

The Mechanism of Interchange Reactions of Halogenoplatinate(IV) Complexes. The $\text{trans-Pt}(\text{CN})_4\text{X}_2^{2-} - \text{I}^-$ Reactions

A. J. Poë and D. H. Vaughan

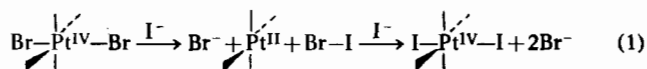
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The kinetics of the reactions with iodide of the complexes $\text{trans-Pt}(\text{CN})_4\text{X}_2^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$) have been studied by means of the "stopped flow" technique. The reactions of the chloro- and bromo-complexes are first order in both complex and iodide concentrations, and the mechanism appears to involve rate determining reduction to $\text{Pt}(\text{CN})_4^{2-}$, followed by fast reoxidation to the *trans*-di-iodo complex provided the iodide concentration is not too high. The reactions are much faster than those of PtCl_6^{2-} and PtBr_6^{2-} with iodide, and the rates appear to be closely related to the thermodynamic ease of reduction. It may be concluded that Pt-X bond breaking, and probably also X-I bond making, play an important part in determining the rates of reaction. The activation parameters for the reaction of the chlorocomplex are $\Delta H^* = 6.0 \pm 0.3$ kcal/mole and $\Delta S^* = -25$ cal.mole⁻¹ deg.⁻¹ at $\mu = 1.0$ M. The iodo-complex undergoes rapid reduction by iodide, and reduction through direct attack by hydroxide also seems to occur. Equilibrium constants for the reduction of the diiodo-complex by iodide, bromide and chloride have been obtained, and rough limiting values of the equilibrium constants for replacement of chloride or bromide by iodide have been estimated. The spectra of solutions of $\text{trans-Pt}(\text{CN})_4\text{X}_2^{2-}$ ($\text{X} = \text{Cl}$ or Br) undergo changes in the presence of a large excess of the corresponding halide which are consistent with the occurrence of charge transfer during collisions between the complex and halide ions.

Introduction

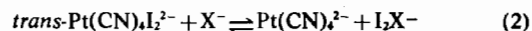
The importance of redox processes in substitution reactions of hexahalogenoplatinate(IV) complexes has been known for some time. In some conditions the $\text{PtCl}_6^{2-} - \text{Cl}^-$ and $\text{PtBr}_6^{2-} - \text{Br}^-$ exchange reactions are believed to go *via* a chain reaction which involves labile platinum(III) intermediates, while the rate of the $\text{PtCl}_6^{2-} - \text{Br}^-$ reaction³ is first order in $[\text{PtCl}_4^{2-}]$, and presumably involves the same sort of redox process by Br^+ transfer as has been postulated for reactions such as $\text{trans-Pt en}_2\text{Cl}_2^{2+} - \text{Cl}^-$ exchange⁴

which is catalysed by Pt en_2^{2+} . In the presence of certain inhibitors, the rates of substitution reactions of PtCl_6^{2-} and PtBr_6^{2-} with iodide are first order in $[\text{I}^-]$,⁵ the latter complex reacting to give PtI_6^{2-} in three distinct stages.⁶ These are thought to involve the successive replacement of three pairs of bromide ions *trans* to each other. (Equation (1)).



Recent work has shown that the $\text{PtCl}_6^{2-} - \text{I}^-$ reaction also proceeds to PtI_6^{2-} in three distinct stages.⁷

We now report studies of the kinetics of the reactions of iodide with the complex $\text{trans-Pt}(\text{CN})_4\text{X}_2^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$), and of the redox equilibria shown in equation (2).



Experimental Section

Materials. Potassium tetracyanoplatinate(II) was prepared by adding a slight excess of potassium cyanide to an aqueous solution of potassium tetrachloroplatinate(II). The precipitate which formed, after concentrating and cooling the solution, was filtered off and dried at 140°C to give the anhydrous salt. Potassium *trans*-dichlorotetracyanoplatinate(IV) dihydrate was prepared by oxidation of a concentrated hydrochloric acid solution of potassium tetracyanoplatinate(II) with chlorine or hydrogen peroxide. The complex which precipitated on concentrating the solution and cooling, was obtained as white crystals which were recrystallised twice from dilute hydrochloric acid. Potassium *trans*-dibromotetracyanoplatinate(IV) dihydrate⁸ was prepared by oxidation of a concentrated hydrobromic acid solution of potassium tetracyanoplatinate(II) with bromine, the resulting solution being concentrated by boiling. After cooling the solution, yellow crystals of the complex were precipitated and these were recrystallised from dilute hydrobromic acid.

(1) R. L. Rich and H. Taube, *J. Amer. Chem. Soc.*, 76, 2608 (1954).

(2) A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, 80, 3865 (1958).

(3) R. Dreyer, *Z. Physik. Chem. (Frankfurt)*, 29, 347 (1961).

(4) F. Basolo, P. H. Wilks, R. G. Pearson, and R. G. Wilkins, *J. Inorg. Nuclear Chem.*, 6, 161 (1958).

(5) A. J. Poë and M. S. Vaidya, *J. Chem. Soc.*, 2981 (1961).

(6) E. J. Bounsall, D. J. Hewkin, D. Hopgood, and A. J. Poë, *Inorganica Chim. Acta*, 1, 281 (1967).

(7) R. C. Delori and A. J. Poë, unpublished work.

(8) "Gmelin's Handbuch der Anorganischen Chemie", 68c, p. 207, Auflage (Pt).

Potassium *trans*-di-iodotetracyanoplatinate(IV) was not isolated as a pure solid owing to partial decomposition while the solution was being concentrated. Stock millimolar solutions of the complex were prepared by adding an aqueous solution of potassium tetracyanoplatinate(II) to one containing equimolar amounts of both iodine and potassium iodide.

$10^{-4} M$ Solutions of the chloro- and bromo-complexes were stable over a period of days, as judged by their unchanging absorption spectra, but those of the iodo-complex were stable only in the presence of an excess of enough tetracyanoplatinate(II) and iodide ions, to prevent reduction and hydrolysis.

The chloro- and bromo-complexes were analysed spectrophotometrically by reduction with an excess of sodium iodide, the tri-iodide formed being estimated spectrophotometrically. The optical density was measured at the maximum at $353 m\mu$, at which wavelength the extinction coefficient of I_3^- is $26.4 \times 10^3 \text{ l.mole}^{-1}\text{cm}^{-1}$.⁹ Weights of complexes were such that absorbances of *ca.* 0.4 were obtained in 1 mm or 1 cm cells. This method was also used to determine the concentrations of the solutions of the iodo-complex. $K_2Pt(CN)_4Br_2 \cdot 2H_2O$: calcd.: Pt, 34.0; found: Pt, 34.9%. $K_2Pt(CN)_4Cl_2 \cdot 2H_2O$: calcd.: Pt, 40.3; found: Pt, 41.0%. The *trans*-configuration was assigned on the basis of the method of preparation and the appearance of only one Pt—X stretching frequency in the Raman spectra of the complexes. Details of the absorption spectra in the near ultra violet, and of the Raman spectra, are given in Table I. The excellent agreement between our data and those of other workers confirms the identity of our complexes.

measuring transmission changes for monochromatic light of wavelength between 230 and 750 $m\mu$ (Hilger Watt monochromator D 246). The light transmitted through the reacting solutions was detected by a photomultiplier (RCA IP 28) and the changes displayed on an oscilloscope screen (Solartron CD 1400) and photographed (Shackman AC/2/25 35 mm oscilloscope camera). After developing the negatives, the traces were projected on to a sheet of graph paper ($16 \times 23 \text{ cm}$) and the transmittance recorded as a function of time. The time was measured relative to the standard mains frequency (50 c.p.s.) which was also displayed on the oscilloscope screen during the reaction. The syringes containing the reactants, the Teflon mixing chamber, and the silica reaction cell (2 mm path length) were all enclosed in a copper jacket through which water, thermostatted at between 15 and 50°, was circulated. Reactions with half times down to *ca.* 5 msec could be followed with this apparatus, the efficiency of mixing being better than 98% by the time the reactants reached

Table II. Rate parameters for carbonic acid decomposition

	k_{18}° (sec^{-1})	E_a (kcal. mole ⁻¹)	Temp. Range (°C)	Technique
This work	11.5	16.0	18-35	stopped flow
Moore ^a	11.5	15.9	23-30	» »
Scheurer <i>et al.</i> ^b	11.8	16.1	23-37	» »
Dalziel ^c	12.3	16.9	19-23	continuous flow

^a Ph. D. Thesis, Northwestern University (1964). ^b *J. Phys. Chem.*, 62, 809 (1958). ^c *Biochem. J.*, 55, 79 (1953).

Table I. Spectroscopic data for the complexes *trans*-Pt(CN)₄X₂²⁻

X	Electronic spectra			Raman spectra		
	λ_{max} (m μ)	ϵ (l.mole ⁻¹ cm ⁻¹)		ν_1 (cm ⁻¹)	Force constant (mdynes/Å)	
	a	b	a	a	c	c
Cl	284	286	522	333	330	2.09
	330 (sh)	330 (sh)	~220			
Br	342	344	1,200	203	(200)	1.73
I	405	—	5,600	142	(141)	1.37

^a This work. ^b I. I. Chernyaev, A. V. Babkov, and N. N. Zheligoyskaya, *J. Inorg. Chem. (U.S.S.R.)*, 8, 1279 (1963). ^c L. H. Jones and J. M. Smith, *Inorg. Chem.*, 4, 1677 (1965); the values in parentheses were obtained indirectly from infrared studies.

Instruments. Uv and visible spectra were measured with a Perkin Elmer 137 UV recording spectrophotometer, and absorbances at a fixed wavelength were measured with a Unicam S.P. 500 spectrophotometer. The Raman spectra were measured with a Carey Laser Raman spectrophotometer, Model 81.

The rates of the reactions studied were sufficiently fast for the stopped-flow technique to be necessary. The apparatus was a slightly modified version of a design by Professor Sturtevant,¹⁰ and was capable of

the reaction cell. The functioning of the apparatus was tested by studying the decomposition of carbonic acid, and the results, compared with those of other workers, are shown in Table II.

Results

The Reaction of Iodide with *trans*-Pt(CN)₄Cl₂²⁻. At low iodide concentrations, the formation of *trans*-Pt(CN)₄I₂²⁻ was followed by observing the decrease in transmittance of the solutions at 405 $m\mu$, an absorption maximum of the di-iodocomplex. The ionic strength was maintained at 0.07 *M* with sodium chloride, the equilibrium constant for replacement of

(9) A. D. Awtrey and R. E. Connick, *J. Amer. Chem. Soc.*, 73, 1842 (1951).

(10) D. J. Hewkin, Ph. D. Thesis, London University (1967); J. M. Sturtevant, "Rapid Mixing and Sampling Techniques in Biochemistry", B. Chance, Ed., Academic Press, Inc., New York, p. 18 (1964).

chloride by iodide being sufficiently large for the reaction to go to completion even in the presence of this amount of free chloride. The results are shown in Table III.

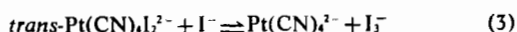
Table III. Rate constants for the reaction $\text{trans-Pt(CN)}_4\text{Cl}_2^{2-} \xrightarrow{\text{I}^-} \text{trans-Pt(CN)}_4\text{I}_2^{2-}$. $[\text{Pt}^{\text{IV}}] = 5.0 \times 10^{-4} M$; $\mu = 0.07 M$

Temp. (°C)	$10^3 [\text{Pt}^{\text{IV}}] (M)$	$10^3 [\text{I}^-] (M)$	$k_{\text{obs}} (\text{sec}^{-1})$	$k_2 (\text{l.mole}^{-1} \text{sec}^{-1})$
22.0	3.4	3.65	0.58	159
»	»	2.42	0.40	165
»	0.8	»	0.45	186
»	1.0	3.65	0.60	164
»	»	»	0.62 ^a	170
30.2	0.8	2.42	0.61	252
38.9	»	»	0.85	351
47.6	»	»	1.10	455
23.4	1.0	4.2	4.01 ^b	954
»	»	»	3.85 ^{b,c}	917

^a $[\text{IrCl}_6^{2-}] = 7 \times 10^{-5} M$. ^b $[\text{Pt}^{\text{IV}}] = 6.9 \times 10^{-4} M$; $\mu = 1.0 M$.
^c $[\text{Cl}^-] = 1.0 M$. $\Delta H^\ddagger = 6.0 \pm 0.3 \text{ kcal./mole}$; $\Delta S^\ddagger = -28 \text{ cal. mole}^{-1} \text{deg}^{-1}$.

$\text{trans-Pt(CN)}_4\text{I}_2^{2-}$ is easily reduced by free iodide ions so that the range of iodide concentrations used was severely limited, even in the presence of an excess of Pt(CN)_4^{2-} . The pseudo first order rate plots were usually linear for 1-2 half times but when, in some cases, the rate plots obtained were curved, the initial slopes were used to calculate the rate constants. Each of the rate constants quoted in Table III was the mean of at least three separate determinations, and an analysis of the data showed that the standard deviation of the quoted values was about $\pm 6\%$. The activation enthalpies and entropies were obtained graphically, and the uncertainties assigned to them are approximate standard deviations, based on the uncertainty of the rate constants.

The reaction was also studied at higher iodide concentrations when extensive reduction of the product iodo-complex occurs, but when pseudo first order conditions are more closely obtained. The rate of reduction of $1.5 \times 10^{-4} M$ iodo-complex by $5 \times 10^{-2} M$ iodide was shown to be too fast to measure with the stopped flow apparatus. These reactions of the chloro-complex were followed by measuring the decrease in transmittance at 353 m μ which accompanies the formation of I_3^- . The ionic strength was maintained at 1.0 M with sodium perchlorate. This method is complicated by the fact that reduction of the product is not complete, so that the proportion of the product which is reduced varies throughout the reaction. The concentration of product, $[\text{Pt(CN)}_4\text{I}_2^{2-}] + [\text{Pt(CN)}_4^{2-}]$, is equal to $[\text{I}_3^-] \{1 + [\text{I}_3^-] / K_r [\text{I}^-]\}$ where K_r is the equilibrium constant for reaction (3).



This was estimated to be 2.4×10^{-2} at 25°C (see below). The effect of the correction term $\{1 + [\text{I}_3^-] / K_r [\text{I}^-]\}$ is to decrease the apparent rate constant by about 7% at the iodide concentration of 0.02 M used

for the determination of the temperature dependence. The same value of K_r was used at each temperature but $|\Delta H^\ddagger|$ would have to be greater than about 5 kcal./mole for this approximation to cause a systematic error of more than 0.5 kcal./mole in the activation enthalpy. The results are given in Table IV. Linear first order rate plots were obtained over 1-2 half times and the standard deviations of the quoted rate constants, each of which is the average of at least three measurements, is about $\pm 3\%$.

Table IV. Rate constants for the reaction $\text{trans-Pt(CN)}_4\text{Cl}_2^{2-} \xrightarrow{\text{I}^-} \text{Pt(CN)}_4^{2-} + \text{I}_3^-$. $[\text{Pt}^{\text{IV}}] = 6 \times 10^{-5} M$; $\mu = 1.0 M$

Temp. (°C)	$10^3 [\text{I}^-] (M)$	$k_{\text{obs}} (\text{sec}^{-1})$	$k_2 (\text{l.mole}^{-1} \text{sec}^{-1})$
20.0	1.0	7.8	780
»	2.0	16.6	830
»	»	16.6	830
»	»	16.5	825
»	5.0	43.3	866
»	7.0	61.3	876
27.6	2.0	22.3	1,120
34.3	»	30.8	1,540
44.9	»	40.1	2,000

$\Delta H^\ddagger = 6.0 \pm 0.3 \text{ kcal./mole}$; $\Delta S^\ddagger = -25 \text{ cal.mole}^{-1} \text{deg}^{-1}$.

The Reaction of Iodide with trans-Pt(CN)₄Br₂²⁻. This is much faster than the reaction of the chloro-complex, and can be studied only at low iodide concentrations by measuring the decrease in transmission at 405 m μ . The results are given in Table V.

Table V. Rate constants for the reaction $\text{trans-Pt(CN)}_4\text{Br}_2^{2-} \xrightarrow{\text{I}^-} \text{trans-Pt(CN)}_4\text{I}_2^{2-}$. Temp. = 20.9°C; $\mu = 0.075 M$ (with NaBr); $[\text{Pt}^{\text{IV}}] = 4.0 \times 10^{-4} M$

$10^3 [\text{I}^-] (M)$	$10^3 [\text{Pt(CN)}_4^{2-}] (M)$	$k_{\text{obs}} (\text{sec}^{-1})$	$10^{-4} k_2 (\text{l.mole}^{-1} \text{sec}^{-1})$
1.45	0.5	108	7.5
1.45	2.1	107	7.4
2.20	2.1	195	8.9

The Reduction of trans-Pt(CN)₄I₂²⁻. An attempt was made to study the rate of reduction of the iodo-complex by iodide at sufficiently low concentrations of iodide for the rate to be measurably slow, and in the presence of hydroxide to remove the I_3^- produced and so drive the reaction to completion. The reaction of I_3^- with OH^- is too fast to measure by the stopped-flow technique. The reactions were followed by measuring the increase in transmission at 405 m μ which accompanies the loss of the iodo-complex, and the results are given in Table VI.

Equilibrium Studies. A study was made of the redox equilibrium, shown in equation (3), by measuring the increase of absorbance, A, at 353 m μ , with increasing amounts of added iodide. The equilibrium was studied in the presence of added Pt(CN)_4^{2-} so that the iodide concentrations corresponding to convenient amounts of reduction were very much greater

Table VI. Rate constants for the reaction $\text{trans-Pt(CN)}_4\text{I}_2^{2-} + \text{I}^-/\text{OH}^- \rightarrow \text{Pt(CN)}_4\text{I}_2^{2-}$. $[\text{Pt}^{\text{IV}}] = 1.5 \times 10^{-4} \text{ M}$; $\mu = 0.05 \text{ M}$; Temp. = 17.1°C

$10^3 \times [\text{OH}^-] (\text{M})$	$10^4 \times [\text{I}^-] (\text{M})$	$k_{\text{obs}} (\text{sec}^{-1})$
1.25	2.00	42
1.25	2.00	44 ^a
2.50	2.00	85
2.50	4.45	106
3.75	2.00	~150

^a $[\text{Pt(CN)}_4\text{I}_2^{2-}] = 7.2 \times 10^{-4} \text{ M}$.

than the concentration of complex. In spite of this, the iodide concentrations were not sufficiently large to prevent some dissociation of I_3^- into I_2 and I^- . However, since the absorbance due to $\text{Pt(CN)}_4\text{I}_2^{2-}$ and I_2 is negligible, the equilibrium constant, K_r , can easily be calculated from equations (i)-(iii), where K is the formation constant⁹ of I_3^- from I_2 and I^- , and ϵ_a and ϵ_b are the extinction coefficients of $\text{trans-Pt(CN)}_4\text{I}_2^{2-}$ and I_3^- , respectively. The subscript zero, here and in equation (iv) below, designates the concentrations in the absence of any reduction.

$$A = \epsilon_a [\text{Pt(CN)}_4\text{I}_2^{2-}]_0 + [\text{I}_3^-] \{ \epsilon_b - \epsilon_a (1 + 1/K [\text{I}^-]) \} \quad (\text{i})$$

$$[\text{Pt(CN)}_4\text{I}_2^{2-}] = [\text{Pt(CN)}_4\text{I}_2^{2-}]_0 - [\text{I}_3^-] (1 + 1/K [\text{I}^-]) \quad (\text{ii})$$

$$[\text{Pt(CN)}_4\text{I}_2^{2-}] = [\text{Pt(CN)}_4\text{I}_2^{2-}]_0 + [\text{I}_3^-] (1 + 1/K [\text{I}^-]) \quad (\text{iii})$$

The experimental data, and the constants derived from them, are given in Table VII.

Table VII. Data for the equilibrium $\text{trans-Pt(CN)}_4\text{I}_2^{2-} + \text{I}^- \rightleftharpoons \text{Pt(CN)}_4\text{I}_2^{2-} + \text{I}_3^-$ at 25°C and $\mu = 0.5 \text{ M}$. $[\text{Pt}^{\text{IV}}]_0 = 2.97 \times 10^{-4} \text{ M}$; $[\text{Pt}^{\text{II}}]_0 = 3.41 \times 10^{-4} \text{ M}$

$10^3 [\text{I}^-]$	0	6.49	9.24	12.0	17.5	21.6	31.9
A^a	0.045	0.216	0.264	0.314	0.371	0.415	0.480
$10^4 K_r$	—	2.15	2.19	2.40	2.35	2.51	2.53
\bar{K}_r	$(2.36 \pm 0.06) \times 10^{-2}$						

^a At 353 m μ in 1 mm cells.

Table VIII. Data for the equilibria $\text{trans-Pt(CN)}_4\text{I}_2^{2-} + \text{X}^- \rightleftharpoons \text{Pt(CN)}_4\text{I}_2^{2-} + \text{I}_2\text{X}^-$ at 25°C and $\mu = 5.0 \text{ M}$.

$[\text{Pt}^{\text{IV}}]_0 = 6.07 \times 10^{-5} \text{ M}$; $[\text{Pt}^{\text{II}}]_0 = 8.31 \times 10^{-5} \text{ M}$; $\epsilon_{\text{I}_2\text{Br}^-} = 1,110 \text{ l.mole}^{-1}\text{cm}^{-1}$ at 405 m μ								
$[\text{Br}^-] (\text{M})$	0	0.156	0.313	0.625	1.25	1.88	2.50	
A^a	1.360	1.042	0.903	0.723	0.535	0.481	0.440	
$10^4 K_r$	—	2.65	2.51	2.56	3.31	2.93	2.91	
\bar{K}_r	$(2.81 \pm 0.12) \times 10^{-4}$							
$[\text{Pt}^{\text{IV}}]_0 = 1.60 \times 10^{-4} \text{ M}$; $[\text{Pt}^{\text{II}}]_0 = 3.08 \times 10^{-4} \text{ M}$; $\epsilon_{\text{I}_2\text{Cl}^-} = 671 \text{ l.mole}^{-1}\text{cm}^{-1}$ at 405 m μ								
$[\text{Cl}^-] (\text{M})$	0	0.74	1.02	1.30	1.85	2.50	3.70	5.00
A^b	0.894	0.796	0.763	0.750	0.700	0.661	0.605	0.551
$10^3 K_r$	—	6.32	6.58	5.82	6.14	5.97	5.76	5.83
\bar{K}_r	$(6.06 \pm 0.11) \times 10^{-5}$							

^a In 4 cm cells. ^b In 1 cm cells.

(11) D. L. Cason and H. M. Neumann, *J. Amer. Chem. Soc.*, **83**, 1822 (1961).

When an attempt was made to determine the equilibrium constants for replacement of chloride or bromide ligands by iodide it was found that free chloride and bromide can also reduce $\text{Pt(CN)}_4\text{I}_2^{2-}$. Increasing amounts of these ions reduced the absorbance at 405 m μ , as expected if they were replacing the iodide in the complex, but addition of small amounts of free iodide failed to reverse the decrease in absorbance. When large amounts of bromide were added to the iodocomplex, there was no evidence for absorption maxima at 240 and 340 m μ , due to the dibromocomplex, but the spectrum resembled instead that of $\text{Pt(CN)}_4\text{I}_2^{2-}$. When $\text{Pt(CN)}_4\text{I}_2^{2-}$ was present initially, a clean isosbestic point at 330 m μ was observed on addition of chloride, and a rather poor one at 350 m μ on addition of bromide. The spectral changes occurred immediately on addition of halide, but at high concentrations of halide the product solutions were not very stable. Spectra were therefore measured immediately after mixing the solutions. The concentrations of chloride or bromide were large enough for all the iodine formed to be present as I_2Cl^- ¹¹ or I_2Br^- ¹² and the equilibrium constants for reduction were calculated from equation (iv) where A_0 and A are the absorbances before and after addition of halide respectively, and ϵ_a and ϵ_b are the extinction coefficients of the di-iodocomplex and of I_2X^- , respectively.

$$K_r = \frac{A_0 - A}{\epsilon_a - \epsilon_b} \cdot \frac{[\text{Pt(CN)}_4\text{I}_2^{2-}]_0 + (A_0 - A)/(\epsilon_a - \epsilon_b)}{[\text{Pt(CN)}_4\text{I}_2^{2-}]_0 - (A_0 - A)/(\epsilon_a - \epsilon_b)} \cdot \frac{1}{[\text{X}^-]} \quad (\text{iv})$$

The absorbance of $\text{Pt(CN)}_4\text{I}_2^{2-}$ in these solutions was negligible. Absorbance data, obtained with the Unicam S.P. 500 spectrophotometer, are shown in Table VIII together with the derived values of the constants.

In 1.0 M solutions of chloride, $\leq 90\%$ conversion of $1.9 \times 10^{-4} \text{ M}$ chlorocomplex into iodocomplex was caused by $6 \times 10^{-4} \text{ M}$ iodide in the presence of $5 \times 10^{-5} \text{ M}$ $\text{Pt(CN)}_4\text{I}_2^{2-}$. Under these conditions about 10% reduction of the iodocomplex had occurred. No attempt to derive accurate equilibrium constants was made in view of the complication introduced by reduction, but an upper limit of ca. 10^5 was obtained

(12) D. Meycrstein and A. Treinin, *Trans. Faraday Soc.*, **59**, 1114 (1963).

for the average constant. Solutions which were $4.8 \times 10^{-5} M$ in bromocomplex, $0.01 M$ in bromide, and $2 \times 10^{-3} M$ in $\text{Pt}(\text{CN})_4^{2-}$, showed isosbestic points at 317 and 365 $m\mu$ for total iodide concentrations above *ca.* $6 \times 10^{-5} M$. These presumably correspond to the overlap of the spectra of the iodobromo- and di-iodocomplexes. Even with this simplification, together with the absence of reduction under these conditions, it proved impossible to obtain self consistent sets of equilibrium constants. An upper limit of *ca.* 10^3 was obtained, however.

Spectroscopic Interactions. The spectra of the chloro- and bromo-complexes were found to change on addition of free halide ions. The increase was linear with concentration of halide up to $4.0 M$ ($\mu = 4.0 M$) for the chlorocomplex at 260 and 280 $m\mu$, and up to $2.0 M$ ($\mu = 5.0 M$) for the bromocomplex at 300 and 320 $m\mu$. No clear maximum was obtained on subtracting the absorbances of the solutions in the absence of free halide from those in its presence. The spectroscopic changes were rapid and were not affected by the addition of substantial amounts of $\text{Pt}(\text{CN})_4^{2-}$. The gradients, expressed as changes in apparent extinction coefficients per unit halide concentration, are given in Table IX. At bromide concentrations above $2.0 M$ the solutions of bromocomplex decomposed sufficiently rapidly to make the measurements unreliable. In the higher chloride concentrations the chlorocomplex also decomposed, but slowly enough for the initial changes to be measured accurately.

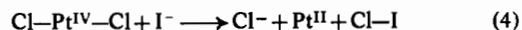
Table IX. Spectroscopic interactions between *trans*- $\text{Pt}(\text{CN})_4\text{X}_2^{2-}$ and X^-

X	λ ($m\mu$)	μ (M)	$10^3[\text{Pt}(\text{CN})_4^{2-}]$ (M)	$\Delta\epsilon/[\text{X}^-]$ ($l^2\text{mole}^{-2}\text{cm}^{-1}$)
Cl	260	4.0	0	62
	270	4.0	0	51
	270	4.0	0.7	50
Br	300	1.0	0	596
	300	1.0	1.0	609
	320	1.0	0	273
	320	1.0	1.0	290
	300	4.0	0	1016
	320	4.0	0	476

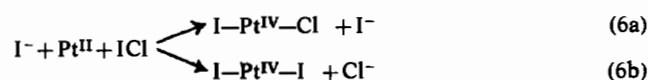
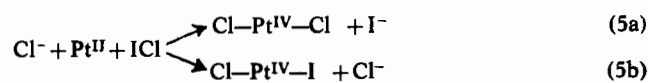
Discussion

Within the limits imposed by the narrow range of iodide concentrations which can be used, the data in Table III show that the rate of replacement of chloride ion in *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ by iodide is first order in iodide concentration. It is unaffected by the presence of 14 mole % of IrCl_6^{2-} , or of quite widely varying amounts of $\text{Pt}(\text{CN})_4^{2-}$. Reaction mechanisms involving labile Pt^{III} or bridged $\text{Pt}^{\text{IV}}\text{-Cl-Pt}^{\text{II}}$ intermediates³ can therefore be rejected. The rate of reduction of the chlorocomplex by iodide is also approximately first order in $[\text{I}^-]$ (Table IV) although there may just possibly be an additional path which is dependent on $[\text{I}^-]^2$. The second order rate constant for reduction at 23.4° can be obtained from the Arrhenius plot, and is the same ($950 \text{ l.mole}^{-1}\text{sec}^{-1}$) as the values for substitution at the same temperature

and ionic strength (Table III). The activation enthalpies for substitution and reduction are also identical within the experimental uncertainty. The slow step in both these reactions would therefore appear to be the reduction reaction (4), the four cyanide ligands



cis to the reacting chloride ligands being omitted for clarity. This reduction can be envisaged as involving the transfer of Cl^+ from the platinum(IV) complex to the iodide ion. If the iodide concentration is sufficiently small, and the platinum(II) concentration sufficiently large, then the reduction is followed by rapid reoxidation of $\text{Pt}(\text{CN})_4^{2-}$. Possible oxidation reactions are shown in equations (5a)-(6b).



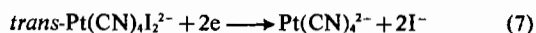
The fact that quite large amounts of chloride do not appreciably retard the replacement reaction (Table III) shows that reaction (5a) is relatively slow. Further studies of the $\text{PtCl}_6^{2-}\text{-I}^-$ reaction at $\mu = 1.0 M$ and at 35.1°C show that it also is not retarded by the presence of chloride ions, the second order rate constants being 0.0826 and $0.0839 \text{ l.mole}^{-1}\text{sec}^{-1}$ when the chloride concentration was 0 and $1.0 M$, respectively. This lack of retardation might be because it is the iodine atom of ICl which re-enters the complex on oxidation in preference to the chlorine atom ((5a) and (5b)). There was also evidence in the studies of the $\text{PtBr}_6^{2-}\text{-I}^-$ reactions that it is the iodine atom and not the bromine atom that re-enters the complex on oxidation.⁶ If the iodochlorocomplex is formed as an intermediate it must be assumed that its reduction by iodide is much faster than that of the dichloro-complex, as would be expected from the high *trans* effect of iodide.

Although the data are very sparse, it seems likely that the dibromo-complex reacts by the same sort of mechanism, the $\text{Br-Pt}^{\text{IV}}\text{-Br}$ group being reduced about 500 times more rapidly than $\text{Cl-Pt}^{\text{IV}}\text{-Cl}$. The data for the reduction of *trans*- $\text{Pt}(\text{CN})_4\text{I}_2^{2-}$ (Table VI) show that the observed rates are not simply due to slow reduction of the complex by iodide, followed by very rapid removal of the iodine formed by hydroxide. On the contrary, the hydroxide appears to play an important part in the rate determining step, and direct reduction by hydroxide seems a likely possibility.

As expected for complexes of platinum(IV), the equilibrium constants for replacement of chloride or bromide by iodide are quite large, although their exact values could not be obtained. Allowing for statistical effects, the replacement of a coordinated bromide ion by iodide is governed by an average equilibrium constant of ≤ 2000 . This can be compared with a value of about 500 found from studies

of the $\text{PtBr}_6^{2-}-\text{I}^-$ equilibria.¹³ It appears, therefore, that the four cyanide ligands have a relatively small effect on the class (b) character¹⁴ or softness¹⁵ of the Pt^{IV} ion. This suggests that the softness of $\text{Co}(\text{CN})_5^{2-}$ ¹⁶ compared with the hardness of $\text{Co}(\text{NH}_3)_5^{3+}$ may be due to a high thermodynamic *trans*-effect of cyanide, such high thermodynamic *trans* effects being known for other Co^{III} complexes.¹⁷

Another way of estimating the ease of replacement of chloride by iodide in these complexes is by comparison of the reduction potentials for reactions (7) and (8). A combination



of the equilibrium constant for reaction (3) with the reduction potential (0.536 volts¹⁸) of $\text{I}_3^- + 2\text{e} \rightarrow 3\text{I}^-$, leads to a value of +0.48 volts for the reduction potential for reaction (7). Subtracting this from the reduction potential of +0.89 volts¹⁹ for reaction (8), a value of 5×10^6 for the average equilibrium constant for replacement of a coordinated chloride by an iodide is obtained. This is very much larger than would be expected in view of the concentration of iodide needed to produce significant amounts of $\text{Pt}(\text{CN})_4\text{I}_2^{2-}$ from $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$, and also in view of the value of ≤ 2000 obtained for replacement of bromide.

Class (b) character is greater the smaller the decrease in bond strengths from the chloro- to the iodo-complexes.²⁰ The force constants quoted in Table I decrease by 30% from the Pt-Cl to the Pt-I bonds. This is much larger than the proportional decrease of the bond strengths. The absolute decrease is usually *ca.* 10 kcal./mole for quite highly class (b) complexes,²⁰ and the absolute strengths of the Pt-Cl and Pt-I bonds must certainly be greater than 30 and 20 kcal./mole, respectively. This suggests that the force constants are not very closely related to the bond strengths, the relative ease of stretching a Pt-I bond over small distances being much greater than that of stretching it to breaking point.

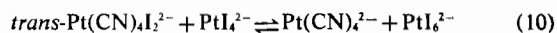
The equilibrium constants for reduction of $\text{Pt}(\text{CN})_4\text{I}_2^{2-}$ by chloride, bromide, and iodide should be related by the equilibrium constants for formation of I_2Cl^- ,¹¹ I_2Br^- ¹² and I_3^- .⁹ Thus $K_r(\text{Cl})$ for equation (9) should be equal to $K_r(\text{I})$, for equation (3), times



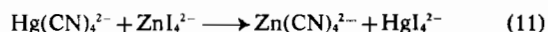
$K_{(\text{I}_2\text{Cl})}/K_{(\text{I}_3)}$. The latter factor is 2.4×10^{-3} so that $K_r(\text{Cl})$ should be 5.8×10^{-5} as compared with the experimental value of 6.1×10^{-5} . The agreement is less good for $K_r(\text{Br})$ which is calculated to be 3.8×10^{-4} as compared with the experimental value of

2.8×10^{-4} . However, not such a clear isosbestic point was observed in the study of the reduction equilibrium with bromide and the possibility arises that some *trans*- $\text{Pt}(\text{CN})_4\text{IBr}^{2-}$ might have been formed. The existence of other equilibria involving I_2Br^- might also complicate the situation.¹²

The equilibrium constant of 2.4×10^{-2} for the reduction of the iodo-complex by iodide (equation (3)) can be combined with the value of 5×10^{-6} for reduction of PtI_6^{2-} ²¹ to give an equilibrium constant of 5×10^3 for reaction (10).



It appears that the stabilities of cyanocomplexes are less dependent than those of iodo-complexes on the softness of the metal ions. Thus the equilibrium constant for reaction (11)



is about 10^8 .²² The large equilibrium constant for reaction (10) can therefore be taken to mean that $\text{I}-\text{Pt}-\text{I}^{2+}$ is softer than Pt^{2+} . This is entirely consistent with the high covalency of the $\text{Pt}^{\text{IV}}-\text{I}$ bond which results in a lower effective ionic charge in $\text{I}-\text{Pt}-\text{I}^{2+}$ than in Pt^{2+} . Nuclear quadrupole resonance data²³ have been interpreted as showing that the effective ionic charge on the Pt ion is 0.28 in both PtBr_6^{2-} and PtBr_4^{2-} , while it is -0.20 in PtI_6^{2-} . The possibility of high oxidation states having relatively high degrees of softness has also been suggested by Jørgensen on the basis of spectroscopic evidence.¹⁶

The existence of a spectroscopic interaction between *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ and Cl^- , and between *trans*- $\text{Pt}(\text{CN})_4\text{Br}_2^{2-}$ and Br^- , is surprising in view of the negative charges on both ions in each pair. The absence of any effect when relatively large concentrations of $\text{Pt}(\text{CN})_4^{2-}$ were added shows that reduction to $\text{Pt}(\text{CN})_4^{2-}$ and X_3^- cannot be occurring. Supposing, however, that the interaction is governed by an equilibrium constant, K , of the same form as an ion-pair association constant, then the apparent extinction coefficient, ϵ , is given by equation (v), where ϵ_a and ϵ_b are

$$\epsilon = \{\epsilon_a + \epsilon_b K [\text{X}^-]\} / \{1 + K [\text{X}^-]\} \quad (v)$$

the extinction coefficients of *trans*- $\text{Pt}(\text{CN})_4\text{X}_2^{2-}$ and the *trans*- $\text{Pt}(\text{CN})_4\text{X}_2^{2-}-\text{X}^-$ interaction product, respectively. Since ϵ increases linearly with $[\text{X}^-]$ up to $[\text{X}^-] \approx 1 \text{ M}$, K must be less than *ca.* 0.1 l.mole⁻¹, and the gradients quoted in Table IX are values for $\epsilon_b K$. The extinction coefficients are therefore of the correct order for charge transfer absorption. Prue has shown,²⁴ on the basis of simple collision theory, that the time that uncharged species can spend close enough to each other for charge transfer to occur is sufficient to give an apparent association constant of about 0.2 l.mole⁻¹.

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For similarly charged ions the apparent association constant will, of course, be less than this, but it is evident that the spectroscopic changes of these platinum complexes are consistent with charge transfer occurring during collision. Similar spectroscopic interactions have been observed between *trans*-Pt-en₂X₂²⁺ and X⁻ (X=Cl and Br)²⁵ and between *trans*-Rh en₂I₂⁺ and I⁻.²⁶

Insofar as data are available, the effects on the rates of reduction of the four ligands *cis* to the X-Pt-X group are closely related to the effects on the equilibrium constants for reduction. Thus *trans*-Pt(CN)₄I₂²⁻ is thermodynamically about 10⁴ times more readily reduced than PtI₆²⁻, whereas *trans*-Pt(CN)₄Cl₂²⁻ and *trans*-Pt(CN)₄Br₂²⁻ are both reduced about 10⁴ times more rapidly by iodide than are PtCl₆²⁻ and PtBr₆²⁻, respectively, under roughly similar conditions.⁶ The kinetic *cis* effect of the cyanide

ligands shows up mainly in the activation enthalpy term. It may be tentatively concluded that the amount of Pt-X bond-breaking, and of X-I bond-making, in the transition state is quite large. This conclusion should be compared with that of Peloso *et al.*²⁷ who studied the rates of reduction of some *trans*-PtL₂X₄ complexes and who concluded that bond making between the reducing agent and the halide was small. (L=P or As donor ligand; X=Cl or Br). Their conclusion was based on the fact that the relative effects of different reducing agents on the kinetics are independent of the substrate.

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