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Substitution Reactions of Five Coordinate Complexes. I. The Replacement of an Apical Monodentate Ligand in Constrained Trigonal Bipyramidal d^8 Metal Complexes

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The kinetics of the reactions $[MQasX]^+ + Y^- \rightarrow [MQasY]^+ + X^-$ *(Qas = tris(o-dimethylarsinophenyl)-arsine; M = Pt, X = Cl, Br, Y =* NO_2^-, N_3^-, NCS^-, I^-, $SC(NH_2)_2$, $P(C_6H_5)_3$; *M = Pd, X = Cl, Y =* NO_2^-*) have been studied in methanol solution. At reasonably high concentrations of Y the rate law under pseudo first order conditions is* $k_{obs} = k_1 + k_2[Y]$ *where both* k_1 *and* k_2 *are dependent on the nature of [Y]. This behaviour is compared with that of the* $[MQASX]^+$ *analogues, QAS = tris(o-diphenylarsino phenyl)arsine, and a mechanism is proposed in which substitution ocurs in planar-4-coordinate intermediates in which one or two of the four arsenics of the quadridentate ligand are temporarily uncoordinated.*

Introduction

The substitution reactions of 4-coordinate planar complexes of d^8 transition metals have been studied extensively for many years.[1,2] Apart from a few exceptional cases, a common mechanistic pattern emerges in which the substitution in associative and involves a reactive five coordinate intermediate. Five coordination in d^8 systems is also quite common and represents the coordinatively saturated situation. One might predict that the substitution reactions of such complexes would follow the reverse of the path adopted by the four-coordinate complexes, *i.e.*, a dissociative mechanism with a planar four-coordinate intermediate. Some years ago, Pearson, *et al.*[3] reported the kinetics of substitution in complexes of the type $[MQASX]^+$, where M = Pd, Pt; X = Cl, Br, and QAS = tris(*o*-diphenylarsinophenyl)-arsine. The kinetics were consistent with an associative mechanism, complicated by ion-pair formation and a six-coordinate intermediate was postulated. The geometry of the ligand prevents the MAs_4 residue adopting a planar configuration and so a simple dissociative mechanism along the lines suggested above is not possible. However, the experimental observations do not rule out the possibility of a rapid and reversible dissociation of a terminal arsenic followed by substitution in the planar four-coordinate MAs_3X intermediate. We have, therefore, examined the kinetics of the substitution reactions of the analogous complexes of the ligand tris(*o*-dimethylarsinophenyl)arsine[4] in the hope that the greater complexing ability and small steric crowding of this ligand might enable us to reach a situation where the dissociation of a terminal arsenic became rate determining.

Experimental Section

The complexes were prepared by the previously reported methods or else were original samples.[4] All gave satisfactory analyses. Other materials used were dried reagent grade stock. No special precautions were taken to dry the Analar grade methanol because the rates of reaction were shown to be unaffected by the addition of small amounts of water and stock solutions of the complexes in methanol were found to be stable over a period of weeks.

Kinetics. The slower kinetics were followed in the thermostatted cell holder of a Unicam SP800B Spectrophotometer, the reagents were separately brought to reaction temperature and mixed in the reaction cell. Most of the studies were made with a stopped flow apparatus consisting of a Teflon mixing chamber and quartz optical cell, the whole encased in a copper block through which water from a thermostat was circulated. The flow was stopped by causing the carriage driving the syringe pistons to hit a metal peg. The progress of the reaction was followed spectrophotometrically by passing light of a known wavelength through the reaction cell and measuring the change in emergent light intensity on a photon multiplier. The signal was displayed on an oscilloscope and recorded in Polaroid film. The scale was linear in time and linear in percent transmission. The latter figures were converted to optical densities for the subsequent calculations. The calibration of the apparatus was tested against a standard reaction, $[Fe(H_2O)_6]^{3+} + SCN^- \rightarrow [FeSCN(H_2O)_5]^{2+} + H_2O$ and the rate constants obtained were in close agreement with literature values.[5]

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(1) F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Second Edition, J. Wiley and Sons, Inc., New York, 1967. p. 351-435.
(2) C.H. Langford and H.B. Gray, Ligand Substitution Processes, W.A. Benjamin, Inc., New York, 1965, p. 18-51.
(3) R.G. Pearson, M.M. Muir, and L.M. Venanzi, *J. Chem. Soc.*, 5521 (1965).
(4) O.St.C. Headley, R.S. Nyholm, C.A. McAuliffe, L. Sindellari, M.L. Tobe, and L.M. Venanzi, *Inorg. Chim. Acta, 4*, 93 (1970).
(5) J.F. Below, R.E. Connick, and C.P. Coppel, *J. Amer. Chem. Soc.*, *80*, 2962 (1958).

Table I. Pseudo First-Order Rate Constants (sec^{-1}) measured in Methanol at 25.0°±0.3°.

$PtQasBr^+ + Y^- \rightarrow PtQasY^+ + Br^-$

Y=I$^-$		Y=NCS$^-$		Y=NO$_2^-$		Y=NO$_3^-$		Y=SC(NH$_2$)$_2$		Y=P(C$_6$H$_5$)$_3$	
$10^4[Y^-]$	k_{obs}	$10^4[Y^-]$	k_{obs}	$10^4[Y^-]$	k_{obs}	$10^4[Y^-]$	k_{obs}	$10^4[Y^-]$	k_{obs}	$10^4[Y^-]$	k_{obs}
1.88	3.2	9.8	4.3	13.4	0.00285	50	0.088	2.0	40	3.0	30
3.75	4.7	16.5	5.3	26.8	0.00592	97	0.136				
4.97	6.2	25.3	8.6	40.1	0.00861	151	0.195				
4.50	9.2	36.2	9.8	53.5	0.0114	194	0.237				
7.70	9.1					302	0.337				
9.95	11.0										
10.0	12.3										
12.2	14.0										
15.0	17.7										
18.8	19.6										
22.0	22.6										
24.8	23.7										
30.0	29.2										
37.3	37										

$PtQasCl^+ + Y^- \rightarrow PtQasY^+ + Cl^-$

Y=N$_3^-$		Y=NO$_2^-$	
$10^4[Y^-]$	k_{obs}	$10^4[Y^-]$	k_{obs}
45	0.188	12.9	0.0076
90	0.35	13.5	0.0071
148	0.48	17.3	0.0094
223	0.75	25.1	0.0131
302	0.95	31.6	0.0170
		38.6	0.0205

$PdQasCl^+ + NO_2^- \rightarrow PdQasNO_2^+ + Cl^-$

$10^4[NO_2^-]$	k_{obs}	$10^4[NO_2^-]$	k_{obs}
12.9	28.6	20.0	40.3
15.5	37.2	25.4	50.9

$PdQasBr^+ + NO_2^- \rightarrow PdQasNO_2^+ + Br^-$

$10^4[NO_2^-]$	k_{obs}
10.0	7.5
12.2	8.5
20.0	13

Result

Apart from some reactions in which iodide was the entering group, all reactions were studied under pseudo first-order conditions with the entering nucleophile present in sufficient excess of the complex. The individual plots of $\log_{10}(D_\infty - D_t)$ against time (D_t and D_∞ are the optical densities at time t and at the end of the reaction) were linear for at least three half lives and values for k_{obs}, (obtained from the slope of the semi logarithm plot) are collected in Table I. Many entries in this Table are the average of at least three separate runs at the same nucleophile concentration. In the few cases where the nucleophile Y was not present in adequate excess, the first-order rate constant was calculated from the initial rate of reaction. These values increase with the concentration of $[Y^-]$ and while it is possible to draw a straight line through the points, the relatively large experimental error does not allow one to decide whether this is a valid relationship or whether there is curvature. Figure 1. In most cases there is a positive intercept at $[Y] = 0$ and the relationship, $k_{obs} = k_1 + k_2[Y]$ appears to be obeyed.

However, unlike the relationship that is usually found for the substitution reactions of planar four-coordinate, d^8, complexes, k_1 is not independent of the nature of Y and cannot be assigned to a parallel bimolecular solvolysis. No attempt was made to maintain constant ionic strength as the addition of an adequate amount of a perchlorate salt led to precipitation of the complex. Pearson *et al.* report that the reactions of the analogous QAS complexes are not sensitive to variation of ionic strength[3] but one must not discount the possibility that the departures from

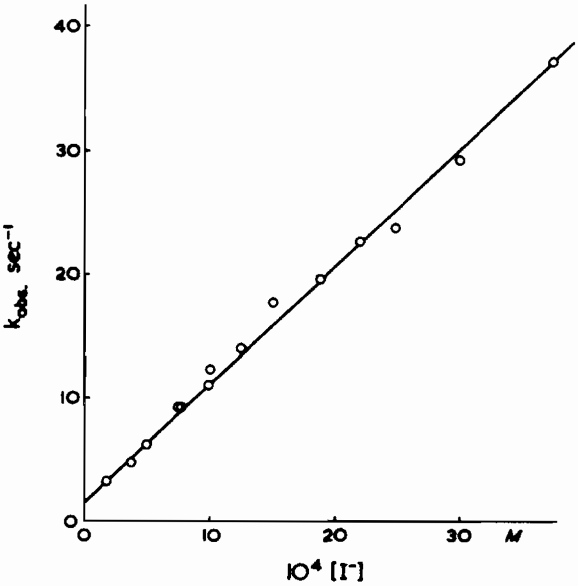

Figure 1. k_{obs} versus $[I^-]$ for the reaction $[Pt\,Qas\,Br]^+ + I^- \rightarrow [Pt\,Qas\,I]^+ + Br^-$ in methanol at 25.0°.

Table II. Slopes (k_2) and intercepts (k_1) of the linear portions of the plot of k_{obs} against [Y] in methanol at 25° for the reaction $[MLX]^+ + Y^- \rightarrow [MLY]^+X^-$

M	X	Y	$n_{Pt}°$	L=Qas 10^2k_1(*sec*$^{-1}$)	L=Qas k_2(M^{-1}*sec*$^{-1}$)	L=QAS[3] 10^2k_1(*sec*$^{-1}$)	L=QAS[3] k_2(M^{-1}*sec*$^{-1}$)
Pt	Cl	NO_2^-	3.22	0.05	5.22	0.011	0.031
		N_3^-	3.58	10	29	0.14	0.56
Pt	Br	NO_2^-	3.22	0.05	2.0	0.0018	0.014
		N_3^-	3.58	3.7	10.3	0.10	0.46
		I^-	5.42	140	9600	10	29
		SCN^-	5.65	190	2300	6.3	97
		$SC(NH_2)_2$	7.17	—	>2x10^5 [a]	18	1400
		$P(C_6H_5)_3$	8.79	—	~10^5	0.08	8.9
Pd	Cl	NO_2^-	3.22	500	18000	—	—
Pd	Br	NO_2^-	3.22	200	5500	—	—
		N_3^-	3.58	—	—	—	~10

[a] from a single measurement neglecting k_1.

linear behaviour are the consequence of variation of ionic strength.

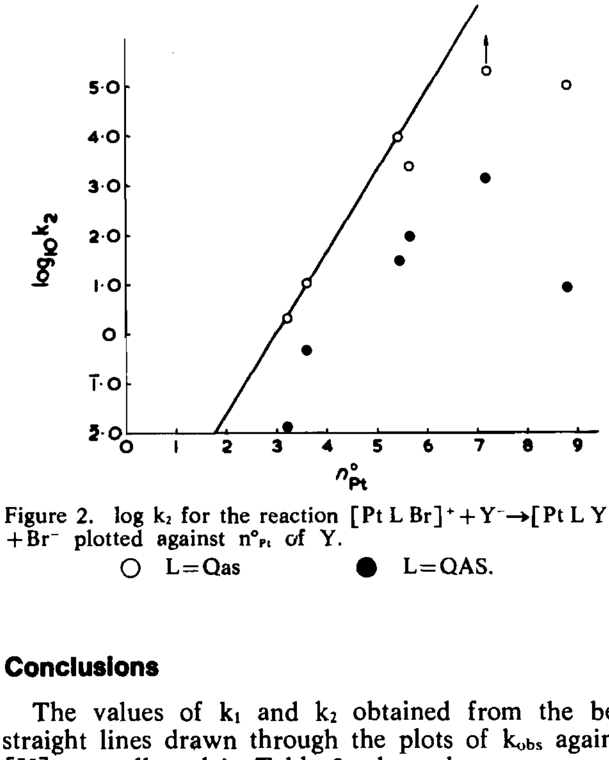

Figure 2. log k_2 for the reaction $[Pt\,L\,Br]^+ + Y^- \rightarrow [Pt\,L\,Y]^+ + Br^-$ plotted against $n°_{Pt}$ of Y.
○ L=Qas ● L=QAS.

Conclusions

The values of k_1 and k_2 obtained from the best straight lines drawn through the plots of k_{obs} against [Y] are collected in Table 2 where they are compared with the data reported by Pearson *et al.*[3] for the corresponding reactions of $[MQASX]^+$. In general, the replacement of the bulky terminal phenyl groups by methyl has not changed the form of the kinetics but the reactivity is significantly increased and the extent of the increase is very much dependent upon the bulk of the entering nucleophile. It is significant to note that this replacement leads to an enormous increase in the reactivity towards triphenylphosphine, by far the bulkiest of the entering nucleophiles. A plot of $\log_{10}k_2$ against $n°_{Pt}$[6] for the entering nucleophiles produces an approximately linear relationship but triphenylphosphine is still considerably less reactive than might be expected on the basis of its $n°_{Pt}$ value. The line drawn represents the maximum slope rather than the best straight line and this correspond to a nucleophilic discrimination factor of 1.64 which is rather high but not excessively so, for planar-4-coordinate platinum(II) complexes. The data for the PtQASBr cation would lie on an approximately parallel line if the anomalous thiourea and triphenylphosphine data are ignored.

In order to account for a k_1 term that is dependent upon the nature of Y, Pearson *et al.*[3] proposed a mechanism in which there is pre-equilibrium between the substrate and the nucleophile (equilibrium constant K) and the substrate and the aggregate or ion-pair could both undergo bimolecular attack by Y with rate constants k_C andk_{IP} respectively. This gave rise to a kinetic form,

$$k_{obs} = \frac{k_C[Y] + k_{IP}K[Y]^2}{1 + K[Y]}$$

and the relationship between k_{obs} and [Y] at low concentrations of Y were said to support this. When $K[Y] \gg 1$ this expression simplifies to

$$k_{obs} = \frac{k_C - k_{IP}}{K} + k_{IP}[Y],$$

not

$$\frac{k_C}{K} + k_{IP}[Y]$$

as is stated in Ref. 3. (See footnote 8). Indeed the statement in that paper, that $k_C \approx k_{IP}$, is not consistent with the observed kinetics and to obtain the form indicated it would require $k_C \gg k_{IP}$. It is not immediately obvious why the association of a potential ligand at the remote and crowded back of the molecule should significantly decrease its reactivity towards bimolecular attack by another ligand. Evidence was put forward to suggest that the association constant equilibrium $[PtQASI]^+ + I^- \rightleftharpoons [PtQASI]^+ \ldots I^-$ is about 3×10^3 M^{-1} in methanol. However, the conductivities of 10^{-3} M solutions of [PtQASX]X (X = Cl, Br, I) in nitrobenzene are not significantly reduced below those expected for a 1:1 electrolyte.[7]

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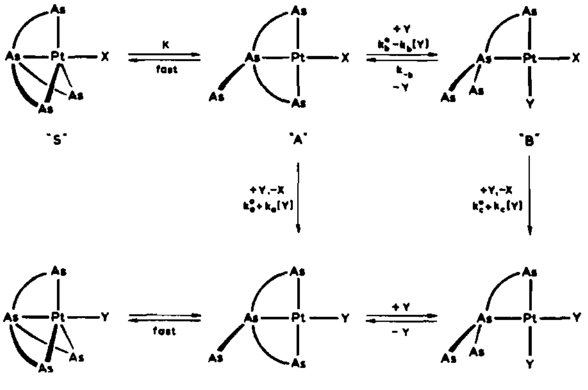
(6) Ref. 1, p. 399.

(7) J.A. Brewster, C.A. Savage, and L.M. Venanzi, *J. Chem. Soc.*, 3699 (1961).

The molar conductivity of a 10^{-3} *M* solution of [Pt-QasI]I in nitromethane (and also [MQasX]X, M = Ni, Pd; X = Br, I)[4] is typical of that expected for a 1:1 electrolyte, suggesting little or no ion-association under these circumstances. (An association constant of 3×10^3 M^{-1} would require that in a 10^{-3} M solution, 60% of the substrate is in the form of the ion-pair). There is no reason to believe that ion association will be far more pronounced in methanol than it is in nitrobenzene or nitromethane. We therefore feel that a mechanism involving parallel bimolecular attack on the substrate and its aggregate is not supported by the bulk of the experimental evidence and would like to suggest an alternative mechanism.

The sensitivity of the rate of reaction to the nature and the concentration of the entering nucleophile and the approximately linear relationship between n°_{Pt} and log k_2 would suggest that substitution takes place in a four coordinate species in accordance with the following reaction scheme.



Scheme 1

Assuming that (i) K≪1 so that only a small fraction of the complex is ever in the 4-coordinate form (ii) the square planar substitution follows the usual two term rate law and (iii) that the replacement of the axial X is irreversible.

$$\frac{-d[S]}{dt}=(k_a^\circ+k_a[Y])[A]+(k_c^\circ+k_c[Y])[B] \tag{1}$$

$$\frac{-d[B]}{dt}=(k_b^\circ+k_b[Y])[A]-k_{-b}[B]-(k_c^\circ+k_c[Y])[B]=0 \tag{2}$$

Then

$$[B]=\frac{(k_b^\circ+k_b[Y])[A]}{k_{-b}+k^\circ_c+k_c[Y]} \tag{3}$$

Also

$$[A]/[S]=K \tag{4}$$

Eliminating [A] and [B] from (1) gives

$$\frac{-d[S]}{dt}=\frac{\{(k_a^\circ k_{-b}+k_a^\circ k_c^\circ+k_c^\circ k_b^\circ)K+(k_ak_{-b}+k_ak_c^\circ+k_a^\circ k_c+k_b^\circ k_c+k_c^\circ k_b)K[Y]+k_c(k_a+k_b)K[Y]^2\}[S]}{(k_{-b}+k_c^\circ)+k_c[Y].}$$

and under pseudo first order conditions

$$k_{obs}=\frac{(k_a^\circ k_{-b}+k_a^\circ k_c^\circ+k_c^\circ k_b^\circ)K+(k_ak_{-b}+k_ak_c^\circ+k_a^\circ k_c+k_b^\circ k_c+k_c^\circ k_b)K[Y]+k_c(k_a+k_b)K[Y]^2}{(k_{-b}+k_c^\circ)+k_c[Y].}$$

This expression differs from that of Pearson *et al.*[3] in that there is a Y independent term in the numerator and so a finite value of k_{obs} when [Y] = 0. The kinetics at low concentration of [Y] are not necessarily diagnostic since retardation by the leaving group X, which has not been taken into account in either mechanism, would add a new complication.

When $k_c[Y]\gg k_{-b}+k_c^\circ$, this expression simplifies considerably and takes on the observed linear form

$$k_{obs}=K(k_a^\circ+k_b^\circ-\frac{k_bk_{-b}}{k_c})+(k_a+k_b)K[Y]$$ [8]

Thus it is possible to equate the observed k_2 with $(k_a+k_b)K$, which is a measure of the reactivity of the MAs_3X unit towards bimolecular substitution by Y and combines the paths leading to the displacement of X (k_a) and As (k_b). The actual magnitude of these rate constants is modified by the constant K, representing the fraction of the substrate in the form of the four-coordinate species. The intercept k_1, is equated to $K[(k_a^\circ+k_b^\circ)-k_bk_{-b}/k_c]$. The first term in the brackets represents the solvolytic reactivity of the substrate and should be independent of the nature of Y but the second term contains three Y dependent, constants. It is not possible to predict the relative reactivities of the $PtAs_3X$ and $PtAs_2XY$ species without a proper knowledge of the relative *cis* effects of As and Y in this type of complex. The ability of Y to act as a leaving group, which controls the k_{-b} term, is probably an important consideration. The intercept, k_1, will therefore be less than expected from the solvolytic reactivity of these complexes, the degree of diminution depending upon the importance of the

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(8) Provided α is not too large, an expression of the type

$$f=\frac{\alpha+\beta Y+\gamma Y^2}{\delta+Y}$$

will become linear when $Y\gg\delta$. However, the simple approximation which ignores δ and divides throughout by Y is incorrect. In order to obtain the correct expression one must calculate the expression for the tangent to this curve and determine the limit for its slope and intercept as [Y] becomes large. Alternatively, and we are indebted to Dr. Thirunamachandran for this suggestion, the expression can be rewritten as

$$f=(\frac{\alpha}{Y}+\beta+\gamma Y)(\frac{\delta}{Y}+1)^{-1}$$

and the second term expanded,

$$f=(\frac{\alpha}{Y}+\beta+\gamma Y)(1-\frac{\delta}{Y}+\ .....)$$

Thus

$$f=\frac{\alpha}{Y}+\beta+\gamma Y-\frac{\alpha\delta}{Y^2}-\frac{\beta\delta}{Y}-\gamma\delta\ .....$$

As Y becomes large all terms with Y in the denominator vanish leaving

$$\mathrm{Lim}\ f_{Y\to\infty}=(\beta-\gamma\delta)+\gamma Y$$

Transposing the appropriate coefficients from the expression for k_{obs} gives the required simplification. The simpler relationship,

$$f=\frac{\beta Y+\gamma Y^2}{\delta+Y}$$

tends to the same limits as Y becomes large.

MAs_2XY intermediate and the competition between the various paths for its consumption. Negative intercepts are not precluded by this mechanism but none have yet been observed.

The proposed mechanism requires that the stable 5-coordinate trigonal bipyramidal form of the substrate and product be dissociately labile with respect to reversible loss of a terminal arsenic donor. Evidence supporting this assumption comes from a study of reactions between the five-coordinate $[MQasX]^+$ (M = Ni, Pd, Pt) complexes and substitutionally labile four-coordinate Pd(II) complexes, such as $[PdCl_3CH_3OH]^-$,[9] where the first stage leads to the formation of an M–Pd dimer in which both metal atoms are four-coordinate and planar. The Pd and Pt complexes react extremely rapidly and dimer formation is much faster than the replacement of the monodentate ligand X. It is suggested that the dimerisation requires initial dissociation of a terminal arsine group which then attacks the labile $[PdCl_3CH_3OH]^-$ species.

The departure from the simple kinetic form for substitution in four-coordinate planar d^8 complexes requires that the reaction path by way of the *cis*–MAs_2XY intermediate makes an important contribution to the process. This, in turn, requires that, in a complex of the type $PtAs_3X^+$, an arsine is a better leaving group than Cl or Br when both are under the *trans* effect of another arsine. Detailed kinetic studies of the reactions of complexes of the type $[PtL_3X]^+$ ($L = AsR_3, PR_3$) do not appear to have been published but there are suggestions from preparative chemistry that such species lose the neutral ligand when attacked by anionic nucleophiles.[10] This is certainly not the case for complexes of the type *trans*–$[ML_2Cl_2]$ (L = phosphine or arsine) where Cl is replaced in preference to L even though it is under the weak *trans* effect of the *trans* chlorine.[11]

The relative reactivities of the analogous Pd(II) and Pt(II) complexes are in the ratio of 3×10^3: 1 which is considerably less than the ratio 10^5: 1 that is generally observed for uncomplicated 4-coordinate planar complexes.[12] This may well reflect the influence of K which ought to be smaller for Pd than Pt as a result of the greater tendency of the former to adopt five-coordination.

The reactions of $[NiQasBr]^+$ were examined briefly but were too fast to be followed by the available equipment. Since the reaction between $[NiQasBr]^+$ and $[PdCl_3CH_3OH]^-$ is relatively slow,[9] the replacement of the monodentate ligand must take place without dissociation of a terminal arsine. It is possible that the nickel complex undergoes substitution through a six-coordinate intermediate.

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(12) Ref. 1, p. 414.