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Bis(ethylenediamine)palladium(II)-Catalyzed Interconversion of *trans*-Dichloro- and *trans*-Dibromobis(ethylenediamine)palladium(IV) Cations

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Received May 18, 1972

The kinetics of chloride replacement in *trans*-$Pd(en)_2Cl_2^{2+}$ by bromide to give *trans*-$Pd(en)_2Br_2^{2+}$ and bromide replacement in *trans*-$Pd(en)_2Br_2^{2+}$ by chloride to give *trans*-$Pd(en)_2Cl_2^{2+}$ have been studied by stopped-flow spectrophotometry. The reactions obey rate laws which contain two terms. Each contains a third-order term which is first order in entering halide, palladium(IV) substrate, and $Pd(en)_2^{2+}$. The third-order rate constant at 25° for the chloride replacement is 9.7×10^6 M^{-2} sec^{-1} ($\mu = 0.10\ M$), while that for the bromide replacement is 2.5×10^5 M^{-2} sec^{-1} ($\mu = 0.15\ M$). The third-order reactions are interpreted in terms of an inner-sphere ligand-transfer process. The second term in the rate law for the chloride replacement is second order and independent of palladium(II). The rate constant is 1.56×10^3 M^{-1} sec^{-1} (25°, $\mu = 0.10\ M$). The second-order reaction is attributed to a reductive attack on coordinated chloride by bromide. The second term in the rate law for the bromide replacement is first order, independent of both palladium(II) and chloride, with a rate constant of 1.42 sec^{-1} (25°, $\mu = 0.15\ M$). This term is interpreted as indicating a dissociative or dissociative interchange process. Spectrophotometric evidence is presented for the association of *trans*-$Pd(en)_2Br_2^{2+}$ and bromide to form an ion pair. An association constant is estimated to be $20 \pm 2\ M^{-1}$.

Introduction

Though the chemistry of octahedral palladium(IV) is commonly believed to be similar to its third-row congener platinum(IV),[1] ligand replacement reactions are poorly characterized and reaction mechanisms are unknown. This is in contrast to numerous studies on platinum(IV) complexes, from which the description of several important reaction paths have emerged.[2-4] One reason for the paucity of information on palladium(IV) is the sensitivity of many palladium(IV) complexes to reduction to palladium(II), which is by far the more common of the two oxidation states. Furthermore, palladium(IV) complexes are more labile than analogous platinum(IV) complexes making kinetic measurements more difficult.

The present paper reports some stopped-flow kinetic measurements on the halide replacement reactions eq 1 and 2 (en = ethylenediamine). The synthesis of the

$$trans\text{-}Pd(en)_2Cl_2^{2+} + 2Br^- \rightarrow trans\text{-}Pd(en)_2Br_2^{2+} + 2Cl^- \tag{1}$$

$$trans\text{-}Pd(en)_2Br_2^{2+} + 2Cl^- \rightarrow trans\text{-}Pd(en)_2Cl_2^{2+} + 2Br^- \tag{2}$$

trans-$Pd(en)_2X_2^{2+}$ (X = Cl, Br) cations was reported recently,[5] though it was necessary to modify the method in the present study. These cations are stable in aqueous solution long enough to characterize the replacement reactions. Further, these reactions are of particular interest for comparison with related reactions of platinum(IV) complexes. From previous work involving halide replacements in *trans*-$Pt(en)_2X_2^{2+}$ and similar complexes, an important reaction path has been characterized. This path involves catalysis by a suitable planar platinum(II) complex such as $Pt(en)_2^{2+}$.[2] The mechanism for these reactions is believed to involve an inner-sphere ligand-transfer process, which is believed to be generally applicable to metals which have two accessible oxidation states differing by two electrons and suitable coordination geometry. Thus, impetus was provided for determining whether this type of path was operative in palladium(IV) chemistry also.

Experimental Section

Preparation of Compounds. The starting material for the preparation of the palladium(IV) complexes was bis(ethylenediamine)-palladium(II) chloride, $[Pd(en)_2]Cl_2$, which was prepared according to the literature method.[6] *Anal.* Calcd for $[Pd(en)_2]Cl_2$: Pd, 35.76; C, 16.15; H, 5.42; N, 18.83. Found: Pd, 35.66; C, 16.15; H, 5.91; N, 18.80. All other chemicals were of reagent grade. Elemental analyses were performed in our laboratories and by Galbraith Laboratories, Inc., Knoxville, Tenn.

***trans*-Dichlorobis(ethylenediamine)palladium(IV) Bis(ethylenediamine)palladium(II) Nitrate, *trans*-$[Pd(en)_2Cl_2Pd(en)_2](NO_3)_4$.** The procedure described in the Russian literature[5] for the synthesis of $[Pd(en)_2Cl_2](NO_3)_2$ was followed exactly. Solid $[Pd(en)_2]Cl_2$ was treated with excess concentrated HNO_3. A dark green crystalline material resulted along with evolution of nitrogen oxides. The green crystals were collected, washed with ice water, absolute alcohol, and ether, and dried *in vacuo* overnight at room temperature. *Anal.* Calcd for $[Pd(en)_2Cl_2Pd(en)_2](NO_3)_4$: Pd, 27.56; C, 12.44; H, 4.17; N, 21.76. Found: Pd, 27.35; C, 12.49; H, 4.42; N, 21.76.

***trans*-Dichlorobis(ethylenediamine)palladium(IV) Bis(ethylenediamine)palladium(II) Perchlorate, *trans*-$[Pd(en)_2Cl_2Pd(en)_2](ClO_4)_4$.** This salt was prepared by dissolving the nitrate salt in aqueous solution and precipitating with cold 72% $HClO_4$. It was also prepared by dissolving $[Pd(en)_2]Cl_2$ in 72% $HClO_4$ and bubbling Cl_2 gas into the solution for 2 min. In each case dark green needlelike crystals were collected, washed with a minimum of ice water, absolute alcohol, and ether, and then dried *in vacuo* overnight at room temperature. *Anal.* Calcd for $[Pd(en)_2Cl_2Pd(en)_2](ClO_4)_4$: Pd, 23.08; C, 10.42; H, 3.49; N, 12.15. Found: Pd, 23.0; C, 10.24; H, 3.72; N, 12.10.

***trans*-Dichlorobis(ethylenediamine)palladium(IV) Perchlorate, *trans*-$[Pd(en)_2Cl_2](ClO_4)_2$.** Solid *trans*-$[Pd(en)_2Cl_2Pd(en)_2](ClO_4)_4$ was moistened with 0.10 *M* $HClO_4$. A solution of 0.20 *M* HCl saturated with chlorine was then added dropwise until all of the dark green solid dissolved. A few drops in excess was added to ensure a slight excess of chlorine. The resulting solution was cooled to ice-bath temperature and treated with an equal volume of cold 72% $HClO_4$. Absolute alcohol was then added to precipitate the product which appeared as light yellow-green platelets. The product was collected on a sintered-glass filter, washed with absolute alcohol, and dried *in vacuo* at room temperature overnight. Washing the product with ether caused some discoloration indicating some decomposition, so washing with this reagent was avoided. *Anal.* Calcd for $[Pd(en)_2Cl_2](ClO_4)_2$: Pd, 21.43; C, 9.68; H, 3.25; N, 11.29; Cl, 28.57. Found: Pd, 21.28; C, 9.66; H, 3.45; N, 11.10; Cl, 28.35.

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(1) See for example F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 1035 ff.

(2) W. R. Mason, *Coord. Chem. Rev.*, 7, 241 (1972), and references cited therein.

(3) L. I. Elding and L. Gustafson, *Inorg. Chim. Acta*, 5, 643 (1971), and references cited therein.

(4) L. E. Cox, D. G. Peters, and E. L. Wehry, *J. Inorg. Nucl. Chem.*, 34, 297 (1972).

(5) A. V. Babaeva and E. Ya. Khananova, *Russ. J. Inorg. Chem.*, 10, 1441 (1965).

(6) "Gmelins Handbuch der anorganischen Chemie," Vol. 65, 8th ed, Verlag Chemie, Weinheim/Bergstr., Germany, 1942, p 357.

Table I. Electronic Spectra: $10^{-3}\ \bar{\nu}$, cm^{-1} (ϵ, M^{-1} cm^{-1})

trans-[Pd(en)$_2$Cl$_2$](ClO$_4$)$_2$ [a]	24.6 (174) [c] 28.8 (943) 39.5 (33,700) 48.3 (22,700)
trans-[Pt(en)$_2$Cl$_2$]Cl$_2$ [b]	26.3 (∼20) [c] 30.1 (105) 38.0 (950)
trans-[Pd(en)$_2$Br$_2$]Br$_2$·2HBr [a]	23.8 (810) 34.8 (7700) [d]
trans-[Pt(en)$_2$Br$_2$]Br$_2$ [b]	27.0 (150) [a] 31.2 (1100) 42.2 (40,000)
[Pd(en)$_2$Cl$_2$Pd(en)$_2$](ClO$_4$)$_4$ [a]	24.6 (170) [c] 28.8 (973) 39.5 (33,600) 49.0 (25,700) [c]
[Pd(en)$_2$Br$_2$Pd(en)$_2$](ClO$_4$)$_4$ [a]	23.8 (505) 36.0 (8400)

[a] Solvent is 0.10 M HClO$_4$. [b] Data from ref 9; solvent is H$_2$O. [c] Shoulder; ϵ is for the value of $\bar{\nu}$ given. [d] Salt concentration 1.63×10^{-4} M.

***trans*-Dibromobis(ethylenediamine)palladium(IV) Bis(ethylenediamine)palladium(IV) Perchlorate, *trans*-[Pd(en)$_2$Br$_2$Pd(en)$_2$]-(ClO$_4$)$_4$.** A solution of [Pd(en)$_2$]Cl$_2$ in excess HClO$_4$ was treated with several drops of bromine with stirring, whereupon an immediate precipitate of bronze-colored crystals resulted. These crystals were collected, washed with ice water, absolute alcohol, and ether, and dried *in vacuo* at room temperature. *Anal.* Calcd for [Pd(en)$_2$Br$_2$Pd(en)$_2$](ClO$_4$)$_4$: Pd, 21.05; C, 9.51; H, 3.19; N, 11.09. Found: Pd, 21.27; C, 9.69; H, 3.24; N, 10.90.

***trans*-Dibromobis(ethylenediamine)palladium(IV) Bromide Di(hydrogen bromide), *trans*-[Pd(en)$_2$Br$_2$]Br$_2$·2HBr.** Solid [Pd(en)$_2$]Cl$_2$ was dissolved in a minimum of water and treated dropwise with a solution of bromine in HBr (approximately 1:3:9 Br$_2$-concentrated HBr-H$_2$O), whereupon an orange precipitate resulted immediately. This was collected by filtration, washed with absolute alcohol, and dried *in vacuo* at room temperature. *Anal.* Calcd for [Pd(en)$_2$Br$_2$]Br$_2$·2HBr: Pd, 15.02; C, 6.78; H, 2.56; N, 7.91; Br, 67.71. Found: Pd, 14.98; C, 6.74; H, 2.33; N, 7.86; Br, 67.4.

Spectral Measurements. Before rate measurements were made, the electronic spectra of the palladium(IV) complexes were determined using a Cary Model 1501 spectrophotometer. Solutions were prepared with 0.10 M HClO$_4$. No changes in the spectrum of *trans*-Pd(en)$_2$Cl$_2$$^{2+}$ were observed for periods up to a 0.5 hr, but small changes were noted in 10–15 min for *trans*-Pd(en)$_2$Br$_2$$^{2+}$. Consequently, fresh solutions were used within minutes of the dissolution of the solid compounds. The spectra of the mixed-valence compounds were nearly identical with the spectra of the simple palladium(IV) cations as expected since the absorptivities of the palladium(IV) complexes are much higher than those for Pd(en)$_2$$^{2+}$.

Measurements were also made on *trans*-[Pd(en)$_2$Br$_2$]Br$_2$·2HBr in solutions of various concentrations of bromide. The absorption between 30,000 and 45,000 cm^{-1} does not obey Beer's law, and marked changes in the spectra are noted as a function of bromide concentration. The absorbance changes are believed to be due to ion-pair formation. At high bromide ion concentration (>0.10 M) the absorbance appears to approach a limiting value. By estimating this limiting value graphically from a plot of absorbance *vs.* [Br$^-$] at a wavelength where a suitably large change occurs, the association constant for the ion-pair formation was calculated using eq 3. In eq 3, A is the measured absorbance at the selected wavelength

$$K = [A - A(\text{reactants})]/[A(\text{products}) - A][\text{Br}^-] \qquad (3)$$

for a given bromide concentration, while A(reactants) is the absorbance for *trans*-Pd(en)$_2$Br$_2$$^{2+}$ in the absence of added bromide at that wavelength, and A(products) is the estimated value of the limiting absorbance at the same wavelength. In view of the Beer's law failure noted above, eq 3 was applied only at constant palladium(IV) concentration. Values of K for five different bromide concentrations were self-consistent to within ±10%.

The spectrum of *trans*-Pd(en)$_2$Cl$_2$$^{2+}$ was unaffected by chloride ion up to concentrations of aproximately 0.10 M.

Kinetics. The kinetics of the halide replacement reactions were studied spectrophotometrically using a Durrum-Gibson stopped-flow spectrophotometer as described previously.[7] The ionic strength of the reaction mixtures was controlled at 0.10 M (NaClO$_4$) for reaction 1 and 0.15 M (NaClO$_4$) for reaction 2. In all experiments the halide concentration was in large excess compared to palladium(IV), and the Pd(en)$_2$$^{2+}$ was regenerated during the course of the reaction, so that under these conditions the kinetics are pseudo first order in palladium(IV). The palladium(IV) product of each reaction was identified by comparing spectra of infinite-time reaction mixtures with authentic samples of the *trans*-Pd(en)$_2$Cl$_2$$^{2+}$ and *trans*-Pd(en)$_2$Br$_2$$^{2+}$ cations. Under the conditions used in this study, the reactions appeared to go to completion.

Rate data were evaluated by a computer fit to an exponential function as described previously.[7] The standard deviations in the computed values of the pseudo-first-order constants, k_{obsd}, were 0.5–1.5% for data taken over 2–5 half-lives of the reaction. Separate kinetic experiments generally could be reproduced to within ±5%. Rate constants for reaction 1 were evaluated by constructing least-squares plots of k_{obsd}/[Br$^-$] *vs.* [Pd(II)]. These plots were linear, and the slope corresponds to the third-order rate constant k_3, while the intercept is the second-order constant k_2. The intercept value was within experimental error of the value of k_{obsd}/[Br$^-$] obtained in the absence of added palladium(II). Values of k_3 were self-consistent to within ±5%; the values of k_2 are of comparable precision. Rate constants for reaction 2 were evaluated by plotting k_{obsd} *vs.* [Pd(II)] at constant [Cl$^-$], or [Cl$^-$] at constant [Pd(II)]. The slope of these linear plots gives k_3[Cl$^-$] or k_3[Pd(II)], respectively, while the common intercept gives the value of k_1. The intercept values were within experimental error of k_{obsd} found in the absence of added palladium(II). Values of k_3 for reaction 2 were self-consistent to within ±4%, and the values of k_1 are of comparable precision.

Results

The synthetic procedure for the preparation of [Pd(en)$_2$]-(NO$_3$)$_2$ described by the Russian chemists[5] resulted in dark green [Pd(en)$_2$Cl$_2$Pd(en)$_2$](NO$_3$)$_4$, apparently a mixed-valence complex of palladium(II) and palladium(IV). Such complexes which result from incomplete oxidation are well known in platinum chemistry[8] and are believed to have chain-type structures with alternating M(II) and M(IV) as in structure I. A modified procedure involving more exhaustive oxidation of Pd(en)$_2$$^{2+}$ was developed and used in

$$\cdots \text{M}^{\text{II}}(\text{en})_2\text{-Cl-M}^{\text{IV}}(\text{en})_2\text{-Cl-M}^{\text{II}}(\text{en})_2\text{-Cl-M}^{\text{IV}}(\text{en})_2\text{-Cl} \cdots$$

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the present study to prepare the simple palladium(IV) cations. It is noteworthy that the mixed-valence compounds could be prepared deliberately by mixing solutions containing equimolar quantities of the *trans*-Pd(en)$_2$Cl$_2$$^{2+}$ or *trans*-Pd(en)$_2$Br$_2$$^{2+}$ and Pd(en)$_2$$^{2+}$ cations.

Table I presents electronic spectral data for the palladium(IV) compounds prepared in this study; spectral data[9] for the *trans*-Pt(en)$_2$X$_2$$^{2+}$ (X = Cl, Br) cations are included for comparison. Figure 1 illustrates typical changes observed for *trans*-Pd(en)$_2$Br$_2$$^{2+}$ in solutions of various concentrations of bromide. These changes are likely due to the interaction of the complex cation and bromide to form an ion pair, eq 4. Similar spectral changes have been observed[9-11] for re-

$$trans\text{-Pd(en)}_2\text{Br}^{2+} + \text{Br}^- \overset{K}{\rightleftharpoons} [trans\text{-Pd(en)}_2\text{Br}_2{}^{2+}, \text{Br}^-] \qquad (4)$$

lated platinum(IV) complexes such as *trans*-Pt(en)$_2$Br$_2$$^{2+}$ and *trans*-Pt(NH$_3$)$_4$Br$_2$$^{2+}$. Since the absorbance at 37,700 cm^{-1} appears to approach a limiting value at high bromide concentration for *trans*-Pd(en)$_2$Br$_2$$^{2+}$, an estimate can be made for the association constant K in eq 4. Values calculated from eq 3 are given in Table II. It should be noted, however, that the validity of these "constants" should be

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(7) W. R. Mason, *Inorg. Chem.*, 9, 2688 (1970).

(8) Reference 1, pp 1030–1031; ref 6, Vol. 68D, 1957, p 616 ff; ref 6, Vol. 68C, 1939.

(9) A. J. Poe, *J. Chem. Soc.*, 183 (1963).

(10) A. J. Poe and D. H. Vaughn, *J. Amer. Chem. Soc.*, 92, 7537 (1970).

(11) R. R. Rettew and R. C. Johnson, *Inorg. Chem.*, 4, 1565 (1965).

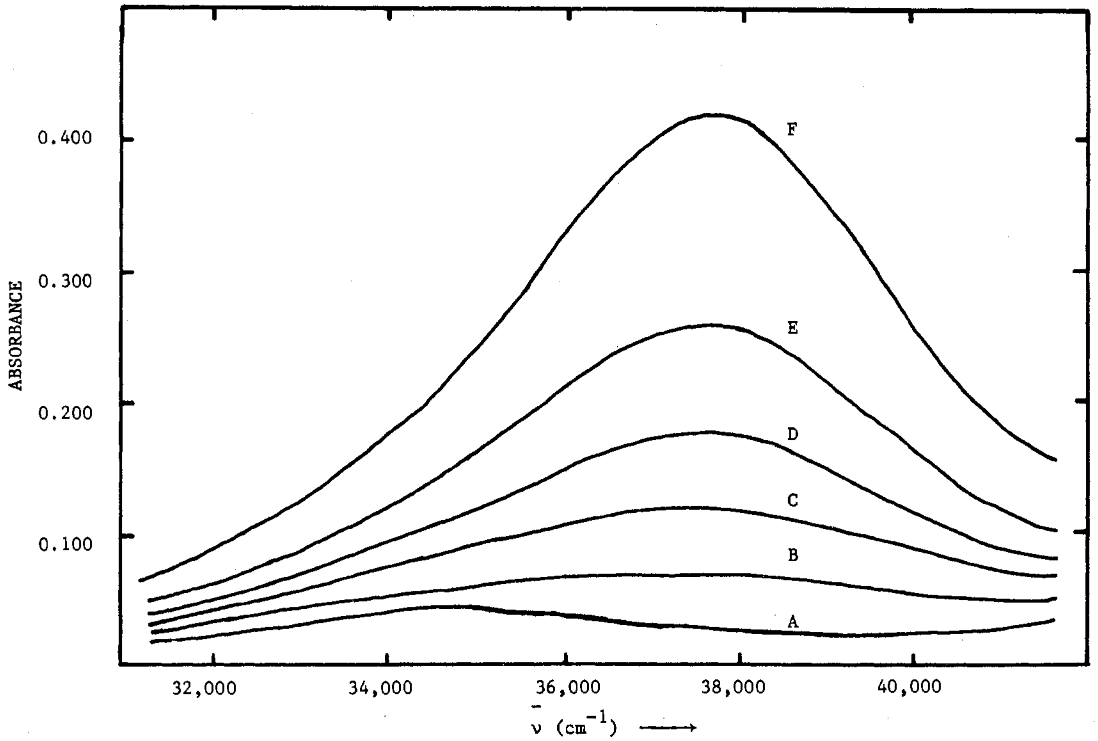

Figure 1. Absorption spectra of *trans*-$[Pd(en)_2Br_2]Br_2 \cdot 2HBr$. For all curves [Pd(IV)] = 2.1×10^{-5} *M*, $[HClO_4]$ = 0.10 *M*, and μ = 0.20 *M* ($NaClO_4$); 25°: A, [NaBr] = 0; B, [NaBr] = 0.0040 *M*; C, [NaBr] = 0.010 *M*; D, [NaBr] = 0.020 *M*; E, [NaBr] = 0.040 *M*; F, [NaBr] = 0.10 *M*.

Table II. Association Constants for *trans*-$Pd(en)_2^{2+}$ and Bromide

$[Br^-]$, *M*	Absorbance at 37,700 cm^{-1}	K_{calcd},[a] M^{-1}	$[Br^{-1}]$, *M*	Absorbance at 37,700 cm^{-1}	K_{calcd},[a] M^{-1}
0.100	0.410	22.8	0.010	0.115	20.2
0.040	0.253	17.7	0.004	0.063	20.3
0.020	0.172	18.5	0	0.021	

[a] At 25°; limiting absorbance 0.580; [*trans*-$Pd(en)_2Br_2^{2+}$] = 2.11×10^{-5} *M*, $[HClO_4]$ = 0.10 *M*, and μ = 0.20 *M* ($NaClO_4$).

viewed with caution since Beer's law failure was noted in the energy region where measurements were made. Nevertheless, the calculated constants probably fairly describe the system's behavior under the experimental conditions employed here.

Rate constants for reactions 1 and 2 are presented in Table III. The data for reaction 1 are consistent with the rate law in eq 5, where $k_2 = 1.56 \times 10^3\ M^{-1}\ sec^{-1}$ (25°, $\mu = 0.10\ M$). The data for reaction 2 are consistent with the rate law given in eq 6, where $k_1 = 1.42\ sec^{-1}$ (25°, $\mu = 0.15\ M$). The rates of both reactions were essentially independent of $[H^+]$ and increased slightly with increasing ionic strength over the limited range studied.

$$-d[trans\text{-}Pd(en)_2Cl_2^{2+}]/dt = [k_2 + k_3[Pd(en)_2^{2+}]][Br^-] \cdot [trans\text{-}Pd(en)_2Cl_2^{2+}] \quad (5)$$

$$-d[trans\text{-}Pd(en)_2Br_2^{2+}]/dt = [k_1 + k_3[Pd(en)_2^{2+}][Cl^-]] \cdot [trans\text{-}Pd(en)_2Br_2^{2+}] \quad (6)$$

Activation parameters were calculated from the temperature dependence of the rates. Values of ΔH^* and ΔS^* are tabulated in Table IV along with rate constants at 25°. Some data on related platinum(IV) reactions[11,12] are included for comparison.

Discussion

Although the structures of the $Pd(en)_2X_2^{2+}$ (X = Cl, Br) cations are not known definitely, it is presumed that they are trans complexes. This geometry is supported, first, by the similarity of the electronic spectra of the palladium(IV) complexes to the spectra of the *trans*-$Pt(en)_2X_2^{2+}$ (X = Cl, Br) cations. Second, the method of synthesis involves oxidations by halogen in halide solutions. For oxidations of platinum(II) complexes, this same method gives trans platinum(IV) complexes.[13] Third, the observation of a stereospecific palladium(II)-catalyzed path for halide replacement strongly suggests a trans geometry by analogy to platinum(II)-catalyzed halide replacements in platinum(IV) complexes.[2] All known examples of platinum(II)-catalyzed halide replacements in trans platinum(IV) substrates are stereospecific giving exclusively trans products. A single example of a catalyzed reaction involving a cis substrate gave a mixture of products.[14]

The prominent dependence of the rates of reactions 1 and 2 on $Pd(en)_2^{2+}$ can be rationalized in terms of a redox ligand-transfer process similar to that postulated for the numerous examples of platinum(II)-catalyzed substitutions in platinum(IV) chemistry.[2] This path is outlined in eq 7-10 for reaction 1 (the two en ligands bound to each metal have been omitted for clarity).

$$Pd^{2+} + Br^- \overset{fast}{\rightleftharpoons} Pd\text{-}Br^+ \quad (7)$$

$$Cl\text{-}Pd\text{-}Cl^{2+} + Pd\text{-}Br^+ \rightleftharpoons Cl\text{-}Pd\text{-}Cl\text{-}Pd\text{-}Br^{3+} \quad (8)$$

$$Cl\text{-}Pd\text{-}Cl\text{-}Pd\text{-}Br^{3+} \rightleftharpoons Cl\text{-}Pd^+ + Cl\text{-}Pd\text{-}Br^{2+} \quad (9)$$

$$Cl\text{-}Pd^+ \overset{fast}{\rightleftharpoons} Cl^- + Pd^{2+} \quad (10)$$

As noted for similar paths for platinum(IV) reactions,[2] the scheme outlined in eq 7-10 is consistent with the observed third-order

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(12) A. Peloso, *Gazz. Chim. Ital.*, **100**, 188 (1970).

(13) W. R. Mason, *Inorg. Chem.*, **10**, 1914 (1971); M. M. Jones and K. A. Morgan, *J. Inorg. Nucl. Chem.*, **34**, 259, 275 (1972).

(14) F. Basolo, M. L. Morris, and R. G. Pearson, *Discuss. Faraday Soc.*, **29**, 80 (1960).

Table III. Rate Data

trans-$Pd(en)_2Cl_2^{2+} + 2Br^- \rightarrow$ *trans*-$Pd(en)_2Br_2^{2+} + 2Cl^-$

$10^4[Pd(en)_2^{2+}]$, M	$10k_{obsd}$, sec^{-1}	10^6k_3, M^{-2} sec^{-1}	$10^4[Pd(en)_2^{2+}]$, M	$10k_{obsd}$, sec^{-1}	10^6k_3, M^{-2} sec^{-1}
	25.0°[a,b]			15.0°[a,j]	
0[c]	0.79		0[c]	0.50	
3.4	2.48	10.1	2.1	1.40	8.6
4.2	2.75	9.4	5.0	2.70	8.8
4.7	5.91[d]	9.2	11.3	5.46	8.8
4.7	12.2[e]	9.7		35.0°[a,k]	
6.2	7.8[d]	10.1			
6.2	15.4[e]	9.9	3.6	2.93	10.2
6.6	4.17	10.2	5.1	3.85	10.8
10.4	5.80	9.6	6.9	4.87	10.9
14.1	7.3	9.2	9.8	6.24	10.5
17.9	9.7	10.0			
3.8	2.40[f]	8.5			
4.0	2.66[g]	9.4			
5.1	4.94[h]	16.3			
5.1	4.32[i]	13.9			

trans-$Pd(en)_2Br_2^{2+} + 2Cl^- \rightarrow$ *trans*-$Pd(en)_2Cl_2^{2+} + 2Br^-$

$10^4[Pd(en)_2^{2+}]$, M	k_{obsd}, sec^{-1}	10^5k_3, M^{-2} sec^{-1}	$10^4[Pd(en)_2^{2+}]$, M	k_{obsd}, sec^{-1}	10^5k_3, M^{-2} sec^{-1}
	25.0°[l,m]			35.0°[l,p]	
0[c]	1.42		0[c]	2.93	
1.37	3.24	2.6	2.7	7.1	3.2
2.7	4.83	2.5	5.4	11.4	3.1
5.5	8.7	2.6	8.1	15.4	3.0
8.2	12.6	2.6		45.0°[l,q]	
13.7	19.2	2.4			
5.5	5.0[n]	2.5	2.7	12.6	4.1
5.5	3.16[o]	2.3	5.4	16.7	3.5
8.2	7.0[n]	2.6	8.1	21.6	3.5
8.2	4.16[o]	2.4			

[a] [*trans*-$Pd(en)_2Cl_2^{2+}$] = (4.5–6.1) × 10^{-5} M, [NaBr] = 5.00 × 10^{-3} M, [$HClO_4$] = 0.100 M, $\mu = 0.10$ M. [b] $k_2 = 1.56 \times 10^3$ M^{-1} sec^{-1}. [c] No added Pd(II). [d] [NaBr] = 1.00 × 10^{-2} M. [e] [NaBr] = 2.00 × 10^{-2} M. [f] [$HClO_4$] = 0.050 M. [g] [$HClO_4$] = 0.200 M, $\mu = 0.200$ M. [h] $\mu = 1.00$ M ($NaClO_4$). [i] $\mu = 0.50$ M ($NaClO_4$). [j] $k_2 = 1.00 \times 10^3$ M^{-1} sec^{-1}. [k] $k_2 = 2.20 \times 10^3$ M^{-1} sec^{-1}. [l] [*trans*-$Pd(en)_2Br_2^{2+}$] = (3.6–4.9) × 10^{-5} M, [NaCl] = 0.050 M; a correction was made for [Cl^-] resulting from the counterion of $Pd(en)_2^{2+}$; [$HClO_4$] = 0.100 M, $\mu = 0.15$ M ($NaClO_4$). [m] $k_1 = 1.42$ sec^{-1}. [n] [NaCl] = 0.025 M. [o] [NaCl] = 0.0125 M. [p] $k_1 = 2.93$ sec^{-1}. [q] $k_1 = 7.0$ sec^{-1}.

Table IV. Rate Constants at 25° and Activation Parameters

Rate constant (μ, M)	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}	Ref
trans-$Pd(en)_2Cl_2^{2+} + 2Br^- \rightarrow$ *trans*-$Pd(en)_2Br_2^{2+} + 2Cl^-$			
$k_3 = 9.7 \times 10^6$ M^{-2} sec^{-1} (0.10)	1.15 ± 0.11	−23 ± 1	This work
$k_2 = 1.56 \times 10^3$ M^{-1} sec^{-1} (0.10)	6.4 ± 0.7	−23 ± 2	
trans-$Pd(en)_2Br_2^{2+} + 2Cl^- \rightarrow$ *trans*-$Pd(en)_2Cl_2^{2+} + 2Br^-$			
$k_3 = 2.5 \times 10^5$ M^{-2} sec^{-1} (0.15)	3.1 ± 0.2	−23 ± 1	This work
$k_1 = 1.42$ sec^{-1} (0.15)	14 ± 2	− 9 ±6	
trans-$Pt(en)_2Cl_2^{2+} + 2Br^- \rightarrow$ *trans*-$Pt(en)_2Br_2^{2+} + 2Cl^-$			
$k_3 = 3.0 \times 10^2$ M^{-2} sec^{-1} (0.066)	6	−27	12
trans-$Pt(NH_3)_4Cl_2^{2+} + Br \rightarrow$ *trans*-$Pt(NH_3)_4ClBr^{2+} + Cl^-$			
$k_3 = 1.1 \times 10^2$ M^{-2} sec^{-1} (0.20)	8	−24	11
trans-$Pt(NH_3)_4ClBr^{2+} + Cl^- \rightarrow$ *trans*-$Pt(NH_3)_4Cl_2^{2+} + Br^-$			
$k_3 = 6.3$ M^{-2} sec^{-1} (0.20)	11	−20	11

kinetics provided eq 7 is a rapidly established equilibrium lying to the left and either eq 8 or eq 9 is assumed to be rate determining. The initial product from eq 7-10 would be *trans*-$Pd(en)_2ClBr^{2+}$, but a similar reaction sequence may be visualized for the second chloride replacement. The observed *trans*-$Pd(en)_2Br_2^{2+}$ product would be formed *via* the bromine-bridged $Cl-Pd-Br-Pd-Br^{3+}$ activated complex.

From studies on related platinum(IV) complexes it is known[2] that reactions involving a bromine bridge are faster than those involving a chlorine bridge by a factor of approximately 400:1, provided the entering, leaving, and in-plane ligands are the same for both cases. Thus, the observation of only the dibromo product for reaction 1 indicates that the second chloride replacement is faster than the first, and thus a similar reactivity order with respect to the bridging ligand must hold for palladium(IV) also. The third-order term in the rate law for reaction 2 and the observation of the dichloro product can be explained in a similar way. In this case, the first bromide replacement would involve a bromine-bridged activated complex and would be expected to be faster than the second replacement involving a chlorine bridge. The stopped-flow spectrophotometric observations were consistent with this expectation. A rapid ($T_{1/2} <$ 2 msec) change in the absorbance of the reactant *trans*-$Pd(en)_2Br_2^{2+}$ was followed by the slower change to give *trans*-$Pd(en)_2Cl_2^{2+}$, which was monitored for the kinetic measurements.

The relative reactivity of the palladium(IV) complexes *via* the catalyzed path is aproximately 32,000:1 (Table IV) compared to platinum(IV). This enhanced reactivity of palladium(IV) is due primarily to the 5 kcal mol^{-1} lower activation enthalpy and to a lesser extent to the slightly more positive activation entropy. The greater reactivity is likely a result of the lower stability of the *trans*-$Pd(en)_2X_2^{2+}$ substrate complexes. Thus, a smaller energetic perturbation is necessary to reach the transition state than for comparable platinum(IV) complexes. The activation is most certainly reductive in character, and considerable charge will be transferred to the palladium(IV) center in the formation of the bridge complex. The halogen-transfer redox process can also be viewed as a halonium ion transfer from one metal center to the other in eq 8 and 9. The formation of $Pd^{II}\cdot\cdot X^+$ from Pd^{IV}-X is expected to be more favorable than the comparable formation for platinum(IV).

The second term in the rate law eq 5 for reaction 1 is second order and independent of palladium(II). The second-order reaction to which it corresponds is characterized by a larger ΔH^* than that for the catalyzed path. Similar platinum(II)-independent reactions have been observed in connection with platinum(II)-catalyzed halide replacements for a variety of platinum(IV) substrates.[2] It has been suggested[10] that these platinum(II)-independent reactions are a result of a direct reductive attack of the entering halide on a coordinated halide of the platinum(IV) substrate. This may be viewed as a transfer of a halonium ion from the substrate to the entering halide giving a halogen in the slow step. A rapid reoxidation to give products is then visualized. Such a process may well be operative here for palladium(IV), since it is observed with the bromide entering ligand which would be more easily oxidized by Cl^+ than an entering chloride by Br^+ for example.

Reaction 2 exhibits a first-order term in the rate law eq 6, indicating a reaction path with a slow step independent of entering chloride and $Pd(en)_2{}^{2+}$. It is reasonable, though admittedly speculative, to ascribe this first-order path to a dissociative or dissociative interchange process of the reactive *trans*-$Pd(en)_2Br_2{}^{2+}$ substrate. In support of this suggestion, the entropy of activation is more positive (though still negative) than ΔS^* observed for the catalyzed path. The Pd^{IV}–Br bond is expected to be more easily ruptured in a purely dissociative process than Pd^{IV}–Cl since the bond energies are likely to be in the order $Pd^{IV}\text{–}Cl > Pd^{IV}\text{–}Br$ as for platinum(IV). Thus, for the *trans*-$Pd(en)_2Br_2{}^{2+}$ cation, this pathway can compete effectively with the catalyzed path.

Finally, the observed changes in the spectra of *trans*-$Pd(en)_2Br_2{}^{2+}$ as a function of bromide ion concentration are ascribed to ion-pair formation, eq 4. Accompanying the increase in absorptivity as the bromide concentration is raised, there is also a notable blue shift to 37,700 cm^{-1} of the charge-transfer band at 34,700 cm^{-1} in *trans*-$Pd(en)_2Br_2{}^{2+}$. This shift of the charge-transfer band, which is presumably ligand to metal in character, is consistent with a reductive interaction between bromide and the complex cation. Partial reduction of palladium(IV) will reduce the positive charge on the metal and therefore destabilize metal acceptor orbitals causing a blue shift for the ligand to metal charge-transfer band. A reasonable suggestion as to the structure of the ion pair might be

$$[Br\text{–}Pd(en)_2\text{–}Br\cdot\cdot\cdot Br]^+$$

It is worth noting that the association constants K for the numerous platinum(IV) complexes which exhibit similar behavior must be appreciably smaller than the value of $20 \pm 2\,M^{-1}$ estimated here for *trans*-$Pd(en)_2Br_2{}^{2+}$, since no evidence of limiting absorbance values has been found.

Registry No. Bis(ethylenediamine)palladium(II) chloride, 16483-18-4; *trans*-dichlorobis(ethylenediamine)palladium(IV) bis(ethylenediamine)palladium(II) nitrate, 9076-08-8; *trans*-$[Pd(en)_2Cl_2Pd(en)_2][ClO_4]_4$, 9047-90-9; *trans*-$[Pd(en)_2Cl_2][ClO_4]_2$, 36245-59-7; *trans*-$[Pd(en)_2Br_2Pd(en)_2][ClO_4]_4$, 9076-07-7; *trans*-$[Pd(en)_2Br_2]Br_2\cdot 2HBr$, 36223-03-7; Br^-, 24959-67-9; Cl^-, 16887-00-6.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Polarized Crystal Spectra of Yellow Cossa's Salt, Potassium Trichloroammineplatinate(II) Monohydrate, and Red Cossa's Salt

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Received May 24, 1972

Evidence is provided that the yellow Cossa's salt is $KPt(NH_3)Cl_3\cdot H_2O$. The red Cossa's salt apparently contains small quantities of the octahedral ions of platinum(IV), $Pt(NH_3)Cl_5{}^-$, which replace the planar ions in the crystals. Crystal spectra for the yellow salt at 300 and 15°K are reported, and the transition assignments are discussed in terms of selection rules for ligand field and vibronic excitations. The temperature dependence of spectra for a red crystal indicate a dipole-allowed transition with its polarization in the stacking direction at 23,800 cm^{-1}. The new compound $K_2[Pt(NH_3)Cl_3][Pt(NH_3)Cl_5]\cdot 2H_2O$ is reported which has alternately stacked planar Pt^{II} and octahedral Pt^{IV} complex anions and a very high absorption for polarization in the stacking direction. It is proposed that the band at 23,800 cm^{-1} in the red crystal constitutes a mixed-valence electron-transfer transition.

Introduction

Polarized crystal spectra in the d ← d region of K_2PtCl_4 have indicated that the absorption of the $PtCl_4{}^{2-}$ ion in the crystal resembles very closely its solution spectrum.[1] The $PtCl_4{}^{2-}$ ion occupies a position of full D_{4h} symmetry in the crystal, and the ions stack along the c axis of the tetragonal crystal with 4.14-Å separations.[2] With its center of symmetry the d ← d transitions are forbidden and can presumably occur only by means of a vibronic mechanism whereby an asymmetric vibration serves as a perturbation which mixes in asymmetric wave functions. According to the vibronic selection rules for $PtCl_4{}^{2-}$, the transition ${}^1A_{2g} \leftarrow {}^1A_{1g}$ ($d_{x^2-y^2} \leftarrow d_{xy}$) is forbidden in z-c polarization and can therefore be unequivocally identified in the polarized crystal spectra. In addition, the spectra at low temperatures confirmed the vibronic model since the absorption intensities were strongly reduced. The better resolution at liquid helium temperatures revealed two additional absorption bands.

Recently, polarized spectra for the molecular crystals of dichloro(ethylenediamine)platinum(II) were reported.[3] These nearly planar molecules do not possess a center of symmetry. Therefore, many transitions may contain a nonzero transition dipole, and selection rules must be based upon the symmetry of the molecule or the "ligand fields." However, these molecules stack with separations of only 3.39 Å and the intermolecular interactions introduce major modifications into the spectra. Indeed, certain absorption

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