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Kinetics and Mechanism of the Substitution Reactions of Four- and Five-coordinate Iridium(I) Complexes. The Detection of a Stable Reaction Intermediate

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The substitution reactions of the four- (X = Cl) and five- (X = I, SCN) coordinate complexes CODIr(phen)X with ethylenediamine have been studied kinetically. The mechanism for the five-coordinate system was dissociative. A stable four- or five-coordinate intermediate CODIr(phen)(en)$^+$ has been detected in the substitution reaction of the four-coordinate system.

Introduction

Kinetic studies on the substitution reactions of four-coordinate square planar complexes revealed an associative mechanism via a five-coordinate transition state [1]. Various groups have lately been looking for a *stable* five-coordinate intermediate and two such claims have already been published [2, 3]. For the substitution reactions of six-coordinate octahedral complexes, either a dissociative mechanism *via* a five-coordinate transition state or an ion pair intermediate is involved in the mechanism [1]. On the basis of this and other work Tolman formulated a 16–18 electron rule [4] which states that diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18 electrons. This rule therefore predicts that the mechanism of the substitution reactions of diamagnetic five-coordinate transition metal complexes will be dissociative:

$$ML_5 \rightleftharpoons ML_4 + L \underset{-Y}{\overset{+Y}{\rightleftharpoons}} ML_4Y \underset{+L}{\overset{-L}{\rightleftharpoons}} ML_3Y \qquad (1)$$

The end product may either be the four-(ML_3Y) or five-(ML_4Y) coordinate complex. Another alternative is that the four-coordinate complex (ML_3Y) may be the end product, but the five-coordinate complex (ML_4Y) may be a stable intermediate.

By studying the substitution reactions of diamagnetic five-coordinate complexes, the possibility of detecting a stable five-coordinate intermediate becomes greater since the complex already strongly favours five-coordination.

Most of the data published on substitution reactions of five-coordinate complexes have been done on paramagnetic Fe [5, 6], Co [5, 7] and Ni [8] complexes which may form stable four-, five- and six-coordinate complexes. The mechanisms of these reactions are therefore not surprisingly both associative and dissociative. Two kinetic studies have been done on diamagnetic five-coordinate Pt^{II} and Pd^{II} tetradentate arsine complex substitution reactions [9, 10]. The kinetic data were unfortunately very complex and interpretations ambiguous due to the fact that the complex can only dissociate with difficulty. N.m.r. studies on neutral-ligand-exchange reactions for five-coordinate complexes have however shown the mechanism to be dissociative [11–13].

The only conclusive kinetic study on diamagnetic five-coordinate substitution reactions was probably done on a Ru^0 system which proved to be dissociative [14];

$$Ru(CO)_4L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(CO)_3L + CO \xrightarrow[L]{k_2} Ru(CO)_3L_2 \qquad (4)$$

on the basis of the limiting rate law:

$$k_{obs} = \frac{k_1k_2[L]}{k_{-1}[CO] + k_2[L]} \qquad (5)$$

We have studied the following system kinetically:

$$CODIr(phen)X + N\text{–}N \xrightarrow{\text{methanol}} CODIr(N\text{–}N)^+ + X^- + phen \qquad (6)$$

(COD = cyclo-octa-1,5-diene, phen = phenanthroline, N–N = ethylenediamine; X = Cl, I, SCN). For X = Cl the complex is four-coordinate in the solid state, while it is five-coordinate for X = SCN, I [15]. Our interest in this system is twofold. Firstly to determine whether the mechanism is associative or dissociative, and secondly to investigate the possibility of the buildup of a stable five-coordinate intermediate.

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Experimental

Materials

CODIrphenX was prepared by the method of Mestroni *et al.* [15]. The yellow endproduct CODIr(en)$^+$ was prepared by addition of ethylenediamine to $[\text{CODIrCl}]_2$ in methanol and precipitation of the cation by BPh_4^-. *Anal.* Calcd for CODIr(en)BPh_4: C, 59.72; H, 6.49; N, 4.10. Found: C, 59.72; H, 6.28; N, 4.07%.

Ethylenediamine was distilled under nitrogen atmosphere. All other materials were of A.R. grade and commercially obtained.

Kinetics

The kinetics of reaction 6 were studied by measuring the rate of disappearance of the visible peaks (565, 565, 545 nm for X = Cl, I, SCN respectively) on a Durrum D110 stopped flow apparatus. Solutions were made up under nitrogen atmosphere, the ionic strength was controlled with LiCl, and iodide solutions were kept in the dark. The ethylenediamine or substituted ethylenediamine concentrations were at all times high enough to ensure pseudo-first-order conditions. Initial complex concentrations were of the order of 10^{-4} *M*.

Spectrophotometric Determination of Equilibrium Constants

The extinction coefficients of the five-coordinate complexes CODIr(phen)I and CODIr(phen)SCN in methanol at 555 nm and 535 nm respectively have been determined in the presence of excess I$^-$ and SCN$^-$ respectively, since these complexes are in equilibrium with the four-coordinate complex CODIr(phen)$^+$. With the extinction coefficient of the four-coordinate complex also known, the ratios of this complex concentration to the I$^-$ or SCN$^-$ concentrations in methanol were varied and the equilibrium constants K_e were calculated using the obtained absorbance values. The ionic strength was kept constant with LiCl at a value of 0.2.

Results

The observed rate constant for reaction 6 showed a limiting dependence on ethylenediamine (en), N-methylethylenediamine (N-en), and N,N-dimethylethylenediamine (N,N-en) concentrations and good straight lines were obtained from $1/k_{obs}$ *vs.* $1/[\text{N–N}]$ plots, therefore

$$\frac{1}{k_{obs}} = \frac{K'}{[\text{N–N}]} + k' \tag{7}$$

Addition of Cl$^-$ to the reaction solution had no effect on the reaction rate and the ionic strength was therefore controlled with LiCl. The slope of equation 7, K′, had a linear dependence of $[\text{X}^-]$ (X = SCN, I), whereas no influence on the intercept k′, was observed:

$$K' = k'' + K''[\text{X}^-] \tag{8}$$

The empirical rate law for this system is thus:

$$k_{obs} = \frac{[\text{N–N}]}{k'' + K''[\text{X}] + k'[\text{N–N}]} \tag{9}$$

When N,N′-dimethylethylenediamine (N,N′-en) was used as incoming ligand, the limiting behavior of the amine concentration in the rate law changed to a linear behavior, while the inverse dependence of $[\text{X}^-]$ still existed for SCN and I:

$$k_{obs} = \frac{[\text{N,N'-en}]}{k''' + K'''[\text{X}^-]} \tag{10}$$

An influence on ionic strength was observed for these reactions. The observed rate constants for the above reactions at different $[\text{X}^-]$, temperatures and [N–N] are given in Table I.

The equilibrium constants K_e, for the equilibria

$$\text{CODIr(phen)}^+ + \text{X}^- \underset{\text{methanol}}{\overset{K_e}{\rightleftharpoons}} \text{CODIr(phen)X} \tag{11}$$

have been determined spectrophotometrically and are given in Table II together with rate and equilibrium constants and activation parameters for reaction 6 which have been calculated on the basis of rate law 13.

Discussion

The following reaction scheme can explain all of the observed data

$$\begin{tikzcd}
\text{CODIr(phen)}^+ + \text{X}^- \arrow[r, shift left, "K_e"] \arrow[d, shift right, "K_1\text{N–N}"'] & \text{CODIr(phen)X} \arrow[l, shift left] \\
\text{CODIr(phen)}^+ \arrow[u, shift right, "\text{N–N}"'] \arrow[r, "k"] & \text{CODIr(N–N)}^+ + \text{phen}
\end{tikzcd} \tag{12}$$

since the derived rate law

$$k_{obs} = \frac{kK_1[\text{N–N}]}{1 + K_1[\text{N–N}] + K_e[\text{X}^-]} \tag{13}$$

for N–N = en, N-en, N,N-en not only fits empirical rate law 9 but also yields values for K_e which are in excellent agreement with the spectrophotometrically determined values (Table II). CODIr(phen)(N–N)$^+$ is a stable intermediate, which may either be four-(both amines have one nitrogen not coordinated) or five-(N–N has one nitrogen not coordinated) coordinated.

From reaction scheme 12 it is evident that the k and K_1 values should not vary on changing from Cl$^-$ to I$^-$ to SCN$^-$ for the same amine. This has been found (Table II). One would expect only the non-

TABLE I. Observed Rate Constants for the Reaction 6 in the Presence of QX.

[N–N] in M	[QX] in *M*	k_{obs} in s^{-1}	[N–N] in *M*	[QX] in *M*	k_{obs} in s^{-1}	[N–N] in *M*	[QX] in *M*	k_{obs} in s^{-1}
X = Cl, T = 25 °C, Q = Li, N–N = en								
0.02	0	3.95	0.02	0.05	3.71	0.02	0.5	3.63
0.04	0	6.60	0.04	0.05	6.24	0.04	0.5	6.10
0.06	0	8.15	0.06	0.05	7.79	0.06	0.5	7.88
0.08	0	9.49	0.08	0.05	9.00	0.08	0.5	9.37
0.1	0	10.66	0.1	0.05	11.18	0.1	0.5	10.50
0.2	0	13.37	0.2	0.05	14.74	0.2	0.5	12.83
0.4	0	15.07	0.4	0.05	16.5	0.4	0.5	15.75
X = Cl, T = 20 °C, N–N = en								
0.02	0	3.41	0.06	0	6.48	0.1	0	8.00
0.04	0	5.41	0.08	0	7.22	0.2	0	9.63
						0.4	0	10.66
X = Cl, T = 30 °C, N–N = en								
0.02	0	4.71	0.06	0	10.66	0.1	0	14.14
0.04	0	8.66	0.08	0	12.83	0.2	0	17.77
						0.4	0	20.69
X = I, T = 25 °C, μ = 0.1, Q = Na, N–N = en								
0.02	0	3.63	0.06	0.01	4.78	0.2	0.015	8.77
0.04	0	6.19	0.08	0.01	5.73	0.4	0.015	11.95
0.08	0	9.12	0.1	0.01	6.73	0.02	0.03	1.03
0.2	0	12.60	0.2	0.01	9.76	0.04	0.03	1.87
0.02	0.005	2.48	0.4	0.01	12.83	0.08	0.03	3.50
0.04	0.005	4.25	0.02	0.015	1.61	0.2	0.03	6.54
0.08	0.005	7.0	0.04	0.015	3.15	0.02	0.065	0.58
0.2	0.005	10.83	0.06	0.015	4.53	0.04	0.065	1.16
0.02	0.01	1.87	0.08	0.015	5.41	0.08	0.065	2.24
0.04	0.01	3.38	0.1	0.015	6.54	0.2	0.065	4.65
X = SCN, T = 25 °C, μ = 0.1, Q = Na, N–N = en								
0.02	0	2.72	0.02	0.015	0.51	0.02	0.04	0.22
0.04	0	4.75	0.04	0.015	1.00	0.04	0.04	0.43
0.08	0	7.30	0.08	0.015	1.93	0.08	0.04	0.87
0.2	0	10.83	0.4	0.015	7.45	0.4	0.04	4.13
0.02	0.005	1.16	0.02	0.03	0.29	0.02	0.05	0.18
0.04	0.005	2.27	0.04	0.03	0.56	0.04	0.05	0.36
0.08	0.005	3.98	0.06	0.03	1.12	0.08	0.05	0.75
0.2	0.005	7.62	0.2	0.03	2.83	0.2	0.05	1.82
X = Cl, T = 25 °C, μ = 0.2, N–N = N,N′-en								
0.02	0	0.022	0.2	0	0.234	0.75	0	1.050
0.04	0	0.045	0.4	0	0.525	1.0	0	1.575
0.06	0	0.069						
X = Cl, T = 25 °C, N–N = N,N-en								
0.02	0	0.021	0.08	0	0.060	0.2	0	0.091
0.04	0	0.041	0.1	0	0.071	0.4	0	0.116
X = Cl, T = 25 °C, N–N = N-en								
0.02	0	1.95	0.06	0	4.59	0.1	0	6.08
0.04	0	3.33	0.08	0	5.54	0.2	0	8.89
						0.4	0	11.55

(Continued overleaf)

TABLE I *(continued from previous page)*

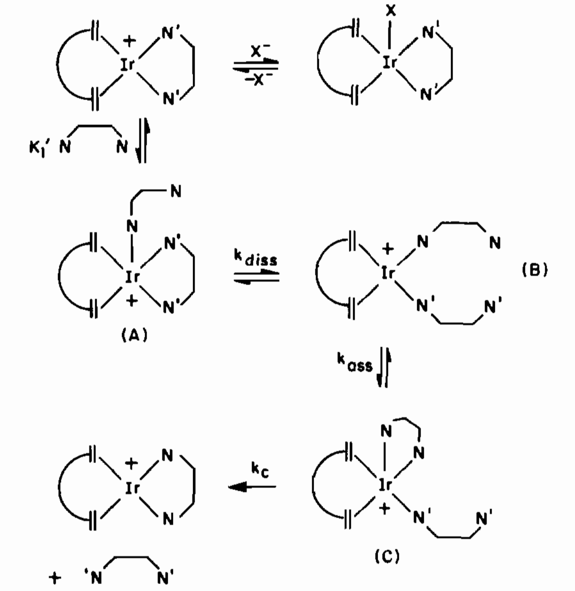
[N–N] in *M*	[QX] in *M*	k_{obs} in s^{-1}	[N–N] in *M*	[QX] in *M*	k_{obs} in s^{-1}	[N–N] in *M*	[QX] in *M*	k_{obs} in s^{-1}
X = I, T = 25 °C, N–N = N,N′-en								
0.02	0	0.024	0.06	0	0.064	0.1	0	0.119
0.04	0	0.045	0.08	0	0.090	0.2	0	0.243
						0.4	0	0.523
X = I, T = 25 °C, μ = 0.2, Q = Na, N–N = N,N′-en								
0.04	0	0.050	0.04	0.01	0.026	0.4	0.02	0.167
0.08	0	0.089	0.06	0.01	0.038	0.04	0.03	0.015
0.1	0	0.124	0.08	0.01	0.050	0.06	0.03	0.022
0.2	0	0.267	0.1	0.01	0.061	0.1	0.03	0.032
0.4	0	0.550	0.2	0.01	0.122	0.2	0.03	0.058
0.02	0.005	0.018	0.4	0.01	0.235	0.3	0.03	0.090
0.04	0.005	0.034	0.02	0.02	0.017	0.4	0.03	0.103
0.06	0.005	0.050	0.08	0.02	0.035	0.1	0.04	0.032
0.1	0.005	0.084	0.1	0.02	0.041	0.2	0.04	0.057
0.2	0.005	0.173	0.2	0.02	0.075	0.3	0.04	0.085
0.4	0.005	0.259	0.3	0.02	0.100			
X = SCN, T = 25 °C, μ = 0.2, Q = Na, N–N = N,N′-en								
0.02	0	0.023	0.1	0.005	0.037	0.1	0.01	0.021
0.04	0	0.044	0.2	0.005	0.077	0.2	0.01	0.042
0.08	0	0.092	0.4	0.005	0.161	0.4	0.01	0.102
0.1	0	0.120	0.04	0.01	0.009	0.06	0.015	0.009
0.2	0	0.248	0.06	0.01	0.013	0.08	0.015	0.012
0.4	0	0.517	0.08	0.01	0.017	0.1	0.015	0.014
0.04	0.005	0.013				0.2	0.015	0.030
0.08	0.005	0.027				0.4	0.015	0.061

TABLE II. Rate and Equilibrium Constants and Activation Parameters for Reaction 6 at 25 °C.

N–N	X	k in s^{-1} × 10^{-1}	K_e in M^{-1} × 10^{-2}	k_1 in s^{-1} M^{-1}	K_1 in M^{-1} × 10^{-1}
en	Cl	1.8 ± 0.1	–	–	1.4 ± 0.2
en	I	1.8 ± 0.1	1.2 ± 0.1	–	1.2 ± 0.2
en	SCN	1.9 ± 0.1	5.9 ± 0.3	–	1.0 ± 0.2
N-en	Cl	1.4 ± 0.1	–	–	0.8 ± 0.1
N,N-en	Cl	0.016 ± 0.002	–	–	0.8 ± 0.1
N,N′-en	Cl	–	–	1.4 ± 0.1	–
N,N′-en	I	–	1.3 ± 0.1	1.4 ± 0.1	–
N,N′-en	SCN	–	5.7 ± 0.3	1.5 ± 0.1	–
a	I	–	1.3 ± 0.2	–	–
a	SCN	–	6.0 ± 0.5	–	–
en	Cl	1.2 ± 0.1 (20 °C)	–	–	–
en	Cl	2.7 ± 0.1 (30 °C)	–	–	–
en	Cl	$\Delta H^{\neq}$ = 58 ± 6 kJ mol^{-1}			
en	Cl	$\Delta S^{\neq}$ = –25 ± 3 J mol^{-1} K^{-1}			

[a] Spectrophotometric determination of equilibrium constants at μ = 0.2 and 25 °C in methanol.

substituted nitrogen in N-en and N,N-en to be coordinated in the four- or five-coordinate CODIr(phen)(N–N)$^+$ and one is therefore tempted to attribute the halving of the equilibrium constant K_1 with steric blocking of one end of ethylenediamine (on changing from N–N = en to N-en or N,N-en) to a statistical factor. However, the k values show a tremendous decrease with building of sterical hindrance on the one end of the bidentate ethylenediamine (from en to N-en to N,N-en). In order to explain this a close look at the mechanism of the pathway described by K_1 and k is necessary. If the intermediate CODIr(phen)(N–N)$^+$ is four-coordinate, then the step described by k is ring closure of the bidentate (N–N), the rate of which will decrease drastically with steric buildup on the nitrogen that is involved in this bond formation step, as has been found. On the other hand, if the CODIr(phen)(N–N)$^+$ intermediate is five-coordinate, the sequence of steps in scheme 14–15 is expected on the basis of the 16–18 electron rule [4] :



Reaction scheme 14–15. Detailed mechanism for reaction 6 where 'N–N' is phenanthroline.

Therefore, if k_{diss} is the rate determining step, one would not expect a decrease in the k values with steric buildings on the non-coordinate nitrogen of N–N, but rather a small increase in rate. If k_{ass} is the rate determining step, there is no reason to invoke the five-coordinate CODIr(phen)(N–N)$^+$ as a stable intermediate and the mechanism is the same as for the four-coordinate case.

On the contrary, if the rate determining step is dissociative (k_{diss}) then one would expect a very small negative or positive $\Delta S^{\neq}$ value, whereas a large negative $\Delta S^{\neq}$ value (–100 to –200 J mol^{-1} K^{-1}) is normal for an associative (k_{ass}) step. The $\Delta S^{\neq}$ value of –25 J mol^{-1} K^{-1} found favours a dissociative mechanism. Furthermore, the likelihood of two bidentate amines only bonding as monodentates in four-coordinate CODIr(phen)(N–N)$^+$, especially in a system lacking protons to protonate the non-coordinate nitrogens, does not appear to be very great. Also, it is well known that the rate of ring closing of the free tooth of a diamine in a square planar complex [16] is extremely high and would thus at the most only appear as a steady state intermediate. It is therefore more likely that the bidentate N–N will coordinate only one nitrogen in five-coordinate CODIr(phen)(N–N)$^+$ since the ring closing step can only follow after ring opening of the phen group, a step which may be very slow and may experience competition from the dissociation of five-coordinate CODIr(phen)(N–N)$^+$ to CODIr(phen)$^+$ + N–N. In order to explain the steric results a neat solution to the problem would be to assume an equilibrium between species A and C in reaction scheme 14, with species B either existing in a steady state condition or as a transition state. The rate determining step k would then be the dissociative step described by k_c while $K_1 = K_1'K_{diss}K_{ass}$. It is now clear that the K_{ass} value will decrease with steric build-up on the one ethylenediamine nitrogen and therefore the K_1 value will decrease with increasing steric hindrance.

When N–N = N,N'-en the steric hindrance of the methyl group on the bonded nitrogen is apparently so big that the stable intermediate CODIr(phen)(N–N)$^+$ becomes unstable and the association process k_1 becomes the rate determining step in reaction scheme 12.

The rate law therefore simplifies to

$$k_{obs} = \frac{k_1[\mathrm{N,N'\text{-}en}]}{1 + K_e[X^-]} \qquad (16)$$

which conforms to empirical rate law 10. Once again the k_1 values for different X^- groups stay constant as is expected and the K_e values confirm the previously kinetically and spectrophotometrically determined values.

The data therefore clearly shows that the substitution reactions of these five-coordinate complexes exclusively proceed via a dissociative mechanism. If an associative pathway also existed, a second term exhibiting a direct $[X^-]$ dependence would have shown up in the rate laws.

The rate law for the reaction [17]

$$\mathrm{CODRh(phen)^+ + en \xrightarrow[k_1]{methanol} CODRh(en)^+ + phen} \qquad (17)$$

was found to be simply

$$k_{obs} = k_1(\mathrm{en}) \qquad (18)$$

with k_1 = 1059 s^{-1} M^{-1} and $\Delta S^{\neq}$ = –96 J mol^{-1} K^{-1}. As expected there is no solvent path but also no stable intermediate as was found for the analogous iridium system. The k_1 value for N–N = N,N'-en (1.4 s^{-1} M^{-1}) in the iridium system is some 700 times slower than that for en in the rhodium system. Ethylenediamine was found to be only about ten times more reactive towards palladium tetrachloride

[18, 19] than N,N′-en, and on that basis rhodium(I) is apparently some 70 times more reactive than iridium(I).

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