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Mechanisms for Oxidative Addition of Molecular Chlorine to Tetracyanoplatinate(II). Formation of *trans*-Dichlorotetracyanoplatinate(IV) via a Platinum(III) Intermediate¹

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Oxidation of $\text{Pt}(\text{CN})_4^{2-}$ in acidic aqueous solutions of chlorine in the presence of a large excess of $\text{Pt}(\text{CN})_4^{2-}$ has been studied by use of stopped-flow spectrophotometry at 25.0 °C for a 1.00 M perchlorate medium. For $0 \leq \text{pH} \leq 1.30$ and $0.010 \text{ M} \leq [\text{Cl}^-] \leq 0.20 \text{ M}$, one single reaction step was observed, in which the product *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ is formed with a first-order rate constant $k_{\text{exptl}} = \{(1.9 \pm 0.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1} / (1.0 \pm 0.1 \text{ M} + [\text{H}^+])\} [\text{Cl}^-] [\text{Pt}(\text{CN})_4^{2-}]$. For $\text{pH} 0$ and $[\text{Cl}^-] \leq 3.5 \times 10^{-4} \text{ M}$ the primary reaction product is *trans*- $\text{Pt}(\text{CN})_4\text{ClOH}_2^-$, which is formed with a first-order rate constant $k_{\text{exptl}} = ((6.4 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}) [\text{Pt}(\text{CN})_4^{2-}]$, whereas the final product *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ is formed in a subsequent step. The reaction path is different from that observed when the oxidation is studied in the presence of an excess of chlorine. The observed kinetics can be interpreted in terms of a mechanism with a rapid and quantitative formation of an intermediate $\text{Pt}(\text{CN})_4^{+}\text{Cl}^-$ as the primary reaction step. In subsequent reactions, this intermediate might react with another $\text{Pt}(\text{CN})_4^{2-}$, forming either *trans*- $\text{Pt}(\text{CN})_4\text{OH}_2^-$ (corresponding to an oxidation of one of the two Pt(II)'s by Cl^+) or, in a parallel process, a chloride-bridged platinum(III) steady-state intermediate in low concentrations, which reacts further with chloride to give *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$.

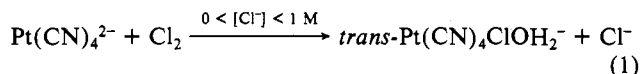
Introduction

Oxidative addition of halogen to square-planar complexes of palladium(II) and platinum(II) involves a two-electron transfer. Only a few kinetic studies on oxidation of platinum(II)⁴⁻⁶ and palladium(II)⁷ complexes have appeared. As a rule, the oxidative-addition step is too fast to be observed with ordinary or flow methods. It is often followed by consecutive substitution reactions at the formed octahedral complexes. These are also fast when the oxidant is bromine.^{6,8-11} The substitution reactions are catalyzed both by residual metal(II) complexes and by free halide.¹²

Oxidation by aqueous solutions of halogens involves parallel oxidation by X_2 , HOX , and OX^- , depending on pH and concentration of free halide X^- .⁴ In some cases, oxidation with HOCl has been interpreted as oxidation with Cl_2 .^{5,6} Equilibrium displacement between X_2 and HOX in aqueous solution might even be rate-controlling for the redox reaction, which then appears to be zero order in the complex.⁴

The few mechanisms for the initial oxidative-addition step that have been proposed so far are inconsistent and incomplete.⁵⁻⁷ Oxidation with I_2 has been suggested to take place via an attack along the z axis of the square-planar complex followed by coordination of the I_2 molecule.⁶ Recently, a solid-state structure that contains an iodine molecule coordinated to platinum(II) in this manner has been described.¹³

In acidic aqueous solution, oxidation of $\text{Pt}(\text{CN})_4^{2-}$ by an excess of molecular Cl_2 gives *trans*- $\text{Pt}(\text{CN})_4\text{ClOH}_2^-$ as the primary reaction product, eq 1.^{4,5} Noteworthy is the fact that the aqua

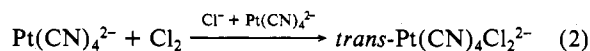


complex is formed even when the concentration of free chloride in the solutions is as high as 1.0 M.¹²

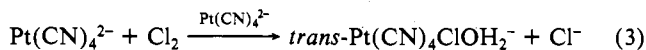
The kinetics for oxidation of $\text{Pt}(\text{CN})_4^{2-}$ by Cl_2 at pH ca. 7 was recently studied.⁴ For an excess of aqueous chlorine (as $\text{Cl}_2 +$

HOCl) the concentration of molecular chlorine in the solutions could be kept very low and constant. For low concentrations of $\text{Pt}(\text{CN})_4^{2-}$ also, the rate of the very rapid redox reaction between Cl_2 and $\text{Pt}(\text{CN})_4^{2-}$ was decreased so much that it could be observed by use of ordinary stopped-flow spectrophotometry (the rate constant is $1.08 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$).⁴

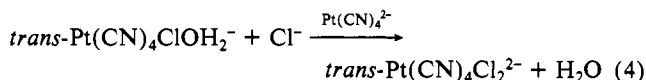
The aim of the present work was to further elucidate this oxidative-addition mechanism by use of experiments with $\text{Pt}(\text{CN})_4^{2-}$ in excess compared to the total concentration of chlorine. The reaction product in this case is *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ also in solutions with very low chloride concentrations. It is formed without an observable intermediate for $0.01 \text{ M} \leq [\text{Cl}^-] \leq 0.20 \text{ M}$ and $0 \leq \text{pH} \leq 1.3$ according to eq 2. For low concentrations



of free chloride ($< 0.35 \text{ mM}$) and $\text{pH} 0$, *trans*- $\text{Pt}(\text{CN})_4\text{ClOH}_2^-$ is formed according to eq 3 via a reaction path different from that



of reaction 1. The *trans*- $\text{Pt}(\text{CN})_4\text{ClOH}_2^-$ formed according to eq 3 reacts further to give *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ according to reaction 4. The kinetics of reaction 4 has been studied previously for $[\text{Cl}^-]$



$\geq 0.2 \text{ M}$, and a rate law has been determined.^{12,14} For such low concentrations of chloride as used in the present experiments ($\leq 0.35 \text{ mM}$), however, reaction 4 is much faster than predicted by the previous rate law,¹² indicating a change of mechanism.

A mechanism that involves a platinum(III) intermediate is proposed for the rapid formation of *trans*- $\text{Pt}(\text{CN})_4\text{Cl}_2^{2-}$ via reaction 2 and via reaction 4 for low chloride concentrations.

Experimental Section

Chemicals and Solutions. $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ (Johnson and Matthey), NaCl (Merck p.a.), HCl (Merck p.a.), and HClO_4 (Baker p.a.) were used directly. NaClO_4 (Baker p.a.) was recrystallized once. Water was doubly distilled from a quartz apparatus. Ca. 70 to 80 mM aqueous solutions of chlorine were prepared from HCl and KMnO_4 (Merck p.a.) and standardized as described previously.⁴ The very dilute solutions of chlorine used for the kinetics were mixed from freshly prepared stock solutions and 1.00 M stock solutions of HCl , HClO_4 , NaCl , and NaClO_4 to give an ionic strength of 1.00 M and the desired concentrations of acid and chloride. They were carefully protected from light and evaporation.

Preliminary Experiments. A 2.0 mM solution of $\text{Pt}(\text{CN})_4^{2-}$ in 1.00 M HClO_4 without extra chloride added was oxidized to *trans*- $\text{Pt}(\text{CN})_4\text{ClOH}_2^-$ by ca. 10 mM chlorine. After the fast reaction residual

- (1) This work continues ref 4 and 12 and is part of a Ph.D. thesis by L.D., Lund University.
- (2) Lund University.
- (3) Chalmers University of Technology.
- (4) Drougge, L.; Elding, L. I. *Inorg. Chem.* **1985**, *24*, 2292.
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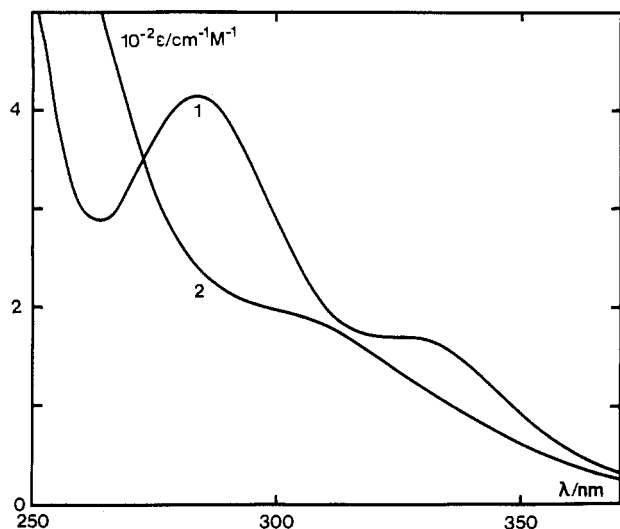


Figure 1. Absorption spectra of *trans*-Pt(CN)₄Cl₂²⁻ (1) and *trans*-Pt(CN)₄ClOH₂⁻ (2).

Table I. Observed Rate Constants for Reaction 2^a

10 ⁴ [Pt(CN) ₄ ²⁻] ₀ /M ^b	10 ⁵ C _{Cl₂} /M	10 ² [Cl ⁻]/M	k _{exptl} /s ⁻¹		
			[H ⁺] = 0.05 M	[H ⁺] = 0.20 M	[H ⁺] = 1.00 M
2.00	1.0	1.00			0.180
2.00	1.0	2.00			0.31
2.00	1.0	4.00		1.29	0.73
2.00	1.0	6.00			1.09
2.00	1.0	8.0		2.36	1.41
2.00	1.0	10.0		3.0	1.79
2.00	1.0	14.0		4.5	2.63
2.00	1.0	20.0		6.0	
0.50	0.5	2.00			0.082
1.00	0.5	2.00		0.294	0.175
2.00	0.5	2.00		0.60	0.34
3.00	0.5	2.00			0.52
4.00	0.5	2.00		1.20	0.75
1.00	1.0	5.00	0.91		
2.00	1.0	5.00	1.55		
4.00	2.0	5.00	3.4		
6.00	2.0	5.00	5.1		

^a 25.0 °C; 1.00 M (H⁺, Na⁺) perchlorate medium; 230 nm. ^b cf. footnote 15.

chlorine was evaporated by flushing with nitrogen. The subsequent chloride anation of *trans*-Pt(CN)₄ClOH₂⁻ to *trans*-Pt(CN)₄Cl₂²⁻ is expected to be extremely slow for the low concentration of free chloride formed in the oxidation (ca. 2 mM) and in the absence of residual platinum(II), according to the published rate law.¹² However, quantitative conversion to *trans*-Pt(CN)₄Cl₂²⁻ was observed within 1 h, as indicated by the spectrum (cf. Figure 1).

Similarly, when 4.0 mM Pt(CN)₄²⁻ was oxidized by 2.0 mM chlorine in 1.00 M HClO₄, the spectral changes for λ > 300 nm, where Pt(CN)₄²⁻ is transparent, showed that all *trans*-Pt(CN)₄ClOH₂⁻ formed had reacted to the *trans*-dichloro complex already a few minutes after mixing, whereas the previous rate law for the Pt(CN)₄²⁻-catalyzed reaction indicates a half-life of about 2 h for [Pt(CN)₄²⁻] ≈ [Cl⁻] ≈ 2 mM.¹²

Kinetics. Spectra of the relevant complexes have been published elsewhere.⁴ Reactions 2 and 3 were followed by use of a modified Durrum-Gibson stopped-flow spectrophotometer at 25.0 ± 0.1 °C and with Pt(CN)₄²⁻ in great excess compared to chlorine (5 × 10⁻⁶–2 × 10⁻⁵ M). The reactions give rise to an absorbance increase at 230 nm, where ε_{Pt(CN)₄²⁻} has a minimum,⁴ *trans*-Pt(CN)₄ClOH₂⁻ and *trans*-Pt(CN)₄Cl₂²⁻ have molar absorptivities of ca. 5.5 × 10³ cm⁻¹ M⁻¹, and chlorine is transparent for the concentrations used. The kinetics were started by mixing equal volumes of solutions containing platinum complex and chlorine and having the same pH and chloride concentration. Tables I and II review the experiments. The solutions used to study reaction 2 contained between 90 and 100% of the chlorine as Cl₂, and those used for reaction 3, between 20 and 50%.⁴ However, the hydrolysis equilibrium of eq 5 was rapidly established in all experiments for the [H⁺] and

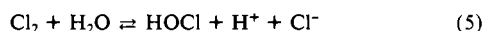


Table II. Observed Rate Constants for Reaction 3^a

10 ⁴ [Pt(CN) ₄ ²⁻] ₀ /M ^b	10 ⁵ C _{Cl₂} /M	10 ⁴ [Cl ⁻]/M	k _{exptl} /s ⁻¹
1.00	0.9	1.00	0.55
2.00	1.0	1.50	1.09
2.20	1.1	1.50	1.18
3.33	1.1	1.50	2.15
4.3	1.1	2.00	2.79
5.0	1.0	3.50	3.4
6.7	1.1	2.50	4.1
10.0	1.1	3.50	6.3

^a 25.0 °C; 1.00 M perchloric acid medium; 230 nm. For pH > 0, the equilibrium displacement HOCl ⇌ Cl₂ according to eq 5 is not sufficiently fast. ^b cf. footnote 15.

[Cl⁻] used⁴ (cf. footnote a, Table II), and oxidation of Pt(CN)₄²⁻ by HOCl was slow enough to be neglected in all cases (k_{HOCl} = 97.9 M⁻¹ s⁻¹).⁴ Thus, Cl₂ was the oxidant in all cases.

Results

Rate constants were calculated directly from the transmittance vs time plots by use of a least-squares program.¹⁵ The experimental results given in Table I yield a rate law for reaction 2 according to eq 6, where k' is (1.75 ± 0.07) × 10⁵, (1.55 ± 0.06)

$$k_{\text{exptl}} = k'[\text{Cl}^-][\text{Pt}(\text{CN})_4^{2-}] \quad (6)$$

× 10⁵, and (0.93 ± 0.03) × 10⁵ M⁻² s⁻¹ for hydrogen ion concentrations of 0.050, 0.200, and 1.00 M, respectively, indicating a pH dependence according to eq 7, where p = (1.9 ± 0.2) × 10⁵ M⁻¹ s⁻¹ and q = 1.0 ± 0.1 M.

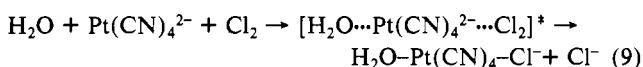
$$k' = p/(q + [\text{H}^+]) \quad (7)$$

Similarly, the rate constant for reaction 3 is given by eq 8, where k'' = (6.4 ± 0.3) × 10³ M⁻¹ s⁻¹ for pH 0.

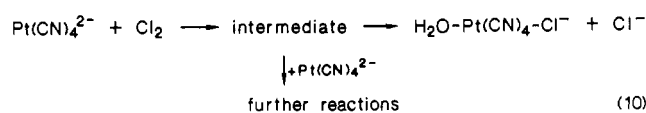
$$k_{\text{exptl}} = k''[\text{Pt}(\text{CN})_4^{2-}] \quad (8)$$

Discussion

Formation of platinum(IV)-chloro complexes as products in all cases studied indicates that the redox reaction between Pt(CN)₄²⁻ and Cl₂ takes place as an inner-sphere process. The present and earlier⁴ experiments show that both the rate and the nature of the reaction product depend on which of the two reactants is present in excess. A direct two-electron transfer according to eq 9 is not possible, since rate and product should



be independent of the nature of the excess reactant for such a mechanism. There must be an intermediate that is sufficiently long-lived to react with the excess reagent present, in this case Pt(CN)₄²⁻, according to eq 10. Equations 6 and 8 show that both



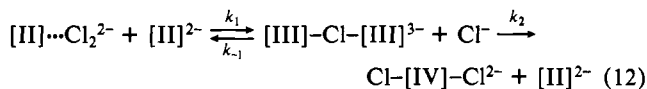
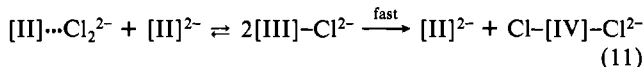
reactions 2 and 3 are first order with respect to Pt(CN)₄²⁻. This means that the intermediate of eq 10 is formed rapidly and quantitatively and that the first-order Pt(CN)₄²⁻ dependence is due to a subsequent and slower reaction step.¹⁶

Formation of *trans*-Pt(CN)₄Cl₂²⁻ according to reaction 2 occurs much faster than via the reaction pathways described previously.^{4,12}

(15) The rate constants were calculated by the use of [Pt(CN)₄²⁻] = [Pt(CN)₄²⁻]₀ - C_{Cl₂}, where C_{Cl₂} denotes the total concentration of chlorine and 0 denotes zero time.

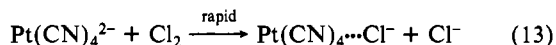
(16) The other alternative, i.e. formation of the intermediate in a rapid preequilibrium between Pt(CN)₄²⁻ and Cl₂ with equilibrium constant K, leads to inconsistencies. With [intermediate] = K[Pt(CN)₄²⁻][Cl₂] and K[Pt(CN)₄²⁻] ≪ 1, *trans*-Pt(CN)₄Cl₂²⁻ should be the product of reaction 1 also, since [Pt(CN)₄²⁻] ≫ [intermediate] during the main course of the reaction.

This might be due to reaction via a Pt(III) complex formed from the intermediate of eq 10 and Pt(CN)₄²⁻. Jones and Morgan⁵ have postulated that a primary intermediate of the type PtCl₄·⁻Cl₂²⁻ is formed rapidly and quantitatively when PtCl₄²⁻ is oxidized by Cl₂. In the present case, there are two possibilities for the subsequent reactions of such an intermediate, eq 11 and 12.¹⁷ The



platinum(III) complex formed in eq 11 is of the type previously assumed for photochemical and some other catalyzed reactions.¹⁸⁻²¹ The final product is expected to be the *trans*-dichloro complex, which then is formed via a rate law independent of [Cl⁻], contradictory to eq 6. Nor is the mechanism of eq 12 probable. With the bridged Pt(III) intermediate present in a low steady-state concentration, the first-order rate constant is $k_1 k_2 [\text{Pt}(\text{CN})_4^{2-}] / (k_{-1} + k_2)$. If the reverse reaction is not significant, the rate constant is simply $k_1 [\text{Pt}(\text{CN})_4^{2-}]$. Those rate expressions are not compatible with the experimental rate law (6).

On the other hand, a [Cl⁻]-dependent rate law for reaction 2 is obtained if a chloride is released already during the very rapid and quantitative formation of the intermediate of eq 10 according to eq 13.

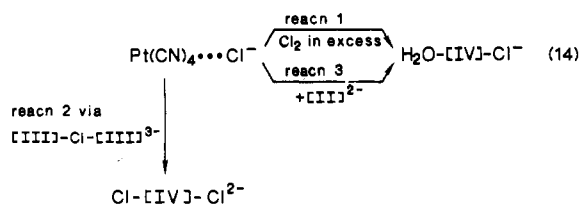


Formally, eq 13 describes an axial addition of Cl⁺ to Pt(CN)₄²⁻. Examples of such addition of various molecules and ions to platinum(II) have been reported.²²⁻²⁵

It is not likely that the complex formed in eq 13 is a Pt(III) species, e.g. of the type [III]·⁻Cl(O)⁻, since such is expected to react rapidly with chloride, forming *trans*-Pt(CN)₄Cl₂²⁻. This product then should be obtained also when Cl₂ is present in excess, which is not the case for reaction 1. Complete electron transfer to Pt(IV) in one single step according to eq 13 can also be excluded by the experimental observations. The intermediate of eq 13 is probably best described as a precursor complex formed from Pt(CN)₄²⁻ and Cl⁺ in which a certain extent of charge displacement has taken place.

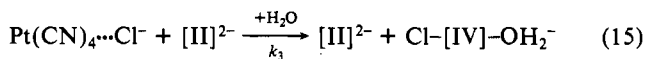
The primary reaction step, eq 13, is independent of which reactant is present in excess. The previously reported constant $k_{\text{Cl}_2} = 1.08 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for oxidation of Pt(CN)₄²⁻ by Cl₂⁴ can therefore be attributed to reaction 13.²⁶

The further reactions, which depend on which reactant is present in excess, are summarized in eq 14.



Transfer of X⁺ in oxidative-addition/reductive-elimination reactions of platinum complexes have previously been proposed.²⁷ Similarly, Cl⁺ might be regarded as the oxidant of Pt(CN)₄²⁻. In this case, it is necessary to postulate that the adduct between Pt(CN)₄²⁻ and Cl⁺ is relatively long-lived.

Reactions 1 and 3 probably occur without a Pt(III) intermediate. Reaction 3 is Pt(CN)₄²⁻-dependent. An attack by a second Pt(CN)₄²⁻ at the chloride side of Pt(CN)₄·⁻Cl⁻ might result either in a two-electron transfer from the incoming platinum(II) to Pt(CN)₄·⁻Cl⁻ or in a platinum(II)-catalyzed electron transfer within Pt(CN)₄·⁻Cl⁻. In both cases, *trans*-Pt(CN)₄ClOH₂⁻ will be the product according to eq 15. A third possibility is that the



chloride-bridged Pt(III) intermediate of reaction 2 is formed. The rate law (16) for reaction 3 then agrees with the experimental eq 8. In eq 16, [Pt(CN)₄·⁻Cl⁻]₀ = C_{Cl₂} at zero time and $k_3 =$

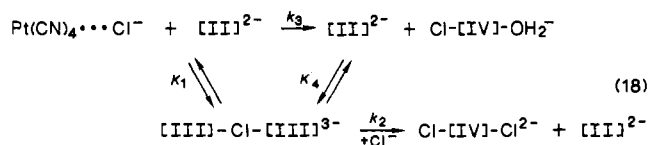
$$\text{rate}(3) = k_3 [\text{Pt}(\text{CN})_4^{2-}] [\text{Pt}(\text{CN})_4\cdots\text{Cl}^-] \quad (16)$$

$(6.4 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at pH 0.

Reactions 2 and 3 are parallel with similar rates; cf. Tables I and II. Reaction 3 can be studied separately, however, if the concentration of free chloride is kept low, which makes reaction 2 slow enough to be neglected. Reaction 2 was studied in the interval $0.01 \text{ M} \leq [\text{Cl}^-] \leq 0.20 \text{ M}$, where the rates of the two reactions are similar; e.g., the observed rate constants are equal for [Cl⁻] = 0.06 M, pH 0. Since the experimental rate constant has the form of eq 6 and not of a two-term expression like eq 17,

$$k = (k'' + k[\text{Cl}^-]) [\text{Pt}(\text{CN})_4^{2-}] \quad (17)$$

the *trans*-Pt(CN)₄ClOH₂⁻ formed must react further to give the final product *trans*-Pt(CN)₄Cl₂²⁻, for instance via path K_4 - k_2 of eq 18. If the equilibria are rapidly established and $K_1 [\text{Pt}(\text{CN})_4^{2-}]$



$\ll 1$ and $K_4 [\text{Pt}(\text{CN})_4^{2-}] \ll 1$, we obtain eq 19 and 20, where A

$$-dA/dt = (k_3 + K_1 k_2 [\text{Cl}^-]) A [\text{Pt}(\text{CN})_4^{2-}] \quad (19)$$

$$-dB/dt = -(k_3 A - K_4 k_2 [\text{Cl}^-] B) [\text{Pt}(\text{CN})_4^{2-}] \quad (20)$$

denotes the concentration of Pt(CN)₄·⁻Cl⁻ and B that of H₂O-⁻[IV]-Cl⁻. Addition of eq 19 and 20 gives eq 21. Since the

$$-d(A + B)/dt = (K_1 A + K_4 B) k_2 [\text{Cl}^-] [\text{Pt}(\text{CN})_4^{2-}] \quad (21)$$

ratio A/B varies during reaction, eq 21 can be integrated to a first-order rate expression, only when the condition (22) is fulfilled.

$$K_1 \approx K_4 = K \quad (22)$$

$$\text{rate}(2) = K k_2 [\text{Cl}^-] [\text{Pt}(\text{CN})_4^{2-}] [\text{complex}] \quad (23)$$

This gives the rate law (23), where complex denotes the disap-

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(24) Elding, L. I.; Gröning, Ö., to be submitted for publication. For instance, a complex of the type PtCl₄²⁻·⁻Hg²⁺ has a formation constant as high as $1.8 \times 10^4 \text{ M}^{-1}$ and a sufficiently long lifetime for a UV-vis absorption spectrum to be recorded.

(25) Venediktov, A. B.; Belyaev, A. V. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1974**, 158.

(26) This reaction was monitored by the use of the disappearance of the intense Pt(CN)₄²⁻ absorption peak at 253 nm, where the further reaction steps cannot be observed. This might be done at 230 nm. When Cl₂ is in excess, however, the disappearance of highly absorbing Cl₂⁻ disturbs the observed kinetics at this wavelength. The Pt(CN)₄²⁻ peak at 253 nm was also observed to disappear when a bridged precursor of the proposed composition H₂O·⁻Pt(CN)₄-Cl-AuCl₂·⁻OH₂²⁻ is formed. Cf.: Drouge, L.; Elding, L. I. *Inorg. Chem.* **1987**, *26*, 1073.

(27) Wilmarth, W. K.; Dooley, R.; Byrd, J. E. *Coord. Chem. Rev.* **1983**, *51*, 125. Wilmarth, W. K.; Fanchiang, Y.-T.; Byrd, J. E. *Coord. Chem. Rev.* **1983**, *51*, 141. Brown, C.; Heaton, B. T.; Sabounchei, J. *J. Organomet. Chem.* **1977**, *142*, 413. The recently studied redox reaction PtCl₄²⁻ + *trans*-Pt(CN)₄ClOH₂⁻ → PtCl₅OH₂⁻ + Pt(CN)₄²⁻ can also be regarded as a transfer of Cl⁺ from the platinum(IV) to the platinum(II) complex.¹²

pearing species, i.e. $\text{Pt}(\text{CN})_4\cdots\text{Cl}^-$ and $\text{H}_2\text{O}-[\text{IV}]-\text{Cl}^-$. The concentration of $\text{trans-Pt}(\text{CN})_4\text{ClOH}_2^-$, which is zero at the start of the kinetics, reaches a maximum concentration at a time t_1 , which depends on the concentration of free chloride. Integration of eq 19 and 21, elimination of A_0 (concentration at zero time), and insertion of the condition $\text{d}B/\text{d}t = 0$ give a value of t_1 . For $[\text{Cl}^-] = 0.06 \text{ M}$ the condition $k_3 = Kk_2[\text{Cl}^-]$ is also valid, which gives eq 24. Thus, t_1' can be identified as the half-life for reaction 2 and $A_{t_1'} = B_{t_1'} = A_0/4$.

$$t_1' = (\ln 2)/(Kk_2[\text{Cl}^-][\text{Pt}(\text{CN})_4^{2-}]); [\text{Cl}^-] = 0.06 \text{ M} \quad (24)$$

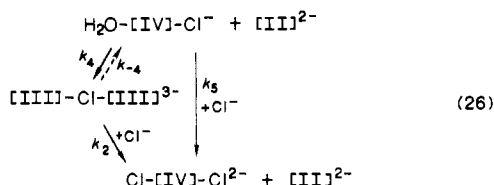
Equation 23 agrees with the observed rate law (6). Identification of the coefficients gives $Kk_2 = (9.3 \pm 0.3) \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ at pH 0.

Both the equilibria for K_1 and K_4 are assumed to be rapidly established during reaction 2. Since formation of the bridged Pt(III) intermediate is expected to be much faster from $\text{Pt}(\text{CN})_4\cdots\text{Cl}^-$ than from $\text{H}_2\text{O}-[\text{IV}]-\text{Cl}^-$, $k_1 \gg k_4$, where $K_1 = k_1/k_{-1}$ and $K_4 = k_4/k_{-4}$. Consequently $k_{-1} \gg k_{-4}$. Approach to the equilibrium for K_1 with the rate constant $(k_1[\text{Pt}(\text{CN})_4^{2-}] + k_{-1})$ might occur rapidly under all experimental conditions, while this is true for the corresponding constant $(k_4[\text{Pt}(\text{CN})_4^{2-}] + k_{-4})$ only for very low concentrations of free chloride. In the model of eq 18, however, the reaction path $k_{-1}-k_3$ gives an additional contribution to the rate constant of the backward reaction $[\text{III}]-\text{Cl}-[\text{III}]^{3-} \rightarrow \text{H}_2\text{O}-[\text{IV}]-\text{Cl}^- + [\text{II}]^{2-}$, which helps to establish the equilibrium for K_4 rapidly.

This additional reaction path is not available when $\text{trans-Pt}(\text{CN})_4\text{ClOH}_2^-$ is the only reactant, as in reaction 4. An intermediate of the type $\text{H}_2\text{O}-[\text{IV}]-\text{Cl}-[\text{II}]^{3-}$ has been proposed for this reaction,¹² which has a rate law according to eq 25, where

$$\text{rate}(4) = k_5[\text{Cl}^-][\text{Pt}(\text{CN})_4^{2-}][\text{H}_2\text{O}-[\text{IV}]-\text{Cl}^-] \quad (25)$$

$k_5 = 38.4 \pm 0.6 \text{ M}^{-2} \text{ s}^{-1}$ for pH 0 and $0.2 \text{ M} \leq [\text{Cl}^-] \leq 1.0 \text{ M}$. Extrapolation of these measurements for $[\text{Cl}^-] \geq 0.2 \text{ M}$ to zero chloride concentration gives a small intercept of ca. $0.5 \text{ M}^{-1} \text{ s}^{-1}$,¹² which can be identified with k_4 of eq 26. The mechanism (26)



gives the rate law (27) for the path occurring via the bridged

$$\text{d[Prod]}/\text{d}t = k_4k_2[\text{Cl}^-][\text{Pt}(\text{II})][\text{Pt}(\text{IV})]/(k_{-4} + k_2[\text{Cl}^-]) \quad (27)$$

platinum(III) intermediate. For high concentrations of chloride ($\geq 0.2 \text{ M}$), $k_2[\text{Cl}^-] \gg k_{-4}$, and the rate is simply $k_4[\text{Pt}(\text{II})][\text{Pt}(\text{IV})]$; i.e., formation of the platinum(III) complex becomes rate-controlling for this reaction path, giving rise to the intercept when extrapolation to zero chloride concentration is made.

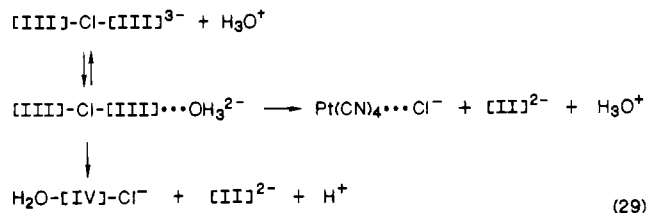
For very low concentrations of chloride, on the other hand, $k_2[\text{Cl}^-] \ll k_{-4}$, and the reaction takes place via the very high rate of eq 28. In this case, the reaction path described by k_5 is

$$\text{rate}(4) = K_4k_2[\text{Cl}^-][\text{Pt}(\text{CN})_4^{2-}][\text{H}_2\text{O}-[\text{IV}]-\text{Cl}^-] \quad (28)$$

negligibly slow. Approach to this mechanism might explain the

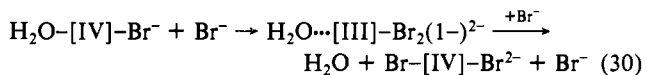
unexpectedly high rates of chloride anation of $\text{trans-Pt}(\text{CN})_4\text{ClOH}_2^-$ observed for low concentrations of chloride.²⁸

The rate of reaction 2 decreases with increasing $[\text{H}^+]$. This might be due to a proton-induced labilization of the bridged platinum(III) intermediate, for instance according to the alternatives of eq 29, being equivalent to a decrease of K with increasing



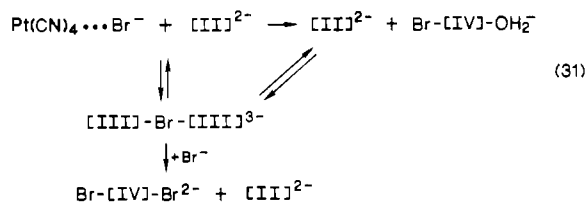
$[\text{H}^+]$; cf. eq 18. It has been shown recently that protonation/deprotonation of terminal aqua ligands of a bridged complex affects the oxidation-state distribution between the two ligand-bridged metal sites.²⁹

The bromide-accelerated anation by bromide of $\text{trans-Pt}(\text{CN})_4\text{BrOH}_2^-$ has a rate constant of ca. $10^5 \text{ M}^{-2} \text{ s}^{-1}$.^{6,8-11} If the reductive ability of bromide is taken into account, this high rate constant might indicate that this reaction also takes place via a platinum(III) intermediate, as in eq 30. Thus, the halide as-



sistance in this case is expected to involve a large extent of charge separation, as suggested previously by Poë and Vaughan.³⁰ This is also discussed elsewhere.¹²

Because of the high efficiency of this bromide-assisted reaction, no slow $\text{Pt}(\text{CN})_4^{2-}$ -accelerated reaction corresponding to reaction 4 should be expected in the bromine system. The fast $\text{Pt}(\text{CN})_4^{2-}$ -accelerated bromide anation of $\text{trans-Pt}(\text{CN})_4\text{BrOH}_2^-$ has been studied for very low concentrations of bromide and has a rate constant of ca. $6 \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$.¹⁰ A mechanism via platinum(III) intermediates of the type described in the present study is likely in this case too, according to eq 31.



To conclude, ligand substitutions in platinum(IV) complexes take place via redox mechanisms. High reaction rates in those systems probably indicate a large extent of charge separation in the intermediate compounds, i.e. participation of platinum(III) intermediates.

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Registry No. Cl_2 , 7782-50-5; $\text{Pt}(\text{CN})_4^{2-}$, 15004-88-3.

(28) A prerequisite for the fast reaction observed in the first of the preliminary experiments is that a small concentration of $\text{Pt}(\text{CN})_4^{2-}$ be reformed when the solution is flushed with nitrogen; cf. rate law 28.

(29) Neyhart, G. G.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 4808.

(30) Poë, A. J.; Vaughan, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 7537.