Mechanisms of Reactions of Binuclear Complexes. II.[1,2]
Preparation of a Diamine-Bridged Complex of Platinum(II)
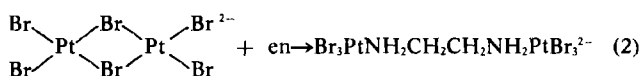
M.M. Muir and E.M. Cancio

The rate of reaction of ethylenediamine with the halogen-bridged binuclear complex, $[(C_2H_5)_4N]_2[Pt_2Br_6]$, was measured in acetone. The product was found to be the ethylenediamine-bridged complex, $[(C_2H_5)_4]_2[Br_3PtNH_2CH_2CH_2NH_2PtBr_3]$. The rate law was like that for cleavage reactions of this complex: rate = $(k_1 + k_2[en])[Pt_2Br_6]$. Evidence for an intermediate with one halogen bridge, obtained by attack by one of the amine groups on a platinum to cleave the first bridge, is discussed.

Introduction

The rates of cleavage of halogen-bridged complexes of platinum(II) have been studied with amines[3] and olefins.[1] Symmetrical cleavage was observed for all monodentate reagents, but with the bidentate olefin, 1,5-cyclooctadiene, the cleavage was unsymmetrical:

$$(1)$$
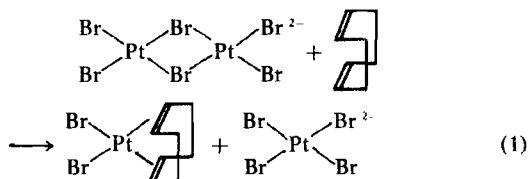
It seemed of interest to examine reactions of the complex with bidentate amines to see if reactions similar to (1) always occurred. The rates of reaction of the complex with ethylenediamine, en, were measured in acetone. The reaction was:

$$(2)$$

Reactions with several other amines were also examined.

Experimental Section

Materials. Ethylenediamine was digested with sodium hydroxide on a steam bath for a day, refluxed

over sodium for two hours, and distilled (bp, 116°). Ethanolamine was given a preliminary distillation followed by several washings with ether. It was then dried over Drierite and magnesium sulfate and fractionally distilled under nitrogen (bp, 170°). Acetone was dried over potassium carbonate for several days and fractionally distilled from Drierite (bp, 56°).

Complexes. $[(C_2H_5)_4N]_2[Pt_2Br_6]$ was prepared by the method of Harris *et al.*[4] $[(C_2H_5)_4N][Pt(NH_2CH_2CH_2OH)Br_3]$ was prepared by the addition of 1 ml of a 0.266 M acetone solution of ethanolamine to an acetone solution of 0.150 g of $[(C_2H_5)_4N]_2[Pt_2Br_6]$. After two days the solution was taken to dryness to yield a brownish oil. When this was treated with ether, a yellow-brown solid formed. *Anal.* Calcd for $C_{10}H_{27}N_2OBr_3Pt$: Pt, 31.2. Found: Pt, 31.2. $[(C_2H_5)_4N]_2[Br_3PtNH_2CH_2CH_2NH_2PtBr_3]$ was prepared by the addition of 1 ml of a 0.221 M solution of ethylenediamine in acetone to an acetone solution of 0.250 g of $[(C_2H_5)_4N]_2[Pt_2Br_6]$. After thirty hours the reaction mixture showed no further spectral change and was taken to dryness. The resulting brownish oil was treated with ether and cooled to 0 °C. Shiny orange crystals appeared. Evaporation of the ether gave dark orange powder. *Anal.* Calcd for $C_{18}H_{48}N_4Br_6Pt_2$: Pt, 32.8. Found: Pt, 32.5; Λ_M, 111 ohm^{-1} cm^2 mole^{-1} for $1 \times 10^{-3} M$ solution in DMF.

Rates of Reaction. Reactions were followed spectrophotometrically as previously described.[1] An excess of amine was used to provide pseudo first-order conditions. It was found to be necessary to use freshly distilled amine. The absorbance of the final reaction mixture remained stable for more than ten half-lives, and the pseudo first-order rate constants, k_{obs}, were obtained from plots which were linear for several half-lives. Products were confirmed by comparison of the spectrum of the final reaction mixture with the spectrum of the expected product.

Analyses were done by ignition of the samples to platinum metal. Molar conductance was measured using a Beckman Model 16 B2 bridge and dip-type cell with a cell constant of 1.054 cm^{-1}. Known compounds of similar size and charge type were measured in the same solvent for comparison with the measurement on the new complex. Infrared spectra of solid compounds in potassium bromide discs were obtained

(1) Paper I. M. M. Muir and E. M. Cancio, *Inorg. Chim. Acta.*, **4**, 565 (1970).
(2) Taken from the thesis submitted by E. M. C. to the University of Puerto Rico in partial fulfillment of the requirements for the degree M. Sc.
(3) R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc.*, **88**, 2163 (1966).
(4) C. M. Harris, S. E Livingstone, and N. C. Stephenson, *J. Chem. Soc.*, 3697 (1958).

on a Perkin Elmer Model 237 spectrophotometer. The apparent molecular weight in acetone of the complex, determined by isothermal distillation with an apparatus similar to that of Wilson et al.,[5,6] was reasonable although the precision of the measurements was poor. Compounds of similar charge and molecular weight were used for calibration.

Results and Discussion

The rate expression, found by plotting k_{obs} against the concentration of ethylenediamine, was the same as that reported previously for cleavage of the complex with monoamines[3] and with olefins:[1]

$$\text{rate} = k_{obs}[\text{Pt}_2\text{Br}_6] \qquad (3)$$

$$k_{obs} = k_1 + k_2[\text{en}] \qquad (4)$$

The same expression was obtained with the monodentate ethanolamine. Values of k_1, the intercept, were small and therefore difficult to determine accurately, but they fell within the range of 10^{-4} to 10^{-5} previously reported for the same solvent.[1,3] Values of k_2, the slope, are given in Table 1.

Table I. Second Order Rate Constants for Reactions of $\text{Pt}_2\text{Br}_6{}^{2-}$ with Amines in Acetone

Temp., °C	Amine	$k_2, M^{-1} \sec^{-1}$ [a]
25.0	pyridine [b]	0.088
25.0	piperidine [b]	0.48
24.4	ethanolamine	0.34±0.04
24.4	ethylenediamine	0.40±0.02
33.4		0.70±0.02
13.9		0.29±0.02

[a] Deviations are standard deviations, from a least squares analysis of the data. [b] Values taken from reference 3.

The close similarity of k_2 for ethylenediamine to the k_2 values for other aliphatic amines, particularly to that for the sterically similar ethanolamine, implies that the rate determining step in the reaction of the complex with ethylenediamine is the same as that for cleavage by monoamines. The rate determining step, which leads to a binuclear intermediate with one halogen bridge, can occur by the two paths shown below. Either solvent or ethylenediamine can attack one platinum from above or below the plane to form a transition state in which that platinum atom is five coordinated.
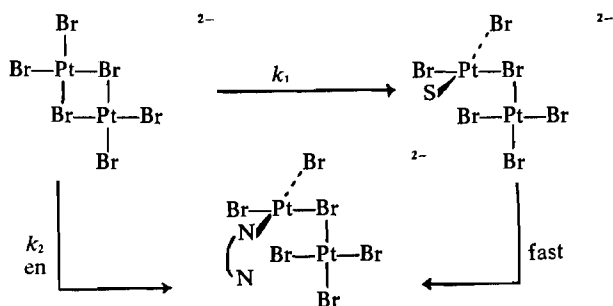
The enthalpy of activation, ΔH^*, for the second order reaction with ethylenediamine was 7.2 kcal/mole. The entropy of activation, ΔS^*, was -36 eu. These values are comparable to the values of 10 kcal/mole and -33 eu for the second order reaction of the complex with pyridine.[7] This is added evidence that the rate determining step is similar for the two reactions.

The singly-halogen-bridged intermediate has several possible paths for subsequent reaction. Ethylenediamine normally forms chelated complexes and might be expected to chelate rapidly after the cleavage of the first bridge. This chelation would cause the cleavage of the second bridge and would yield two products, PtenBr_2 and $\text{PtBr}_4{}^{2-}$, as shown in scheme I below. The $\text{PtBr}_4{}^{2-}$ could undergo further reaction with ethylenediamine at a slower rate. It is evident that scheme I is not followed, since the spectrum of the final reaction mixture does not correspond to the spectrum of PtenBr_2, of $\text{PtBr}_4{}^{2-}$, or to a mixture of the two. The kinetics showed no subsequent slow reaction. The unsymmetrical cleavage of scheme I was observed, however, for the diolefin, 1,5-cyclooctadiene.[1]
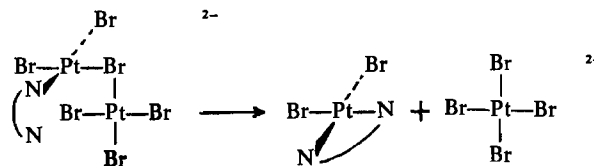
Scheme 1.

A second possibility is that the second bridge is cleaved, by solvent or amine, before chelation of the coordinated ethylenediamine could occur, with subsequent reactions to give PtenBr_2, as in scheme II. Since the expected products were not obtained, scheme II can also be discarded.

Scheme 2.

The products of scheme II would also be obtained if chelation of the first ethylenediamine occurred without cleavage of the second bridge, to give a singly-halogen-bridged intermediate with one five-coordinate platinum(II), $\text{Br}_2\text{N} \frown \text{NPtBrPtBr}_3{}^{2-}$. Since the products of scheme II were not observed, this five-coordinate intermediate is also unlikely.

(5) A. Wilson, L. Bini, and R. Hofstader, Anal. Chem., 33, 135 (1961).
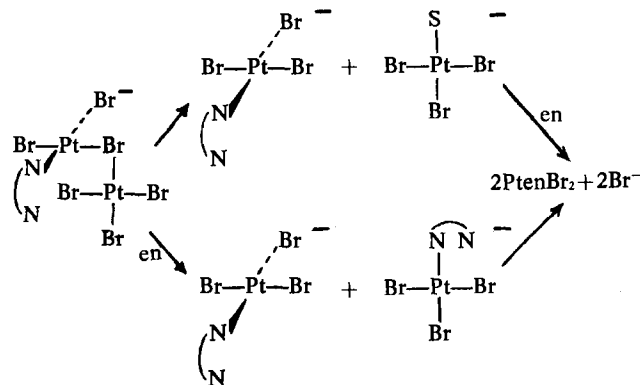(6) Details of the apparatus will be described elsewhere.

(7) M. M. Muir, Ph. D. Dissertation, Northwestern University, Evanston, Illinois, 1965.

If scheme II is not followed, the singly-bridged intermediate apparently lasts long enough to allow scheme III, in which after the initial cleavage the second Pt^{II} is attacked by the free end of the coordinated ethylenediamine. Examination of molecular models shows this is sterically reasonable. The attack on the second platinum cleaves the second halogen bridge and gives a binuclear species with a bridging ethylenediamine. This product has been isolated and characterized.
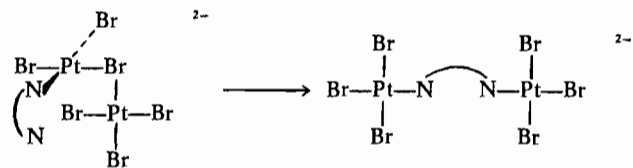
Scheme 3.

The visible-UV spectrum of the product corresponds to spectra of complexes of the type $Pt(amine)Br_3^-$. Since no further reaction is observed, the reaction product is not $Br_3PtN\frown N^-$, which would be produced by scheme II, but which should react to give chelated product.

Although ethylenediamine usually chelates, there are reports of complexes with bridging ethylenediamine, so the above complex is not unreasonable. Truter and Cox[8] have reported X-ray data for a complex of Pt^{II} with bridging ethylenediamine. Helman[9] synthesized the complex
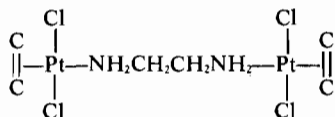
which was further characterized by Powell and Sheppard.[10] Since the latter authors reported a significant difference in the infrared spectra of complexes with chelated and with bridging ethylenediamine,[10] the infrared spectra of $[(C_2H_5)_4N]_2[Br_3PtenPtBr_3]$, PtenBr$_2$, and $[(C_2H_5)_4N]Br$ were compared. The data listed in Table II are very similar to that reported by Powell and Sheppard.[10] The much simpler spectrum for the bridged complex, after neglecting bands due to the cation, is in agreement with the higher symmetry possible for bridging ethylenediamine than for chelating ethylenediamine.

Attempts to follow reactions of $Pt_2Br_6^{2-}$ with other bidentate amines were not successful. Reactions with 4-aminopyridine gave a finely dispersed solid in the

Table II. Infrared Absorption Frequencies from 750 to 1600 cm^{-1} for Complexes with Ethylenediamine

$[(C_2H_5)_4N]_2[Br_3PtenPtBr_3]$ [a]	PtenBr$_2$
1548 m	1550 s
1452 m	1447 m
	1453 m
1376 w	1375 m
	1360 w
1260 w	1305 w
	1280 m
1240 w	1240 w
	1180 m
	1125 m
1100 m	1110 m
	1060 s
	1005 vw
900 m	940 vw
	905 vw
	905 m

[a] Frequencies which occurred in the spectrum of tetraethylammonium bromide were identified with the cation and are not listed above for the bridged complex.

spectrophotometer cell during the reaction. Since 4-aminopyridine should form bridges readily the precipitate is possibly a polymeric diamine-bridged material. Reactions with 3-aminopyridine, 2-aminopyridne, and 2,2'-bipyridyl did not give stable final reaction mixtures or linear pseudo first-order kinetic plots. It may be that both bridging and chelation were occurring. Further work with other bidentate ligands should prove of interest.

The formation of the ethylenediamine-bridged complex following cleavage of the initial halogen bridge is further evidence that the intermediate with one halogen bridge exists, since it seems unlikely that the diamine bridged product would be obtained if cleavage of the two halogen bridges occurred simultaneously. This is of significance in view of the work on exchange recations of Pt^{II} complexes in which singly-bridged intermediates have been postulated.[11,12]

The mechanism discussed above suggests that complexes with a variety of bridging bidentate ligands could be prepared from halogen-bridged binuclear complexes. The properties of such complexes may increase understanding of reactions involving binuclear complexes.

(8) M. R. Truter and E. G. Cox, *J. Chem. Soc.*, 948 (1956).
(9) A. D. Helman, *Comp. rend. sci. U.R.S.S.*, 38, 243 (1943).
(10) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 3089 (1959).

(11) J. E. Teggins, D. R. Gano, M. A. Tucker, and D. S. Martin, Jr., *Inorg. Chem.*, 6, 69 (1967).
(12) J. E. Teggins and D. S. Martin, Jr., *Inorg. Chem.*, 6, 1003 (1967).