ϵ_{Ir} and ϵ_{Co} are the extinction coefficients of IrCl_6^{3-} and $\text{Co}(\text{CN})_5\text{OH}_2^{2-}$, respectively, the known final products of the reaction.¹⁷ The values of ϵ_{app} calculated from eq 2 in the wavelength region 600–250 nm are plotted in Figure 1. Included in the figure for comparative purpose are the absorption spectra of $\text{Co}(\text{CN})_5\text{Cl}^{3-}$ and IrCl_6^{3-} .

Discussion

The absorbance changes observed on mixing solutions of IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ demonstrate that, under the experimental conditions used, the overall reaction



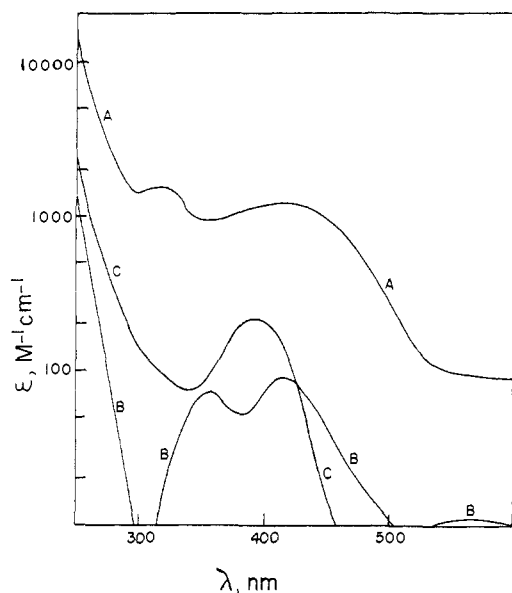
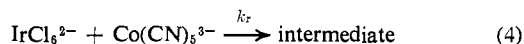
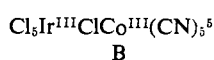
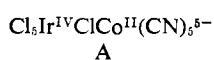


Figure 1. Absorption spectra of (A) intermediate $\text{Cl}_3\text{IrClCo}(\text{CN})_5^{5-}$; (B) IrCl_6^{2-} ; (C) $\text{Co}(\text{CN})_5\text{Cl}^{3-}$.

proceeds in at least two stages. The first stage corresponds to the very rapid disappearance of the IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ reactants to produce, at least in part, an intermediate. The second stage corresponds to the somewhat slower first-order decay of the intermediate by a process independent of the initial concentrations of IrCl_6^{2-} , $\text{Co}(\text{CN})_5^{3-}$, CN^- , and OH^- . It is reasonable to assume that the rapid disappearance of the reactants in the first stage is a second-order process, and, consequently, the reaction sequence given by eq 4 and 5 adequately represents the two steps demanded by the observations. Moreover, since the amount of inter-



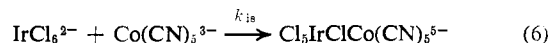
mediate produced in the first stage is proportional to the initial concentration of IrCl_6^{2-} (the limiting reagent), but independent of the excess concentration of $\text{Co}(\text{CN})_5^{3-}$, it is concluded that the formation of the intermediate in eq 4 is a thermodynamically favored process with an equilibrium constant larger than $3 \times 10^6 \text{ M}^{-1}$.¹⁸ It is noteworthy that, although the kinetic and stoichiometric studies provide conclusive evidence for the existence of an intermediate, these studies give no direct information about the yield, composition, or structure of the intermediate. However, there is little doubt that the intermediate is the chloride-bridged, binuclear complex $\text{Cl}_3\text{IrClCo}(\text{CN})_5^{5-}$. A chloride-bridged structure, rather than a cyanide-bridged one, is favored on the basis of the ready availability of the sixth coordination position on $\text{Co}(\text{CN})_5^{3-}$ and the slow substitution rate on IrCl_6^{2-} . Two alternative formulations are possible for the binuclear, chloride-bridged structure.



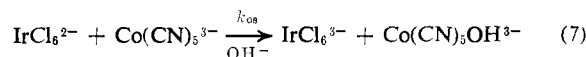
(18) This figure is obtained by recognizing that at the lowest IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ concentrations used, reaction 3 proceeds to at least 90% completion.

Formulation B is strongly favored over formulation A on the basis of the following arguments. An equilibrium constant larger than $3 \times 10^6 \text{ M}^{-1}$ for the formation of A from IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ appears unreasonable. Although the sixth coordination position of $\text{Co}(\text{CN})_5^{3-}$ is readily attained kinetically, there is little thermodynamic tendency for $\text{Co}(\text{CN})_5^{3-}$ to increase its coordination number. For example, the upper limit for the formation constant of $\text{Co}(\text{CN})_6^{4-}$ from $\text{Co}(\text{CN})_5^{3-}$ and CN^- has been estimated as 0.1 M^{-1} .¹⁹ On the other hand, an equilibrium constant of at least $3 \times 10^6 \text{ M}^{-1}$ for the formation of B is quite consistent with the known oxidation potentials of the $\text{Ir}(\text{III})/\text{IV}$ and $\text{Co}(\text{II})/\text{III}$ couples. The spectrum of the intermediate presented in Figure 1 provides additional support for formulation B. It has been noted^{5,20,21} that binuclear complexes for which interaction absorption does not obtain display absorption spectra similar to those of the parent mononuclear complexes, the absorption maxima of the binuclear complexes being somewhat shifted and more intense. Although the detailed interpretation of the spectrum in Figure 1 depends on an assumption about the absolute yield of the intermediate (*vide infra*), the similarity of the spectrum of the intermediate (maximum at 420 nm) with the spectra of IrCl_6^{2-} (maximum at 417 nm) and $\text{Co}(\text{CN})_5\text{Cl}^{3-}$ (maximum at 393 nm) suggests that the correct oxidation states of the cobalt and iridium atoms in the intermediate are those given in formulation B.

On the basis of these arguments, it is concluded that the intermediate has structure B, and, consequently reaction 4 is formulated as the inner-sphere redox reaction



One question that we have been unable to resolve satisfactorily is related to the absolute yield of the intermediate. Although the results demonstrate that IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$ react *via* the inner-sphere reaction to produce the intermediate (eq 6), a parallel outer-sphere reaction (eq 7) giving products directly cannot be ruled out on the basis of the kinetic measurements. Nor



can eq 7 be ruled out on the basis of the calculated values of ϵ_{app} , as will be seen from the following considerations. Assume that the IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ proceeds *via* parallel inner- and outer-sphere reactions according to eq 6 and 7. The fraction of reaction leading to the formation of the intermediate is denoted as f ($\equiv k_{is}/k_{is} + k_{os}$). It can be shown that ϵ_{app} is related to ϵ_{int} , the extinction coefficient of the intermediate at a particular wavelength, by eq 8. For ϵ_{int} to be

$$\epsilon_{\text{app}} = f\epsilon_{\text{int}} + (1 - f)(\epsilon_{\text{Ir}} + \epsilon_{\text{Co}}) \quad (8)$$

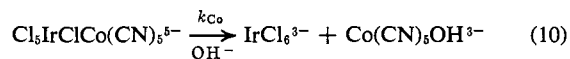
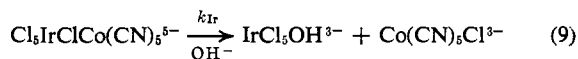
positive or zero, as required by the physical significance of the quantity ϵ_{int} , it is necessary that $\epsilon_{\text{app}} \geq (1 - f) \cdot (\epsilon_{\text{Ir}} + \epsilon_{\text{Co}})$. This inequality will be obeyed for any value of f in the interval $0 < f \leq 1$ as long as $\epsilon_{\text{app}} \geq \epsilon_{\text{Ir}} + \epsilon_{\text{Co}}$. However, if $\epsilon_{\text{app}} < \epsilon_{\text{Ir}} + \epsilon_{\text{Co}}$, it would be possible to

(19) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Amer. Chem. Soc.*, **85**, 2517 (1963).

(20) A. W. Adamson and E. Gonick, *Inorg. Chem.*, **2**, 129 (1963).

(21) J. P. Birk, *ibid.*, **9**, 125 (1970).

set an upper limit (within the 0–1 interval) on f . Unfortunately, for all wavelengths investigated (in the 600–250-nm region) it was found that $\epsilon_{\text{app}} > \epsilon_{\text{Ir}} + \epsilon_{\text{Co}}$, and consequently, it is not possible to set an upper limit on f on the basis of the requirement $\epsilon_{\text{int}} \geq 0$. However, a lower limit on f can be obtained by considering the results of the stoichiometry of the overall reaction. In order to develop the argument, it is necessary to recognize that the intermediate can dissociate *via* Ir–Cl or Co–Cl bond rupture (eq 9 or 10).



On the basis of reactions 6, 7, 9, and 10, the yield of IrCl_6^{3-} (expressed as the ratio of IrCl_6^{3-} produced divided by $(\text{IrCl}_6^{2-})_0$) is given by the expression $1 - k_{\text{Ir}}/(k_{\text{Ir}} + k_{\text{Co}})$. Since the average value of the yield of IrCl_6^{3-} is 0.985, $f = 0.015(k_{\text{Ir}} + k_{\text{Co}})/k_{\text{Ir}}$, and therefore $1 \geq f \geq 0.015$.

On the basis of the information presented so far it is not possible to decide whether IrCl_6^{3-} and $\text{Co}(\text{CN})_5\text{OH}^{3-}$ are formed in an outer-sphere reaction (eq 7) and/or by decomposition of the intermediate *via* Co–Cl bond rupture (eq 10). However, some additional arguments, albeit indirect, will be advanced in favor of the mechanism given by eq 6, 9, and 10. In previous work¹⁹ it has been demonstrated that, when a suitable bridging ligand is present in the oxidant, $\text{Co}(\text{CN})_5^{3-}$ reacts rapidly and *via* an inner-sphere mechanism. However, when such a ligand is absent, the oxidation of $\text{Co}(\text{CN})_5^{3-}$ becomes extremely slow, or even ceases, and an outer-sphere path involving the species $\text{Co}(\text{CN})_6^{4-}$, in equilibrium with $\text{Co}(\text{CN})_5^{3-}$ and CN^- , becomes important.¹⁹ Invoking an outer-sphere reaction between $\text{Co}(\text{CN})_5^{3-}$ and IrCl_6^{2-} would clearly violate the above reactivity pattern. First, the redox stage of the IrCl_6^{2-} – $\text{Co}(\text{CN})_5^{3-}$ is extremely rapid, as expected for an inner-sphere reaction mediated by a chloride bridge. Second, although kinetic studies of the redox stage were precluded by the rapidity of the reaction, the independence of the yield of the intermediate upon the excess cyanide ion concentration (Table II) clearly demonstrates that $\text{Co}(\text{CN})_6^{4-}$ is not implicated as a reactive species in this system, and, consequently, that an outer-sphere mechanism between IrCl_6^{2-} and $\text{Co}(\text{CN})_6^{4-}$ is unimportant. Admittedly, the arguments are insufficient to rule out an outer-sphere reaction between IrCl_6^{2-} and $\text{Co}(\text{CN})_5^{3-}$. However, the arguments suggest that such a reaction is unlikely to be important.

A second approach to the problem involves an examination of the significance of the ϵ_{app} values plotted in Figure 1. The extinction coefficients of the intermediate, ϵ_{int} , are related to ϵ_{app} by eq 8, and it will be seen that in order to calculate ϵ_{int} it is necessary to know f . As already indicated, f , the fraction of the redox reaction proceeding *via* the inner-sphere pathway, cannot be determined. However it is instructive to calculate the values of ϵ_{int} for the two limiting values of f . When $f = 1$, $\epsilon_{\text{int}} = \epsilon_{\text{app}}$, and the values obtained (for example ϵ_{int} at 420 nm = $1250 \text{ M}^{-1} \text{ cm}^{-1}$) are considered reasonable for a binuclear complex containing two metal ions with d^6 electronic configurations.^{20, 22–24}

When $f = 0.015$, the calculated values of ϵ_{int} at 550, 420, 300, and 250 nm are 6.2×10^3 , 7.3×10^4 , 7.9×10^4 , and $8.8 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. These values are several orders of magnitude higher than those observed for the entirely analogous binuclear complexes $(\text{NC})_5\text{FeCNC}(\text{Co}(\text{CN})_5)^{6-}$,²² $(\text{NC})_5\text{FeCNC}(\text{CoEDTA})^{5-}$,^{20, 23} $(\text{NH}_3)_5\text{CoNCC}(\text{Co}(\text{CN})_5)^{4+}$,²⁴ $(\text{H}_2\text{O})_5\text{RuClCr}(\text{H}_2\text{O})_5^{4+, 8, 25}$ $(\text{NH}_3)_4\text{CrRuClCr}(\text{H}_2\text{O})_5^{3+, 6}$ and $\text{Cl}_5\text{IrClCr}(\text{H}_2\text{O})_5^{5-}$. These comparisons suggest that the lower limit $f = 0.015$ is much too conservative, and, in fact, that the upper limit $f = 1$ is probably approached.

The suggested mechanism, eq 6 and 10 with a minor contribution from reactions 7 and/or 9, is entirely analogous to the one previously proposed for the $\text{Fe}(\text{CN})_6^{3-}$ – $\text{Co}(\text{CN})_5^{3-}$ and $\text{Fe}(\text{CN})_6^{3-}$ – $\text{Co}(\text{EDTA})^{2-}$ reactions,^{20, 22, 23} but contrasts, in part, with the mechanism recently postulated for the IrCl_6^{2-} – Cr^{2+} reaction.⁵ The portion of the latter reaction that proceeds *via* the inner-sphere pathway produces the bridged intermediate $\text{Cl}_5\text{IrClCr}(\text{H}_2\text{O})_5$, which decomposes by Ir–Cl bond fission, and, consequently, in the overall reaction, chloride transfer from iridium to chromium obtains. In contrast, the $\text{Fe}(\text{CN})_6^{3-}$ – $\text{Co}(\text{CN})_5^{3-}$, $\text{Fe}(\text{CN})_6^{3-}$ – CoEDTA^{2-} , and IrCl_6^{2-} – $\text{Co}(\text{CN})_5^{3-}$ reactions proceed *via* inner-sphere mechanisms without transfer of the bridge, *e.g.*, following the dissociation of the binuclear complexes the bridging ligand is retained in the coordination sphere of the reduced form of the oxidant. These results demonstrate that transfer of the bridging ligand from oxidant to reductant is not, at least for these systems,⁷ an essential feature of the inner-sphere mechanism. Whether or not ligand transfer obtains depends on the position of bond scission in the bridged binuclear complexes. The dissociation of the binuclear complexes may be viewed as metal-catalyzed aquations of the parent complexes, and it is noteworthy, although the available data are admittedly limited, that the position of bond breaking appears to depend on the rate constants rather than the activation energies for aquation of the parent complexes. The pertinent information is summarized in Table IV. It is also

Table IV. Rate Constants and Activation Parameters for Dissociation of Chloride-Bridged Binuclear Complexes and for Aquation of Mononuclear Chloride Complexes

Complex	Bond ruptured	k , sec^{-1} (25°)	ΔH^\ddagger , kcal mol^{-1}	ΔS^\ddagger , eu	Ref
$\text{Cl}_5\text{IrClCo}(\text{CN})_6^{5-}$	Co–Cl	4.0	15.4	–4.2	<i>a</i>
$\text{Cl}_5\text{IrClCr}(\text{OH})_2$	Ir–Cl	4.2×10^{-2}	21.8	8.4	<i>b</i>
IrCl_6^{3-}	Ir–Cl	9.4×10^{-6}	29.4	19	<i>c</i>
$\text{Co}(\text{CN})_5\text{Cl}^{3-}$	Co–Cl	6.4×10^{-5}	23.2	0	<i>d</i>
$\text{Cr}(\text{OH})_5\text{Cl}^{3+}$	Cr–Cl	2.8×10^{-7}	24.4	–7	<i>e</i>

^a This work. ^b Reference 5. ^c Reference 9. ^d From data in ref 26 and a single measurement at 30°. ^e T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

noteworthy that the acceleration in the rates of metal-chloride bond rupture of the intermediate as compared to the parent complexes is associated with a decrease of

(22) A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **83**, 509 (1961).

(23) D. Huchital and R. G. Wilkins, *Inorg. Chem.*, **6**, 1022 (1967).

(24) R. Castello, C. Piriz, N. Egen, and A. Haim, *ibid.*, **8**, 699 (1969).

(25) The values in column 5 of Table I of ref 8 must be multiplied by 10^3 (N. Sutin, private communication).

(26) R. G. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).

ca. 8 kcal in activation energy. Moreover, in common with other aquations of pentacyano-cobaltate(III) complexes, the dissociation of $\text{Cl}_5\text{IrClCo}(\text{CN})_5^{5-}$ proceeds at a rate independent of hydroxide ion concentration, and, presumably, yields as the primary cobalt(III) product the pentacoordinate species $\text{Co}(\text{CN})_5^{2-}$.²⁶

Finally, the results of the present study must be compared with those of the study of the IrCl_6^{2-} -CoEDTA²⁻ reaction.²⁷ In the latter system, no intermediate was detected, but the authors suggested an inner-sphere mechanism *via* the intermediate $\text{Cl}_5\text{IrClCoEDTA}^{4-}$, with the chloride bridge being retained by the iridium following the dissociation of the intermediate. If this mechanism is correct, then the position of bond rupture in the $\text{Cl}_5\text{IrClCoEDTA}^{4-}$ postulated intermediate would correlate with the activation energies for aquation of the parent complexes, rather than the rate constants.²⁸ Moreover, this system would provide an additional example of an inner-sphere reaction which does not result in transfer of the bridging ligand, and would conform to the findings in the related $\text{Fe}(\text{CN})_6^{3-}$ -CoEDTA²⁻, $\text{Fe}(\text{CN})_6^{3-}$ - $\text{Co}(\text{CN})_5^{3-}$, and IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$ systems. However, it is surprising, in view of the stability of the intermediates produced in the latter three systems, that the intermediate $\text{Cl}_5\text{IrClCoEDTA}^{4-}$ was not detected. Furthermore, some anomalies become apparent when the rates of these reactions are compared. The second-order rate constants (25°) for the redox stages of the latter three inner-sphere reactions are 1.3×10^5 ,²³ 4.5×10^4 ,²⁹ and $>10^7$ $M^{-1} \text{sec}^{-1}$, respectively. The second-order rate constant for the IrCl_6^{2-} -CoEDTA²⁻ reaction is 4×10^3 $M^{-1} \text{sec}^{-1}$ at 22°.²⁷ The rate order for oxidation of CoEDTA²⁻, $\text{Fe}(\text{CN})_6^{3-} > \text{IrCl}_6^{2-}$, is opposite to that pre-

dicted on the basis of either free energy considerations and/or the relative electron mediating abilities of chloride and cyanide ions. It would appear that this unexpected order is caused by an abnormally fast rate for $\text{Fe}(\text{CN})_6^{3-}$ rather than a slow rate for IrCl_6^{2-} . This is seen by comparing the rates of reduction of $\text{Fe}(\text{CN})_6^{3-}$ by CoEDTA²⁻ and $\text{Co}(\text{CN})_5^{3-}$. The order $\text{CoEDTA}^{2-} > \text{Co}(\text{CN})_5^{3-}$ is opposite to that predicted on the basis of either free energy considerations and/or general reactivity patterns in reductions by CoEDTA²⁻ or $\text{Co}(\text{CN})_5^{3-}$. It was noted previously²³ that the $\text{Fe}(\text{CN})_6^{3-}$ -CoEDTA²⁻ reaction proceeds ca. 10^5 times faster than predicted on the basis of Marcus' equation $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$,³⁰ and this was attributed to the rate accelerating action of an inner-sphere process. This explanation must be at least incomplete, since the $\text{Co}(\text{CN})_5^{3-}$ reduction of $\text{Fe}(\text{CN})_6^{3-}$ also proceeds *via* an inner-sphere mechanism, but with a slower rate than the CoEDTA²⁻ reduction. A satisfactory rationalization for all the observed trends is not available. However, it is noteworthy that the rate constant for the IrCl_6^{2-} -CoEDTA²⁻ reaction calculated³¹ using Marcus' equation for outer-sphere reactions gives a value of 2×10^3 $M^{-1} \text{sec}^{-1}$, in remarkable agreement with the measured value 4×10^3 $M^{-1} \text{sec}^{-1}$. It is tempting to suggest, on the basis of this agreement, that the IrCl_6^{2-} -CoEDTA²⁻ reaction proceeds *via* an outer-sphere mechanism. If the outer-sphere mechanism obtains, then it is easy to understand why an intermediate was not detected in this system. But then the question would remain: why is an inner-sphere mechanism so ineffective for bringing about the IrCl_6^{2-} -CoEDTA²⁻ reaction, when for the analogous systems $\text{Fe}(\text{CN})_6^{3-}$ -CoEDTA²⁻, IrCl_6^{2-} - $\text{Co}(\text{CN})_5^{3-}$, and $\text{Fe}(\text{CN})_6^{3-}$ - $\text{Co}(\text{CN})_5^{3-}$ the inner-sphere mechanism represents the major pathway to products?

(27) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 2802 (1963).

(28) The rate constant and activation enthalpy for loss of chloride from CoEDTACl^{2-} are $2.8 \times 10^{-6} \text{sec}^{-1}$ and 22.8 kcal mol⁻¹, respectively: R. Dyke and W. C. E. Higginson, *ibid.*, 1998 (1960).

(29) B. Grossman and A. Haim, unpublished measurements.

(30) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

(31) The values used are $k_{11} = 2 \times 10^{-7} M^{-1} \text{sec}^{-1}$, $k_{22} = 2 \times 10^5 M^{-1} \text{sec}^{-1}$, and $K_{12} = 10^8$.