

Figure 2. Nmr spectra of $[\text{Pt}(\text{en})\text{G}_2]\text{Cl}_2$ (left) and $[\text{Pt}(\text{en})\text{X}_2]\text{Cl}_2$ (right).

to the platinum atom along the z axis, this would also favor higher frequencies for the amine complexes.

Pyridine complexes (see bottom of Table I) are not very stable in the solid state at room temperature and were not studied further. Adenosine complexes were also studied and nmr spectra showed several species due to different binding sites (N_1 and N_7). We shall report the details of these reactions elsewhere.

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Registry No. *cis*- $[\text{Pt}(\text{NH}_3)_2\text{G}_2]\text{Cl}_2$, 50790-41-5; *cis*- $[\text{Pt}(\text{en})\text{G}_2]\text{Cl}_2$, 40790-42-6; *cis*- $[\text{Pt}(\text{NH}_3)_2\text{X}_2]\text{Cl}_2$, 50790-42-6; *cis*- $[\text{Pt}(\text{en})\text{X}_2]\text{Cl}_2$, 50790-44-8; *cis*- $[\text{Pt}(\text{NH}_3)_2\text{In}_2]\text{Cl}_2$, 50883-28-8; *cis*- $[\text{Pt}(\text{en})\text{In}_2]\text{Cl}_2$, 50790-45-9; *cis*- $[\text{Pt}(\text{py})_2\text{G}_2]\text{Cl}_2$, 50790-46-0; *trans*- $[\text{Pt}(\text{py})_2\text{G}_2]\text{Cl}_2$, 50883-29-9; guanosine, 118-00-3; xanthosine, 550-26-5; inosine, 58-63-9.

Contribution from the William Ramsay and Ralph Forster Laboratories, University College, Gower Street, London, W. C. 1., England

Entering Group, Leaving Group, and Cis Effects of Alicyclic Primary Amines in Substitution Reactions of Platinum(II) Complexes Containing Sulfur-Bonded Dimethyl Sulfoxide¹

P. D. BRADDOCK,² R. ROMEO,² and M. L. TOBE*

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Series of complexes of the types *cis*- $[\text{Pt}(\text{am})_2(\text{DMSO})\text{Cl}]\text{Cl}$, *cis*- $[\text{PtCl}_2(\text{am})(\text{DMSO})]$, and $[\text{Pt}(\text{am}')(\text{DMSO})(\text{am})\text{Cl}]\text{Cl}$, where am is an alicyclic primary amine, $\text{C}_n\text{H}_{2n-1}\text{NH}_2$ ($n = 3-8$), am' is cyclopropylamine, and DMSO is dimethyl sulfoxide bonded through the sulfur, have been prepared and characterized. The kinetics of the forward and reverse steps of the process, *cis*- $[\text{PtCl}_2(\text{DMSO})(\text{am})] + \text{am} \rightleftharpoons \text{cis}-[\text{Pt}(\text{am})_2(\text{DMSO})\text{Cl}]^+ + \text{Cl}^-$ (and also the analogous reaction with cyclopropylamine as entering group), have been studied in methanol at 30.0° at constant ionic strength and the equilibrium constants have been determined. The normal two-term rate law is observed but the first-order (nucleophile-independent) path is of little importance. In addition to the expected dependence of rate on the basicity of the leaving group, a very strong cis effect is observed where the least basic amine produces the most reactive substrate. This cis effect is as dependent on basicity as the leaving group effect. It is concluded that the very strong trans effect of S-bonded dimethyl sulfoxide is due to transition-state stabilization that results from the π -acceptor properties of the sulfur in this ligand.

Introduction

Although a number of studies have been made of the way in which the nature of the leaving group affects the reactivity of four-coordinate, planar d^8 metal ion complexes,³ little

attention has been paid to a systematic study of the relationship between the basicity and the lability of coordinated amines. Some studies have been made with Au(III) substrates⁴⁻⁶ and a small amount is known about Pd(II) com-

(1) Presented, in part, with Dr. A. R. Khokhar, at the Second International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy, Oxford, England, April 16-18, 1973.

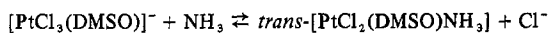
(2) On leave from the Istituto di Chimica-Fisica dell'Universita di Messina, Messina, Sicily.

(3) See, for example, L. Cattalini, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One*, 9, 278 (1972).

(4) L. Cattalini and M. L. Tobe, *Inorg. Chem.*, 5, 1145 (1966).

(5) L. Cattalini, A. Orio, and M. L. Tobe, *Inorg. Chem.*, 6, 75 (1967).

plexes^{7,8} but the general inertness of the Pt-N bond toward substitution has precluded any systematic study of the role of amines as leaving groups in such systems. As part of an extensive study of the relationship between the reactivity and antitumor properties of complexes of the type *cis*-[Pt(am)₂-Cl₂] (am = amine), it was necessary to examine the *cis*, *trans*, and leaving group effects of a range of amine ligands coordinated to Pt(II) and so it was decided to make use of complexes that contained a strong *trans*-labilizing ligand in order to loosen the amine sufficiently to allow its replacement to be studied. There has been a great deal of interest, recently, especially in the work of Kukushkin, in dimethyl sulfoxide complexes of platinum(II) and the reported strong *trans* effect of this ligand,^{9,10} and the reversibility of the reaction¹⁰



has led us to examine the kinetics of the displacement of amines from complexes of the type *cis*-[Pt(am)₂(DMSO)Cl]⁺, where am is a primary amine with an alicyclic substituent in the sequence cyclopropylamine to cyclooctylamine. These alicyclic amines were chosen partly because of the special therapeutic activity of the *cis*-[PtCl₂(am)₂] complexes that they formed¹¹ and partly because they present a homologous series in which the basicity can be changed over some 1.4 p*K*_a units simply as a result of the bond angle strain at the carbon adjacent to the nitrogen¹² without any discontinuous solvation changes that result from the variation of polar substituents usually varied to change the p*K*_a. In addition, the steric effects (as far as congestion about the reaction center is concerned) remain constant in the amines where the maximum change of p*K*_a is encountered (*n* = 3–5) and only become important when the alicyclic ring becomes puckered (*n* = 6–8), bond angle strain diminishes, and the p*K*_a values remain almost constant. In the course of this work it was found to be necessary to separate the leaving group effect from the rather large *cis* effect that was encountered and so a series of mixed-amine complexes was prepared in which the amine *cis* to dimethyl sulfoxide was varied and that *trans* was held constant as cyclopropylamine.

Experimental Section

Preparations. *cis*-Dichlorobis(dimethyl sulfoxide)platinum(II) was prepared from K₂PtCl₄ and aqueous dimethyl sulfoxide by the method of Wayland, *et al.*¹³

***cis*-Chlorobis(cyclopropylamine)(dimethyl sulfoxide)platinum(II) Chloride.** Cyclopropylamine (0.114 g) was added to a solution of [PtCl₂(DMSO)₂] (0.42 g) in methanol (75 ml). After standing at room temperature for 1 day, the methanol was removed under reduced pressure without heating. The addition of a small amount of acetone, followed by ether, to the oily residue produced a white crystalline product which was washed with ether and air-dried. The yield and analytical data are reported in Table I.

***cis*-Chlorobis(cyclobutylamine)(dimethyl sulfoxide)platinum(II) Chloride.** [PtCl₂(DMSO)₂] (0.20 g) was suspended in methanol (15 ml) and the mixture heated with an excess of cyclobutylamine (0.08

g) for 15 min until the yellow color had disappeared. Addition of ether and subsequent cooling in ice gave a white crystalline product which was recrystallized from methanol-ether. The analytical data, etc., are in Table I.

***cis*-Chlorobis(cyclopentylamine)(dimethyl sulfoxide)platinum(II) chloride, *cis*-chlorobis(cyclohexylamine)(dimethyl sulfoxide)platinum(II) chloride, *cis*-chlorobis(cycloheptylamine)(dimethyl sulfoxide)platinum(II) chloride, and *cis*-chlorobis(cyclooctylamine)(dimethyl sulfoxide)platinum(II) chloride** were prepared in a similar way using an excess of the appropriate amine. The analytical data, etc., are collected in Table I.

***cis*-Dichloro(cyclohexylamine)(dimethyl sulfoxide)platinum(II), *cis*-[Pt(cyclohexylamine)₂(DMSO)Cl]Cl** was dissolved in methanol and twice the stoichiometrically required amount of perchloric acid was added. The solution, which slowly assumed a yellow color, was left to stand at room temperature for 2 days and then evaporated under reduced pressure to small bulk. The pale yellow crystals that formed were filtered off, washed with ether, and air-dried. The analytical data are reported in Table I.

***cis*-Dichloro(cyclopropylamine)(dimethyl sulfoxide)platinum(II), *cis*-dichloro(cyclobutylamine)(dimethyl sulfoxide)platinum(II), *cis*-dichloro(cyclopentylamine)(dimethyl sulfoxide)platinum(II), *cis*-dichloro(cycloheptylamine)(dimethyl sulfoxide)platinum(II) and *cis*-dichloro(cyclooctylamine)(dimethyl sulfoxide)platinum(II)** were prepared in an analogous way from the corresponding *cis*-diamino complex. The analytical and other data are reported in Table I.

***trans*-(Cyclopropylamine)(dimethyl sulfoxide)-*trans*-chloro(cyclohexylamine)platinum(II) Chloride.** *cis*-[PtCl₂(cyclohexylamine)(DMSO)] was dissolved in methanol and an equimolar quantity of cyclopropylamine was added. The solution was left to stand for 1 day at room temperature and the methanol was removed by distillation at reduced pressure. The white residue was dissolved in the minimum amount of methanol and the pure complex was precipitated by adding acetone and ether, filtered off, washed with ether, and air-dried. The analytical and other data for the white crystalline solid are reported in Table I.

***trans*-(Cyclopropylamine)(dimethyl sulfoxide)-*trans*-chloro(cyclobutylamine)platinum(II) chloride, *trans*-(cyclopropylamine)(dimethyl sulfoxide)-*trans*-chloro(cyclopentylamine)platinum(II) chloride, *trans*-(cyclopropylamine)(dimethyl sulfoxide)-*trans*-chloro(cycloheptylamine)platinum(II) chloride, and *trans*-(cyclopropylamine)(dimethyl sulfoxide)-*trans*-chloro(cyclooctylamine)platinum(II) chloride** were prepared in a similar way by treating cyclopropylamine with the appropriate *cis*-[PtCl₂(am)(DMSO)] complex. Analytical data are given in Table I.

Cyclobutylamine was purchased from Fluka A.G. and the other alicyclic amines were purchased from Emanuel Ltd. Methanolic solutions of these amines were made up by weight and standardized by titration with acid. Close agreement was found between the results of the two methods of standardization. Methanol, perchloric acid (72%), and lithium chloride and perchlorate were of AnalaR grade.

Kinetics. For the reactions involving the displacement of the amines, separate solutions of the diamino complex in methanol and the other reagents (LiCl, LiClO₄, HClO₄) in methanol were brought to the reaction temperature. The reaction was started by mixing appropriate amounts of the two solutions in a standard volumetric flask, the volume was adjusted by adding prewarmed methanol and the reaction mixture was transferred to the spectrophotometer cell which was placed in the thermostated cell compartment of a Unicam SP 800 spectrophotometer. The spectrum was then scanned over the range 250–450 nm at appropriate times. In the faster reactions the reagent solution was placed in the spectrophotometer cell and the prethermostated complex solution was added by means of a calibrated hypodermic syringe to start the reaction. The wavelength was locked at 290 nm and the recorder bed was allowed to move at a fixed known rate. All reactions were carried out in the presence of a sufficient excess of chloride to ensure first-order kinetics and the pseudo-first-order rate constants were determined graphically from the plot of log (A_∞ - A_t) against time (A_t and A_∞ are the absorbances at 290 nm at time "t" seconds after 10 half-lives, respectively). The reactions involving the entry of amine were too fast for this method to be used and so were followed with a Durrum-Gibson D110 stopped-flow spectrophotometer. The output from the photomultiplier was displayed on a Servoscribe RE 511.20 potentiometric recorder and the change in absorbance at 295 nm used to follow the course of the reaction. In order to avoid Schlieren effects on mixing it was necessary to adjust the ionic strength of both the amine and the complex solution to 0.5. The spectra of the solutions at the end of all the reactions corresponded exactly with those of the independently synthesized reaction products.

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Table I. Analytical Data, Yields, and S-O Stretching Frequencies

am	am'	Formula	% C		% H		% N		% yield	ν_{S-O} , cm^{-1}
			Calcd	Found	Calcd	Found	Calcd	Found		
(a) Complexes of the Type [Pt(am)(am')(DMSO)Cl]Cl (am' Trans to DMSO)										
C ₃ H ₇ NH ₂	C ₃ H ₅ NH ₂	C ₈ H ₂₀ Cl ₂ N ₂ OSPt	21.0	21.1	4.39	4.35	6.11	6.01	40	1128
C ₄ H ₇ NH ₂	C ₄ H ₇ NH ₂	C ₁₀ H ₂₄ Cl ₂ N ₂ OSPt	24.7	25.1	4.97	4.73	5.76	5.95	77	1132
C ₅ H ₉ NH ₂	C ₅ H ₉ NH ₂	C ₁₂ H ₂₈ Cl ₂ N ₂ OSPt	28.0	28.1	5.49	5.61	5.45	5.40	93	1127
C ₆ H ₁₁ NH ₂	C ₆ H ₁₁ NH ₂	C ₁₄ H ₃₂ Cl ₂ N ₂ OSPt	31.0	30.6	5.95	5.73	5.16	4.90	96	1133
C ₇ H ₁₃ NH ₂	C ₇ H ₁₃ NH ₂	C ₁₆ H ₃₆ Cl ₂ N ₂ OSPt	33.7	34.0	6.36	6.14	4.90	4.92	88	1122
C ₈ H ₁₅ NH ₂	C ₈ H ₁₅ NH ₂	C ₁₈ H ₄₀ Cl ₂ N ₂ OSPt	36.1	35.9	6.74	6.66	4.68	4.68	89	1118
C ₄ H ₇ NH ₂	C ₃ H ₅ NH ₂	C ₉ H ₂₂ Cl ₂ N ₂ OSPt	22.9	22.7	4.69	4.52	5.93	5.83	90	1126
C ₆ H ₉ NH ₂	C ₃ H ₅ NH ₂	C ₁₀ H ₂₄ Cl ₂ N ₂ OSPt	24.7	24.3	4.97	4.71	5.76	5.65	90	1125
C ₆ H ₁₁ NH ₂	C ₃ H ₅ NH ₂	C ₁₁ H ₂₆ Cl ₂ N ₂ OSPt	26.4	26.0	5.24	5.01	5.60	5.41	92	1131
C ₇ H ₁₃ NH ₂	C ₃ H ₅ NH ₂	C ₁₃ H ₂₈ Cl ₂ N ₂ OSPt	28.0	27.6	5.49	5.28	5.45	5.31	90	1120
C ₈ H ₁₅ NH ₂	C ₃ H ₅ NH ₂	C ₁₃ H ₃₀ Cl ₂ N ₂ OSPt	29.5	28.7	5.72	5.44	5.30	5.04	88	1127
(b) Complexes of the Type <i>cis</i> -[PtCl ₂ (am)(DMSO)]										
C ₃ H ₇ NH ₂		C ₅ H ₁₃ Cl ₂ NOSPt	15.0	15.1	3.27	3.21	3.49	3.60	35	1125
C ₄ H ₇ NH ₂		C ₆ H ₁₅ Cl ₂ NOSPt	17.4	17.3	3.64	3.58	3.37	3.31	80	1122
C ₅ H ₉ NH ₂		C ₇ H ₁₇ Cl ₂ NOSPt	19.6	19.5	3.99	3.87	3.26	3.19	74	1119
C ₆ H ₁₁ NH ₂		C ₈ H ₁₉ Cl ₂ NOSPt	21.7	22.0	4.32	4.25	3.16	3.11	100	1117
C ₇ H ₁₃ NH ₂		C ₉ H ₂₁ Cl ₂ NOSPt	23.6	24.3	4.63	4.66	3.06	3.06	60	1118
C ₈ H ₁₅ NH ₂		C ₁₀ H ₂₃ Cl ₂ NOSPt	25.5	25.5	4.92	4.94	2.97	3.24	70	1121

Results

Two series of cationic and neutral complexes of platinum(II) containing coordinated dimethyl sulfoxide, alicyclic primary amines, and chloride were synthesized from PtCl₂(DMSO)₂. This species, obtained as yellow crystals from the reaction between K₂PtCl₄ and dimethyl sulfoxide, has variously been assigned the *cis*^{13,14} and the *trans*¹⁵ configuration. Although the infrared spectrum indicates a *cis* configuration and the complex is not isomorphous with the corresponding Pd(II) complex which is known, from X-ray diffraction studies, to have a *trans* configuration,¹⁶ the chemical behavior is more in keeping with a *trans* configuration.^{16a} There is general agreement that in the platinum(II) complexes with one or two dimethyl sulfoxides, the ligands are bonded to platinum through sulfur. In all of the complexes reported in Table I the presence of a strong peak at 1125 ± 8 cm⁻¹, which is assigned to the S-O stretch, is taken to indicate bonding through the sulfur,¹⁷ since this is shifted to higher frequency than the corresponding vibration in the free ligand. The white complexes of the type *cis*-[Pt(am)₂(DMSO)Cl]Cl are all typically 1:1 electrolytes in methanol and can also be prepared by the solvolysis of the corresponding *cis*-[Pt(am)₂Cl₂] in anhydrous or even aqueous dimethyl sulfoxide. This method, while establishing the *cis* configuration of the complexes, is less convenient and produces poorer yields than the method finally adopted. The pale yellow compounds of the type *cis*-[PtCl₂(am)(DMSO)] were prepared from the bis(amine) complexes by reaction with an excess of perchloric acid and were shown to be nonconductors, at least initially, in methanol solution. The mixed-amine complexes of the type [Pt((DMSO)(cyclopropylamine))((am)Cl)]Cl were obtained by the reaction of the appropriate *cis*-[PtCl₂(am)(DMSO)] complex with cyclopropylamine in methanol. In general, the preparation and handling of the complexes containing the most labile (and labilizing) ligand, cyclopropylamine, required special care. For example, an excess of

cyclopropylamine with [Pt(DMSO)₂Cl₂] yields the [Pt(am)₄]Cl₂ species. Recrystallization of the *cis*-[Pt(cyclopropylamine)₂(DMSO)Cl]Cl complex can lead to the formation of the mono(amine) complex if great care is not taken.

Kinetics of the Displacement of Amine by Chloride. Preliminary studies indicated that neutral aqueous or methanolic solutions of *cis*-[Pt(chx)₂(DMSO)Cl]Cl (chx = cyclohexylamine) were stable and no significant change in spectrum was observed over periods of days. However, addition of dilute hydrochloric acid led to a slow change in spectrum that was not consistent with the formation of a dichlorodiamineplatinum(II) species (displacement of DMSO). A pH Stat experiment at pH 3 indicated that 1 equiv of acid was consumed per mole of complex reacted and so one, and only one, of the two amines had been displaced. The reaction product was isolated and shown by analysis to be [PtCl₂(chx)(DMSO)] and comparison with independently prepared samples showed this to be the *cis* isomer.

The systematic kinetics of this reaction were studied in methanol at 30.0° in the presence of 0.01 M HClO₄ at constant ionic strength (0.50, maintained by the addition of lithium perchlorate). Preliminary experiments had shown that, at constant chloride concentration, the rate of reaction was independent of the concentration of acid over the range 0.005–1.0 M. The acid serves simply to protonate the released amine and to prevent the reverse reaction. If less than 1 equiv of acid is present, the reaction ceases when all the acid has been consumed; the approach to this point is still first order in complex and the rate constant is the same as that found in the presence of excess acid. In solutions containing acid stronger than 1.0 M a second stage in the reaction was observed. The rate of this reaction is proportional to acid concentration and increases as a function of the chloride concentration but the kinetics are not properly reproducible. Preliminary studies have indicated that platinum(IV) complexes containing dimethyl sulfide are present as intermediates. Kukushkin, *et al.*, have reported a similar reaction with PtCl₂(DMSO)₂ and concentrated HCl.¹⁵ The pseudo-first-order rate constants for the reaction of the Pt(II) complex in 0.01 M acid were determined at six separate chloride concentrations within the range 0.05–0.5 M and the plot of these constants (*k*_{obsd}) against [Cl⁻] was linear. Unlike the usual behavior observed in the substitution reactions of platinum(II) complexes, this particular plot passed through the origin within the limits of experimental error. The behavior of the

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Table II. Rate and Equilibrium Constants for the Reactions^{a,h}

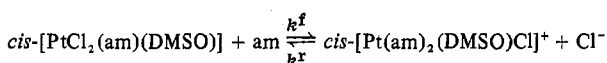
$$\left[\begin{array}{c} \text{am} \\ \diagup \\ \text{Pt} \\ \diagdown \\ \text{Cl} \end{array} \begin{array}{c} \text{DMSO} \\ \diagdown \\ \text{Pt} \\ \diagup \\ \text{Cl} \end{array} \right] + \text{am}' \xrightleftharpoons[k_1^r + k_2^r[\text{Cl}^-]]{k_1^f + k_2^f[\text{am}]} \left[\begin{array}{c} \text{am} \\ \diagup \\ \text{Pt} \\ \diagdown \\ \text{Cl} \end{array} \begin{array}{c} \text{DMSO} \\ \diagdown \\ \text{Pt} \\ \diagup \\ \text{am}' \end{array} \right]^+ + \text{Cl}^-$$

am	am'	$10^3 k_1^f, \text{sec}^{-1}$	$M^{-1} k_2^f, \text{sec}^{-1}$	$10^3 k_1^r, \text{sec}^{-1}$	$M^{-1} k_2^r, \text{sec}^{-1}$	$K = k_1^f/k_1^r$
Cyclopropylamine ^b	Cyclopropylamine	4.0 ± 1.0	4.82	5.0 ± 1.0	14.8	320
Cyclobutylamine ^c	Cyclobutylamine	2.0 ± 1.0	3.60	0.0 ± 1.0	3.2	1120
Cyclopentylamine ^d	Cyclopentylamine	4.0 ± 1.0	1.96	1.0 ± 1.0	1.22	1610
Cyclohexylamine ^e	Cyclohexylamine	3.0 ± 1.0	1.73	0.0 ± 1.0	1.16	1490
Cycloheptylamine ^f	Cycloheptylamine	6.0 ± 1.0	1.38	0.0 ± 1.0	1.37	1010
Cyclooctylamine ^g	Cyclooctylamine	2.0 ± 1.0	1.22	0.0 ± 1.0	1.37	890
Cyclobutylamine	Cyclopropylamine	2.0 ± 1.0	2.37	10.0 ± 1.0	9.0	264
Cyclopentylamine	Cyclopropylamine	4.0 ± 1.0	1.67	6.0 ± 1.0	4.6	363
Cyclohexylamine	Cyclopropylamine	2.0 ± 1.0	1.56	8.0 ± 1.0	4.35	360
Cycloheptylamine	Cyclopropylamine	2.0 ± 1.0	1.53	7.5 ± 1.0	4.35	352
Cyclooctylamine	Cyclopropylamine	2.0 ± 1.0	1.22	5.0 ± 1.0	4.00	305

^a In methanol at 30.0°; $\mu = 0.50$ (LiClO₄); [complex] = 1.0×10^{-3} M for forward reaction, 2.0×10^{-3} M for reverse reaction; [H⁺] = 0.01 M for reverse reaction. ^b pK_a = 8.66.¹² ^c pK_a = 9.34.¹² ^d pK_a = 9.95.¹² ^e pK_a = 9.84,¹² 9.82.¹⁸ ^f pK_a = 9.99.¹⁸ ^g pK_a = 10.01.¹⁸
^h Values in ref 12 are half-point scale readings in 50% water-ethanol, while those in ref 18 are measured in 80% Methyl Cellosolve-water.

cyclohexylamine complex was mirrored by all the other complexes of the type *cis*-[Pt(am)₂(DMSO)Cl]⁺ and also the mixed amine-cyclopropylamine complexes. All lost the amine trans to the dimethyl sulfoxide at a rate that was independent of the concentration of the acid and all gave linear plots of k_{obsd} vs. [Cl⁻]. In some cases there was a finite intercept (k_1^r), occasionally well outside experimental error but always small so that the precision of its evaluation was poor. Values for the rate constants k_1^r and k_2^r (the slope of the plot of k_{obsd} vs. [Cl⁻]) are collected in Table II.

Kinetics of the Displacement of Chloride by Amine. In the absence of acid the position of equilibrium of the reaction



lies well over to the right. The forward reaction can therefore be studied by adding the amine to a solution of *cis*-[PtCl₂(am)(DMSO)]. The reaction in methanol is relatively fast and the final spectrum corresponds exactly to that of the corresponding diamino complex. The kinetics were followed in methanol at 30.0° at constant ionic strength (0.50, LiClO₄) using a stopped-flow technique. A sufficiently large excess of amine was used to ensure pseudo-first-order kinetics and the rate constants were measured at six separate amine concentrations in the range 0.01–0.15 M. The plot of k_{obsd} against [am] was linear and, as in the case of the reverse reaction, the nucleophile-independent term, k_1^f , was small and contributed little to the reaction except at the lowest amine concentrations. Values of the slope (k_2^f) and the intercept (k_1^f) are collected in Table II.^{12,18}

Discussion

The presence of S-bonded dimethyl sulfoxide in the complexes of the type *cis*-[Pt(am)₂(DMSO)Cl]Cl provides sufficient *trans*-labilizing power for it to be possible to observe the displacement of the *trans* amine by other nucleophiles, such as chloride, provided acid is present to protonate the released amine and thereby suppress the reverse reaction. The major part of the substitution goes by way of the chloride-dependent (k_2^r) path and in some cases the solvolytic path contribution (k_1^r) is too small to be detected. This is somewhat unusual for substitution in platinum(II) complexes

by a nucleophile as weak as chloride but the small importance of the k_1 term is well marked in substitution reactions of gold(III) complexes.¹⁹ It is possible that the k_1 term is masked by an unusually large k_2 arising from the enhancement of reactivity through interaction of the cationic substrate with an anionic reagent and this view is supported by the fact that, in the displacement of amine from the uncharged *trans*-[PtCl₂(am)(DMSO)] by chloride, which will be reported elsewhere,²⁰ the k_1 term is still within the range found for the cationic diamine complexes while the k_2 term is reduced by two or three orders of magnitude. Indeed, in those complexes, the nucleophile-independent path dominates the substitution. However, the reaction between *cis*-[PtCl₂(am)(DMSO)] and amines, where such charge effects should be negligible, also goes mainly by way of the amine-dependent path. It is likely that a proper understanding of the factors that control the magnitude of the solvolytic-dependent rate constant in square-planar substitution still awaits the accumulation of much more data.

The second-order rate constants for the replacement of amine in *cis*-[Pt(am)₂(DMSO)Cl]⁺ by chloride show a clear relationship with the basicity of the amine in which the least basic amine forms the most reactive substrate and a rough LFER can be found in the plot of log k_2^r against the pK_a of am. The best straight line has a slope of -0.91 (Figure 1). This sensitivity to basicity is considerably greater than that observed in the replacement of the amine in [AuCl₃(am)] by chloride (slope -0.61)⁵ and contains a contribution from the *cis* effect of the other amine that remains bonded to the platinum throughout. In order to evaluate this contribution, we examined the reactivity of an analogous series of complexes where the amine *trans* to dimethyl sulfoxide and replaced by chloride was held constant (cyclopropylamine) and the *cis* amine was varied. The plot of log k_2^r against the pK_a of the *cis* amine indicates that there is quite a marked *cis* effect and that the relationship is essentially linear with a slope of -0.43 (Figure 1). This is the strongest basicity-related *cis* effect so far reported. Cattalini²¹ examined the displacement of chloride from complexes of the type *trans*-

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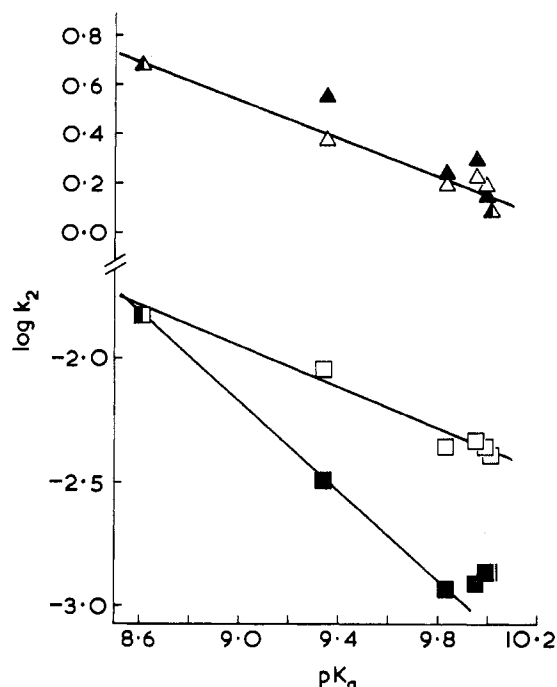


Figure 1. The relationship between pK_a of the cis amine, am, and (i) $\log k_f^2$, entering group = cyclopropylamine, Δ , (ii) $\log k_f^2$, entering group = am, \blacktriangle , (iii) $\log k_r^2$, leaving group = am, \blacksquare , and (iv) $\log k_r^2$, leaving group = cyclopropylamine, \square .

$[\text{Pt}(\text{am})_2\text{Cl}_2]$ where am is a substituted pyridine and, although he was concerned with the relationship between the basicity of the cis amine and the nucleophilic discrimination factor (the slope of the plot of $\log k_2$ against the n_{Pt} value for a range of nucleophiles reacting with one substrate), it is possible to see from his data that there is a linear relationship between $\log k_2$ and pK_a of the cis amine for a constant nucleophile and a range of substrates. The slope depends upon the nature of the entering group and lies within the range -0.2 to -0.3 . Rund²² examined the reaction between $[\text{Pt}(\text{phen-X})\text{Cl}_2]$ and dithiooxamide and showed that the rate constant for the displacement of the chloride increased as the pK_a of the substituted phenanthroline (phen-X) decreased. The plot of $\log k_2$ against the pK_a of the amine has a slope of -0.25 but since, in this case, it was not possible to distinguish between cis and trans effects the authors have attributed this to a position nonspecific effect of the nonparticipating ligands.

The rate of the entry of amine is almost completely dominated by the cis effect. For entry of cyclopropylamine into the series of $\text{cis-}[\text{PtCl}_2(\text{am})(\text{DMSO})]$ complexes there is a reasonably good linear relationship between $\log k_f^2$ and the pK_a of the cis amine with slope -0.39 (Figure 1). This is not significantly different from that observed in the reverse reaction. For the series of reactions in which the entering amine and the cis amine are varied at the same time, a greater scatter of points is observed but the data are served by the same straight line. This is good indication that the nucleophilicity of the alicyclic primary amines toward platinum does not vary much with basicity.

Since the contribution from the k_1 path is negligibly small, it is possible to calculate the equilibrium constant for the process by taking the ratio of the forward and reverse second-order rate constants. These values are collected in Table II. Two contributions to the behavior can be picked out. With a small amine trans to the DMSO the cis effect virtually

disappears; *i.e.*, the equilibrium constants for the series of complexes with cyclopropylamine trans to the dimethyl sulfoxide have only a marginal dependence upon the basicity of the cis amine, but in the series $\text{cis-}[\text{Pt}(\text{am})_2(\text{DMSO})\text{Cl}]^+$ where the cis and the trans amines are varied, the increase in stability with increasing basicity of am that is observed on going from cyclopropylamine to cyclopentylamine and, which is expected as a consequence of the increasing strength of the Pt-N bond, is reversed on going from cyclopentylamine to cyclooctylamine where basicity does not change markedly. It is suggested that this decrease in stability is an indication of steric hindrance when two of the bulkier amine ligands are adjacent in the same complex.

The absence of an electronic cis effect in the equilibrium constant indicates either that the destabilizing effect of the amine in the ground state acts equally on its cis ligand irrespective of whether it is chloride or another amine or else that it is negligible and that the observed cis effect is a transition-state effect. The latter seems to be most likely and it can be seen that the least basic amine, by virtue of its weakest donation of charge to the metal, will least oppose the binding of the incoming group. Conceptually, this statement is closely equivalent to that of Cattalini,²¹ who spoke in terms of the least basic amine producing the most electrophilic platinum atom. The magnitude of the cis effect in this group of complexes is somewhat larger than expected. The reactivity of the complex toward substitution is almost as sensitive to the basicity of the cis amine as it is to that of the leaving group. This strengthens the idea that the bond between the incoming ligand and the reaction center is well developed in the rate-determining transition state. It may be inferred, therefore, that the trans effect of dimethyl sulfoxide owes more to the π -acceptor properties of the sulfur, which will lead to a transition-state stabilization trans effect than to its relatively low electronegativity (ground-state bond-weakening trans effect). It is to be expected that, on going from R_2S (thioether) to R_2SO (sulfoxide), the σ -donor capacity of the sulfur decreases while its π -acceptor properties increase. This would lead to the predictions (a) that the trans effect of a sulfoxide is greater than that of a thioether and (b) that, if there was any difference in the bond lengths of ligands trans to R_2S and R_2SO in otherwise equivalent Pt(II) complexes, the bond trans to the thioether would be longer.

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Registry No. *cis*-Chlorobis(cyclopropylamine)(dimethyl sulfoxido)platinum(II) chloride, 50830-75-6; *cis*-chlorobis(cyclobutylamine)(dimethyl sulfoxido)platinum(II) chloride, 50830-76-7; *cis*-chlorobis(cyclopentylamine)(dimethyl sulfoxido)platinum(II) chloride, 50830-77-8; *cis*-chlorobis(cyclohexylamine)(dimethyl sulfoxido)platinum(II) chloride, 50830-78-9; *cis*-chlorobis(cycloheptylamine)(dimethyl sulfoxido)platinum(II) chloride, 50830-79-0; *cis*-chlorobis(cyclooctylamine)(dimethyl sulfoxido)platinum(II) chloride, 50830-80-3; *trans*-(cyclopropylamine)(dimethyl sulfoxido)-*trans*-chloro(cyclobutylamine)platinum(II) chloride, 50830-81-4; *trans*-(cyclopropylamine)(dimethyl sulfoxido)-*trans*-chloro(cyclopentylamine)platinum(II) chloride, 50830-82-5; *trans*-(cyclopentylamine)(dimethyl sulfoxido)-*trans*-chloro(cyclohexylamine)platinum(II) chloride, 50830-83-6; *trans*-(cyclopropylamine)(dimethyl sulfoxido)-*trans*-(cycloheptylamine)platinum(II) chloride, 50830-84-7; *trans*-(cyclopropylamine)(dimethyl sulfoxido)-*trans*-chloro(cyclooctylamine)platinum(II) chloride, 50830-85-8; *cis*-dichloro(cyclopropylamine)(dimethyl sulfoxido)platinum(II), 50830-86-9; *cis*-dichloro(cyclobutylamine)(dimethyl sulfoxido)platinum(II), 50830-87-0; *cis*-dichloro-

(cyclopentylamine)(dimethyl sulfoxido)platinum(II), 50830-88-1; *cis*-dichloro(cyclohexylamine)(dimethyl sulfoxido)platinum(II), 50830-89-2; *cis*-dichloro(cycloheptylamine)(dimethyl sulfoxido)-

platinum(II), 50830-90-5; *cis*-dichloro(cyclooctylamine)(dimethyl sulfoxido)platinum(II), 50830-91-6; dichlorobis(dimethyl sulfoxido)-platinum(II), 15274-33-6.

Contribution from the Department of Chemistry,
Northern Illinois University, DeKalb, Illinois 60115

Anion-Cation Interaction in Tetrakis(alkyl isocyanide)platinum(II) Tetracyanoplatinate(II) Double Complexes in the Solid State and in Solution¹

HUSEYIN ISCI and W. ROY MASON*

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Three double-complex salts $[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{or } t\text{-C}_4\text{H}_9$) exhibit low-energy electronic absorption bands in the solids (at 22.25 and 22.30 kK for the methyl and ethyl compounds, respectively, in KBr pellets and at 17.70 kK for the *tert*-butyl compound in a Nujol mull) which are absent in the solution spectra of the anion or cation complexes with simple counterions. These low-energy bands, which are responsible for the intense colors of the solids, are ascribed to metal \rightarrow ligand charge transfer which has been red shifted by Davydov interaction between anion and cation complexes in the solid lattice. The ethyl and *tert*-butyl compounds are also slightly soluble in acetonitrile, and the ethyl compound is slightly soluble in water and ethanol. These solutions exhibit a low-energy band near 30 kK which is also absent in anion or cation spectra. The concentration dependence of the solution spectra does not obey Beer's law, and the solution conductance is lower than expected for 1:1 electrolytes. These results are interpreted in terms of an anion-cation association equilibrium. Association constants in acetonitrile at 24° were found to be $(4.0 \pm 0.5) \times 10^4 \text{ M}^{-1}$ for $[\text{Pt}(\text{CNC}_2\text{H}_5)_4]^{2+}$ and $[\text{Pt}(\text{CN})_4]^{2-}$ from spectrophotometric and conductance data and $(2.0 \pm 0.5) \times 10^5 \text{ M}^{-1}$ for $[\text{Pt}(\text{CN}-t\text{-C}_4\text{H}_9)_4]^{2+}$ and $[\text{Pt}(\text{CN})_4]^{2-}$ from spectrophotometric data. A model is proposed for the structure of the associated complex, and the origin of the low-energy absorption is discussed.

Introduction

Double-complex salts of the type $[\text{PtA}_4][\text{PtX}_4]$ consisting of square-planar cations and square-planar anions of equal ionic charges are fairly common in platinum(II) chemistry, and numerous examples have been known for many years.² One of the most notable examples of such a salt is green $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, first reported by Magnus in 1828³ and commonly called Magnus' green salt (MGS). Solid MGS has intrigued investigators for years because its color is "abnormal," since it is not like that of either the cation (colorless) or the anion (red) complexes with simple counterions.⁴ The abnormal color and also anisotropic electrical conductivity of the solid reported recently⁵ are believed due to a structural feature of the crystal which allows anion-cation interaction. The structure⁶ of MGS consists of an infinite stack of alternating planar cations and anions along the crystal *c* axis forming a chain with uniform Pt-Pt distances of 3.24 Å. The color of MGS results from a strong solid-state perturbation of the PtCl_4^{2-} ligand field spectra, causing a red shift of the $^1\text{A}_{1g} \rightarrow ^{1,3}\text{E}_g$ ligand-field transitions by about 4000 cm^{-1} , leaving a "window" near 20 kK in the green region of the spectrum.⁴ Numerous other related double-complex salts of platinum(II) have structures which are similar to, if not isomorphous with, that of MGS; Pt-Pt distances along the chain direction range from 3.2 to 3.6 Å.⁷ The colors of the solids and other features of their

electronic spectra are related to the anion-cation Pt-Pt distance.

Nearly all of these double-complex salts, including MGS, are highly insoluble. Consequently anion-cation interaction phenomena have been investigated only in the solid state. In the present paper we report the preparation and characterization of three tetrakis(alkyl isocyanide)platinum(II) tetracyanoplatinate(II) double-complex salts, $[\text{Pt}(\text{CNR})_4][\text{Pt}(\text{CN})_4]$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{or } t\text{-C}_4\text{H}_9$), two of which ($\text{R} = \text{C}_2\text{H}_5$ or $t\text{-C}_4\text{H}_9$) show a low but definite solubility in acetonitrile; the ethyl compound is also slightly soluble in water and ethanol. Thus in addition to spectral measurements on the solid salts, the solution properties of the two salts were investigated, and evidence is presented for anion-cation interaction in solution.

Experimental Section

Preparation of Compounds. The starting material for the double complex salts was potassium tetracyanoplatinate(II), $\text{K}_2[\text{Pt}(\text{CN})_4]$, which was prepared by the literature method⁸ and converted to the *n*-butylammonium salt.⁹ The complex $[\text{Pt}(\text{CNC}_2\text{H}_5)_4][\text{BF}_4]_2$ was prepared by alkylating $\text{Pt}(\text{CN})_4^{2-}$ with triethylxonium tetrafluoroborate according to the method described for the methyl compound.¹⁰ A sample of $[\text{Pt}(\text{CNCH}_3)_4][\text{BF}_4]_2$ was kindly supplied by Professor P. M. Treichel.¹⁰ The *tert*-butyl isocyanide ligand was prepared and purified according to the method of Casanova, *et al.*¹¹ Tetra-*n*-butylammonium tetrachloroplatinate(II) was prepared as described previously.⁹ All other chemicals were reagent grade; solvents were Spectro Grade and were used without further purification.

Tetrakis(ethyl isocyanide)platinum(II) Tetracyanoplatinate(II),

(1) Taken in part from the Ph.D. dissertation of H. I., Northern Illinois University, DeKalb, Ill., 1974.

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