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Exchange Reaction of Pt^{II} Complexes. II. Thiocyanate Exchange with Complexes of the Type $Pt(A\text{-}A)(SCN)_2$

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The kinetics of the isotopically labelled ligand exchange reaction

$$Pt(A{-}A)(SCN)_2 + {}^*SCN^- \rightleftharpoons Pt(A{-}A)(SCN)({}^*SCN^-) + SCN^-$$

where A–A is a series of substituted ethylenediamines of increasingly bulky substituents have been investigated. Activation parameters were determined and are discussed in terms of the importance of steric factors in the reaction mechanism for square-planar complexes. The normal two-term rate law $k_{obs} = k_1 + k_2[Y]$ *for square-planar complexes is observed. For A–A = N,N'-dimethylethylenediamine,* $H_2* = 16.8$ *Kcal mole*$^{-1}$*;* $S_2* = -16$ *e.u. For A–A = N,N'-diethylethylenediamine* $H_2* = 20.1$ *Kcal mole*$^{-1}$*;* $S_2* = -6$ *e.u. For A–A = N,N'-diisopropylethylenediamine,* $H_2* = 16.5$ *Kcal mole*$^{-1}$*;* $S_2* = -19$ *e.u. For A–A = stilbenediamine (1,2 diphenyl, 1,2 diaminoethane);* $H_2* = 14.0$ *Kcal mole*$^{-1}$*;* $S_2* = -14$ *e.u.*

Introduction

The influence of steric factors on the kinetics and mechanism of the reactions of complexes of Pt^{II}, has been the subject of a number of papers.[1-7] It has been shown that if the complex substrate is sterically hindered, there is a marked effect on the reaction rate, and similarly, sterically hindered incoming groups also show significant rate variations.[6,7] Baddley and Basolo[8] have also demonstrated that the kinetic pattern followed by highly sterically hindered Pd^{II} complexes departs from the usual behaviour of square-planar complexes. These studies concerning sterically hindered complexes may be divided into two types. In the one, typified by the work of Basolo *et al.*[1] on the reaction $Pt(PEt_3)_2LCl + py \rightleftharpoons Pt(PEt_3)_2Lpy^+ + Cl^-$ where L = phenyl, *o*-tolyl or mesityl, the steric blocking of the sites of reaction of the complex is gradually increased. The results show that as the extent of substitution on the phenyl ring increases the rate of reaction decreases. Since the effect is far greater for the *cis* compounds than for the *trans*, this is interpreted as showing that the incoming ligands are hindered in their approach to the molecule along a direction perpendicular to the plane of the molecule.

In the second type of study,[2,3] comparison is made between the totally unhindered compound $Pt(dien)Cl^+$, and the almost completely sterically blocked compounds $Pt(Et_4dien)Cl^+$, where a marked rate decrease was found, and in addition the latter compound does not obey the well documented rate law.[9]

$$k_{obs} = k_1 + k_2[Y]$$

for square-planar complexes. There is no rate dependence on the concentration of the nucleophile, and its reactions closely resemble those of octahedral systems.

In all these cases, only rate constants have been determined, and no attempts were made to determine activation parameters.

In this study, an attempt is made to evaluate the importance of steric blocking by gradually changing the size of bulky substituents of the ligands in the compelx, and determining the activation parameters.

The ligand exchange reaction $Pt(A{-}A)(SCN)_2 + {}^*SCN^- \rightleftharpoons Pt(A{-}A)(SCN)({}^*SCN^-) + SCN^-$ (A–A = a substituted ethylenediamine) was chosen, rather than a substitution reaction to avoid the complications of having different incoming and leaving groups.

Experimental Section

Ligands. Stilbenediamine 2,3-diphenyl-ethylenediamine (stien) was prepared by the methods of Drew and Head[10] and Mills and Quibell.[11] Ten ml of benzaldehyde were treated with 100 ml conc. ammonia (spec. gravity = 0.880) in the cold and allowed to solidify overnight, after vigorous initial shaking.[12]

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[3] R. Wanguo, Master's Thesis, Northwestern University, 1965, quoted in Ref. 26, F. Basolo, in «Advances in Chemistry Series» No. 49 (American Chem. Soc. 1965).

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[12] A. I. Vogel, «Practical Organic Chemistry», Third Ed., Longman's Green, London (1956).

Solid hydrobenzamide thus obtained was recrystallised from ethanol. Fifty grams of hydrobenzamide were heated on an oil-bath at 120°-130°C for five hr. To the reaction mixture, a viscous yellow liquid at 120°C, was added, while hot, 80 ml acetic anhydride and 1.5 g sodium acetate. The solution was boiled for three hr after which 15 ml conc. hydrochloric acid and 150 ml water was added. Heating on a water-bath for 2 hr ensured that this reaction went to completion. The product, N-benzoyl, N′-acetyl-2,3-diphenylethylenediamine(I) was filtered washed with water and hot ethanol, and dried in an oven at 120°C.

The entire yield of (I) was added to 600 ml 1:1 sulphuric acid and heated to boiling. A current of steam was passed through the reaction mixture to prevent charring by concentration of the acid. After 3 hr the mixture was cooled in an ice-bath and treated with 300 ml conc. ammonia. Solids that separated were filtered off and discared. The filtrate was rendered alkaline with conc. ammonia, whereupon stilbenediamine separated from solution. The product was recrystallised from boiling water (M.Pt. 115°C; yield = 5%).

N,N′-diisopropylethylenediamine was prepared by the reaction of ethylenedichloride and isopropylamine in an autoclave for 18 hr at 120°C, as described elsewhere.[13,14] The diamine was separated from the reaction mixture by addition of 40 *M* potassium hydroxide. The organic layer was separated and distilled under reduced pressure (B.Pt. at 37 mm Hg = 84°C). The amine itself is strongly hygroscopic and absorbs water so quickly that it was found extremely difficult to isolate the pure liquid amine even by distillation over solid potassium hydroxide. Instead it was obtained by acidification of aqueous solution of the distillate with hydrochloric acid, as the dihydrochloride salt. It was characterised by n.m.r. and i.r. spectra.

N,N′-dimethyl- and N,N′-diethylethylenediamine are commercially available.

*Complexes.** The complexes were all prepared by methods published elsewhere,[15] with minor modifications in the case of the stilbenediamine and N,N′-diisopropylethylenediamine compounds. A solution of stilbenediamine in hot water was added to a solution of $Pt(SCN)_4^{2-}$, and the complex separated by filtration.

A solution of N,N′-diisopropyl-en 2HCl in H_2O was neutralised with 1 *M* potassium hydroxide and added to a solution of $Pt(SCN)_4^{2-}$. The pH was maintained at 7-8 by periodic addition of 1 *M* potassium hydroxide. The solution was maintained at 0°C for about a week, and the complex filtered off and recrystallised from DMF-water mixtures.

All complexes were characterised by analysis, and infrared and electronic spectra for the complexes of alkyl substituted ethylenediamines.[15,16] The n.m.r. spectrum of the diisopropyl compound confirms the nature of the substituted ethylenediamine present.

$Pt(stien)(SCN)_2$ required Pt = 37.31; C, 36.70. Found: Pt, 37.95; C, 36.79. $Pt(N,N'{-}Me_2{-}en)(SCN)_2$ requires C, 18.05; H, 3.01; N, 14.04; S, 16.04. Found: C, 18.06; H, 2.87; N, 13.93; S, 16.11. $Pt(N,N'{-}Et_2{-}en)(SCN)_2$ requires C, 22.48; H, 3.75; N, 13.11; S, 14.99. Found: C, 22.76; H, 3.76; N, 13.08; S, 14.85. $Pt(N,N'{-}iPr_2{-}en)(SCN)_2$ requires C, 26.37; H, 4.40; N, 12.31; S, 14.07. Found: C, 26.25; H, 4.22; N, 12.15; S, 13.95.

Chemicals. Isotopically labelled thiocyanate containing radioactive ^{35}S was prepared as described elsewhere.[17] N,N′-dimethylformamide was dried over calcium oxide and fractionated through a glass head column (B.Pt 155-157°C). All other chemicals were analytical reagent grade and were recrystallised, and dried to constant weight before use. Distilled water was used throughout.

Kinetics. The exchange of isotopically labelled thiocyanate with the complex was followed by the same technique as described elsewhere, and the results were treated in the same manner.[17] The observed rates as a function of the thiocyanate concentration for the various complexes are listed in Tables I-IV. Rate constants are listed in Table V and Table VI contains the activation parameters for the reactions of the different complexes.

Table I. Kinetic data for the Reaction $Pt(N,N'{-}Me_2{-}en)(SCN)_2 + {}^*SCN^- \rightleftharpoons Pt(N,N'{-}Me_2{-}en)(SCN)({}^*SCN^-) + SCN^-$. $[Pt(N,N'{-}Me_2{-}en)(SCN)_2] = 0.2$; $\mu = 0.6$

$[SCN^-]$	$10^5 R_{obs}$ (*M* sec^{-1})			
(*M*)	20.0°C	25.0°C	30.1°C	35.0°
0.06	1.45	1.95	3.64	5.56
	1.47	2.12	4.06	4.22
				5.85
0.15	3.29	4.96	8.35	11.17
	2.90	4.66	8.80	10.78
			7.55	13.22
0.225				19.35
				15.59
0.30	5.64	9.16	14.26	22.8
	5.89	8.81	14.60	24.5
				23.9
0.45	7.86	12.31	21.65	29.8
	8.30	12.15	10.09	
			19.41	
0.54	9.22	15.22	29.10	
	9.48	16.01	27.40	
			26.40	

Results and Discussion

Values of k_2 are obtained from the least squares slopes of R_{obs} *vs.* $[SCN^-]$ while values of k_1 are obtained from the intercepts of these lines. The k_1 path contributes little to the overall reaction rate, and the values of the intercepts are extremely small. The uncertainty in the temperature dependence studies were thus relatively large. Although reasonable

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(*) Me=methyl; Et=ethyl; IPr=isopropyl; en= ethylenediamine).

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Table II. Kinetic data for the Reaction $Pt(N,N'-Et_2-en)(SCN)_2 + {}^*SCN^- \rightleftharpoons Pt(N,N'-Et_2-en)(SCN)({}^*SCN^-) + SCN^-$. $[Pt(N,N'-Et_2-en)(SCN)_2] = 0.12\ M$; $\mu = 0.6$

$[SCN^-]$ (M)	10^5 R_{obs} (M sec^{-1}) 25.6°C	 30.4°C	 35.1°C
0.060	0.44	1.35	2.39
	0.40	1.37	3.18
	0.73		
0.150	1.24	3.05	5.05
	1.56	3.57	5.04
0.231			7.69
			8.04
0.300	2.81	4.47	12.01
	2.70	5.39	11.41
0.450	4.23	9.99	15.81
	4.21	9.64	15.17
0.540	5.13	12.51	
	4.90	12.00	

Table III. Kinetic data for the Reaction $Pt(N,N'-iPr_2-en)(SCN)_2 + {}^*SCN^- \rightleftharpoons Pt(N,N'-iPr_2-en)(SCN)({}^*SCN^-) + SCN^-$. $[Pt(N,N'-iPr_2-en)(SCN)_2] = 0.09$; $\mu = 0.6$

[SCN] (M)	10^5 R_{obs} (M sec^{-1}) 20.0°C	 25.0°C	 30.0°C
0.06	0.51	0.64	1.54
	0.41	0.60	1.38
0.15	0.93	1.34	3.11
		1.42	2.11
0.30	1.78	2.05	5.30
	1.82	2.20	4.75
0.45	2.22	2.86	6.72
	2.32	2.89	5.96
0.54		3.75	7.35
		3.24	7.16
		3.83	

Table IV. Kinetic data for the Reaction $Pt(stien)(SCN)_2 + {}^*SCN^- \rightleftharpoons Pt(stien)(SCN)({}^*SCN^-) + SCN^-$. $[Pt(stien)(SCN)_2] = 0.1911\ M$; $\mu = 0.6$

$[SCN^-]$ (M)	10^5 R_{obs} (M sec^{-1}) 34.2°C	 44.1°C	 50.0°C
0.0417	0.64	1.59	2.55
0.1250			4.49
0.2500	2.72	5.77	9.00
0.4000	4.14	8.30	13.69
0.5000	5.25	10.08	16.55

Table V. Rate Constants for the Reaction $Pt(A-A)(SCN)_2 + {}^*SCN- \rightleftharpoons Pt(A-A)(SCN)({}^*SCN) + SCN^-$.

Temp. (°C)	10^6 k_1 (sec^{-1})	10^4 k_2 (M sec^{-1})
	$(A-A) = N,N'-Me_2-en$	
20.0	16.6	4.00
25.0	14.1	6.82
30.1	26.8	11.51
35.0	40.1	17.21
	$(A-A) = N,N'-Et_2-en$	
25.6		4.73
30.4		9.35
35.1		14.24
	$(A-A) = N,N'-iPr_2-en$	
20.0	13.06	2.63
25.0	18.68	3.32
30.0	49.40	6.76
	(A–A) = stien	
34.2	1.25	5.20
44.1	3.67	10.38
50.0	6.25	15.81

Table VI. Activation Parameters for the Reaction $Pt(A-A)(SCN)_2 + {}^*SCN^- \rightleftharpoons Pt(A-A)(SCN)({}^*SCN) + SCN^-$.

A–A	k_2 path ΔH^*(Kcal mole^{-1})	ΔS^*(e.u.)
en [a]	23.4	15
pn [a]	23.4	15
$N,N'-Me_2-en$	16.8	–16
$N,N'-Et_2-en$	20.1	–6
$N,N'-iPr_2-en$	16.5	–19
stien	14.0	–14
	k_1 path ΔH^*(Kcal mole^{-1})	ΔS^*(e.u.)
en [a]	10.6	–39
pn [a]	8.0	–47

[a] From Ref. 17.

values of ΔH_1^* and ΔS_1^* were obtained, it is felt that the steric influence on the k_1 path could probably be better assessed *via* a substitution reaction and this forms the basis of a separate paper. Discussion is limited here to the k_2 path and the k_1 path for the en and pn compounds previously published.

For the $N,N'-Et_2-en$ compound, the experimental scatter was such that although a reliable slope was obtained, from which k_2 was calculated, the value of the intercept was insufficiently reliable for acceptable k_1 values to be obtained.

Although the k_1 path values are not discussed in this paper the observed rate followed the general rate law for square-planar complexes, *viz.*,

$$k_{obs} = k_1 + k_2[SCN]$$

even at high values of the thiocyanate concentration. Martin *et. al.*[18-20] have shown than in exchange reactions involving bromoplatinum systems, bridged bromo species of kinetic importance are formed. In the $Pt^{IV}-Pt^{II}$ electron exchange reaction, thiocyanate ions have been shown to act as bridging groups, and it is well known that the thiocyanate group bonds either through the nitrogen or the sulphur atom.[21-25]

It might have been expected thus, that thiocyanate bridged species of kinetic importance would be indicated. This, however, was not observed, and

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the ligand behaves « normally », as it does in ordinary substitution reactions,[9,26] *i.e.* no higher order Pt^{II} terms in the rate expression.

Previous studies on steric effects in Pt^{II} systems have in the main, been directed at proving the associative nature of the now generally accepted mechanism of substitution at square-planar complexes. The argument used was that the presence of bulky groups in the complex substance would hinder the approach of the incoming group, and the rate would suffer a retardation in comparison with unhindered systems. Rate constants under the same experimental conditions were compared, and showed to agree with the above argument.[1-4] Observed increases in rate were taken as evidence for the operation of a dissociative type of mechanism.[26]

This study has revealed the danger of this direct comparison of rate constants. For the exchange reaction of the complex $Pt(en)(SCN)_2$ with labelled thiocyanate,[17] k_2 at 34.2°C was found to be 59.50×10^{-5} M^{-1} sec^{-1}. Molecular models confirm the suggestion that N,N′-dialkyl substituted ethylenediamines show significant steric hindrance. On this basis, a significant rate retardation could be expected for the complexes of these substituted ligands. In fact the values found for k_2 at the indicated temperatures are, for N,N′-di-methylethylenediamine 115.1×10^{-5} M^{-1} sec^{-1} (30.1°C); for N,N′-diethylethylenediamine 93.5×10^{-5} M^{-1} sec^{-1} (30.4°C) and for N,N′-diisopropylethylenediamine 67.6×10^{-5} M^{-1} sec^{-1} (30.0°C). Thus even at lower temperatures, the reactions of the sterically hindered compounds are faster than the reaction of the reference unsubstituted ethylenediamine complex.

On the basis of the foregoing arguments, this would lead to a conclusion of the operation here of a dissociative mechanism which is totally at variance with virtually all of the vast Pt^{II} documentation. The apparent anomaly is, however, explained by reference to the activation parameters for the reaction.

It should be remembered that the slope of a graph of log k against 1/T for a reaction contains the activation energy for the reaction. If within a series of related compounds, the activation energy changes significantly, log k *vs.* 1/T plots may yield straight lines that intersect one another. Comparison of rates constants, therefore, depends on the rather fortuitous value of the temperature at the point of intersection. Whereas one reaction may be slower than another at a given temperature, this relationship may be inverted at a higher temperature. In such a case, the only valid comparisons that can be made are between the activation parameters for the reaction.

The values of the activation parameters for the k_2 path are listed in Table VI, together with the activation parameters for both k_1 and k_2 path for the en and pn complexes obtained previously. The difference in ΔS_1^* values between the en and pn compounds was attributed to the action of the methyl group in imposing a degree of order on the reactants in the pn system. For solvation of the complex by solvent molecules to occur, the orientation of the molecules with respect to one another is important. In the en complex, the DMF molecule can approach the square plane of the complex from almost any direction, whereas the presence of the extra methyl group in the pn complex excludes certain directions of attack, thus conferring a degree of orientation onto the pn system and lowering its activation entropy. Because the physical geometry of the system has oriented the substrate favourably with respect to the incoming solvent molecule, the energy of activation is reduced.

For the en and pn systems, no difference in the activation enthalpy or entropy was observed for the k_2 path. The thiocyanate group, being physically much smaller than the DMF molecule, does effectively not « see » the extra methyl group of the pn. However, as Basolo *et al.*[1] have shown the closer the bulky group is to the site of reaction, the greater is the steric effect. Thus *cis* substituents hinder reactions far more than *trans*-substituents.

In the present study, three compounds of increasingly bulky substitution were introduced onto the nitrogen atoms of the ethylenediamine group. These substituents were thus much closer than the C-methyl group and steric interaction could more readily be expected to occur. This is in fact found to be the case, and drastic changes in activation entropies are observed, as well as smaller but significant changes in activation enthalpies.

These changes are explained in exactly the same way. The bulky groups so close to the reaction sites, exclude the entry of the incoming ligand from any direction, but impose a significant orientation on it. The degree of orientation is reflected directly in the negative ΔS_2^* values, and in turn in the reduced ΔH_2^* values. It is interesting that the stilbenediamine compound has activation parameters close to those of the N,N′-dialkyl substituted compounds. This would suggest that although the substituent phenyl group is further away from the reaction site on the C-atom, it is so big that the incoming ligand encounters marked steric interference. This view is supported by the fact that molecular models show the environment immediately above and below the platinum atom in the plane to be very similar for the stien and N,N′-dimethylethylenediamine compounds. It is possible, however, that this rate difference is due to change in the *trans*-labilisation properties of the nitrogen atoms caused by the introduction of aromatic character in the metal-en chelate ring.[27] A resultant reduction in electron density would be transmitted across the plane of the molecule as described by Chatt[28] and Orgel[29] in their theories of the *trans* effect. The weakened Pt–S bond would result in a greater lability for the thiocyanate group.

Within the N,N′-dialkylethylenediamine series, the diethyl compound appears to be anomalous cf. to the dimethyl and diisopropopyl compounds which are very similar. It is possible that the incoming ligand, « sees » the same steric repulsion above and below

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the plan eof the complex for the latter two compounds. Molecular models show that it is possible that the steric hindrance in the case of the diethyl compound is actually less than either of the other two, because the chain structure of the ethyl group places the majority of the bulk of the substituent relatively far from the site of reaction.

These and other problems are currently being investigated by the utilisation of substitution reactions using ligands of fair size.

It is possible that these activation parameter differences are due to changes in the relative energies of the d-orbitals of the metal. Spectroscopic studies on these complexes[16] have shown that the d-orbitals are seriously perturbed by the introduction of bulky groups, but it is as yet not clear what correlation may be drawn between the spectroscopic data, and the kinetic results reported here.