Table IV. Bond Strength Sums for $Na_3ON(SO_3)_2 \cdot 3H_2O$

	Na(1)	Na(2)	S	H(51)	H(52)	H(61)	H(62)	Total
O(1)	0.19^a	0.18					0.19	0.75^c
O(2)		0.17^b 0.12^b	1.51	0.16				1.96
O(3)	0.13		1.54		0.18			1.85
O(4)	0.15	0.18^b	1.58					1.91
O(5)	0.19 0.15			0.84	0.82			2.00
O(6)	0.13^a					0.86 0.14	0.81	2.07
Total	0.94	1.12	4.63^c	1.00^d	1.00^d	1.00^d	1.00^d	

[a] Occurs twice in horizontal sum. [b] Occurs twice in vertical sum. [c] Bond to nitrogen ignored. [d] Assumed.

polyhedra are contained in Table III.

The three water molecules in the formula unit are located in the vicinity of one of the glide planes in the structure. The operation of this glide plane generates a continuous ribbon three water molecules wide which runs through the structure in the *c* direction. One hydrogen atom per formula unit is involved in hydrogen bonding within this ribbon; the others are in bonds to the neighboring anions, two of the five being to other sheets. Details of these hydrogen bonds are contained in Table III.

Bond lengths and bond angles within the anion are also given in Table III and are illustrated in Figure 2, along with some averaged molecular geometries for the related species $\{H[ON(SO_3)_2]_2\}^{5-}$ in its rubidium salt and the anion of Fremy's salt, $[ON(SO_3)_2]^{2-}$, determined by Howie et al.[3] It shows that the bond lengths and overall geometry of the isolated nitrosyl-*N*,*N*-disulfonate anion are not significantly different from those of the corresponding moiety in its rubidium acid salt, while the nitrosodisulfonate anion, differing only by one electron, has a markedly shorter N–O distance and a nearly planar conformation at nitrogen.

Bond strength sums were calculated using the formula and constants of Brown and Shannon.[8] The results are given in Table IV. The hydrogen atom positions were assumed to give a bond strength sum of 1.00 around the hydrogen atom, assuming a straight-line O–H···O conformation. The large contribution of 0.75 valence unit to O(1) due to bonds external to the anion illustrates its strongly basic nature and is therefore consistent with the formation of the symmetric dimeric species $\{H[ON(SO_3)_2]_2\}^{5-}$ in other salts. The unusually low bond strength totals for O(2) to O(4), the sulfonate oxygen atoms, may be related to the low thermal motion in this structure compared to many of those used by Brown and Shannon to determine their S–O curve.

Registry No. $Na_3[ON(SO_3)_2] \cdot 3H_2O$, 55904-77-3.

Supplementary Material Available. Table I, containing the observed and calculated structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W. Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC50304O-10-75.

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Outer-Sphere One-Equivalent Changes in the Vanadium(II) Reductions of Hexachloroplatinate(IV) and Chloropentaammineplatinum(IV)

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Received February 20, 1975 AIC501358

The V^{2+} reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$, $2V^{II} + Pt^{IV} \rightarrow 2V^{III} + Pt^{II}$, have been studied in aqueous perchloric acid solutions, $I = 1.0$ *M* ($LiClO_4$). No VO^{2+} is generated in the initial redox steps, and a reaction sequence, (i) and (ii),

$$V^{II} + Pt^{IV} \rightarrow V^{III} + Pt^{III} \tag{i}$$

$$V^{II} + Pt^{III} \xrightarrow{\text{fast}} V^{III} + Pt^{II} \tag{ii}$$

involving 1-equiv changes, is consistent with all observations. Both reactions are independent of $[H^+]$ in the range 0.10–1.00 *M*. At 25° the rate constant for the reaction of $PtCl_6^{2-}$ is 3.36 (±0.13) × 10^4 M^{-1} sec^{-1} ($\Delta H^\ddagger = 4.6 \pm 0.2$ kcal mol^{-1}, $\Delta S^\ddagger = -22.4 \pm 0.7$ cal K^{-1} mol^{-1}), and for $Pt(NH_3)_5Cl^{3+}$ it is 1.15 ± 0.10 M^{-1} sec^{-1} ($\Delta H^\ddagger = 9.9 \pm 0.5$ kcal mol^{-1}, $\Delta S^\ddagger = -25.1 \pm 1.7$ cal K^{-1} mol^{-1}). The V^{2+} reduction of $PtCl_6^{2-}$ is too fast for an inner-sphere process to occur. A rate constant of 110 ± 10 M^{-1} sec^{-1} has been obtained for the $Ru(NH_3)_6^{2+}$ reduction of $Pt(NH_3)_5Cl^{3+}$ at 25°, $I = 0.1$ *M* ($LiClO_4$), and using a linear correlation of data for other V^{2+} and $Ru(NH_3)_6^{2+}$ reductions, an outer-sphere mechanism is also assigned to the V^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$. The Cr^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$ has previously been studied, and evidence has been obtained for a two-electron inner-sphere process. Reasons for this different behavior of Cr^{2+} and V^{2+} are considered.

Introduction

It has been demonstrated that the V^{2+} reduction of mercury(II) proceeds by concurrent 1- and 2-equiv paths.[1] Since the vanadium(III) reduction of mercury(II) is known to be slow,[2] the 2-equiv change must occur within the lifetime of a single binuclear adduct. The Cr^{2+} reduction of mercury(II) on the other hand proceeds solely by 1-equiv reactions.[3] Beattie and Basolo[4] have concluded that the Cr^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$ proceeds via a 2-equiv change with intermediate formation of chromium(IV). Since vanadium(IV) is generally easier to generate than chromium(IV), it seemed likely that the V^{2+} reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$ would proceed with formation of vanadium(IV). The studies reported here demonstrate that neither reaction conforms to this prediction.

Rate constants for the reduction of $Pt(NH_3)_5Cl^{3+}$ by $Ru(NH_3)_6^{2+}$, an outer-sphere reductant, were determined to help in the assignment of a mechanism to the V^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$.

Experimental Section

Reactant Solutions. Ammonium hexachloroplatinate(IV), $(NH_4)_2PtCl_6$ (Johnson Matthey Chemicals Ltd.), gave a spectrum of λ_{max} 262 nm (ϵ 2.45×10^4 M^{-1} cm^{-1}) and 454 nm (ϵ 48 M^{-1} cm^{-1}), in good agreement with previous values[5] and was used without further purification. Chloropentaammineplatinum(IV) was prepared by treating 1 g of potassium hexachloroplatinate(IV) (Johnson Matthey Chemicals Ltd.) with disodium hydrogen phosphate (2 g), 20% ammonia solution (20 ml) and water (30 ml).[6] The mixture was stirred until the solution became colorless (ca. 20 min). The pale yellow precipitate of the phosphate salt was filtered off and washed with water (ca. 30 ml). This was then dissolved in 0.1 M HCl and the chloride salt precipitated by addition of concentrated HCl (ca. 10 ml). Finally the solid was recrystallized twice from 0.1 M $HClO_4$, first at 50° and then at room temperature. Anal. Calcd for $[Pt(NH_3)_5Cl](ClO_4)_3$: H, 2.44; N, 11.4; Cl, 23.1. Found: H, 2.6; N, 11.2; Cl, 22.7. Aqueous solutions give a peak at 286 nm (ϵ 186 M^{-1} cm^{-1}) in good agreement a previous value.[7]

Vanadium(IV) perchlorate was prepared from the sulfate salt (B.D.H. reagent grade) by exchanging onto an Amberlite IR-120(H) cation-exchange column, washing free from sulfate, and then eluting with 1.0 M $HClO_4$. Vanadium(II) perchlorate (ϵ 3.22 M^{-1} cm^{-1} at 850 nm) was prepared by reduction of the vanadium(IV) solution at a mercury-pool cathode. Vanadium(III) perchlorate (ϵ 8.3 M^{-1} cm^{-1} at 400 nm) was obtained by mixing equivalent amounts of the V^{2+} and VO^{2+} solutions.

Hexaammineruthenium(III) trichloride (Johnson Matthey Chemicals Ltd.) was purified as previously described (λ_{max} 275.5 nm, ϵ 472 M^{-1} cm^{-1})[8] and reduced to hexaammineruthenium(II) (λ_{max} 275 nm, ϵ 640 M^{-1} cm^{-1}) using a Jones reductor column, containing amalgamated zinc shot (Hopkin and Williams, AnalaR grade), under argon gas.[9]

Perchloric acid was of AnalaR grade purity (72%, B.D.H.). Lithium perchlorate was prepared by addition of lithium carbonate to perchloric acid and recrystallizing three times.

Experimental Procedure. All experiments were carried out under anaerobic conditions, deoxygenation being achieved by bubbling nitrogen or argon gas (for Ru) through reactant solutions. Teflon needles were used in the deoxygenation and transference of platinum(IV) solutions, since platinum(IV) reacts with stainless steel needles. All platinum(IV) solutions were stored in flasks covered with aluminum foil to prevent photochemical reactions.[10] Fresh solutions of platinum(IV) complexes were prepared each day. By addition of small quantities of chloride, generally 0.01 M (see Results), aquation of $PtCl_6^{2-}$ was minimized.

Products and Stoichiometries. At 25° with $[V^{2+}] = 8.7 \times 10^{-3}$ M, $[PtCl_6^{2-}] = 1.0 \times 10^{-2}$ M, and $[H^+] = 1.00$ M, an upper limit for the formation of VO^{2+} (λ_{max} 760 nm, ϵ 17.2 M^{-1} cm^{-1}) was 6–8%. A more precise determination was not possible at this temperature due to the incidence of the V^{3+} reduction of $PtCl_6^{2-}$. Contributions from the latter were more marked at lower $[H^+]$ values. At 2° the secondary reaction made a much smaller contribution, and for a run with $[V^{2+}] = 2.4 \times 10^{-3}$ M, $[PtCl_6^{2-}] = 2.5 \times 10^{-3}$ M, and $[H^+] = 1.0$ M, it was concluded that there was <1.2% of the 2-equiv reaction yielding VO^{2+}. By diluting the final solution (50 times) and determination of $PtCl_6^{2-}$ at the 262-nm peak (ϵ 2.45×10^4 M^{-1} cm^{-1}), a stoichiometry of 2.1 mol of V^{2+} to 1.0 mol of $PtCl_6^{2-}$ was obtained. The reaction under investigation can thus be expressed as in (1). Final

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

absorbance readings at 454 nm were consistent with the formation of $PtCl_4^{2-}$ (ϵ 15.7 M^{-1} cm^{-1}).[11]

The V^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$ also gave a 2:1 stoichiometry as in (1). This was determined at 15° by the reaction of 1.7×10^{-3} M reactant solutions, $[H^+] = 1.0$ M, and equating absorbance changes at 300 nm to absorption coefficients for $Pt(NH_3)_5Cl^{3+}$ (136 M^{-1} cm^{-1}), $Pt(NH_3)_4^{2+}$ (37 M^{-1} cm^{-1}), V^{2+} (21.2 M^{-1} cm^{-1}), and V^{3+} (2.6 M^{-1} cm^{-1}). Experiments monitored at 760 nm indicated no formation of VO^{2+} prior to the much slower reaction of V^{3+} with excess $Pt(NH_3)_5Cl^{3+}$, which requires a period of up to 16 hr to proceed to completion.

A 2:1 stoichiometry was also required to explain data for the $Ru(NH_3)_6^{2+}$ reduction of $Pt(NH_3)_5Cl^{3+}$.

Kinetic Studies. The V^{2+} reduction of $PtCl_6^{2-}$ was studied using a Durrum-Gibson stopped-flow spectrophotometer. The apparatus was constructed so that only glass, Kel-F, and Teflon surfaces came into contact with reactant solutions. A modification to the drive syringe containing the V^{2+} enabled a stream of N_2 gas to pass around and occupy the space behind the piston, thus preventing the loss of traces of V^{2+} and permitting the use of low concentrations of the latter. It was necessary to have the $PtCl_6^{2-}$ reactant in excess of the V^{2+}, thereby avoiding further reduction of $PtCl_4^{2-}$ product to platinum metal. Rate constants k_1 were evaluated by plotting $\log \{1 + ([PtCl_6^{2-}]_0 - 0.5[V^{2+}]_0)\Delta\epsilon l/\Delta A\}$ against time, where subscript zero denotes initial made up concentrations, $\Delta\epsilon$ the change in absorption coefficients for the stoichiometric reaction, l the optical path length (1.95 cm), and ΔA the change in absorbance at time t. For runs monitored at 290, 300, and 312 nm $PtCl_6^{2-}$ is the only significant absorbant (ϵ 4609 M^{-1} cm^{-1} at 300 nm). Absorption coefficients at 454 nm are for $PtCl_6^{2-}$ (48 M^{-1} cm^{-1}), $PtCl_4^{2-}$ (15.7 M^{-1} cm^{-1}), V^{3+} (2.1 M^{-1} cm^{-1}), and V^{2+} (0.8 M^{-1} cm^{-1}).

Rate constants k_2 for the V^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$ were obtained by conventional spectrophotometry at 300 nm (shoulder for $Pt(NH_3)_4^{2+}$ product).[11] For those runs with stoichiometric amounts of reactants k_2 was obtained by plotting $\Delta\epsilon/\Delta A$ against time, where absorption coefficients (ϵ) are as listed above.

Experiments at 760 nm in which the decrease in V^{2+} (2.14 M^{-1} cm^{-1}) was monitored were highly relevant in considering whether V^{3+} or VO^{2+} is generated as a primary product. At this wavelength ϵ's were determined for $Pt(NH_3)_5Cl^{3+}$ (0.82 M^{-1} cm^{-1}) and for $Pt(NH_3)_4^{2+}$ and V^{3+} (both <0.2 M^{-1} cm^{-1}). If VO^{2+} (ϵ 17.2 M^{-1} cm^{-1}) is formed in significant amounts, the absorbance would first increase and then decrease as the reaction of V^{2+} with VO^{2+} (rate constant 1.6 M^{-1} sec^{-1} at 25°) became dominant.[12] Since the rate constant for the reaction of V^{2+} with $Pt(NH_3)_5Cl^{3+}$ determined at 300 nm is 1.15 M^{-1} sec^{-1} at 25°, it can be concluded that for the reactant concentrations and conditions chosen the absorbance should increase for >25% of reaction if VO^{2+} is a primary product. No increase was detected and the rate constant observed is in excellent agreement with those obtained at 300 nm. For other runs with nonstoichiometric amounts of V^{2+} and $Pt(NH_3)_5Cl^{3+}$ rate constants were evaluated by the same standard procedure as used for $PtCl_6^{2-}$.

The $Ru(NH_3)_6^{2+}$ reduction of $Pt(NH_3)_5Cl^{3+}$ was studied by conventional spectrophotometry at 275 nm, where both $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_6^{3+}$ exhibit maxima. At this wavelength other absorption coefficients are $Pt(NH_3)_5Cl^{3+}$ (164 M^{-1} cm^{-1}) and $Pt(NH_3)_4^{2+}$ (35 M^{-1} cm^{-1}).

Results

The V^{2+} Reduction of $PtCl_6^{2-}$. The range of reactant concentrations was limited by the need to have $PtCl_6^{2-}$ in excess. By working with 1:1 and 7:1 molar ratios of reactants and varying the wavelength, see Table I, a 30-fold variation in $[V^{2+}]$ and 12-fold variation in $[PtCl_6^{2-}]$ was achieved. Second-order plots were linear to 80% completion at 290, 300, and 312 nm, but to only ca. 60% at 454 nm when a faster time base was required (because of the higher concentrations) and the signal:noise ratio was less satisfactory. No dependence on added chloride was observed, $[Cl^-] = 0.005$–0.10 M, but rate constants were somewhat erratic and up to 30% less in the absence of chloride. From the data presented, Table I, it can be concluded that the rate law is as in (2). The reaction

$$-d[Pt^{IV}]/dt = k_1[V^{II}][Pt^{IV}] \qquad (2)$$

was independent of $[H^+]$, which was varied from 0.1 to 1.0 M, $I = 1.0$ M ($LiClO_4$), and $[V^{III}]_0 = 3 \times 10^{-3}$ M added initially similarly had no effect on the evaluated rate constants. Runs monitored on the stopped-flow apparatus at the 760-nm VO^{2+} peak position gave no evidence for formation of VO^{2+} prior to the complete oxidation of V^{2+}. The V^{2+} reaction with VO^{2+} [12] is not sufficiently rapid for it to be effective on the

Table I. Rate Constants for the V^{2+} Reduction of $PtCl_6^{2-}$, $I = 1.0\ M$ ($LiClO_4$)[f]

Temp, °C	λ, nm	$[H^+]$, M	$10^4[V^{2+}]$, M	$10^4[PtCl_6^{2-}]$, M	$10^{-4}k$, M^{-1} sec^{-1}
25.0	454	1.00	7.68	12.1	3.29 (2)[a]
	454	1.00	7.16	12.3	3.22 (2)[c]
	454	1.00	5.26	11.6	3.53 (2)[b]
	454	1.00	4.00	14.8	3.40 (2)[a]
	454	1.00	3.34	7.60	3.46 (2)[a]
	290	1.00	0.77	1.45	3.45 (2)[e]
	290	1.00	0.65	1.45	3.36 (2)
	300	1.00	0.62	1.19	3.28 (2)[d]
	312	1.00	0.37	2.39	3.39 (2)
	290	1.00	0.34	1.42	3.05 (2)[d]
	300	0.50	0.83	1.49	3.25 (2)
	454	0.10	4.37	12.0	3.54 (2)
	300	0.10	1.01	1.48	3.47 (2)
15.0	454	1.00	13.1	12.0	2.47 (2)
	300	1.00	0.44	1.24	2.33 (2)
	312	1.00	0.31	2.39	2.69 (2)
	454	0.10	5.04	12.0	2.37 (2)
5.0	454	1.00	9.74	12.0	1.78 (2)
	312	1.00	0.63	2.39	1.92 (2)
	300	1.00	0.45	1.24	1.75 (2)
	454	0.10	8.06	12.0	1.77 (2)

[a] No chloride added. [b] $[Cl^-] = 0.005\ M$. [c] $[Cl^-] = 0.05\ M$. [d] $[Cl^-] = 0.10\ M$. [e] $[V^{III}] = 2.96 \times 10^{-3}\ M$ initially. [f] The number of runs averaged are as indicated in parentheses. Chloride concentrations were 0.01 M except where stated.

Table II. Rate Constants for the V^{2+} Reduction of $Pt(NH_3)_5Cl^{3+}$, $I = 1.0\ M$ ($LiClO_4$)[a]

Temp, °C	$[H^+]$, M	$10^3[V^{2+}]$, M	$10^3[Pt(NH_3)_5Cl^{3+}]$, M	k_2, M^{-1} sec^{-1}
35.0	1.00	3.47	1.73	2.08
	1.00	0.87	0.43	1.88
25.0	1.00	6.93	3.46	1.17[b]
	1.00	3.47	1.73	1.04
	1.00	0.87	0.43	1.26
	0.85	0.87	0.43	1.27[c]
	0.10	3.47	1.73	1.13
15.0	1.00	9.48	0.93	0.65
	1.00	3.47	1.73	0.61
	1.00	1.64	1.84	0.60
	0.50	6.93	3.46	0.59

[a] λ 300 nm except as stated. [b] λ 760 nm. [c] $[V^{III}] = 2.6 \times 10^{-3}\ M$ initially.

time scale of (1). From the temperature dependence of k_1 and an unweighted least-squares treatment of log (k_1/T) against $1/T$, activation parameters $\Delta H^\ddagger = 4.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -22.4 \pm 0.7$ cal K^{-1} mol^{-1} were determined.

The V^{2+} Reduction of $Pt(NH_3)_5Cl^{3+}$. This reaction could be studied with the V^{2+} reactant in excess without further reduction of the platinum(II) and precipitation of Pt metal. All experiments were consistent with a rate law as in (2), with k_2 for k_1. Second-order rate constants k_2 are as listed in Table II. The kinetics are independent of $[H^+] = 0.1$–$1.00\ M$, and $[V^{III}]_0 = 2.6 \times 10^{-3}\ M$ added initially. At 25° $k_2 = 1.15 \pm 0.10\ M^{-1}$ sec^{-1} and activation parameters from a least-squares fit are $\Delta H^\ddagger = 9.9 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = -25.1 \pm 1.7$ cal K^{-1} mol^{-1}.

The $Ru(NH_3)_6^{2+}$ Reduction of $Pt(NH_3)_5Cl^{3+}$. Sufficient runs were carried out at 1.5–12.8° to allow a rate constant, $k_3 = 110 \pm 10\ M^{-1}$ sec^{-1} at 25°, to be obtained by extrapolation. A low range of temperatures, as well as low $[H^+]$ (10^{-3} M), and $[ClO_4^-]$ ($I = 0.1\ M$), was desirable in order to avoid side reactions of $Ru(NH_3)_6^{2+}$.[13] The data obtained are listed in Table III.

Discussion

The V^{2+} reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$ proceed in 1-equiv steps with the formation of V^{3+}, (3) and (4).

Table III. Rate Constants for the $Ru(NH_3)_6^{2+}$ Reduction of $Pt(NH_3)_5Cl^{3+}$ at $[H^+] = 10^{-3}\ M$ and $I = 0.10\ M$ ($LiClO_4$)

Temp, °C	$10^5[Ru(NH_3)_6^{2+}]$, M	$10^5[Pt(NH_3)_5Cl^{3+}]$, M	k_3, M^{-1} sec^{-1}
1.5	8.90	9.03	8.02
2.0	5.70	6.10	9.15
5.5	8.85	9.03	10.7
10.0	8.90	9.03	24.4
12.8	5.60	6.10	28.8

$$V^{II} + Pt^{IV} \rightarrow V^{III} + Pt^{III} \tag{3}$$

$$V^{II} + Pt^{III} \xrightarrow{\text{fast}} V^{III} + Pt^{II} \tag{4}$$

Experiments at 760 nm, a peak position for VO^{2+}, clearly indicate that VO^{2+} is not a primary product and that this ion is only formed in the much slower secondary reactions of V^{3+} with excess Pt(IV). No dependence on hydrogen ion concentration was observed, $[H^+] = 0.1$–$1.0\ M$, which is consistent with observations that VO^{2+} is not formed. Reactions in which VO^{2+} is generated from either V^{2+} or V^{3+} generally give a dependence on $[H^+]^{-1}$ due to the increase in the degree of hydrolysis of the product.[1,14] The addition of $[V(III)]_0$ = ca. $3 \times 10^{-3}\ M$ does not affect the rate of (1) or the linearity of plots, and it is concluded that the reactions of V^{3+} with Pt(III) and Pt(IV) do not make significant contributions.

Evidence that the Pt(III) intermediate formed in the reduction of $PtCl_6^{2-} \rightarrow PtCl_4^{2-}$ has a formula $PtCl_4^-$ has been obtained previously.[15] The rate constant for the Fe^{2+} reduction of $PtCl_4^-$ has been determined, and is fast ($2.8 \times 10^6\ M^{-1}$ sec^{-1} at ca. 20°), in accordance with the fast stage (4) which is proposed in the present study.

The rate constant (25°) of $3.36 \times 10^4\ M^{-1}$ sec^{-1} is too high for substitution into the inner coordination sphere of V^{2+} [16] and $PtCl_6^{2-}$ [10] to occur, and this reaction must therefore be outer sphere. The same argument does not hold for the V^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$, and kinetic data do not emphatically rule out a V^{2+} substitution-controlled process, which typically has rate constants in the range 1–50 M^{-1} sec^{-1}, enthalpies of activation ca. 11–13 kcal mol^{-1}, and entropies of activation ca. −17 cal K^{-1} mol^{-1}.[17,18] Thus for 2+ and 3+ reactants, a rate constant at the low end of the range (1.15 M^{-1} sec^{-1}), with $\Delta H^\ddagger$ smaller than is generally observed (9.9 kcal mol^{-1}) and $\Delta S^\ddagger$ more negative (−25.1 cal K^{-1} mol^{-1}) might just be acceptable. To clarify the situation we therefore made a brief study of the $Ru(NH_3)_6^{2+}$ reduction of $Pt(NH_3)_5Cl^{3+}$. Rate constants for the V^{2+} and $Ru(NH_3)_6^{2+}$ reductions of $Pt(NH_3)_5Cl^{3+}$ give excellent correspondence with the existing correlation of rate constants for outer-sphere reactions of these same two reductants with a series of common oxidants.[18,19] On this basis we assign an outer-sphere mechanism to the V^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$ as highly probable. Two other arguments may be cited in support of this assignment. First if the reactions were inner sphere, then a 2-equivalent process might in this instance be expected to contribute as in the reduction of mercury(II). No such contribution is observed. Second chloride does not appear to be a suitable bridging ligand for V^{2+} reductions, since it has previously been demonstrated that the V^{2+} reductions of $Co(NH_3)_5X^{2+}$, $X^- = Cl^-$, Br^-, and I^-, are outer sphere, whereas with $X^- = F^-$ the reaction is inner sphere.[18] Vanadium(II) would seem to prefer hard rather than soft bridging ligands.

The $>10^4$ difference in rate constants for the V^{2+} reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$ at 25° warrants further comment. It has previously been noted that exchange reactions of $Pt(NH_3)_4^{2+}$ (in the presence of free Cl^-) with *trans*-$Pt(NH_3)_4Cl_2^{2+}$ and *trans*-$Pt(en)_2Cl_2^{2+}$ are approximately 10^3–10^4 times faster than those with $Pt(NH_3)_5Cl^{3+}$ and *cis*-$Pt(NH_3)_4Cl_2^{2+}$.[20] Although inner-sphere activated complexes, bonding Pt–Cl–Pt, are believed to be formed, the identity of the nonbridging trans ligand of the Pt(IV) reactant clearly has a marked effect on the rate. Electrons have to be accommodated in the d_{z^2} orbital of the Pt(IV) when reduction occurs, and cleavage of the Pt–NH_3 bond is also necessary. Both are more difficult to achieve when the trans ligand is NH_3. The same reasoning is expected to apply for the one-electron outer-sphere reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$ with a result that the latter reacts much more slowly. A difference in reduction potentials may also be relevant. Whereas the standard reduction potential for the $PtCl_6^{2-}$–$PtCl_4^{2-}$ couple (in 1 *M* HCl) is known (0.68 V),[21] that for $Pt(NH_3)_5Cl^{3+}$–$Pt(NH_3)_4^{2+}$ does not appear to have been measured. The charge product also favors the reaction of $PtCl_6^{2-}$.

Finally it is appropriate to comment on the Cr^{2+} and V^{2+} reductions of $Pt(NH_3)_5Cl^{3+}$ and the fact that the first but not the second of these reactions proceeds by a 2-equiv change. Chromium(IV) is unstable in aqueous solution and is more difficult to generate than vanadium(IV). Thus with the strong oxidant Tl(III) both Cr^{2+} [22] and V^{2+} [23] undergo 2-equiv changes, but with the milder oxidant Hg(II) only the V^{2+} reductant undergoes a 2-equiv change.[1,3] With $Pt(NH_3)_5Cl^{3+}$ as oxidant the opposite pertains and the mechanism of the reaction appears to be of overriding importance. With Cr^{2+} as reductant the intermediate Pt^{III}–Cl–Cr^{III} is presumably sufficiently long-lived to permit a 2-equiv change. With V^{2+} on the other hand the mechanism is outer sphere, and a 2-equiv change cannot occur within the short lifetime of the outer-sphere adduct involving the two reactants. The results obtained add considerable weight therefore to earlier suggestions that 2-equiv electron-transfer reactions are only tenable if an inner-sphere reaction path obtains.[1,24] At present the only possible exception to this would appear to be the thallium(I)–thallium(III) exchange, which it has been concluded proceeds by a 2-equiv change.[25] On this basis there are grounds for supposing that an inner-sphere mechanism should prevail. However, such a mechanism requires H_2O to function as a bridge for the dominant [H^+]-independent path,[26] and generally H_2O is a poor bridging ligand.[27]

Acknowledgment. We are grateful to the Ruder Bošković Institute, Zagreb, for a leave of absence (to A.B.). We thank the U.K. Science Research Council for a research studentship (to T.D.H.).

Registry No. V^{2+}, 15121-26-3; $PtCl_6^{2-}$, 16871-54-8; $Pt(NH_3)_5Cl^{3+}$, 18372-92-4; $Ru(NH_3)_6^{2+}$, 19052-44-9.

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Polarized Crystal Spectra of Potassium Tetrachloropalladate(II) and Potassium Tetrabromopalladate(II)

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Received March 24, 1975 AIC502117

Absorption spectra have been recorded for aqueous solutions and single crystals of K_2PdCl_4 and K_2PdBr_4. For both compounds ${}^1A_{2g}$ and ${}^1E_g$ peaks are not resolved in *a* polarization although the ${}^1A_{2g}$ peak has the much stronger vibrational structure at 15°K. For K_2PdCl_4 the ${}^1A_{2g}$ and ${}^1E_g$ states are assigned at 21,700 and 23,200 cm^{-1}, respectively, and for K_2PdBr_4 they are at 20,200 and 21,700 cm^{-1}. The ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ($M \leftarrow L\pi$) charge-transfer bands have surprisingly low intensity and are observed at 37,400 and 30,900 cm^{-1} for K_2PdCl_4 and K_2PdBr_4. The ${}^1B_{1g}$ transition appears to be hidden by the ${}^1A_{2u}$ transition in the *c* polarization. Weak spin-forbidden bands were observed in both polarizations for both compounds. For K_2PdBr_4 exceptional vibrational structure has been recorded at 15°K. Also, in K_2PdBr_4 two weak transitions at 37,000 and 43,200 cm^{-1} have been assigned as forbidden charge-transfer transitions.

Introduction

Electronic spectra of square-planar palladium complexes in solution have been available for some time.[1-4] In addition, polarized crystal spectra for K_2PdCl_4 were reported by Day et al.[5] and more recently by Francke and Moncuit (FM).[6] These experimental results have provided a stimulus for extensive theoretical treatments of these systems.[7-12] In spite of the numerous studies, controversies about the transition assignments have continued. In the previous experimental work, transition assignments have been based on vibronic and ligand field selection rules. These selection rules for D_{4h} have been recently summarized in a review of square-planar platinum(II) complexes.[13]

The spectral interpretations of K_2PdCl_4 and K_2PdBr_4 have been influenced by earlier investigations of K_2PtCl_4[14,15] and K_2PtBr_4.[16] All of the compounds are isomorphous and the