Kinetic Data for Outer-sphere V^{2+} and $[Ru(NH_3)_6]^{2+}$ Reductions of Platinum(IV) Complexes and a Correlation of Rate Constants

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The kinetics of 2 : 1 V^{2+} and $[Ru(NH_3)_6]^{2+}$ reductions of six Pt^{IV} complexes: *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$, *trans*-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$, $[Pt(NH_3)_5Cl]^{3+}$, $[Pt(NH_3)_5Br]^{3+}$, *mer*-$[Pt(NH_3)_3Cl_3]^{+}$, and $[PtCl_6]^{2-}$ have been studied. Reactions involve one-equivalent changes, $Pt^{IV} \longrightarrow Pt^{III} \longrightarrow Pt^{II}$ where the first step is rate determining and Pt^{III} is a transient intermediate. A linear correlation of second-order rate constants (15 °C) k_V and k_{Ru}, log k_V =0.89 log k_{Ru}− 1.68, is obtained at I = 0.10M ($LiClO_4$), consistent with outer-sphere reactions, and non-utilization (by V^{2+}) of inner-sphere pathways involving Cl^- and Br^- bridges. The occurrence of outer-sphere reactions appears to preclude two-equivalent changes. Rate constants for the V^{2+} reductions of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ > $[Pt(NH_3)_5Cl]^{3+}$ differ by a factor of 60, whereas those for corresponding $[Pt(NH_3)_4]^{2+}$ reductions, which involve two-equivalent changes, have previously been shown to differ by a factor 10^4. Activation parameters have been determined for five of the V^{2+} reductions. Those for the reduction of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ and *trans*-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$ differ significantly indicating an influence of the methyl groups.

THE present investigations are an extension of earlier studies on the V^{2+} reductions of Pt^{IV} complexes $[PtCl_6]^{2-}$ and $[Pt(NH_3)_5Cl]^{3+}$ [equation (1)] in which outer-sphere

$$2V^{II} + Pt^{IV} \longrightarrow 2V^{III} + Pt^{II} \qquad (1)$$

electron transfer in one-equivalent steps was indicated.[1] Evidence for this assignment was based on (*a*) failure to observe intermediate formation of vanadium(IV) under conditions when this would otherwise have been spectrophotometrically detectable, and (*b*) the magnitude of rate constants for the V^{2+} reduction of $[PtCl_6]^{2-}$, which were too large to permit substitution into either coordination sphere and formation of an inner-sphere bridged precursor complex. The first step in the $Pt^{IV} \longrightarrow Pt^{III} \longrightarrow Pt^{II}$ conversion is rate determining and is the focal point of the present investigations. Studies with the one-equivalent substitution-inert reductant $[Ru(NH_3)_6]^{2+}$, complement the V^{2+} studies and help to further substantiate the outer-sphere assignment.

EXPERIMENTAL

Preparation of trans-$[Pt(NH_3)_4Cl_2]Cl_2$.—The procedure for preparing this compound has been described previously.[2] Chlorine gas was passed through a solution of *ca.* 1.5 g of the Pt^{II} complex $[Pt(NH_3)_4]^{2+}$ (see below) in a minimum of 6M-HCl for 30 min. Pale yellow *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$ crystals were filtered off, and washed with ethanol and ether {Found: H, 3.1; Cl, 35.3; N, 13.7. Calc. for $[Pt(NH_3)_4Cl_2]Cl_2$: H, 2.96; Cl, 35.1; N, 13.8%}. The spectrum in H_2O gave $\lambda_{max.}$ 335 nm (ε 101 l mol^{-1} cm^{-1}).[3]

Preparation of trans-$[Pt(NH_2CH_3)_4Cl_2]Cl_2$.[4]—Methylamine solution (33%, 6.25 ml) was added to $Na_2[PtCl_4]$ (Johnson Matthey, 1.66 g) in H_2O (60 ml). A colour change, dark red ⟶ yellow, was observed after the mixture had been warmed on a steam-bath for 15 min. The residue from rotary evaporation to dryness of the mixture (when excess of methylamine was removed) was treated with Cl_2 as above. The yellow product was washed with cold water, ethanol, and ether. Recrystallization was from water by addition of concentrated HCl {Found: C, 10.5; H, 4.45. Calc. for $[Pt(NH_2CH_3)_4Cl_2]Cl_2$: C, 10.4; H, 4.34%}. The spectrum in H_2O gave $\lambda_{max.}$ 340 nm, (ε 116.8 l mol^{-1} cm^{-1}).

Preparation of $[Pt(NH_3)_5Br](ClO_4)_3 \cdot 3H_2O$.—Potassium hexabromoplatinate(IV) (Johnson and Matthey; 2 g), disodium hydrogen phosphate (4 g), and 20% ammonia solution (40 ml) were mixed with H_2O (60 ml). The mixture was heated on a steam-bath at *ca.* 80 °C for 40 min. Pale yellow crystals began to form, and the solution was cooled in ice. The crystals, the phosphate salt of $[Pt(NH_3)_5Br]^{3+}$, were filtered off and washed with ice-cold ethanol, and then ether. The solid was dissolved in a minimum volume of 0.1M-$HClO_4$, and the perchlorate salt obtained by addition of small amounts of ice-cold $HClO_4$ (72%). The spectrum gave $\lambda_{max.}$ 323 nm (ε 273 l mol^{-1} cm^{-1}) {Found: H, 2.7; Br, 11.5; Cl, 14.3; N, 9.2. Calc. for $[Pt(NH_3)_5Br](ClO_4)_3 \cdot 3H_2O$: H, 2.9; Br, 11.1; C., 14.9; N, 9.8%}.

Preparation of mer-$[Pt(NH_3)_3Cl_3]Cl \cdot H_2O$.[5]—The Pt^{II} complex (see below) $[Pt(NH_3)_3Cl]Cl$ (1 g) was dissolved in 6M-HCl (250 ml), and a stream of Cl_2 gas was passed through for *ca.* 40 min. A yellow precipitate of *trans*-$[Pt(NH_3)_4Cl_2]Cl_2$ formed during the oxidation and was discarded. The filtrate was left to evaporate on a steam-bath until yellow crystals were obtained. The mixture was then cooled, and the yellow product filtered off. Recrystallization was from a minimum of H_2O with addition of conc. HCl. The spectrum in H_2O gave $\lambda_{max.}$ 402 nm (ε = 53 l mol^{-1} cm^{-1}); λ(sh) 330 (ε 220 l mol^{-1} cm^{-1}). The meridional assignment is consistent with the preparative procedure,[5] and Pt^{II} products in this study. Calc. for $[Pt(NH_3)_3Cl_3]Cl \cdot H_2O$: H, 2.2; Cl (total), 35.0; Cl (ionic), 8.74; N, 10.3 [Found: H, 2.7; Cl (total), 34.8; Cl (ionic), 9.1; N, 10.2%]. Ionic chloride was determined by a potentiometric method using a Ag/AgCl electrode.[6]

Other Pt^{IV} *Complexes*.—Samples of ammonium hexachloroplatinate(IV) (Johnson and Matthey), $\lambda_{max.}$ 262 nm (ε 2.45 × 10^4 l mol^{-1} cm^{-1}) and $\lambda_{max.}$ 454 nm (ε 48 l mol^{-1} cm^{-1}), and chloropenta-ammineplatinum(IV) perchlorate, $\lambda_{max.}$ 286 nm (ε 186 l mol^{-1} cm^{-1}) were as used previously.[1]

Preparation of cis-$[Pt(NH_3)_2Cl_2]$.—This Pt^{II} complex was prepared by dissolving $K_2[PtCl_4]$ (Johnson and Matthey) in dilute HCl, and treating the solution with NH_3 in the presence of NH_4Cl (buffer control to prevent formation of hydroxo-complexes) as described previously.[7] Yellow *cis*-$[Pt(NH_3)_2Cl_2]$ was separated from a small amount of insoluble Magnus's Green salt $[Pt(NH_3)_4][PtCl_4]$. The spectrum of an unrecrystallized sample gave $\lambda_{max.}$ 302 and 366 nm in satisfactory agreement with literature values.[8]

Preparation of $[Pt(NH_3)_3Cl]Cl$.[9]—The *cis*-$[Pt(NH_3)_2Cl_2]$ complex (1 g) and cyanate (0.7 g, KNCO) were dissolved in H_2O (20 ml). After the solution had been boiled for 1 min a bright orange solution was obtained, at which stage concentrated HCl (0.4 ml) was added. Yellow unchanged *cis*-$[Pt(NH_3)_2Cl_2]$ was filtered off. Addition of an excess of $K_2[PtCl_4]$ gave a precipitate of Magnus's Green salt, $[Pt(NH_3)_4][PtCl_4]$, and $[Pt(NH_3)_3Cl]_2[PtCl_4]$. These were separated (Magnus's Green is the least soluble) by treatment with hot water acidified with a few drops of HCl. The filtrate yielded a flesh-pink solid, which was redissolved (dilute HCl) and treated with $[Pt(NH_3)_4]Cl_2$. The $[PtCl_4]^{2-}$ component was removed as insoluble Magnus's Green salt, and a solution of $[Pt(NH_3)_3Cl]^+$ and excess of $[Pt(NH_3)_4]^{2+}$ remained. The latter crystallized first and was filtered off. A sample of $[Pt(NH_3)_3Cl]Cl$ was obtained by leaving the solution over P_2O_5 in a desiccator. The spectrum gave $\lambda_{max.}$ 325 (ε 34.5 l mol^{-1} cm^{-1}) and 250 nm (ε 122) in good agreement with literature values,[8] which are quoted for $[Pt(NH_3)_3Cl]_2SO_4$.

Preparation of $[Pt(NH_3)_4]Cl_2$.[10]—To samples of Magnus's Green $[Pt(NH_3)_4][PtCl_4]$ from the previous preparation (*ca.* 0.3 g), were added H_2O (25 ml), concentrated HCl (2 ml), and NH_3 (*d* 0.880, 100 ml). The solution was boiled (*ca.* 1 h) until the solid had dissolved, the solution being maintained at *ca.* 100 ml by addition of NH_3. The solution was concentrated to *ca.* 50 ml and dilute HCl was added to the filtrate until the solution was just acid to litmus; concentrated HCl (1 ml) was then added. A solid sample was obtained by addition of (×10 volumes) ethanol–acetone (1 : 1). The spectrum in H_2O gave $\lambda_{max.}$ 287 cm^{-1} (ε 44 l mol^{-1} cm^{-1}) (lit.,[8] ε 36 l mol^{-1} cm^{-1}).

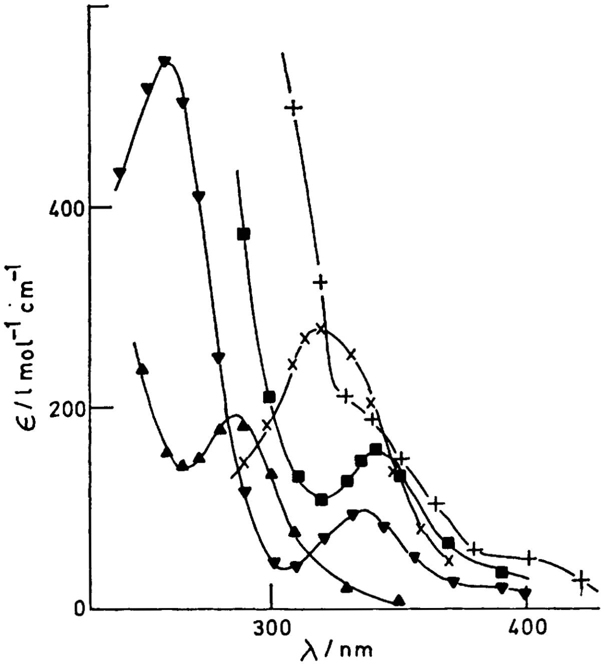

FIGURE 1 U.v. spectra of Pt^{IV} complexes *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ (▼), *trans*-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$ (■), $[Pt(NH_3)_5Cl]^{3+}$ (▲), $[Pt(NH_3)_5Br]^{3+}$ (×), and *mer*-$[Pt(NH_3)_3Cl_3]^+$ (+) in H_2O

Reductants.—Solutions of hexaquovanadium(II) perchlorate (hereafter V^{2+}) in dilute perchloric acid were prepared by electrolytic reduction of vanadium(IV) perchlorate. Hexa-ammineruthenium(II) solutions were prepared by Zn/Hg reduction of the chloride salt [11] of the Ru^{II} analogue in 0.01M-$HClO_4$, and standardized as previously described.[12]

Product Analyses.—Detailed spectrophotometric analyses were carried out for the V^{2+} reductions of Pt^{IV} complexes. It has previously been demonstrated that with $[PtCl_6]^{2-}$ and $[Pt(NH_3)_5Cl]^{3+}$ little or no V^{IV} is formed and that the 2 : 1 reactions, (1), proceed in consecutive one-equivalent steps. Here we have further confirmed that no V^{IV} is formed in the reaction of V^{2+} with *mer*-$[Pt(NH_3)_3Cl_3]^+$. The identity of the Pt^{II} products is also relevant. The V^{2+} reactant was in *ca.* 5% excess of the stoicheiometric 2 : 1 ratio. Reactions were at 25 °C, $[H^+]$ = 1.0M, and I = 1.0M (perchlorate). Final spectra were corrected for V^{2+}/V^{3+} absorbance. Relevant Pt^{IV} and Pt^{II} spectra are shown in Figures 1 and 2.

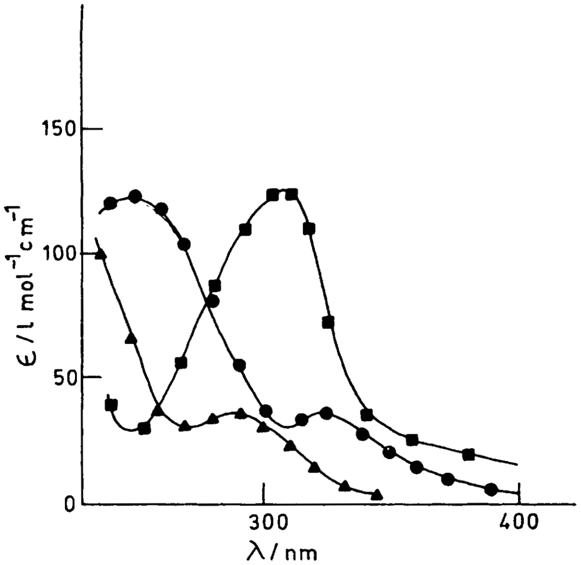

FIGURE 2 U.v. spectra of *cis*-$[Pt(NH_3)_2Cl_2]$ (■), $[Pt(NH_3)_3Cl]^+$ (●), and $[Pt(NH_3)_4]^{2+}$ (▲) in H_2O

Spectra of *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ are given in ref. 8. It was found that for the V^{2+} reduction of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ the product was at least 75% $[Pt(NH_3)_4]^{2+}$. With $[Pt(NH_3)_5Cl]^{3+}$ as oxidant $[Pt(NH_3)_4]^{2+}$ is the product, and with *mer*-$[Pt(NH_3)_3Cl_3]^+$ the product is $[Pt(NH_3)_3Cl]^+$. The final spectrum in the latter case gave $\lambda_{max.}$ 325 nm (ε 26 l mol^{-1} cm^{-1}) as compared to $\lambda_{max.}$ 325 nm (ε 34 l mol^{-1} cm^{-1}) for $[Pt(NH_3)_3Cl]^+$. Since *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$ have much stronger absorption at $\lambda_{max.}$ 302 (ε 128 l mol^{-1} cm^{-1}) and 315 nm (ε 60) peaks respectively,[8] these products can be excluded.

Kinetics.—Reactions were monitored at Pt^{IV} absorbance peak positions by the stopped-flow method. The V^{2+} reductant was generally in large (>10-fold) excess when plots of absorbance changes $\log(A_t - A_\infty)$ against time (linearity > 80% completion) gave slopes of $2k_V\,[Pt^{IV}]_0/2.303$ from which second-order rate constants k_V could be evaluated. Rate constants k_V for V^{2+} reactions with the latter in smaller excess were obtained from the slope (×2.303) of plots $\log\{1 + ([V^{2+}]_0 - 2[Pt^{IV}]_0)\Delta\varepsilon l/(A_t - A_\infty)\}$ against time, where $\Delta\varepsilon(\text{l mol}^{-1}\text{ cm}^{-1}) = (\varepsilon_{Pt^{IV}}/2 + \varepsilon_{V^{II}}) - (\varepsilon_{Pt^{II}}/2 + \varepsilon_{V^{III}})$, l is the optical path length (2 cm),

TABLE 1

Rate constants, k_V, for the V^{2+} reduction of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$, $I = 1.00$M ($LiClO_4$) except as stated, λ 325 nm

(t/°C)	[H^+]/M	$10^3[V^{2+}]$/M	$10^4[Pt^{IV}]$/M	k_V/l mol^{-1} s^{-1}
35.0	0.50	7.4	3.46	95
	0.50	3.7	1.85	107
	0.50	3.7	1.67	107 [a]
	0.10	9.8	2.86	114
	0.10	6.5	2.86	95
25.0	1.00	9.8	4.57	53
	1.00	4.9	4.57	53
	1.00	2.4	4.57	67
	0.50	3.7	1.67	55 [a]
	0.10	9.8	2.86	63
	0.10	6.5	2.86	64
	0.10	6.5	1.33	56
	0.10	3.3	1.33	59
15.0	0.10	9.8	2.86	32
	0.10	6.5	1.33	28
	0.10	3.3	1.33	25
	0.09	5.3	2.30	15.1 [b]

[a] [Cl^-] = 0.01M added initially. [b] $I = 0.10$M ($LiClO_4$). Average of 4 runs.

and initial concentrations are indicated. Most $[Ru(NH_3)_6]^{2+}$ reductions were carried out with the Pt^{IV} reactant in excess of the stoicheiometric amount, when second-order rate constants were obtained from plots of $\log\{1 + (2[Pt^{IV}]_0 - [Ru^{II}]_0)\Delta\varepsilon l/(A_t - A_\infty)\}$ against time. For consistency with these equations correction factors are required to rate constants for the V^{2+} reduction of $[PtCl_6]^{2-}$, and the $[Ru(NH_3)_6]^{2+}$ reduction of $[Pt(NH_3)_5Cl]^{3+}$, (all $\times \frac{1}{2}$) reported in the previous paper.[1]

Ionic strengths of reactant solutions were made up to $I = 1.00$ and 0.10M with V^{2+}, and 0.10M with $[Ru(NH_3)_6]^{2+}$ as the reductant using $HClO_4/LiClO_4$.

Treatment of Data.—Activation parameters for the V^{2+} reductions were obtained using a non-linear least-squares programme [13] with $1/k^2$ weighting factor. Errors in other cases were estimated using a standard (unweighted) least-squares treatment.

Results. Second-order rate constants, k_V, for the V^{2+} reductions of Pt^{IV} complexes, rate law (2), are listed in

$$-d[Pt^{IV}]/dt = k_V[V^{2+}][Pt^{IV}] \quad (2)$$

Tables 1—4 for *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$, *trans*-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$, $[Pt(NH_3)_5Br]^{3+}$, and *mer*-$[Pt(NH_3)_3Cl_3]^+$ respectively. All rate constants quoted are an average of at least two duplicate runs. Rate constants at 15 °C, $I = 0.10$M ($LiClO_4$), were required for the correlation described below. No dependence on [H^+] and [Cl^-] is observed. Activation parameters were determined for the first three of these reactions, and these are shown alongside values for $[Pt(NH_3)_5Cl]^{3+}$ and $[PtCl_6]^{2-}$ at $I = 1.00$M ($LiClO_4$), in Table 5.

TABLE 2

Rate constants, k_V, for the V^{2+} reduction of *trans*-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$, $I = 1.00$M ($LiClO_4$) except as stated, λ 340 nm

t/°C	[H^+]/M	$10^2[V^{2+}]$/M	$10^3[Pt^{IV}]$/M	k_V/l mol^{-1} s^{-1}
35.0	0.90	4.88	2.03	258
	0.90	0.49	0.24	250
	0.10	0.85	0.45	262 [a]
25.0	0.90	4.88	2.03	195
	0.90	1.69	0.96	192
	0.90	0.49	0.24	192
	0.10	0.85	0.45	184
	0.10	0.42	0.45	199
15.0	0.90	1.69	0.96	130
	0.10	0.42	0.45	138
	0.09	0.53	0.26	57 [b]

[a] [Cl^-] = 0.010M added initially. [b] $I = 0.10$M ($LiClO_4$).

Second-order rate constants, k_{Ru}, are defined by a rate law of the same form as (2). All studies were at 15 °C, $I = 0.10$M ($LiClO_4$), Table 6. Difficulties in working with this reductant at higher [H^+] and [ClO_4^-], and at higher temperatures, have been referred to previously.[12]

TABLE 3

Rate constants, k_V, for the V^{2+} reduction of $[Pt(NH_3)_5Br]^{3+}$, $I = 1.00$M ($LiClO_4$), λ 323 nm

t/°C	[H^+]/M	$10^2[V^{2+}]$/M	$10^3[Pt^{IV}]$/M	k_V/l mol^{-1} s^{-1}
35.0	0.95	0.75	4.81	14.2
	0.90	2.24	11.5	
	0.10	1.23	5.85	14.6
25.0	0.95	1.23	5.92	10.4
	0.95	0.75	4.81	10.9
	0.90	2.24	11.5	10.2
	0.50	0.72	2.89	10.6
	0.10	1.23	5.85	9.5
15.0	0.95	0.75	4.81	5.8
	0.90	2.24	11.5	5.6
	0.50	0.72	2.89	6.5
	0.10	1.23	5.85	6.0

TABLE 4

Rate constants (15.0 °C), k_V, for the V^{2+} reduction of *mer*-$[Pt(NH_3)_3Cl_3]^+$, $I = 1.00$M ($LiClO_4$) except as stated, λ 400 nm

[H^+]/M	$10^3[V^{2+}]$/M	$10^4[Pt^{IV}]$/M	k_V/l mol^{-1} s^{-1}
0.10	4.30	5.35	177
0.30	4.30	4.30	158
0.50	4.30	6.42	141
0.55	2.92	5.35	169
0.75	2.92	4.27	186
1.00	2.92	3.20	140
1.00	2.92	6.42	146
0.09	2.88	5.25	71 *

* $I = 0.10$M ($LiClO_4$).

Table 7 lists k_V and k_{Ru} values at 15 °C, $I = 0.10$M ($LiClO_4$), relevant to the rate constant correlation in Figure 3. Rate constants for the V^{2+} and $[Ru(NH_3)_6]^{2+}$ reductions of $[PtCl_6]^{2-}$, and the V^{2+} reduction of $[Pt(NH_3)_5Cl]^{3+}$ at $I = 0.10$M were not previously reported. A linear fit was obtained, see equation (6) below, using all k_{Ru} values in Table 7. Errors for k_V were assumed to be of the same magnitude as observed for the more extensive studies at $I = 1.00$M ($LiClO_4$).

TABLE 5

Summary of rate constants (25 °C) and activation parameters for the V^{2+} reduction of Pt^{IV} complexes, $I = 1.00$M ($LiClO_4$)

Oxidant	k_V/l mol^{-1} s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}
trans-$[Pt(NH_3)_4Cl_2]^{2+}$	28.3	10.7 ± 0.6	−14.5 ± 2.0
trans-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$	134	5.1 ± 0.3	−31.0 ± 0.9
$[Pt(NH_3)_5Cl]^{3+}$ [a]	0.61	9.9 ± 0.5	−25.1 ± 1.7
$[Pt(NH_3)_5Br]^{3+}$	6.0	7.5 ± 0.5	−28.8 ± 1.6
mer-$[Pt(NH_3)_3Cl_3]^+$	159		
$[PtCl_6]^{2-}$ [b]	1.23×10^4	4.6 ± 0.2	−23.9 ± 0.7

[a] Ref. 1. [b] Ref. 1, rate constants corrected ($\times \frac{1}{2}$) see Experimental section.

TABLE 6

Rate constants (15 °C), k_{Ru}, for the $[Ru(NH_3)_6]^{2+}$ reduction of Pt^{IV} complexes, I = 0.10M ($LiClO_4$), λ 335 nm

Oxidant	$\frac{[H^+]}{M}$	$\frac{10^4[Ru(NH_3)_6{}^{2+}]}{M}$	$\frac{10^4[Pt^{IV}]}{M}$	$\frac{10^{-3}k_{Ru}}{l\ mol^{-1}\ s^{-1}}$
trans-$[Pt(NH_3)_4Cl_2]^{2+}$	0.10	1.93	6.05	2.07
	0.01	4.61	6.05	2.00
	0.01	1.08	1.01	2.36
trans-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$	0.10	1.12	2.13	9.3
	0.01	2.45	5.85	6.5
	0.01	0.82	2.10	6.7
$[Pt(NH_3)_5Br]^{3+}$	0.10	0.52	2.29	0.163
	0.01	1.24	2.41	0.198
	0.01	0.20	1.21	0.187
mer-$[Pt(NH_3)_3Cl_3]^+$	0.01	5.8	1.30	16.0
	0.01	5.8	0.73	16.0
	0.02	4.8	0.73	19.5
	0.02	4.8	0.73	17.6
	0.03	3.4	1.09	15.8
	0.04	1.9	0.73	19.8
	0.04	1.9	1.09	16.0
	0.10	6.3	2.43	21.5

DISCUSSION

With other redox partners both the V^{2+} and Pt^{IV} reactants have been shown to be capable of two-equivalent changes. Although in the case of the Cr^{2+} reduction of $[Pt(NH_3)_5Cl]^{3+}$ a considerable barrier is presented in that Cr^{IV} is not easy to generate in aqueous solution, such a two-equivalent inner-sphere pathway appears more favourable than the alternative involving formation of Pt^{III}.[14] Oxidation of V^{2+} to V^{IV} should occur more readily since V^{IV} (as VO^{2+}) is a stable species.[15] However no contributions from the two-electron step, $V^{II} + Pt^{IV} \longrightarrow V^{IV} + Pt^{II}$, which with excess of V^{2+} is followed by further reactions $V^{II} + V^{IV} \longrightarrow V^{III}{}_2 \longrightarrow 2V^{III}$, are observed. This alone suggests an outer-sphere assignment, if (as seems likely) the more extensive reorganisation attendant on a two-equivalent change is difficult to achieve in an outer-sphere process.

TABLE 7

Summary of rate constants for the V^{2+} and $[Ru(NH_3)_6]^{2+}$ reduction of Pt^{IV} complexes at 15 °C, I = 0.10M ($LiClO_4$)

Oxidant	$\frac{k_V}{l\ mol^{-1}\ s^{-1}}$	$\frac{k_{Ru}}{l\ mol^{-1}\ s^{-1}}$
trans-$[Pt(NH_3)_4Cl_2]^{2+}$	15.1	2.14×10^3
trans-$[Pt(NH_2CH_3)_2Cl_2]^{2+}$	57	7.5×10^3
$[Pt(NH_3)_5Cl]^{3+}$	0.26 [a]	17.7 [b]
$[Pt(NH_3)_5Br]^{3+}$		1.8×10^2
mer-$[Pt(NH_3)_3Cl_3]^+$	71	1.78×10^4
$[PtCl_6]^{2-}$	2.14×10^4 [c]	7.9×10^6 [d]

[a] $[V^{2+}] = 3.0 \times 10^{-3}$M; $[Pt^{IV}] = 1.5 \times 10^{-3}$M; $[H^+]$ = 0.08M. [b] Rate constants from ref. 1 corrected (× ½), see Experimental section. [c] $[V^{2+}] = 6.5 \times 10^{-4}$M; $[Pt^{IV}] = 7.6 \times 10^{-4}$M; $[H^+]$ = 0.09M. [d] Error ±30%; $[Ru(NH_3)_6{}^{2+}] = (8.4 - 23.5) \times 10^{-6}$M; $[Pt^{IV}] = 6.8 \times 10^{-6}$M.

For the six Pt^{IV} oxidants now investigated all observations are in accordance with a reaction sequence (3)—(4). Further confirmation of the outer-sphere assignment to reaction (3) was sought by comparison of rate constants k_V with k_{Ru} for the corresponding

$$V^{II} + Pt^{IV} \xrightarrow{k_V} V^{III} + Pt^{III} \qquad (3)$$

$$V^{II} + Pt^{III} \xrightarrow{\text{fast}} V^{III} + Pt^{II} \qquad (4)$$

$[Ru(NH_3)_6]^{2+}$ reductions. A plot of log k_V against log k_{Ru} (Figure 3) shows satisfactory linearity and since the slope approaches 1.0 as required by the modified Marcus approach,[16] outer-sphere assignments can be made for both reductants. Initially however the V^{2+} studies were at I = 1.00M ($LiClO_4$), whereas the $[Ru(NH_3)_6]^{2+}$ studies had to be at a lower ionic strength, I = 0.10M ($LiClO_4$). These results (open circles in Figure 3) give a slope similar to that of the broken line, which summarizes existing log k_V and log k_{Ru} data for the reaction of some 24 Co^{III} oxidants [equation (5)].[17] With Pt^{IV} as oxidant a wide range of charges from −2 to +3 were investigated, and we therefore saw fit to obtain further data with V^{2+} as reductant at I = 0.10M ($LiClO_4$). A significant change in slope is observed, where the shaded points now give a fit to [equation (6)]. It is difficult to

$$\log k_V = 0.81 \log k_{Ru} - 0.64 \qquad (5)$$

$$\log k_V = (0.89 \pm 0.01) \log k_{Ru} - (1.68 \pm 0.06) \qquad (6)$$

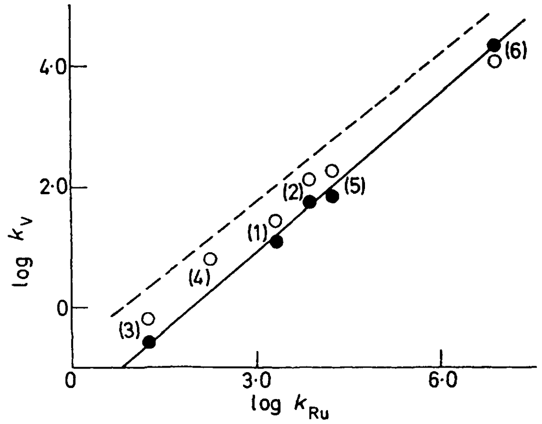

FIGURE 3 Correlation of rate constants for V^{2+} (k_V) and $[Ru(NH_3)_6]^{2+}$ (k_{Ru}) reductions of Pt^{IV} complexes *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ (1), *trans*-$[Pt(NH_2CH_3)_4Cl_2]^{2+}$ (2), $[Pt(NH_3)_5Cl]^{3+}$ (3), $[Pt(NH_3)_5Br]^{3+}$ (4), *mer*-$[Pt(NH_3)_3Cl_3]^+$ (5), and $[PtCl_6]^{2-}$ (6). Rate constants k_{Ru} at I = 0.10M ($LiClO_4$), and k_V at I = 1.00M ($LiClO_4$) (○), and I = 0.10M ($LiClO_4$) (●)

reappraise the Co^{III} studies making due allowance for effects of I (charges on the Co^{III} complexes vary much less in any case), but we suspect that the slope may also be closer to 1.0,[18] than indicated by equation (5). Correlations involving Cr^{2+},[19,20] $[Cr(bipy)_3]^{2+}$,[21,22] Eu^{2+},[18] have been shown to be close to 1.0. A notable exception appears to be with $[TiOH]^{2+}$ as reductant (slope *ca.* 0.55) an effect which as yet is not fully understood.[23] The possibility that this correlation is in fact curved has been suggested but additional data are required.

The correlation in Figure **3** leads to an outer-sphere assignment for the V^{2+} reduction of the complex $[Pt(NH_3)_5Br]^{3+}$. It is concluded that Br^- like Cl^- does not readily function as a lead-in group for inner-sphere V^{2+} reduction, an interesting observation bearing in mind that the rate constants (25 °C) for $[Pt(NH_3)_5Br]^{3+}$ (6.0 l mol^{-1} s^{-1}) and $[Pt(NH_3)_5Cl]^{3+}$ (0.61 l mol^{-1} s^{-1}) do not necessarily exclude an inner-sphere contribution. There are two points to make. One is that V^{2+} has an aversion for the softer halide ions which can be rationalized in terms of hard and soft acid-base theory (V^{2+} is hard).[23] Secondly, assuming that formation of an inner-sphere precursor complex can occur, subsequent electron-transfer might be slow. We believe the first of these is relevant, since the V^{2+} reduction of $[Co(NH_3)_5Br]^{2+}$ (30 l mol^{-1} s^{-1}) and $[Co(NH_3)_5Cl]^{2+}$ (10.2 l mol^{-1} s^{-1}) are also outer-sphere.[22] The V^{2+} reduction of $[Co(NH_3)_5F]^{2+}$ on the other hand is inner-sphere,[22] and reduction of Pt^{IV} fluoro-complexes [*e.g.* $Pt(NH_3)_5F^{3+}$] would be of interest since they might also proceed by an inner-sphere pathway, and thus provide conditions, appropriate for a two-electron transfer.

Studies on Pt^{II}–Pt^{IV} exchange reactions have provided evidence for Cl^- bridging and an inner-sphere mechanism.[24] A two-equivalent change involving simultaneous or near-simultaneous transfer of two electrons may occur in these reactions. The rate constants for the $[Pt(NH_3)_4]^{2+}$ exchange with *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ is 10^4 greater than for the exchange with $[Pt(NH_3)_5Cl]^{3+}$. This difference is presumed to stem from the presence of a stronger *trans* Pt–NH_3 bond in $[Pt(NH_3)_5Cl]^{3+}$, making the accompanying octahedral—square-planar geometry change (some bond stretching will be required in the activated complex) more difficult to achieve. For the outer-sphere V^{2+} and $[Ru(NH_3)_6]^{2+}$ reductions rate constants exhibit much smaller differences of ×60 and $\times 10^2$ respectively, consistent with the less demanding $Pt^{IV} \rightarrow Pt^{III}$ change. Enthalpies of activation are, moreover, very similar for these two V^{2+} reductions (Table 5) whereas for the $[Pt(NH_3)_4]^{2+}$ reductions of $[Pt(NH_3)_5Cl]^{3+}$ (16.7 kcal mol^{-1}) and *trans*-$[Pt(en)_2Cl_2]^{2+}$ (11.5 kcal mol^{-1}) the differences account for the rate constant pattern. The V^{2+} reduction of $[Pt(NH_3)_5Cl]^{3+}$ might be slower than for *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ because Pt–N bond vibrations *trans* to the Cl^- are less conducive to electron transfer into the e_g orbital aligned in this direction.[25] Rate constants for the reductions of *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ and *mer*-$[Pt(NH_3)_3Cl_3]^+$ complexes are very similar, as in the corresponding $[Pt(NH_3)_4]^{2+}$ reductions.

Of further interest is the effect of replacing NH_3 by CH_3NH_2 in *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$, when activation parameters (Table 5) change in a way which we do not fully understand, but which could be related to the presence of the hydrophobic methyl groups. The trends are self compensating since rate constants k_V show little variation and are within a factor of ×5.

Platinum(II) reaction products were identified spectrophotometrically, and these indicate that geometry changes accompanying the redox change occur by Cl^- rather than NH_3 loss. Unfortunately our data do not include a study of a *cis*-dichloro-complex. Beattie and Starink [26] have shown that for the two-equivalent Cr^{2+} reduction of *cis*-$[Pt(pn)_2Cl_2]^{2+}$ (pn = propylenediamine) the Pt^{II} product is $[Pt(pn)(pnH)Cl]^+$, whereas for the one-equivalent Eu^{2+} reduction (probably inner-sphere) the final Pt^{II} product is $[Pt(pn)_2]^{2+}$. For a one-equivalent outer-sphere V^{2+} reduction loss of two *cis*-chloride ligands is to be expected.

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