Gordon[2] studied the effect of the perchloric acid concentration of 0.05–0.5 M on the reaction of iron(II) ion with ferriin and found that the rate decreased with increasing acidities. They have also explained this effect by postulating the formation of $\mathrm{HFe(phen)_3}^{4+}$. The rate of oxidation reaction of solvents of water, methanol, and ethanol by ferriin becomes sluggish with increasing acidities. In particular, it is of interest to note that ferriin becomes extremely stable in 11 M perchloric acid and only slowly oxidizes even iron(II) ion.[6] A strong association shell between $\mathrm{Fe(phen)_3}^{3+}$ and $\mathrm{ClO_4}^-$ may inhibit iron(II) ion to approach to the ferriin molecule.

Registry No. $\mathrm{Fe(phen)_3}^{3+}$, 13479-49-7; I^-, 20461-54-5; Fe^{2+}, 15438-31-0.

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Solution Chemistry of Silver Porphyrins. 1. Demetalation[1]

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Kinetics of the reaction between a water-soluble silver(II) porphyrin and nitric acid were investigated. In salt solutions, where the predominant species is dimeric, the reaction is first order in porphyrin concentration and first order in hydrogen ion concentration. In 25% methanolic solutions, where the predominant porphyrin species is monomeric, the reaction is found to be second order in porphyrin and first order in hydrogen concentration. Under both conditions, the product solution consisted of equimolar amounts of silver(III) porphyrin and dication of the metal-free porphyrin. A probable mechanism involving disproportionation of silver(II) is proposed.

Introduction

Chemistry of higher oxidation states of silver has been a subject of considerable interest to inorganic chemists. In aqueous solution the di- and trivalent states of silver are highly reactive and unstable. Many catalytic activities of silver(I) have been explained in terms of the involvement of these oxidation states.[2] Recently several coordination compounds of these higher states of silver with N-donor ligands have been synthesized and characterized.[3] Though the silver(II) complexes of porphyrins have been known for a long time, their aqueous solution chemistry has not been investigated. Results of such a study that we have undertaken comprise this series of articles.

Based on the ease with which a given metal ion is replaced by protons when the respective metalloporphyrin is placed in acids of varying concentration, an order of acid stability has been devised:[4] Pt(II) > Pd(II) > Ni(II) > Co(II) > Ag(II) > Cu(II) > Zn(II) > Mg(II) > $(\mathrm{Na^{I}_2})$ > $(\mathrm{Ag^{I}_2})$. Even those metalloporphyrins which are unstable toward acids undergo demetalation on reduction.[5] In aqueous solution zinc(II) and magnesium(II) porphyrins have been the subject of all the kinetic studies of this reaction.[6] The general rate law for this reaction in water appears to be rate = $k[\mathrm{MP}]\cdot[\mathrm{H^+}]^2$. A unique mode of demetalation observed for tetrakis(*p*-sulfonatophenyl)porhinatosilver(II) ($\mathrm{Ag^{II}TPPS}$) (Figure 1) is reported here.

Experimental Section

Tetraphenylporphine was synthesized by the method of Adler et al.[7] and sulfonated.[8] Chemicals such as $\mathrm{HNO_3}$ (AR Grade, Mallinckrodt), $\mathrm{NaNO_3}$ (AlFA Products), methanol (North-Strong), silver acetate (reagent grade, Allied Chemical), and potassium persulfate (Baker Analyzed) were used as obtained.

A Beckman Model CIII Acta UV–visible spectrophotometer was used for spectral studies. Kinetic studies were carried out employing a Durrum Model D110 stopped-flow spectrophotometer, thermostated at 30.0 ± 0.1 °C. Kinetics of the disappearance of the silver porphyrin were monitored at 412 nm ($\lambda_{\max}$ of the dimer) for reactions in water solutions and at 421 nm ($\lambda_{\max}$ of the monomer) for reactions in 25% methanolic solutions. Pseudo-first-order rate constants were obtained either from the slope of a plot of $\ln (A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbances of the solution at time "t" and at the end of the reaction, or by using a nonlinear least-squares program. These plots were linear over at least 3 half-lives. The pseudo-second-order rate constants were obtained by computation from the slope of a plot of $1/A_t$ vs. time, where A_t is the absorbance of the solution at time "t". The rate constant, k_{obsd}, is equal to the product of the slope × light path length × change in molar extinction coefficient. The changes in molar extinction coefficients were $2.03 \times 10^5\ \mathrm{M^{-1}\ cm^{-1}}$ at 421 nm in 25% methanolic solution and $9.02 \times 10^4\ \mathrm{M^{-1}\ cm^{-1}}$ at 412 nm in water solutions. The rate constants for duplicate runs were found to deviate less than 5%. Magnetic susceptibilities were determined in solution by the method of Evans[9] and in the solid state by the Faraday method.

Synthesis of $\mathrm{Ag^{II}TPPS}$. In a 150-mL beaker, 1.0 g $\mathrm{Na_4TPPS}$ was dissolved in 50 mL of water and heated. Little more than twice the stoichiometric amount of silver(I) acetate was added with stirring to the porphyrin solution, when it was about to boil and the solution was set aside to cool. In about 30 min, the solution was filtered, passed through a column (30 × 2 cm) of cation-exchange resin, Dowex 50W-X8 in sodium form, and evaporated to dryness. The crude product was Soxhlet extracted with methanol, precipitated from the methanolic solution by two volumes of acetone, filtered, and dried in an oven at 100 °C for 30 min. Anal. Calcd for $\mathrm{C_{44}H_{24}N_4S_4O_{12}Na_4Ag\cdot 10H_2O}$: C, 40.37; H, 3.36; N, 4.28; S, 9.79. Found: C, 40.37; H, 3.07; N, 3.95; S, 9.92. Molecular weight calculated for the above formula is 1308. Molecular weight determined by demetalation after reduction is 1310. The number of water molecules was chosen to fit the analytical data. Magnetic moment is 1.76 μ_{B}.

Synthesis of $\mathrm{Ag^{III}TPPS}$. In a 250-mL beaker, 1.2 g of pure $\mathrm{Ag^{II}TPPS}$ was dissolved in 50 mL of water. The solution was made slightly alkaline with a few drops of dilute (0.1 M) sodium hydroxide solution. The solution was heated to boil, 0.15 g of potassium persulfate was added to the solution, and the mixture was constantly stirred while the heating continued. Intermittently a few drops of the solution were tested spectrophotometrically for completion of oxidation. Incomplete

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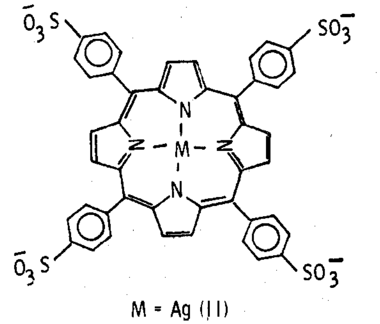

Figure 1. Tetrakis(*p*-sulfonatophenyl)porphinatosilver(II).

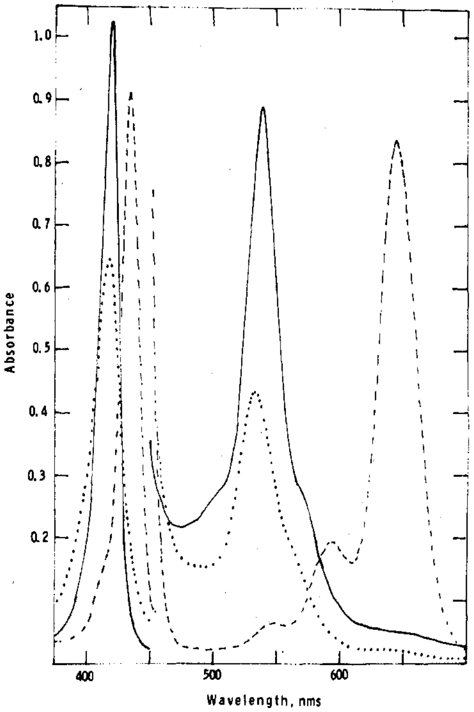

Figure 2. Spectra of $Ag^{II}TPPS$ (—), $Ag^{III}TPPS$ (···), and H_4TPPS^{2+}, (- - -). (Absorbance scale in the 375–450-nm region is 10 times that in the 450–700-nm region.) (See ref 10.)

reaction is indicated by a spectrum which is a composite of silver porphyrin and the dication form of the porphyrin. After about 15 min, if the reaction was still incomplete, an additional 50-mg portion of persulfate was added to complete oxidation. When the reaction was complete (about 10 min after the second addition) the solution was cooled and passed through a column (30 × 2 cm) of cation-exchange resin, Dowex 50W-X8, in sodium form. The effluent was concentrated to 20 mL by evaporation and cooled, and 80 mL of acetone was added with continuous stirring. The $Ag^{III}TPPS$ precipitated as a fine powder. It was filtered on a sintered funnel, washed with acetone, and dried to a constant weight in a vacuum desiccator. Anal. Calcd for $C_{44}H_{24}N_4S_4O_{12}Na_3Ag{\cdot}6H_2O$: C, 43.53; H, 2.97; N, 4.62; S, 10.55. Found: C, 42.91; H, 3.19; N, 3.99; S, 10.39. The compound was diamagnetic. The number of water molecules was chosen to fit the analytical data. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

Results and Discussion

In Figure 2, the spectra of $Ag^{II}TPPS$, $Ag^{III}TPPS$, and the dication H_4TPPS^{2+} are presented.[10] In our earlier study[11] we found that those metalloporphyrins which contain a four-coordinated metal ion in the center and anionic substituents at the periphery tend to dimerize in water. One of the porphyrins we found to dimerize was $Ag^{II}TPPS$. In Figure 3, the absorbances of the $Ag^{II}TPPS$ solution at varying salt concentrations are presented. At an ionic strength of 0.4 F, the $Ag^{II}TPPS$ exists completely as a dimer. The reaction between this dimeric $Ag^{II}TPPS$ and acids was investigsted over a hydrogen ion concentration range of 1.0×10^{-3} to 2.0×10^{-1} M at an ionic strength of 0.4 F ($NaNO_3$). Under these conditions[12] the $Ag^{II}TPPS$ undergoes a fast first-order reaction followed by a relatively slower second-order reaction. In Figure 4, a plot of the observed pseudo-first-order rate constants k_0 vs. the H^+ is presented. This reaction is first order in both the dimer and the hydrogen ion concentrations. Thus the rate law for this reaction is

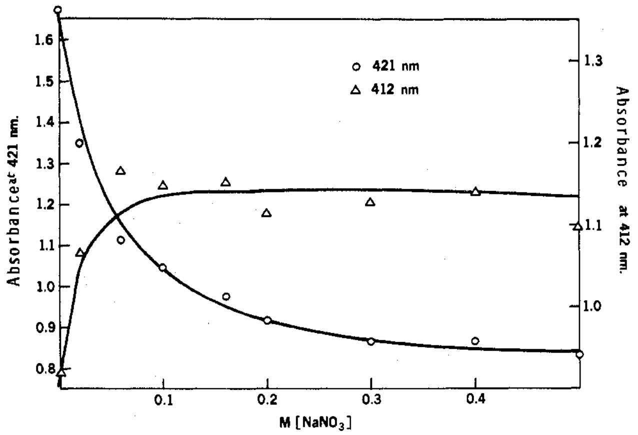

Figure 3. Changes in the absorbance of the $Ag^{II}TPPS$ solution as a function of the salt concentration.

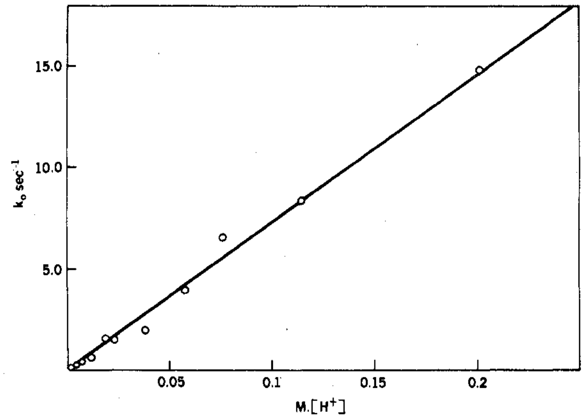

Figure 4. Dependence of the observed pseudo-first-order rate constants, k_{obsd}, for the reaction of dimeric $Ag^{II}TPPS$ on concentrations of nitric acid.

Table I. The Observed Pseudo-Second-Order Rate Constants for the Slower Process in the Reaction between Nitric Acid and $Ag^{II}TPPS$

$[H^+]$, M	$10^{-4}k_{obsd}$, $M^{-1}\ s^{-1}$	$[H^+]$, M	$10^{-4}k_{obsd}$, $M^{-1}\ s^{-1}$
0.2017	20.85	0.05709	5.910
0.1522	15.99	0.03806	2.790
0.1142	13.89	0.02284	2.011
0.07612	6.870	0.01903	1.854

$$\text{rate} = \mathrm{d}[(Ag^{II}TPPS)_2]/\mathrm{d}t = k_1'[(Ag^{II}TPPS)_2][H^+]$$

The observed pseudo-second-order rate constants for the slower process are listed in Table I. This slower process is also first order in $[H^+]$.

In order to verify the nature of this slower pseudo-second-order reaction the following experiments were carried out. As it is known that addition of nonaqueous solvents such as methanol or acetone to a solution of porphyrin prevents dimerization,[13] the reaction was carried out in 25% methanolic solution. Under these conditions only one pseudo-second-order reaction was observed. In Figure 5 the observed pseudo-

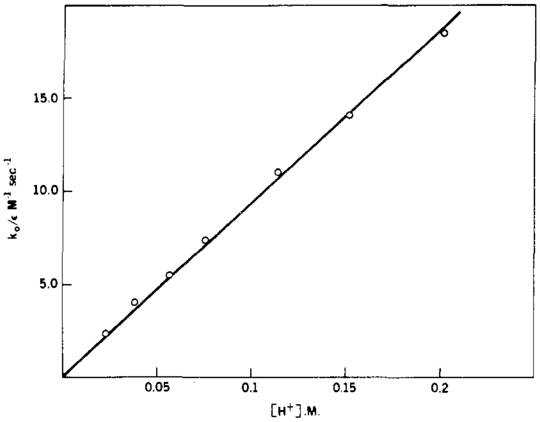

Figure 5. Variation of the observed pseudo-second-order rate constants for the reaction of monomeric $Ag^{II}TPPS$ with various concentrations of nitric acid in 25% methanolic solution.

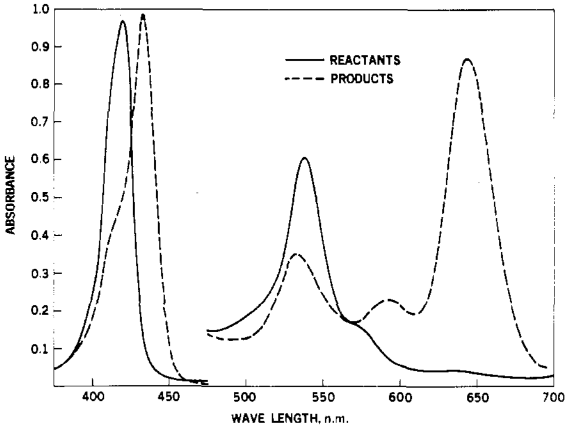

Figure 6. The spectrum of the product solution from the kinetic experiments.

second-order rate constants are plotted as a function of the hydrogen ion concentrations. The rate law for this reaction is

$$\text{rate} = d[Ag^{II}TPPS]/dt = k_2[Ag^{II}TPPS]^2[H^+]$$

Thus the slower second-order process observed in water solution appears to be due to the $Ag^{II}TPPS$ monomers, which would exist under very dilute conditions.[12] In Figure 6, the spectrum of the product solution from the kinetic experiments is presented. This spectrum indicates the presence of the silver porphyrin species in the solution in addition to the dication form of the porphyrin, H_4TPPS^{2+}. To establish the stoichiometry of the reaction, a dilute solution of the $Ag^{II}TPPS$ was treated with acid under the conditions of the kinetic runs. Based on the known extinction coefficients of the dication (H_4TPPS^{2+}), a 9.48×10^{-6} M solution of $Ag^{II}TPPS$ produced 4.8×10^{-6} M H_4TPPS^{2+} on reaction with acid. Qualitatively the presence of silver(I) ion in the product solution could be detected, but the same test on the reactant solution was negative. The presence of silver porphyrin in the product could only be justified if the product silver porphyrin is of different oxidation state and the spectrum of this metalloporphyrin is not so sensitive to the changes in the oxidation state of the metal ion. The spectra of $Co^{II}TPPS$ (λ_{max} 411 and 527 nm) and $Co^{III}TPPS$ (λ_{max} 427 and 539 nm)[14] are very similar. The silver(III) octaethylporphyrin was reported to be similar to that of silver(II) octaethylporphyrin.[15] The same is found to be true in the case of $Ag^{III}TPPS$ and $Ag^{II}TPPS$ also (see Figure 2).[10] Thus the overall reaction appears to be

$$2Ag^{II}TPPS + 4H^+ \rightarrow H_4TPPS^{2+} + Ag^{III}TPPS + Ag^+$$

In addition, the presence of monovalent silver in the product solution was verified qualitatively, supporting the reaction. Several reports of the dipositive silver with water in acidic solutions have appeared in the chemical literature.[16-21] Though various mechanisms have been proposed for these reactions, they all postulate a preequilibrium of the type $2Ag^{2+} \rightleftharpoons Ag^{3+} + Ag^+$, in common and subsequent reaction of the tripositive silver with water. Yet no direct evidence for the presence (or formation) of Ag^{3+} has been observed. The above reaction appears to confirm this postulate.

The following mechanism is proposed for the demetalation of silver(II) porphyrin:

$$2Ag^{II}TPPS \overset{K_1}{\rightleftharpoons} (Ag^{II}TPPS)_2 \tag{1}$$

$$(Ag^{II}TPPS)_2 \overset{K_2}{\rightleftharpoons} Ag^{III}TPPS\text{-}Ag^{I}TPPS \tag{2}$$

$$Ag^{III}TPPS\text{-}Ag^{I}TPPS + H^+ \xrightarrow{k_1} Ag^{III}TPPS + HAg^{I}TPPS \tag{3}$$

$$HAg^{I}TPPS + 3H^+ \xrightarrow{\text{fast}} H_4TPPS^{2+} + Ag^+ \tag{4}$$

Then

$$-d[(Ag^{II}TPPS)_2]/dt = k_1K_2[(Ag^{II}TPPS)_2][H^+]$$

and

$$-d[Ag^{II}TPPS]/dt = k_1K_2K_1[Ag^{II}TPPS]^2[H^+]$$

In this mechanistic scheme, the first step is the previously studied aggregation equilibrium, with an equilibrium constant K_1. The second step is an intramolecular oxidation–reduction equilibrium. Though there is no actual evidence for the species such as $Ag^{III}TPPS\text{–}Ag^{I}TPPS$ being present in the solution, it is highly improbable that the residual basicity of the porphyrinic nitrogen when it is bound to a divalent metal is large enough to attract a proton. So an equilibrium of this type is proposed with an associated equilibrium constant K_2. Hydrogen ion breaking the dimer into a silver(III) porphyrin and monovalent silver porphyrin is the rate-determining step (step 3). The monovalent metalloporphyrins are usually unstable in acid solutions. So with a very rapid addition of hydrogen ions demetalation results (step 4).

Hence $k_1K_2 = k_1'$ and $k_1K_2K_1 = k_2$. The observed values are $k_1' = 73 \pm 3$ M^{-1} s^{-1} and $k_2 = (1.08 \pm 0.01) \times 10^7$ M^{-2} s^{-1} in water and $(1.85 \pm 0.03) \times 10^6$ M^{-1} s^{-1} in 25% methanolic solutions. The equilibrium constant K_1 calculated as k_2/k_1' is (2.50×10^4 M^{-1} in methanolic solutions) 1.5×10^5 M^{-1} in water and determined independently from a Beer's law plot at $\mu = 0.06$ F is 9.0×10^5 M^{-1}. The agreement between those two values of k_1 upholds the internal consistency of this mechanism.

Aggregation followed by disproportionation is well-known in the cyclic-tetrapyrrole chemistry.[22] Because of its importance in the primary process of photosynthesis, aggregation of chlorophyll has been thoroughly investigated.[23] Porphyrin radicals have been shown to undergo second-order disproportionation into phlorin and porphyrin.[24] But this silver porphyrin is probably the only instance of a disproportionation at the metal center in the prophyrin-aggregate investigated thus far.

When $Ag^{II}TPPS$ monomers aggregate to form dimers, the Soret band in the absorption spectrum shifts to shorter wavelengths from 421 to 412 nm and the visible absorption also shifts though toward longer wavelengths. These changes in the absorption spectrum would indicate a strong interaction of the π clouds of the porphyrin molecules. So it would appear that the channel for electron transfer is already open in forming the dimer. It is not clear whether hydrogen ions promote such an internal electron transfer in this case or hydrogen ions take advantage of an already existing equilibrium as proposed in step 2 above and compete for the porphyrin nitrogens with the univalent silver. Electrochemical investigation currently in progress might resolve this.

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Registry No. $Ag^{II}TPPSNa_4$, 66810-80-8; $Ag^{III}TPPSNa_3$, 66810-81-9; nitric acid, 7697-37-2.

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Thermal and Photochemical Cis–Trans Isomerization of PtL_2Cl_2 (L = Dialkyl Sulfoxide) Complexes. Kinetics and Mechanisms for Thermal Isomerization

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trans-$Pt(n\text{-}Pr_2SO)_2Cl_2$, where n-Pr_2SO = di-*n*-propyl sulfoxide, has been isolated as a solid kinetic product where the cis form is the thermodynamically stable species. Photolyzing deuteriochloroform solutions containing predominantly cis isomers of $Pt(Me_2SO)_2Cl_2$, $Pt(Et_2SO)_2Cl_2$, and $Pt(n\text{-}P_2SO)_2Cl_2$, where Me_2SO = dimethyl sulfoxide and Et_2SO = diethyl sulfoxide, results in enrichment of the trans isomer. The three trans complexes thermally isomerize in solution to cis–trans equilibrium mixtures. The forward, k_f, and reverse, k_r, rate constants have been determined by NMR for the first-order kinetic process

$$trans\text{-}Pt(L)_2Cl_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} cis\text{-}Pt(L)_2Cl_2$$

where L = Et_2SO or n-Pr_2SO. Temperature dependence of the rate constants suggest the trans isomer is enthalpy favored and the cis isomer entropy favored. Free-ligand additions to isomerizing *trans*-$Pt(n\text{-}Pr_2SO)_2Cl_2$ solutions have permitted several mechanisms to be proposed for the isomerization. The interchange in $Pt(L)_2Cl_2$ solutions of Me_2SO for Et_2SO, and i-Am_2SO, where i-Am_2SO = diisoamyl sulfoxide, has been followed by proton NMR. These interchanges occur with retention of geometric configuration. The intermediate $Pt(Me_2SO)(L)Cl_2$ complexes and the thermal isomerization of these intermediates are described.

Introduction

Cis–trans isomerization of platinum(II) and palladium(II) complexes has received increasing attention in recent years. Earlier reports of the thermal[1–4] and photochemical[5–8] interconversions of the cis–trans isomers of $Pt(L)_2X_2$, where L = various phosphorus, nitrogen, and sulfur donor ligands and X = halogen, have been succeeded by more recent studies which focus on the mechanism of isomerization since this phenomenon is pertinent to the broader topic of square-planar substitution reactions. Two hypotheses have emerged which account for the isomerization of platinum(II) phosphine complexes where isomeric equilibrium occurs in the presence of free catalyzing phosphine ligand, L. The first involves an association of L to give a distorted five-coordinate intermediate $[L_3PtX_2]$ which undergoes fluxional change interconverting axial and equatorial ligands resulting in isomerization.[9] The second, which has found wider support, involves a consecutive displacement process in which an ionic intermediate $[Pt(L)_3X^+]X^-$ is formed which then takes up a halide ion to form the new isomer.[10–15] In the case of uncatalyzed isomerization of similar platinum complexes, where no free ligand is present, the process is believed to proceed by a dissociative mechanism in which the rate-determining step is the breaking of the Pt–X bond.[16,17]

We previously reported a series of complexes of the form $Pt(L)_2Cl_2$ where L = dialkyl sulfoxide.[18] Sulfoxide ligands

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