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The Mechanism for Chloride Anation of *trans*-Tetracyanochloroaquaplatinate(IV)

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The rate law for the chloride anation of $PtCl_5H_2O^-$ in the presence of $PtCl_4^{2-}$

$$PtCl_5H_2O^- + Cl^- \xrightarrow{PtCl_4^{2-}} PtCl_6^{2-} + H_2O \qquad (1)$$

was recently reported:[1]

$$\text{Rate} = \frac{k' + k''[Cl^-]}{1 + k'''[Cl^-]}[PtCl_4^{2-}][PtCl_5H_2O^-] \qquad (2)$$

To describe the kinetics it was necessary to modify the usual Basolo, Pearson scheme[2-5] for platinum(IV) substitutions in the presence of platinum(II). Our experiments indicated that the entering chloride ligand was added after the formation of the bridged intermediate, as shown by Fig. 1. A primary formation of a five-coordinate chloro complex, *i.e.*

$$PtCl_4^{2-} + Cl^- \rightleftarrows PtCl_5^{3-} \qquad (3)$$

followed by the formation of the bridged intermediate could be excluded in this case since the value of the parameter k''' obtained from the experimental rate expression (2) was too large to be identified with the formation constant for $PtCl_5^{3-}$ according to reaction (3). The appearance of aqua complex intermediates in several other platinum(IV) substitutions (*cf.* Ref. 1) also speaks in favour of the suggested mechanism in other cases.

The present communication reports a rate law of the same form as eqn. (2) for the process

$$trans\text{-}[Pt(CN)_4ClH_2O^-] + Cl^- \xrightarrow{Pt(CN)_4^{2-}} trans\text{-}[Pt(CN)_4Cl_2^{2-}] + H_2O \qquad (4)$$

which gives further experimental support to the mechanism in Figure 1. In the absence of tetracyanoplatinate(II) the chloride anation of $Pt(CN)_4ClH_2O^-$ is extremely slow, even at 50 °C.

Experimental

Potassium tetracyanoplatinate(II) (Johnson and Matthey) was used without further purification. Solutions of *trans*-$[Pt(CN)_4ClH_2O^-]$ were prepared by oxidation of 3×10^{-3} *M* or 6×10^{-3} *M* solutions of potassium tetracyanoplatinate(II) with chlorine in 1.00 *M* perchloric acid solution as described previously.[1] The kinetics were started by mixing equal volumes of one solution containing platinum (IV) complex and another containing tetracyanoplatinate(II) and chloride directly in the thermostated spectrophotometer cell, using thermostated syringes. The ionic strength and hydrogen ion concentration were 1.00 *M*, supported by perchloric acid. The reaction was followed at (25.0 ± 0.1) °C using a Zeiss PMQ II Spectrophotometer equipped with a Goertz compensation recorder. The absorption maximum of *trans*-$[Pt(CN)_4Cl_2^{2-}]$ at 288 nm was used. The blank contained tetracyanoplatinate(II) in appropriate concentration.

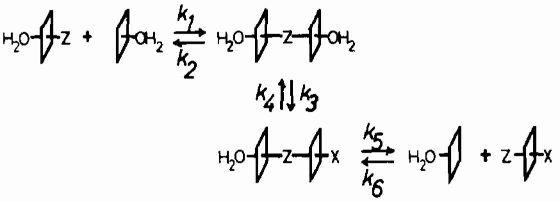

Fig. 1. Proposed mechanism for reactions (1) and (4) (*cf.* Ref. 1). Z = X = Cl. The four ligands in the plane around the platinum atoms have been omitted.

The Table reviews the experiments. Pseudo-first-order kinetics were obtained, since chloride was in large excess and $Pt(CN)_4^{2-}$ was regenerated in the reaction and its concentration therefore constant. One-electron reducing or oxidizing agents had no effect on the observed rate constants (*cf.* Table).

Results and Discussion

Plots of the observed rate constant *vs.* the concentration of tetracyanoplatinate(II) are linear with small intercepts (*cf.* Figure 2). These intercepts probably indicate small amounts of platinum(II) in the platinum(IV) solutions, present because of incomplete oxidation, although a reaction path independent of platinum(II) cannot be excluded.

Figure 3 shows that the observed rate constant corrected for the intercept in Figure 2 is given by the eqn.

$$k_{\text{exp,corr}} = \frac{k''}{1 + k'''[Cl^-]}[Cl^-][PtCN_4^{2-}] \qquad (5)$$

A least-squares analysis gave $k'' = (47 \pm 1)\ s^{-1}\ M^{-2}$, $k''' = (0.76 \pm 0.07)\ M^{-1}$. Thus, the rate constant for reaction (4) is a function of the concentration of the entering ligand and the platinum(II) complex of the same form as that for reaction (1) – *cf.* eqn. (2).

TABLE. Chloride Anation of *trans*-$[Pt(CN)_4ClH_2O^-]$ in the Presence of $Pt(CN)_4^{2-}$. The concentration of platinum(IV) complex was 1.5×10^{-3} M. The errors in k_{exp} were less than 3%.

$[Cl^-]$ $\times 10^3/M$	$[Pt(CN)_4^{2-}]$ $\times 10^3/M$	k_{exp} $\times 10^3/s^{-1}$	Added Substance
25	9.76	12.0	
50	2.50	6.2	
100	2.00	8.3	
100	3.00	12.8	
100	5.00	21.4	
200	2.02	16.6	
300	2.02	23.1	
500	0.52	10.3	
500	1.02	20.7	
500	1.40	28.2	
500	1.40	26.9	$FeCl_3$ [a]
500	1.40	27.5	$(NH_4)_2Fe(SO_4)_2$ [a]
500	1.40	27.4	$CeCl_3$ [a]
500	1.40	26.8	Hydroquinone[a]
500	1.81	32.8	
500	2.02	34.6	
500	2.58	46	
750	0.26	9.4	
750	0.45	13.2	
750	0.77	22.4	
750	0.90	22.6	
750	1.29	35.6	
750	1.81	44.8	

[a] 1.5×10^{-4} M.

In the present case, the reverse reaction is completely negligible, which means that the parameter k' is too small to be determined. The mechanism in Figure 1 gives a consistent expression for the rate constant using the steady-state approximation (reverse reaction neglected):

$$k_{exp} = \frac{\dfrac{k_1k_3k_5}{k_2(k_4+k_5)}}{1+\dfrac{k_3k_5[Cl^-]}{k_2(k_4+k_5)}}\,[Cl^-]\,[Pt(CN)_4^{2-}] \qquad (6)$$

For the same reasons as discussed in Ref. 1, the value of the parameter $k''' = 0.76\ M^{-1}$ is probably much too large to be identified with the equilibrium constant for the process

$$Pt(CN)_4^{2-} + Cl^- \rightleftarrows Pt(CN)_4Cl^{3-} \qquad (7)$$

For instance, the absorption spectra of $Pt(CN)_4^{2-}$ in 1 M perchloric acid and 1 M hydrochloric or hydrobromic acid are practically identical in the region 220 to 300 nm.

Thus, reaction (4) is a further example of a platinum(II)-"catalyzed" platinum(IV) substitution, the kinetics of which can be described by the scheme in Fig. 1. This is probably also applicable to some previous studies on platinum(IV) substitutions in the presence of $Pt(CN)_4^{2-}$.[6-8]

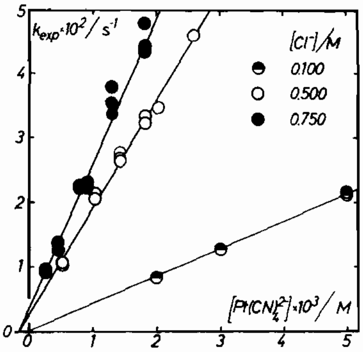

Fig. 2. The observed rate constant for reaction (4) as a function of the concentration of tetracyanoplatinate(II) for different concentrations of chloride.

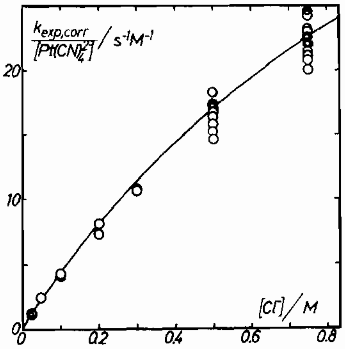

Fig. 3. $k_{exp}/[Pt(CN)_4^{2-}]$ for reaction (4) as a function of chloride concentration.

Pt(III)-catalysis of the type proposed by Rich and Taube[9] cannot account for the experimental results. Inhibitors have no effect on the observed rate constants (*cf.* Table) and mechanisms involving Pt(III) require square-root terms in the rate expressions.

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References

1 L. I. Elding and L. Gustafson, *Inorg. Chim. Acta, 19,* 00 (1976).
2 F. Basolo, P. H. Wilks, R. G. Pearson, and R. G. Wilkins, *J. Inorg. Nucl. Chem., 6,* 161 (1958).
3 F. Basolo, A. F. Messing, P. H. Wilks, R. G. Wilkins, and R. G. Pearson, *J. Inorg. Nucl. Chem., 8,* 203 (1958).
4 F. Basolo, M. L. Morris, and R. G. Pearson, *Disc. Faraday Soc., 29,* 80 (1960).
5 W. R. Mason, *Coord. Chem. Rev., 7,* 241 (1972).
6 W. R. Mason, *Inorg. Chem., 8,* 1756 (1969).
7 W. R. Mason, *Inorg. Chem., 9,* 1528 (1970).
8 K. A. Morgan and M. M. Jones, *J. Inorg. Nucl. Chem., 34,* 275 (1972).
9 R. L. Rich and H. Taube, *J. Am. Chem. Soc., 76,* 2608 (1954).