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LETTER

The hydrolysis products of *cis*-diamminedichloroplatinum(II)
8. Kinetics of the base hydrolysis of $\text{PtCl}_2(\text{AA})$ (AA = en, chxn, tn, Me_2tn) and *trans*- $\text{PtCl}_2(\text{NH}_3)_2$

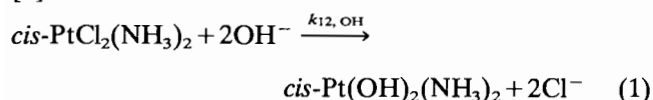
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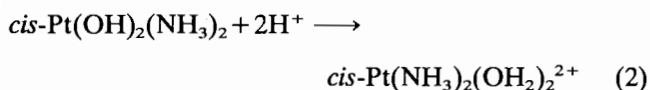
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Introduction

The reaction between *cis*- $\text{PtCl}_2(\text{NH}_3)_2$ and hydroxide ion (eqn. (1)) proceeds to completion in two steps of comparable rate and with retention of stereochemistry [1].



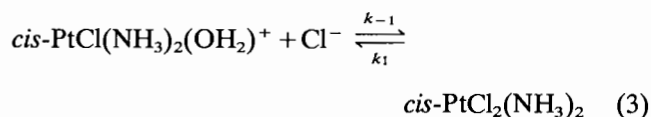
The resultant dihydroxo species is after acidification (eqn. (2)) a useful source of the labile diaqua ion [2].



In the absence of added nucleophile, the background chloride ion from eqn. (1) will slowly react with the diaqua to give a dichloro, chloroaqua, diaqua, equilibrium mixture, with the chloroaqua predominating [2]. By addition of controlled amounts of chloride ion, the rates of chloride anation of the diaqua and chloroaqua can be separately measured [2, 3].

Indeed, for the latter reaction with excess chloride ion, plots of chloride ion versus k_{obs} (the observed first order anation rate constant) are linear. The slope of such plots corresponds to the second order anation rate constant (k_{-1}) and the intercept to the forward

first order acid hydrolysis rate constant (k_1) (eqn. (3)) [3].



To provide comparative data, we now report rate constants for reaction (1) for the series of complexes $\text{PtCl}_2(\text{AA})$ (AA = en, chxn, tn, Me_2tn)** and *trans*- $\text{PtCl}_2(\text{NH}_3)_2$.

Experimental

The Pt(II) complexes used in this study were either commercially available (*cis*- $\text{PtCl}_2(\text{NH}_3)_2$, *trans*- $\text{PtCl}_2(\text{NH}_3)_2$, $\text{PtCl}_2(\text{RR-chxn})$) or prepared from the diamines and *cis*- $\text{PtCl}_2(\text{dmsO})_2$, as described previously [3].

Sodium hydroxide solutions (0.1 M) were prepared from VOLUCON ampoules. More concentrated solutions were prepared from weighed amounts of solid NaOH.

Base hydrolysis kinetics $k_{12, \text{OH}}$ (eqn. (1))

Standard sodium hydroxide solutions (10 ml) were allowed to reach thermal equilibrium in a rectangular 4.00 cm cell, placed in an electrically heated temperature controlled cell block in a Perkin-Elmer λ -2 recording spectrophotometer. Small samples of the solid complex (~0.3 mg) were added, and after dissolution (usually within 1 min but 2–3 min for *trans*- $\text{PtCl}_2(\text{NH}_3)_2$ at low temperatures), the repeat scan data collection mode was started.

The reactions were monitored for 6–8 half-lives and satisfactory first order rate constants (Table 1) were calculated from the absorbance ($\lambda \sim 300$ nm) versus time data using the normal equations.

Similar procedures were used for $\text{PtCl}_2(\text{RR-chxn})$, except that the changes in circular dichroism ($\lambda = 270$ nm) were monitored with time.

Base hydrolysis kinetics, $k_{2, \text{OH}}$ (eqn. (5))

Solutions of $\text{PtCl}(\text{AA})(\text{OH}_2)^+$ (AA = en, chxn, tn, Me_2tn and *trans*- $(\text{NH}_3)_2$) ($\sim 1.4 \times 10^{-3}$ M) in 0.01 M HClO_4 were prepared as described previously [2]. Samples of these stock solutions (2.0 ml) were made basic with 1.0 ml, 0.3 M NaOH solution, both at thermal equilibrium, and repeat scan data were collected for the hydrolysis of $\text{PtCl}(\text{OH})(\text{AA})$ in 0.1 M NaOH. The subsequent spectrophotometric changes for *trans*-

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**IUPAC recommended abbreviations [4] have been used: $\text{Me}_2\text{tn} = \text{NH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NH}_2$.

TABLE 1. Spectrophotometrically determined rate constants ($k_{12, \text{OH}}$) for the base hydrolysis of $\text{PtCl}_2(\text{AA})$ (eqn. (1)) in aqueous 0.1 M NaOH^a

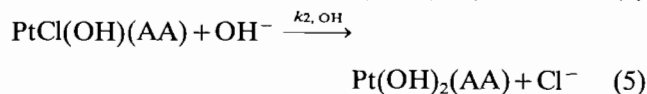
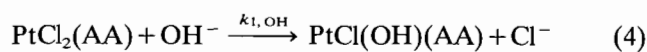
Complex	T (°C)	$10^5 \times k_{12, \text{OH}} \text{ (s}^{-1}\text{)}$	
		Obs. ^b	Calc. ^c
<i>trans</i> - $\text{PtCl}_2(\text{NH}_3)_2$	25.0		2.41
	35.0	9.30	9.52
	45.8	39.4	38.1
	52.2	115	118
$\text{PtCl}_2(\text{en})$	25.0		1.78
	33.8	7.20	7.44
	45.8	26.0	25.6
	50.3	46.6	43.6
	54.8	66.4	73.0
$\text{PtCl}_2(\text{RR-chxn})^{\text{d}}$	25.0		3.81
	40.9	20.7	19.0
	42.7	21.8	22.6
	44.8	26.1	27.5
		30.9 ^e	
	47.3	35.5	34.4
	48.5	37.4 ^f	38.4
	49.6	41.9	42.9
	51.9	49.7	53.2
	53.7	67.0	62.4
55.4	69.8	71.9	
$\text{PtCl}_2(\text{tn})$	25.0		3.63
	35.8	11.0	11.6
	44.8	37.7	35.2
	49.8	64.6	59.8
	54.8	90.8	99.8
$\text{PtCl}_2(\text{Me}_2\text{tn})$	25.0		2.97
	35.5	9.90	9.81
	44.7	25.8	26.2
	55.2	76.0	75.4

^aThese data are reproducible to $\pm 5\%$. ^bIndividual experiments or the mean of two determinations. ^cCalculated from the activation parameters cited in Table 3. ^dDetermined spectropolarimetrically at 270 nm. ^eDetermined spectrophotometrically at 305 nm. ^fContaining 0.1 M NaCl ($I = 0.2 \text{ M}$).

$\text{PtCl}(\text{OH})(\text{NH}_3)_2$, generated using such procedures [3], were too small to obtain accurate rate constants.

Results and discussion

Solutions of $\text{PtCl}_2(\text{AA})$ ($\text{AA} = \text{en}, \text{chxn}, \text{tn}, \text{Me}_2\text{tn}$) in 0.1 M NaOH have an initial absorption maximum near 300 nm and a minimum near 250 nm. As reaction (1) proceeds the absorption intensity at 300 nm decreases and that at 250 nm increases to give a final, more or less featureless increasing absorbance from 350 to 220 nm [2]. Initially, a single isobestic point is observed (corresponding to eqn. (4)), but this shifts slightly as eqn. (5) dominates.



Nevertheless, the data corresponding to the total spectrophotometric change can be satisfactorily analysed assuming a single first order rate process ($k_{12, \text{OH}}$, eqn. (1)) (Table 1) [2].

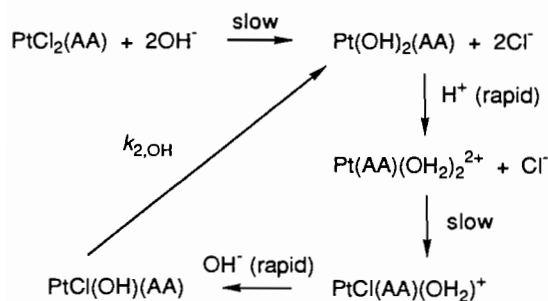
In principle, it is possible to analyse the total data in terms of two sequential rate processes [5], but as there is some uncertainty in this procedure [6], and as $\text{PtCl}(\text{OH})(\text{AA})$ can be generated, we were able to measure the second step (eqn. (5)) directly.

$\text{PtCl}(\text{OH})(\text{AA})$ ($\text{AA} = \text{en}, \text{chxn}, \text{tn}, \text{Me}_2\text{tn}$) was formed in solution, from the dichloro species, via the reaction sequence outlined in Scheme 1. The absorption spectra of each solution so generated (in 0.1 M NaOH) changed with time, as expected, to give the corresponding dihydroxo species with a sharp isobestic point (at 271, 273, 266 or 266 in the above order, respectively) and first order rate constants were calculated from the absorbance versus time data (Table 2).

TABLE 2. Spectrophotometrically determined rate constants ($k_{2, \text{OH}}$) for the base hydrolysis of $\text{PtCl}(\text{OH})(\text{AA})$ (eqn. (5)) in aqueous 0.1 M NaOH^a

Complex	T (°C)	$10^5 \times k_{2, \text{OH}} \text{ (s}^{-1}\text{)}$	
		Obs. ^b	Calc. ^c
$\text{PtCl}(\text{OH})(\text{en})$	25.0		2.81
	34.5	8.56	8.72
	35.3	8.92	9.57
	35.5	9.34	9.79
	40.1	20.0	16.7
	54.2	78.2	82.0
$\text{PtCl}(\text{OH})(\text{chxn})$	25.0		1.85
	35.2	6.62	6.93
	44.8	24.3	22.3
	50.0	41.5	40.7
	54.2	61.5	65.3
$\text{PtCl}(\text{OH})(\text{tn})$	25.0		5.56
	35.2	17.0	17.1
	44.8	47.9	46.1
	49.7	70.8	74.7
	54.7	123	121
	$\text{PtCl}(\text{OH})(\text{Me}_2\text{tn})$	25.0	
35.3		9.19	9.25
40.2		17.1	18.4
44.7		34.6	30.1
50.5		55.6	54.9
54.4		83.3	87.8

^aThese data are reproducible to $\pm 5\%$. ^bIndividual experiments or the mean of two determinations. ^cCalculated from the activation parameters cited in Table 3.



Scheme 1.

The absorption spectrum of *trans*-PtCl₂(NH₃)₂ dissolves in 0.1 M NaOH ($\lambda_{\text{max}}=265$ nm) showed an increase with time at all wavelengths (320–240) and no isosbestic points were developed. The final spectrum had a prominent shoulder at about 290 nm on the side of the increasing absorbance. Satisfactory first order rate constants were obtained assuming a single process was occurring [7]. It was not possible to measure $k_{2,\text{OH}}$ directly for the system as the absorption changes corresponding to eqn. (5) were too small, over the concentration range where satisfactory data were obtained for the other systems.

It was also possible to measure $k_{12,\text{OH}}$ for PtCl₂(RR-chxn) using the time dependent changes in the CD spectrum at 270 nm. Variation of ionic strength or addition of chloride ion had no effect on the reaction rate, a finding similar to that observed for *cis*-PtCl₂(NH₃)₂ [2].

The problem of analysis of sequential rate processes (e.g. eqns. (4) and (5)), where $k_{1,\text{OH}} \sim k_{2,\text{OH}}$ has been nicely discussed by Jackson *et al.* [6]. Values for $k_{2,\text{OH}}$

(Table 2) have been obtained by direct measurement, and we would interpret $k_{12,\text{OH}}$ (Table 1) as being close to the values for $k_{1,\text{OH}}$ although $\epsilon[\textit{cis}\text{-PtCl}(\text{OH})(\text{AA})]$ is not equal to $\epsilon[\textit{cis}\text{-Pt}(\text{OH})_2(\text{AA})]$. Nevertheless, this assumption leads to reasonable values for the time of maximum concentration [6] of *cis*-PtCl(OH)(AA) in all systems except AA = Me₂tn.

For the complexes studied here, it is not possible to measure $k_{1,\text{OH}}$ directly using the wavelength of the isosbestic point for the $k_{2,\text{OH}}$ reaction (5), because the close proximity of the first isosbestic point (eqn. (4)) results in a very small absorbance change. The activation parameters associated with $k_{12,\text{OH}}$ and $k_{2,\text{OH}}$ are presented in Table 3.

The accepted *trans* effect order, Cl⁻ > NH₃ > OH⁻ > OH₂ [8] would predict that *trans*-PtCl₂(NH₃)₂ should lose the first chloro ligand faster than the *cis* isomer in both acid and base media. While we confirm this prediction in basic solution ($k_{12,\text{OH}}^{\text{trans}}/k_{12,\text{OH}}^{\text{cis}}=1.3$ at 25 °C), our previous measurements [3] in acid solution ($k_{\text{H}}^{\text{trans}}/k_{\text{H}}^{\text{cis}}=0.4$ at 25 °C) do not agree with the above order. The *trans* effect difference between Cl⁻ and NH₃ is, however, rather small [9] and reversals of this type can be expected.

We would also emphasise that these rate comparisons may have little validity, as the activation parameters (Table 3) associated with the rate constants for the *cis* and *trans* isomers are not identical. The trend is for reactions of the *trans* isomer to have a higher activation enthalpy and a lower activation entropy than for similar reactions of the *cis* analog. Such a situation results in similar values for the rate constants for both complexes.

TABLE 3. Activation parameters for the hydrolysis of some PtCl(X)(AA) complexes (X = Cl, OH) at 25 °C (*I* = 0.1 M)

Complex	Rate constant ^b	10 ⁵ × k_x (s ⁻¹)	ΔH [#] (kJ mol ⁻¹)	ΔS [#] (J K ⁻¹ mol ⁻¹)	Ref.
<i>cis</i> -PtCl ₂ (NH ₃) ₂	$k_{12,\text{OH}}$	1.90	84 ± 4	-52 ± 8	2
<i>cis</i> -PtCl(OH)(NH ₃) ₂	$k_{2,\text{OH}}$	1.43	84 ± 5	-55 ± 10	2
<i>cis</i> -PtCl ₂ (NH ₃) ₂	k_{H}	5.24	87 ± 3	-34 ± 14	1, 3
<i>trans</i> -PtCl ₂ (NH ₃) ₂	$k_{12,\text{OH}}$	2.41	102 ± 7	+10 ± 14	^a
<i>trans</i> -PtCl ₂ (NH ₃) ₂	k_{H}	1.90	92 ± 8	-26 ± 16	3
PtCl ₂ (en)	$k_{12,\text{OH}}$	1.78	98.8 ± 9	-4 ± 18	^a
PtCl(OH)(en)	$k_{2,\text{OH}}$	2.81	88.4 ± 6	-35 ± 12	^a
PtCl ₂ (en)	k_{H}	3.20	97 ± 2	-5 ± 6	3
PtCl ₂ (chxn)	$k_{12,\text{OH}}$	3.81	76.2 ± 4	-74 ± 8	^a
PtCl(OH)(chxn)	$k_{2,\text{OH}}$	1.85	96.6 ± 5	-11 ± 10	^a
PtCl ₂ (chxn)	k_{H}	7.25	69 ± 2	-97 ± 4	3
PtCl ₂ (tn)	$k_{12,\text{OH}}$	3.63	87.9 ± 6	-35 ± 12	^a
PtCl(OH)(tn)	$k_{2,\text{OH}}$	5.56	81.7 ± 3	-52 ± 6	^a
PtCl ₂ (tn)	k_{H}	5.88	97 ± 3	-1 ± 6	3
PtCl ₂ (Me ₂ tn)	$k_{12,\text{OH}}$	2.97	84.7 ± 1	-47 ± 2	^a
PtCl(OH)(Me ₂ tn)	$k_{2,\text{OH}}$	2.95	91.2 ± 5	-26 ± 10	^a
PtCl ₂ (Me ₂ tn)	k_{H}	8.40	83 ± 3	-46 ± 6	3

^aThis research. ^b k_{H} corresponds to k_1 in eqn. (3).

For both, $k_{12, \text{OH}}$ and $k_{2, \text{OH}}$, the reaction rate is dependent of $[\text{OH}^-]$ and added Cl^- and proceeds to completion. This is consistent with a mechanism where a water molecule binds to the Pt(II) center, deprotonation occurs and the chloro ligand is displaced, as in all but the *trans*-(NH_3)₂ case, $k_{12, \text{OH}}$ is smaller than k_{H} the acid hydrolysis rate constant (Table 3). Indeed, there is a general close similarity between the activation parameters for $k_{12, \text{OH}}$ and $k_{2, \text{OH}}$ for any particular AA group.

An associative mechanism of this type may well be influenced by small changes in the square planar geometry or the nature of the non-replaced ligands, and we have argued previously [2] that $\text{NH}\dots\text{OH}_2$ hydrogen bonds could be important in stabilising the five coordinate transition region. Thus the higher activation energy associated with k_{H} and $k_{12, \text{OH}}$ for *trans*- $\text{PtCl}_2(\text{NH}_3)_2$ relative to *cis*- $\text{PtCl}_2(\text{NH}_3)_2$ or with k_{H} for $\text{PtCl}_2(\text{en})$ relative to $\text{PtCl}_2(\text{chxn})$ may be related to the relative ease of approach of the incoming water molecule.

Activation entropy patterns can be related to solvation effects, and while chloride is a constant leaving group in all the systems studied, the trend is for ΔS^\ddagger associated with $k_{12, \text{OH}}$ or $k_{2, \text{OH}}$ to be more negative than that associated with k_{H} , reflecting the different charge on the Pt(II) product in the two situations. The more positive ΔS^\ddagger associated with both $k_{12, \text{OH}}$ and k_{H} for *trans*- $\text{PtCl}_2(\text{NH}_3)_2$ relative to *cis*- $\text{PtCl}_2(\text{NH}_3)_2$ would sug-

gest that the transition region for the *trans* isomer is more easily solvated.

Acknowledgements

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References

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