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Ligand Field Analysis of Substitution Reactions in Square Planar Pt(II) Complexes

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A ligand field analysis has been carried out for a number of substitution reactions in square planar Pt(II) complexes. The complete set of 12 rate constants describing the progressive transformation of MA_4 to MB_4 and vice versa has been considered in detail.

Each metal–ligand interaction is characterized by two independent spectrochemical parameters. The different ligands are assumed to make additive contributions to the ligand field matrix. On the basis of this model, the ligand field activation energies are calculated to be in exactly the same order as would be anticipated from the experimentally observed rate constants.

Introduction

Ligand field stabilization energy (LFSE) and ligand field activation energy (LFAE) have been shown to be very useful concepts in the kinetic study of certain transition metal complexes[1–3]. Of course, the LFAE is only *one* of the different contributions to the total activation energy; changes in the metal–ligand and the ligand–ligand interactions often constitute equally important or even more important contributions. Yet, in some cases, it has been possible to rationalize the relative inertness of otherwise comparable complexes by considering only the ligand field part of the activation energy. It is the purpose of this note to show how this line of reasoning might be extended, so as to explain qualitatively the relative magnitude of a series of reaction rate constants.

Substitution Reactions in Square Planar Pt(II) Complexes

A general scheme of the successive substitution reactions of a square planar ML_4 complex is shown in Figure 1. It is not easy to obtain the complete set of 12 rate constants describing the progressive transformation of Ma_4 to MB_4 and *vice versa*. The best data seem to be provided by the work of Elding[4–8]. Table I

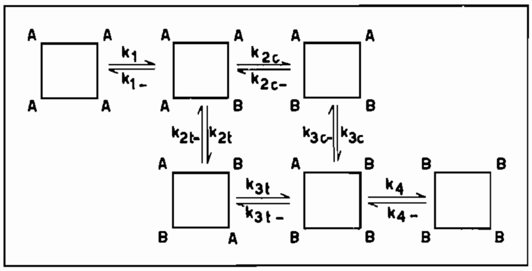

Figure 1. Substitution reactions of a square planar ML_4 complex.

TABLE I. Rate Constants (at 25° C) of Pt(II) Substitutions $PtA_nB_{4-n} \underset{A}{\overset{B}{\rightleftharpoons}} PtA_{n-1}B_{5-n}$ where A = Cl^-, Br^- and B = H_2O. The results have been taken from the work of Elding[4–8]; the rate constants are expressed in s^{-1} for the aquation reactions (k_1 through k_4) and in $M^{-1}s^{-1}$ for k_{1-} through k_4. Values in parentheses are uncertain. The subscripts of the rate constants refer to Fig. 1.

	A = Cl^-	A = Br^-		A = Cl^-	A = Br^-
k_1	3.6×10^{-5}	1.9×10^{-4}	k_{1-}	2.8×10^{-3}	9×10^{-2}
k_{2c}	6×10^{-5}	6×10^{-4}	k_{2c-}	7.5×10^{-2}	3.3
k_{2t}	2.8×10^{-8}	1.4×10^{-8}	k_{2t-}	4.6×10^{-5}	1.8×10^{-4}
k_{3c}	2×10^{-7}	10^{-6}	k_{3c-}	10^{-3}	3.3×10^{-2}
k_{3t}	10^{-4}	–	k_{3t-}	0.53	–
k_4	(3×10^{-7})	–	k_{4-}	(3×10^{-2})	–

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shows the rate constants of the successive aquation reactions of Pt(II) chloride and bromide complexes.

Both the forward and the backward reaction rates span a range of approximately four orders of magnitude. No obvious or simple regularity is apparent from the data in Table I, except for the fact that one finds the same relative sequance in both cases. This sequence

$$\begin{array}{l} k_{3t} > k_{2c} > k_1\ (> k_4) > k_{3c} > k_{2t} \\ k_{3t-} > k_{2c-} > (k_{4-} >)\ k_{1-} > k_{3c-} > k_{2t-} \end{array} \tag{1}$$

may be a general characteristic for the Pt(II) substitutions[18]; as far as the data are available, it also applies to the hydrolysis rates of mixed chloride–ammonia complexes[2,9], and to the direct chloride–ammonia exchange.[10]

There are very good reasons to believe that the different substitutions of Figure 1 all proceed in an identical manner *via* a transition state of enhanced coordination number[2,11]. Indeed, a dissociative mechanism does not explain the observed stereospecificity of the reactions, nor does it explain the large differences between k_{2c} and k_{2t}. A schematic representation of a substitution in a square planar complex is shown in Figure 2, where the transition state is taken to be a regular trigonal bipyramid. Although some details may be different, the main features of Figure 2 should represent a reasonably accurate description of the reaction path.

From the temperature dependence of the rate constants, it appears that the activation entropy does not vary too much in different square planar substitutions[12]; apparently, there is some justification in limiting oneself to the *energy* changes of the system in an attempt to explain the kinetic behaviour.

Characterization of the d-Orbital Energies

The angular overlap model associates two parameters to any given metal–ligand interaction[13–17]. Consider one ligand A, situated on the z-axis; the d-orbital set gives rise to three different energy levels E_A^σ (z^2), E_A^π (xz, yz) and E_A^δ (xy, x^2-y^2). The energy splittings

$$\begin{array}{l} \sigma_A = E_A^\sigma - E_A^\delta \\ \pi_A = E_A^\pi - E_A^\delta \end{array} \tag{2}$$

can be considered as empirical parameters, having an immediate and obvious chemical significance.

If more ligands are added to the coordination sphere of the central metal ion, the resulting energy matrix elements will be a function of (i) the spectrochemical parameters associated with each ligand, (ii) the angular position of the different ligands.

As an example, consider the energy matrices relevant to the reaction

$$MA_4 + B \rightarrow M(A_2B)(A_2) \rightarrow MA_3B + A$$

For the square MA_4 molecule, one finds a diagonal matrix. For the transition state, one obtains the following matrix:

$$\begin{array}{llllll}
M(A_2B)(A_2) & (z^2)' & (xz)' & (yz)' & (xy)' & (x^2-y^2)' \\
\hline
(z^2)' & \frac{5}{2}E_A^\sigma+\frac{3}{2}E_A^\delta+\frac{1}{4}E_B^\sigma+\frac{3}{4}E_B^\delta & & & & \frac{\sqrt{3}}{4}[(E_B^\delta-E_A^\delta)-(E_B^\sigma-E_A^\sigma)] \\
(xz)' & & \frac{5}{2}E_A^\pi+\frac{3}{2}E_A^\delta+E_B^\pi & & & \\
(yz)' & & & \frac{7}{2}E_A^\pi+\frac{1}{2}E_A^\delta+E_B^\delta & & \\
(xy)' & & & & \frac{19}{8}E_A^\delta+\frac{9}{8}E_A^\sigma+\frac{1}{2}E_A^\pi+E_B^\pi & \\
(x^2-y^2)' & \frac{\sqrt{3}}{4}[(E_B^\delta-E_A^\delta)-(E_B^\sigma-E_A^\sigma)] & & & & \frac{17}{8}E_A^\delta+\frac{3}{8}E_A^\sigma+\frac{3}{2}E_A^\pi+\frac{3}{4}E_B^\sigma+\frac{1}{4}E_B^\delta
\end{array} \tag{3}$$

For the square planar MA_3B molecule, one finds:

$$\begin{array}{llllll}
MA_3B & z^2 & xz & yz & xy & x^2-y^2 \\
\hline
z^2 & \frac{3}{4}E_A^\sigma+\frac{1}{4}E_B^\sigma+\frac{9}{4}E_A^\delta+\frac{3}{4}E_B^\delta & & & & \frac{\sqrt{3}}{4}[(E_B^\delta-E_A^\delta)-(E_B^\sigma-E_A^\sigma)] \\
xz & & E_A^\pi + E_B^\pi + 2E_A^\delta & & & \\
yz & & & 2E_A^\pi+E_A^\sigma+E_B^\delta & & \\
xy & & & & 3E_A^\pi + E_B^\pi & \\
x^2-y^2 & \frac{\sqrt{3}}{4}[(E_B^\delta-E_A^\delta)-(E_B^\sigma-E_A^\sigma)] & & & & \frac{9}{4}E_A^\sigma+\frac{3}{4}E_B^\sigma+\frac{3}{4}E_A^\delta+\frac{1}{4}E_B^\delta
\end{array} \tag{4}$$

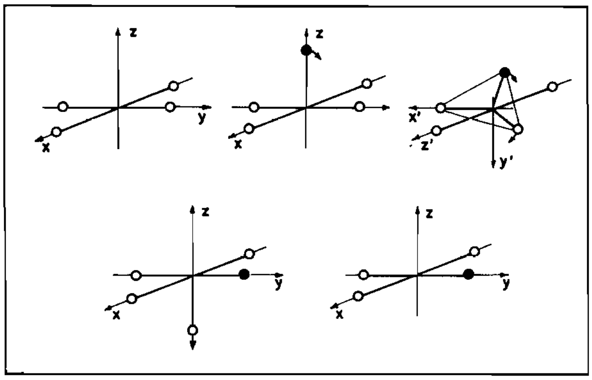

Figure 2. Associative substitution reaction proceeding *viă* a trigonal bipyramidal transition state.

In the d^8 complexes under consideration, the LFSE is given by twice the energy of the non-occupied orbital – at least when this energy is referred to the barycenter of the d-orbital set. The relevant energies can be calculated from matrices such as (3) and (4). Carrying out an exact diagonalization would in general lead to unwieldy expressions. Instead, it is well to realize that the off-diagonal elements are in general small quantities. If A = B, both matrices (3) and (4) become completely diagonal: if A ≠ B, the diagonal elements will still provide an acceptable first approximation for the orbital energies. Therefore, one can write:

$$E_i \simeq H_{ii} + \sum_j \frac{H_{ij}^2}{\Delta E_{ij}} \qquad (5)$$

and similarly:

$$LFSE = LFSE^{(1)} + LFSE^{(2)}$$

where $LFSE^{(1)}$ contains the contributions of the diagonal elements, and $LFSE^{(2)}$ contains the (much smaller) contributions arising from the offdiagonal elements.

Ligand Field Stabilization and Activation Energies

Using the procedure and the notation introduced in the previous Section, one finds the values of $LFSE^{(1)}$ and $LFSE^{(2)}$ shown in Tables II and III

As an example, Figure 3 shows a complete d-orbital correlation diagram for the reaction $MA_4 + B \rightarrow MA_3B + A$. The LFSE corresponding to the square planar molecules (MA_4, MA_3B) and the trigonal bipyramidal transition state (MA_2BA_2) can be found from Tables II and III.

An obvious symmetry is apparent from the energy expressions, in that the LFSE of MA_nB_{4-n} can be obtained from the LFSE of $MA_{4-n}B_n$ by interchanging (σ_A, π_A) and (σ_B, π_B); a similar remark can be made on the LFSE of the trigonal bipyramids. As a matter of fact, the different reactions can be subdivided into groups of two, complementary reactions, as for instance:

$$MA_3B \xrightarrow{B} M(A_2B)(AB) \rightarrow cis\text{-}MA_2B_2 \qquad (k_{2c})$$

and

$$MB_3A \xrightarrow{A} M(B_2A)(BA) \rightarrow cis\text{-}MB_2A_2 \qquad (k_{3c-})$$

All energy expressions, both LFSE and LFAE, relevant to the k_{3c-} reaction can be obtained from the k_{2c} reaction, by interchanging (σ_A, π_A) and (σ_B, π_B). The exchange-related reactions are (k_1, k_{4-}), (k_{2c}, k_{3c-}), (k_{2t}, k_{3t-}), (k_{3c}, k_{2c-}), (k_{3t}, k_{2t-}) and (k_4, k_{1-}).

If also the LFAE is separated into $LFAE^{(1)}$ (main contribution, due to the diagonal elements) and $LFAE^{(2)}$ (correction due to the off-diagonal elements), one obtains for the forward reactions

$$LFAE^{(1)} = (1/10)(8\pi_B + r\sigma_A + s\sigma_B) \qquad (7)$$

and for the backward reactions

$$LFAE^{(1)} = (1/10)(8\pi_A + t\sigma_A + u\sigma_B) \qquad (8)$$

where the coefficients r, s, t and u are shown in Table IV

TABLE II. Ligand Field Stabilization Energies $LFSE = LFSE^{(1)} + LFSE^{(2)}$ for the different square planar complexes MA_nB_{4-n}. In general it can be shown that $LFSE = 11/10[n\sigma_A + (4-n)\sigma_B] - 4/5[n\pi_A + (4-n)\pi_B]$. We define $\Delta\sigma = \sigma_B - \sigma_A$.

	$LFSE^{(1)}$	$LFSE^{(2)}$
MA_4	$(1/10)(44\sigma_A - 32\pi_A)$	0
MA_3B	$(1/10)[(33\sigma_A - 24\pi_A) + (11\sigma_B - 8\pi_B)]$	$(3/4)\frac{(\Delta\sigma)^2}{3\sigma_A + \sigma_B}$
cis-MA_2B_2	$(1/10)[(22\sigma_A - 16\pi_A) + (22\sigma_B - 16\pi_B)]$	0
trans-MA_2B_2	$(1/10)[(22\sigma_A - 16\pi_A) + (22\sigma_B - 16\pi_B)]$	$(3/2)\frac{(\Delta\sigma)^2}{\sigma_A + \sigma_B}$
MAB_3	$(1/10)[(11\sigma_A - 8\pi_A) + (33\sigma_B - 24\pi_B)]$	$(3/4)\frac{(\Delta\sigma)^2}{3\sigma_B + \sigma_A}$
MB_4	$(1/10)(44\sigma_B - 32\pi_B)$	0

TABLE III. Ligand Field Stabilization Energies LFSE = LFSE$^{(1)}$ + LFSE$^{(2)}$ for the Different Trigonal Bipyramidal Transition States. $\Delta\sigma = \sigma_B - \sigma_A$.

		LFSE$^{(1)}$	LFSE$^{(2)}$
	$M(A_3)(A_2)$	$(7/2)\sigma_A - 4\pi_A$	0
k_1	$M(A_2B)(A_2)$	$(1/10)(34\sigma_A + \sigma_B) - (1/5)(16\pi_A + 4\pi_B)$	$\frac{3(\Delta\sigma)^2}{17\sigma_A - 4\sigma_B - 12\pi_A}$
k_{2c}	$M(A_2B)(AB)$	$(1/10)(18\sigma_A + 17\sigma_B) - (1/5)(12\pi_A + 8\pi_B)$	$\frac{3(\Delta\sigma)^2}{9\sigma_A + 4\sigma_B - 12\pi_A}$
k_{2t}	$M(AB_2)(A_2)$	$(1/10)(33\sigma_A + 2\sigma_B) - (1/5)(12\pi_A + 8\pi_B)$	$\frac{3(\Delta\sigma)^2}{12\sigma_A + \sigma_B - 12\pi_B}$
k_{3c}	$M(AB_2)(AB)$	$(1/10)(17\sigma_A + 18\sigma_B) - (1/5)(8\pi_A + 12\pi_B)$	$\frac{3(\Delta\sigma)^2}{4\sigma_A + 9\sigma_B - 12\pi_B}$
k_{3t}	$M(A_2B)(B_2)$	$(1/10)(2\sigma_A + 33\sigma_B) - (1/5)(8\pi_A + 12\pi_B)$	$\frac{3(\Delta\sigma)^2}{\sigma_A + 12\sigma_B - 12\pi_A}$
k_4	$M(AB_2)(B_2)$	$(1/10)(\sigma_A + 34\sigma_B) - (1/5)(4\pi_A + 16\pi_B)$	$\frac{3(\Delta\sigma)^2}{-4\sigma_A + 17\sigma_B - 12\pi_B}$
	$M(B_3)(B_2)$	$(7/2)\sigma_B - 4\pi_B$	0

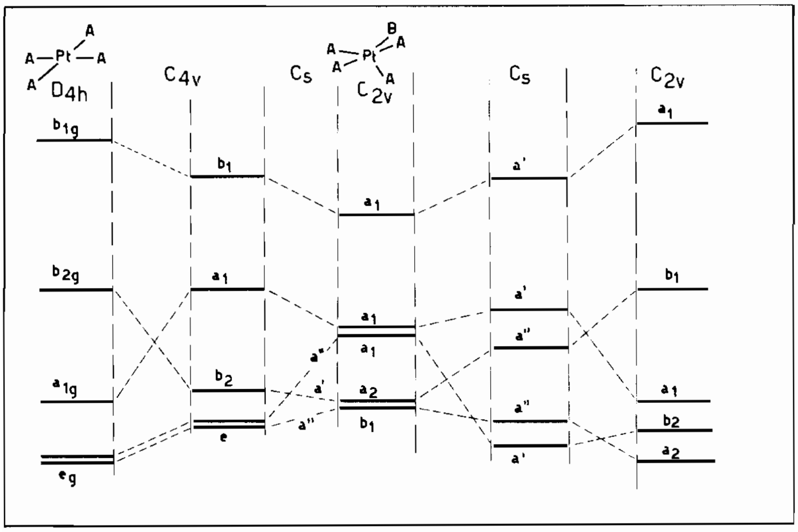

Figure 3. Orbital Correlation Diagram for the Reaction $PtA_4 + B \rightarrow PtA_3B + A$ *via* a trigonal bipyramidal transition state.

If $\sigma_A < \sigma_B$, this leads to a sequence of the reaction constants which is almost precisely the one found experimentally and given in Eq (1).

The seemingly irregular sequence of Eq (1) can thus be traced back directly to the nature of the different trigonal bipyramidal transition states. If $\Delta\sigma$ remains small, the "second-order" contributions given in Table II are not very important. They will affect the linearity of the LFAE expressions implied by Eqs 7 and 8, but they can hardly be expected to change the relative order of the rate constants. It is true, though, that the corrected values of k_1 and k_4 will no longer be equal. Indeed, it appears from Tables II and III that the second order correction to the reaction (1) is given by

$$\mathrm{LFAE}^{(2)} = -\frac{3(\Delta\sigma)^2}{17\sigma_A - 4\sigma_B - 12\pi_A} \qquad (9)$$

TABLE IV. The r, s, t and u Coefficients of the LFAE$^{(1)}$ Expressions. Obviously r + s = t + u = 9 in all cases; indeed, the twelve reactions under consideration reduce to $MA_4 + A \rightarrow MA_5$, if A = B. In this case the LFAE equals $(1/10)(8\pi_A + 9\sigma_A)$. If $\sigma_B > \sigma_A$, the (3t ±) reactions have the smallest LFAE$^{(1)}$: $(1/10)(8\pi_B + 20\sigma_A - 11\sigma_B)$ and $(1/10)(8\pi_A + 9\sigma_A)$ respectively; the reactions are in order of increasing activation energy, that is, in order of increasing s (or u) coefficients.

k_n			k_{n-}		
	r	s		t	u
k_{3t}	20	−11	k_{3t-}	9	0
k_{2c}	15	−6	k_{2c-}	4	5
k_1, k_4	10	−1	k_{4-}, k_{1-}	−1	10
k_{3c}	5	4	k_{3c-}	−6	15
k_{2t}	0	9	k_{2t-}	−11	20

and for reaction (4), one obtains

$$\mathrm{LFAE}^{(2)} = (3/4)\frac{(\Delta\sigma)^2}{3\sigma_B + \sigma_A} - \frac{3(\Delta\sigma)^2}{17\sigma_B - 4\sigma_A - 12\pi_B} \quad (10)$$

Therefore if $\Delta\sigma$ becomes larger, one expects reaction (1) to become faster than reaction (4). Similarly, reaction (4−) will become faster than 1− for small values of $\Delta\sigma$; for larger values of $\Delta\sigma$, reaction 1− will become predominant. Figure 4 shows how the LFAE varies as a function of $\Delta\sigma$; arbitrarily π_A and π_B were kept constant and equal.

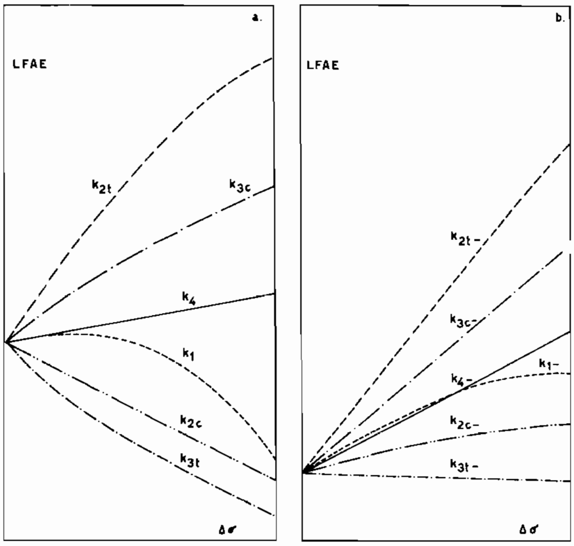

Figure 4. Qualitative variation of the LFAE for the forward (a) and backward (b) reactions, as a function of $\Delta\sigma = \sigma_B - \sigma_A$. The parameters π_A and π_B were arbitrarily set equal to each other and to $1/2\sigma_A$.

Conclusion

The experimental constants for the Pt(II) substitution reactions are in the same sequence as predicted from LFAE calculations. The only relevant parameters in the LFAE expressions are σ_A and σ_B; whether one particular substitution reaction is faster or slower than another one, depends only on the relative σ-bonding (or antibonding) abilities of A and B. This is not unreasonable, since neither of the two relevant orbitals – (x^2-y^2) in the plane square and $(z^2)'$ in the trigonal bipyramid – exhibits any π-bonding with the ligands.

It is obvious that the ideas outlined in the previous sections are purely qualitative; the absolute values that could be calculated from Eqs 7–10 can certainly not be expected to match the experimental data. Yet, the present approach allows for a qualitative insight into the nature of the substitution reactions. It can also be extended so to contribute to a better understanding of the kinetic *trans* effect.[18]

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References

1 N.S. Hush, *Australian J. Chem., 15,* 378 (1962).
2 F. Basolo and R.G. Pearson, "Mechanism of Inorganic Reactions", Wiley, New York, N.Y., 1967.
3 S.T. Spees, J.R. Perumareddi and A.W. Adamson, *J. Am. Chem. Soc., 90,* 6626 (1968).
4 L.I. Elding, *Acta Chem. Scand., 24* (4), 1331 (1970).
5 L.I. Elding, *Acta Chem. Scand., 24* (4), 1341 (1970).
6 L.I. Elding, *Acta Chem. Scand., 24* (5), 1527 (1970).
7 L.I. Elding, *Acta Chem. Scand., 24* (7), 2546 (1970).
8 L.I. Elding, *Acta Chem. Scand., 24* (7), 2557 (1970).
9 M.A. Tucker, C.B. Colvin and D.S. Martin, Jr., *Inorg. Chem., 3,* 1373 (1964).
10 H.B. Gray, *J. Am. Chem. Soc., 84,* 1548 (1962).
11 C.H. Langford and H.B. Gray, "Ligand Substitution Processes", Benjamin, New York, N.Y., 1965.
12 U. Belluco, R. Ettore, F. Basolo, R.G. Pearson and A. Turco, *Inorg. Chem., 5,* 591 (1966).
13 D.S. McClure, "Advances in the Chemistry of Coordination Compounds", Ed. S. Kirschner, 498, New York, McMillan, 1961.
14 C.K. Jorgensen, R. Pappalardo and H.-H. Schmidtke, *J. Chem. Phys., 39,* 1422 (1963).
15 C.E. Schäffer, *XIIth International Conference on Coordination Chemistry, UIPAC,* 361 (1970).
16 C.E. Schäffer, *Struct. Bonding, 14,* 69 (1972).
17 C. Görller-Walrand and L. Vanquickenborne, *J. Chem. Phys., 54,* 4178 (1971).
18 L. Vanquickenborne, J. Vranckx and C. Görller-Walrand, *J. Am. Chem. Soc., 96,* 4121 (1974).