Exchange Reaction of Pt^{II} Complexes. I. Thiocyanate Exchange with Complexes of the Type Pt(A-A)(SCN)$_2$
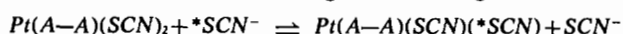
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The isotopically labelled ligand exchange reaction

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

has been investigated in dimethylformamide solution. A two term rate law is observed

$$R_{obs} = \{k_1 + k_2[SCN^-]\}[Pt(A-A)(SCN)_2]$$

Activation parameters are determined, and are discussed in terms of the role played by bulky ligands in the substitution mechanism. For A–A = ethylenediamine, $k_1 = 5.40 \times 10^{-6}$ sec^{-1}; $k_2 = 59.50 \times 10^{-5}$ M^{-1} sec^{-1} at 50°C; $H_1^* = 10.6 \pm 1.5$ Kcal mole^{-1}; $S_1^* = -39 \pm 2$ e.u.; $\Delta H_2^* = 23.4 \pm 2$ Kcal mole^{-1}; $S_2^* = 15 \pm 2$ e.u. For A–A propylenediamine, $k_1 = 3.50 \times 10^{-6}$ sec^{-1}, $k_2 = 60.10 \times 10^{-5}$ M^{-1} at 50°C; $H_1^* = 8.0 \pm 1.5$ Kcal mole^{-1}; $\Delta S_1^* = -47 \pm 2$ e.u.; $H_2^* = 23.4$ Kcal mole^{-1}; $\Delta S_2^* = 15 \pm 2$ e.u.

Introduction

The general two term rate law for substitution reactions at square-planar complexes $R_{obs} = \{k_s + k_y[Y]\}[complex]$—(1) has been well established.[1,2] A special case of the substitution reaction is where the incoming group and leaving group are chemically identical, so that no nett chemical change occurs. These reactions, which are followed by radioisotopic labelling techniques, have, despite their theoretical importance, enjoyed, by comparison with the more common substitution reactions, relatively little attention. Martin has reviewed the field of ligand exchange reactions,[3] and found that these have been of two basic types. In the one, the « normal » rate law (1) above is found to be obeyed. « Abnormal » exchanges exhibit rate laws involving other higher power terms, interpreted as evidence for the intervention of kinetically important bridged intermediates. Bromocomplex systems appear particularly sensitive to the formation of bridged polynuclear compounds.[4-7]

Previous studies[8-12] of the influence of steric properties of bulky ligands on the rate law for square-planar complexes have involved the use of substitution rather than exchange techniques, and furthermore, have generally concerned themselves only with a comparison of relative rates. Although much data on steric effects is available, little systematic work appears to have been done.

This study reports the exchange reactions of two complexes of the type Pt(A–A)(SCN)$_2$ with labelled thiocyanate, with the aim of investigating the influence of the steric properties of bulky ligands on the rate law (1), with special reference to the information obtained from a temperature dependence study of the reaction.

Experimental Section

Complexes. Pt(en)(SCN)$_2$ and Pt(pn)(SCN)$_2$ were prepared by previously published methods[13] and were characterised by analysis and conductivity measurements in N,N'-dimethyl formamide (DMF). Pt(en)(SCN)$_2$ requires Pt, 52.60; C, 12.93; H, 2.16; N, 15.09; S, 17.23. Found: Pt, 52.48; C, 13.07; H, 2.15; N, 15.04; S, 17.11. Pt(pn)(SCN)$_2$ requires Pt, 50.70; C, 15.60; H, 2.60; N, 14.51; S, 16.58. Found: Pt, 50.42; C, 16.08; H, 2.69; N, 14.04; S, 16.42.

Isotopically labelled thiocyanate. Isotopically labelled potassium thiocyanate incorporating radioactive ^{35}S was prepared from « carrier-free » sodium sulphate supplied by the Radiochemical Centre, Amersham, Harts., England, by the methods of Briske, Hartehorne and Stranks[14] and Adamson.[15] ^{35}S, a weak beta emitter has a conveniently long half-life of 87 days.

(1) F. Basolo and R. G. Pearson, « Mechanisms of Inorganic Reactions », 2nd. ed., Wiley, N. Y., (1967). Chap. 5, and references therein.
(2) C. H. Langford and H. B. Gray, « Ligand Substitution Process », Benjamin, N. Y., (1965). Chap. 2, and references therein.
(3) D. S. Martin, Jr., *Inorg. Chim. Acta Reviews.*, 1, 87 (1967).
(4) A. A. Grinberg and G. A. Shagisultanova, *Izv. Akad. Nauk. SSSR*, 6, 981 (1955).
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(9) R. G. Pearson, H. B. Gray and F. Basolo, *J. Am. Chem. Soc.*, 82, 787 (1960).
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(11) R. Wanguo, Master's thesis, North Western University, 1965, quoted in ref. 2; F. Basolo, in « Advances in Chemistry Series, » No. 49, *J. Am. Chem. Soc.*, (1965).
(12) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, 86, 2075 (1964).
(13) R. J. Mureinik and W. Robb, *Spectrochim. Acta*, 24A, 837 (1968).
(14) C. Briske, N. H. Hartehorne and D. R. Stranks, *Inorg. Syn.*, 7, 116 (1963).
(15) A. N. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, 76, 3379 (1954).

Chemicals. N,N'-dimethyl formamide (DMF) was dried over calcium oxide and fractionated through a glass bead 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. Solutions of the appropriate cocnentration of complex together with the appropriate concentration of ammonium thiocyanate were made up, and allowed to equilibrate at the temperature of the experiment. Ionic strength was maintained constant with ammonium perchlorate. Temperature control was effected in two ways. The reaction vessel for the experiments at 34.2°C was maintained in an ether vapour bath which gave temperature constant to within 0.1°C. Other experiments were carried out in a water bath with the temperature thermostatically regulated to within 0.1°C.

A « spike » of labelled thiocyanate contained in 0.01 ml solution was injected into the reaction vessel. The time of mixing was taken as the zero time for the reaction . The solution was vigorously shaken at regular intervals. Aliquots of 0.4 ml were withdrawn at regular intervals and the complex precipitated from solution by addition to 5 ml of ice-cold water, with vigorous shaking. (Sometimes solid ice was present as well, as an aid to precipitation). The solutions were filtered under suction through sintered glass discs of known weight. The same filtration apparatus was used throughout so that the mounted samples had the same diameter, thus keeping the geometry of the counting process uniform. Using this filtration technique, separation of the complex from the mother liquor was complete within 30 seconds, a time negligible with respect to the half-life of the reaction.

The samples were dried under an infrared lamp and weighed. Counting was done on a conventional Geiger-Muller end-window counter, and recorded on a Philips Electronic Counter P.W. 4035 Scalar Unit.

Samples recovered from the exchange experiment were found by analysis, infrared and electronic spectral measurements to be identical to the starting product.

« Infinite time » samples were taken at times greater than twelve half-lives of the reaction. These were checked for equilibrium distribution of the isotopic label with samples taken a few half-lives of reaction later.

Results

The specific activities of all samples taken during the course of the exchange reaction were determined and expressed as counts per minute per milligram.

The results were treated using the McKay equation,[16,17] as detailed by Friedlander and Kennedy.[18]

The fraction of exchange, F, at time t, for each

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sample was determined, where F is given by

$$F = \frac{x_t}{x_\infty}$$

and

$$x_t = \text{specific activity at time } t$$
$$x_\infty = \text{specific activity at infinite time.}$$

The half-time of reaction $t_{1/2}$ (the time at which $F = \frac{1}{2}$) was obtained from least squares plots of $\log(1-F)$ against t, and used to evaluate the observed rate in the equation

$$R_{obs} = \frac{0.693}{t_{1/2}} \cdot \frac{ab}{a+b}$$

where a = 2[complex]. The factor 2 allows for the fact that the bound thiocyanate ligands are kinetically equivalent and b = [SCN⁻].

Zero time exchange was found not to occur. Extrapolation of $\log(1-F)$ versus time plots to zero time showed that within experimental error no excess exchange occurred over and above that monitored in the rate process. Also, samples taken just after injection of the « spike » were shown to be of very low activity indeed.

Separation-induced exchange was found not to occur by the fact that a suspension of $Pt(en)(SCN)_2$ in water in the presence of large amounts of labelled thiocyanate, does not show activity on separation from the slurry.

Table I. Rate Data for the Reaction $Pt(en)(SCN)_2 + SCN^- \rightleftharpoons Pt(en)(SCN)(*SCN) + SCN^-$.

A. [SCN⁻] (M)	$10^6 R_{obs}$ (M sec⁻¹)			
	34.2°C	40.0°C	44.1°C	50.0°C
$[Pt(en)(SCN)_2] = 0.2050\ M$; $\mu = 0.6000$				
0.0625	2.83	5.74	—	18.48
0.1250	5.26	11.41	—	29.95
				32.55
0.1520	6.95	13.30	21.05	—
0.2500	10.18	19.42	—	67.00
0.2980	12.38	24.75	—	—
0.3333	13.75	—	—	84.30
0.3760	15.78	30.85	50.20	—
0.4000	—	—	—	97.40
0.5000	20.30	38.45	—	123.1
0.5760	22.90	44.70	76.30	—
$[Pt(en)(SCN)_2] = 0.1480$; $\mu = 0.6$				
0.0625	—	—	6.75	—
0.1250	—	7.30	12.59	22.20
0.2500	—	15.50	25.90	46.10
0.3333	—	19.30	32.70	58.50
0.5000	—	29.50	48.80	89.40
B. $[Pt(en)(SCN)_2]$		$[SCN^-] = \mu = 0.4930$		
0.1670	9.17	—	—	—
0.2065	12.02	—	—	—
0.2870	16.40	—	—	—
0.4510	25.70	—	—	—

Rate *vs.* time plots were found to be linear with both an intercept and slope, in agreement with the general rate law for platinum complexes

$$R_{obs} = \{k_1 + k_2[SCN^-]\}[complex]$$

Values of k_1 were small, and due to the inherent inaccuracy of the counting technique, it was not clear whether these values were real. Confidence tests, as well as the behaviour of k_1 with temperature showed, however, that the intercept did represent a chemical reaction, and not an experimental error.

Rate data are collected in Table I for the en complex, and in Table II for the pn complex. Rate constants and activation parameters obtained in the usual way are listed in Tables III and IV. A typical rate plot is shown in Figure 1.

Table II. Rate data for the Reaction $Pt(pn)(SCN)_2 +$ $*SCN^- \rightleftharpoons Pt(pn)(SCN)(*SCN^-) + SCN^-$.
$[Pt(pn)(SCN)_2] = 0.1947\,M$; μ 0.6000

[SCN⁻] (M)	10⁶ R_obs (M sec⁻¹)			
	34.2°C	40.0°C	44.1°C	50.0°C
0.0417	1.75	4.15	6.48	9.45
0.1250	5.19	10.97	17.24	32.65
0.2500	9.54	20.80	33.60	59.50
0.4000	14.90	33.00	53.20	94.90
0.5000	18.00	40.90	66.30	117.7

Table III. Rate constants for the Reaction $Pt(A-A)(SCN)_2 +$ $*SCN^- \rightleftharpoons Pt(A-A)(SCN)(*SCN^-) + SCN^-$

A—A	Temp. °C	10⁶k₁ (sec⁻¹)	10⁵k₂ (M⁻¹ sec⁻¹)
en	34.2	2.22	9.55
	40.0	3.45	18.80
	44.1	4.16	32.55
	50.0	5.40	59.50
pn	34.2	1.50	9.08
	40.0	2.16	20.50
	44.1	2.66	33.33
	50.0	3.50	60.10

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

A—A	k₁ path		k₂ path	
	ΔH₁* (Kcal/mole)	ΔS₁* (e.u.)	ΔH₂* (Kcal/mole)	ΔS₂* (e.u.)
en	10.6±1.5	−39±2	23.4±2	15±2
pn	8.0±1.5	−47±2	23.4±2	15±2

Discussion

Rate plots for both complexes at both temperatures as a function of the concentration of thiocyanate yield straight lines with a small, but definite non-zero intercept. Despite some experimental scatter, there is no evident deviation from linearity even at high values of the thiocyanate concentration. The rate also shows a linear dependence on the complex con-

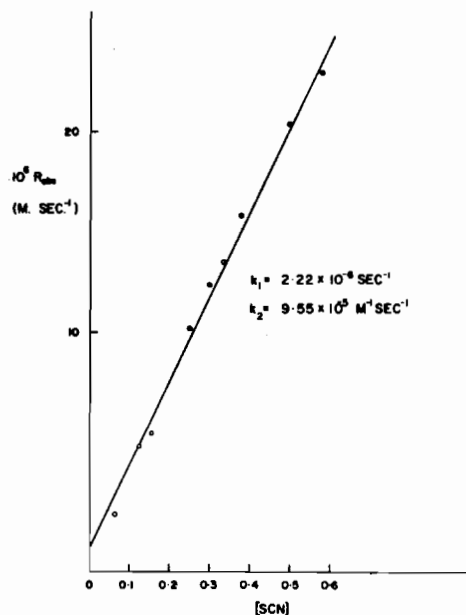centration, with no evidence for higher-order complex dependence.

Figure 1. $Pt(en)(SCN)_2 + *SCN^- \rightleftharpoons Pt(en)(SCN)(*SCN^-) + SCN^-$, $\mu = 0.6$. $[Pt(en)(SCN)_2] = 0.2050\,M$; $T = 34.2°C$.

The general rate law (1) applies in this case and no higher terms appear, thus excluding reaction paths involving a bridged binuclear species of the type found by Martin.[3] In view of the known bridging function of the thiocyanate ion in the $Pt^{IV}-Pt^{II}$ electron-transfer reaction, this is perhaps surprising,[19] until it is remembered that in substitution reactions, the ligand behaves « normally. »[1,2]

In passing it may be noted that the rate was found to show a strong ionic strength dependence. This will form the basis of a separate publication. All the data discussed in this paper were obtained at constant ionic strength.

The general two term rate law been found to apply in many different solvents apart from water, notably methanol[20] where the rates of reaction of *trans*-Pt-(py)₂Cl₂ with various ligands have successfully been used to establish a quantitative nucleophilicity scale. Relatively little work has been done on dipolar aprotic solvents systems, but Belluco *et. al.*[21] have shown that the two term rate equation is found for the reactions of *trans*—Pt(pip)₂Cl₂* in DMF, acetonitrile, DMSO and nitromethane. This is in contrast to the behaviour of DMF as the solvent for the chloride exchange with *trans*—Pt(py)₂Cl₂ reported by Pearson *et. al.*,[22] where only second-order kinetic behaviour, *i.e.* no solvent path, was observed.

The relative role of the solvating power of the

(*) pip = piperidine; DMSO = dimethylsulphoxide.
(19) R. C. Johnson and F. Basolo, *J. Inorg. Nucl. Chem.*, **13**, 36 (1960).
(20) U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).
(21) U. Belluco, A. Orio and M. Martelli, *Inorg. Chem.*, **5**, 1370 (1966).
(22) R. G. Pearson, H. B. Gray and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787, (1960).

solvent, and its donor characteristics in providing a solvo-intermediate in the reaction scheme has not been adequately evaluated,[23,24] but on both counts DMF can be viewed as a « good » solvent. The $>C=O$ system possesses π-orbitals of the right energy and symmetry for its interaction with the metal atom to be appreciable. For metal ions that are soft in the Pearson sense,[25] an aprotic dipolar solvent is a more active solvating species than a protic solvent.[23] Thus viewing DMF in either light, a significant solvent path is to be expected, and this is confirmed in the results presented in this discussion. The size of the solvent molecule is a factor that has not really been considered before in determing the role of the solvent, although Belluco et. al.[23] have suggested that the solvation of the metal ion decreases on going to the transition state for steric as well as electronic reasons. The steric requirements of the solvent are discussed more fully below.

A number of studies on steric factors have been reported,[8-12] the majority of them undertaken to provide evidence for the associative nature of substitution reactions of Pt complex. The general picture of the reaction process views the incoming group, either substituting ligand or solvent, as approaching the molecule from a direction perpendicular to the plane of the molecule. If access along this vertical direction could be denied the incoming group, it was argued that a rate retardation should be observed. Thus, for instance, in the reaction[8]

$$[Pt(PEt_3)_2RCl]^+ + py \rightarrow [Pt(PEt_3)_2Rpy]^{2+} + Cl^-$$

it was observed that for the trans compounds the relative rates for R = mesityl, o-tolyl and phenyl are 1 : 5 : 36. For the cis compound, the change of rate is even more striking. For R = mesityl, o-tolyl and phenyl, the ratio is 1 : 200 : 80000.

It was suggested that the presence of o-methyl groups on the phenyl nucleus, hinder the approach of the incoming ligand and result in a rate retardation. The fact that the effect is so striking for cis compounds as opposed to trans compounds is direct evidence in support of the idea of steric blocking, for in the cis compounds, the bulky groups are a lot closer to the sites of reaction.

The importance of steric blocking was shown by the fact that whereas [Pt(dien)Cl]$^+$ shows normal square-planar kinetic behaviour[10] with $k_1 = 10^{-4}$ sec^{-1} at 25°C, the totally sterically hindered [Pt(Et$_4$-dien)Cl]$^+$ shows only a k_1 path with $k_1 = 8.5 \times 10^{-6}$ sec^{-1} at 80°C.[11] The kinetic behaviour of the latter compound resembles that of octahedral complexes, and shows that the steric requirements of bulky ligands have rendered inoperable the associative type of mechanism. This study represents a comparison of a non-sterically hindered complex, with a totally sterically hindered complex, which results in a drastic mechanistic difference. In the current study of steric hindrance, a series of closely related chemical constitution, but incorporating a series of ligands whose bulkiness increases gradually, is used in an attempt to determine the exact nature of the effect of bulky groups.

Table III lists the values of the rate constants obtained for the en and pn compounds. Comparison of the k_2 values for the two compounds at all temperatures shows no significant differences. This is reflected in the activation parameters for the k_2 path where the values $\Delta H_2^* = 23.4$ Kcal/mole and $\Delta S_2^* = 15$ e.u. are obtained for both compounds.

The fact that ΔH_2^* is the same for both compounds is interpreted as showing that there is no difference in the nature of the Pt–S bonding for the two compounds. This verifies the treatment of rate data for the pn compound, for it could be claimed that the presence of an asymmetrically substituted ethlenediamine in the complex could lead to kinetically inequivalent thiocyanate groups. The linearity of the rate plots for the exchange with the pn complex shows that only one reaction is kinetically observable, while the constancy of ΔH_2^* shows that the incorporation of an extra methyl group has not had any trans-labilising effect. This is consistent with the fact that virtually no difference in the Pt–S or Pt–N stretching frequencies is observed in the infrared spectra of the compounds.[13]

The fact that ΔS_2^* is also constant indicates that there is very little difference in the transition states of the two complexes. The magnitude of ΔS_2^* is perhaps unusual in that it has a positive value. The general view that for square-planar complexes ΔS^* should be negative appears to stem from an incomplete survey of activation parameters[26] for substitution of some square-planar complexes. However, this survey ignores the work, for example of D. S. Martin et. al.[27] who found a positive activation entropy for the reaction of an ion and dipole in solution. Other examples of positive activation entropies have been found.[28,29]

The variation of k_1 with temperature (Table IV) yields an activation enthalpy of 10.6 Kcal/mole for the solvolytic path with an activation entropy of –39 e.u. for the en complex. The corresponding values for the pn complex are 8.0 Kcal/mole and –47 e.u. Direct comparison of the first order rate constants at 50°C, viz. 5.40×10^{-6} sec^{-1} for the en complex, and 3.50×10^{-6} sec^{-1} for the pn complex, seem to suggest that the extra methyl group of the propylenediamine bidentate group had slightly influenced the rate of the solvolytic reaction.

It could well be reasoned that steric repulsion between the methyl group and the methyl groups of the solvent were responsible for the rate retardation. The fact that no effect was shown on the k_2 path could be attributed to the fact that the steric requirements of the thiocyanate anion are much smaller than those of the bulkier DMF molecule, so that the incoming thiocyanate does not « see » the extra methyl group. The nature of the extended structure of the solvent

(23) U. Belluco, M. Graziani, M. Nicolini and P. Rigo, Inorg. Chem., 6, 721 (1967).
(24) R. S. Drago, V. A. Mode and J. G. Kay, Inorg. Chem., 5, 2051, (1966).

(25) R. G. Pearson, J .Am. Chem. Soc., 85, 3533 (1963).
(26) U. Belluco, R. Ettore, F. Basolo, R. Pearson and A. Turco, Inorg. Chem., 5, 591 (1966).
(27) F. Aprile and D. S. Martin, Jr., Inorg. Chem., 1, 551 (1962).
(28) W. Robb, Inorg. Chem., 6, 382 (1967).
(29) W. J. Louw, M. Sc. Thesis, University of South Africa, (1966).

however, brings into play the steric needs of a bulky group at a greater distance from the site of reactions.

This is in keeping with the findings, quoted above, of Basolo *et. al.,*[8] that *cis* groups show greater steric hindrance than *trans* bulky groups.

However, the temperature dependence studies of k_1 yield information of more interest. Not only is there a change in activation entropy, but in activation enthalpy as well. It cannot be argued that this change in activation enthalpy reflects *trans*-labilising properties of the additional methyl group, since this effect would surely have been observed in the k_2 path as well. (The uncertainties in the values determined in the k_2 path are inherently smaller, since k_2 values are obtained from the slope of a line, while small errors can affect intercept values and hence k_1 considerably).

The changes in the entropy term are explained as follows. For solvation between solvent molecule and metal atom to occur, the orientation of the two molecules with respect to one another is important. In the pn complex, the presence of a methyl group interferes with the randomness of direction with which the DMF molecule can approach. In other words a greater degree of orientation is conferred on the pn system compared to the en system. This orientation effect could be expected to be transmitted some distance into the bulk solvent, so that the net effect is to increase the ordering on going to the 5 co-ordinate intermediate, for pn as compared to en.

This explanation is in accordance with that advanced for negative ΔS^* values by Belluco *et. al.*[26] Solvation « freezes out » solvent molecules from the bulk solvent. Increase in the extent of bonding in the transition state explains the negative ΔS^* values obtained. Solvation of the pn complex is hindered with respect to that in the en complex, so that less solvent molecules can effectively be removed from the bulk medium.

The changes observed in ΔH_1^* can be explained as follows. Because of the stricter orientation of solvent that occurs for the pn complex, they could be regarded as being energetically more suited for bonding, and hence for stabilising the intermediate. This would result in the lowering of the activation enthalpy that is observed in going from en to pn.

It is by no means impossible that this activation energy difference has its origin in the influence of bulky groups on the energy differences between the d-orbitals of th central metal atom. Electronic spectra of these compounds show that there are marked changes in the energy splittings between the various d-orbitals[30] but as yet it is not clear what correlation may be validly drawn.

(30) R. J. Mureinik and W. Robb, *Spectrochim. Acta.*, in the press.