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Substitution Reactions at Palladium(II) Complexes Producing Dimeric Species: Stability Constants Determination for Simultaneous Equilibria

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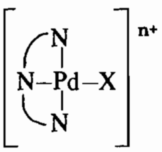
Substitution equilibria in Pd(dien)-like aquocomplexes are parallel to dimerization equilibria of the starting monomeric species. Accurate potentiometric measurements of the hydrogen ion concentration lead to the simultaneous determination of the stability constants of both kinds of equilibria: $Pd(dien)H_2O^{2+} + X^- \rightleftarrows Pd(dien)X^+ + H_2O$, *and* $2\ Pd(dien)H_2O^{2+} + X^- \rightleftarrows [Pd(dien)]_2X^{3+} + 2H_2O$.

For the monomeric complexes, the following relative stability series was ascertained: $X^- = Cl^- < Br^- < I^- < SCN^- < OH^-$. *The bridging ligand affects the relative stability of the dimeric species in the order:* $X^- = I^- \ll OH^- < SCN^-$.

Introduction

The coordination of a ligand X to a metal center is the fundamental step for achieving a change in its usual reactivity. This step of the so-called metal-promoted molecular activation may proceed either through an addition of X to a vacant coordination site or, more often, by a ligand substitution reaction. Suitable models for studying the substitution of a single ligand around the metal are the Pd(dien)-like complexes:



where n = 2 or 1 according to whether X is a molecule (H_2O) or a monovalent anion (Cl^-, Br^-, I^-, SCN^-, OH^-), and were $\widehat{N\,N\,N}$ is either diethylenetriamine (dien), or 1,1,7,7 tetraethyldiethylenetriamine (Et_4dien), or 1,1,4,7,7 pentamethyldiethylenetriamine (Me_5dien). For simplicity, we would indicate such complexes as MX, disregarding the charges; and, in particular, (M1)X, (M2)X and (M3)X for Pd(dien)X^{n+}, Pd(Et_4dien)X^{n+} and Pd(Me_5dien)X^{n+} respectively. The main characteristics of these model compounds are: i) they contain Pd(II), a very labile metal center active in catalytic processes [1], ii) a single coordination site is potentially available on the metal for substitution reactions, iii) the substitution reactions can be carried out in aqueous solution.

In spite of the simplicity of the model, we found that the substitution of the ligand (or the release of H^+ from MOH_2) is parallel to a dimerization of the starting monomeric unit. This finding, observed under dynamic conditions in solution, is rather important because of the dependence of the molecular activation on the nuclearity of the metallic systems. While being very well identified as concerns their structure in the solid state, the genesis and the presence of polynuclear species in solution is a vexing question. The stability constants concerning a formation of polynuclear complexes are, in particular, scarcely known and difficult to measure.

Concerning this point, we suggest an experimental method suitable for getting equilibrium constants for simultaneous reactions, such as substitution and dimerization. It consists of adding, as in titrations, increasing amounts of the ligand to the solutions containing both MOH_2 and MOH, and in measuring the equilibrium concentrations of the hydrogen ion by suitably standardized glass electrodes. While it recalls the method of A. W. Thomas [2] and the subsequent improvements of Bjerrum [3], we would emphasize that, in the present case, the pH control is maintained by the conjugated system MOH_2–MOH, instead of by hydrolysis of the ligand. The acid–base equilibria of MOH_2 are, of course, the first subject of attention.

As for the equilibrium constants we stated, for simplicity, to concern ourselves only with molar stoicheiometric quotients at fixed ionic strength and practically constant composition.

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Experimental

The equilibria were studied at 25 ± 0.02 °C and at ionic strength 0.5 ± 0.02 *M*, generally in $NaClO_4$ solutions. Some measurements (and the corresponding standardisations) were repeated in $NaNO_3$ solutions, as the perchlorates of (M2)SCN, (M2)I, (M3)SCN, (M3)I, and of (M2)Br are only slightly soluble. The supporting electrolyte ($NaClO_4$ or $NaNO_3$) was always in great excess as compared with X and with the complexes, in order to avoid any appreciable variation of the composition and the ionic strength, which could affect both the activity coefficients and the junction potentials. All solutions were prepared using conductivity-grade water. The aquocomplexes were obtained from the corresponding halide complexes (the chlorides for $(M1)OH_2$ and $(M2)OH_2$, the iodide for $(M3)OH_2$), and from $AgClO_4$ in the ratio 2:1. The endpoint for Ag^+ was potentiometrically detected, this being a useful test to prove the purity of the halide complexes. After filtering, the solutions were diluted by means of $NaClO_4$ (or $NaNO_3$) solutions up to a concentration of 5×10^{-3}–3×10^{-2} *M*, and were titrated with both NaOH and NaX 0.5 *M* solutions. Nitrogen was used to prevent pollution from CO_2.

The pH values were measured by using a Delta acque 107 potentiometer. The reference electrode (Ag, AgCl/NaCl 0.5 *M*) was connected to the test solution through a 0.5 *M* $NaClO_4$ (or $NaNO_3$) salt bridge, in order to minimize the Cl^- diffusion which seriously interferes with the measurements. The glass electrode was standardized in terms of p[H] (*i.e.*, $-\log_{10}[H^+]$) using known amounts of $HClO_4$ in $NaClO_4$ (or $NaNO_3$) solution at $I = 0.5$ *M* [4]. When titrated with NaOH, the perchloric acid was directly added to the test solution.

The OH^- molar concentrations were correlated to p[H] by assuming 1.9×10^{-14} and 2.1×10^{-14} as the stoicheiometric molar K_w in 0.5 *M* $NaClO_4$ and 0.5 *M* $NaNO_3$ respectively*, according to some literature data [5, 6]. A rather high relative error in $[OH^-]$ is, of course, possible, but even 10% or 20% errors do not appreciably change the results when pH values range below 9 (as it usually was).

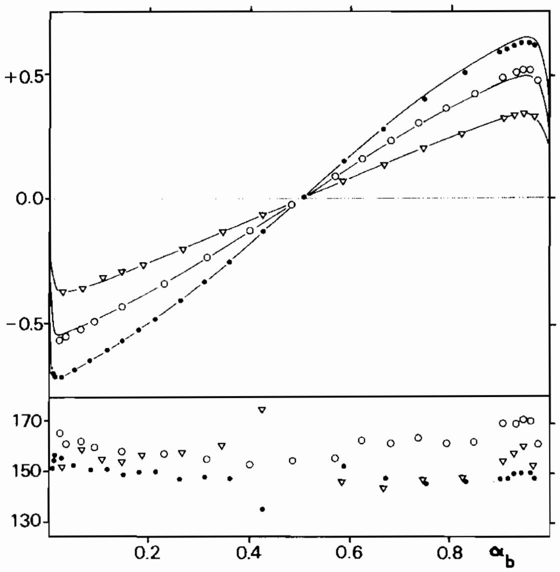

Fig. 1. Upper section, experimental $\Delta p[H]$ as a function of the titrated fraction α_b, for three titrations of $(M1)OH_2$ in $NaClO_4$ solution. Starting concentrations of $(M1)OH_2$: 9.96×10^{-3} *M* (▽), $1.77_5 \times 10^{-2}$ *M* (○), $3.06_5 \times 10^{-2}$ *M* (●) (the corresponding $p[H]_{0.5}$ were 7.58_8, 7.58_5 and 7.59_3 respectively). Full lines: theoretical $\Delta p[H]$ for $K_D = 156$. Lower section: K_D values calculated from each experimental p[H] in the same titrations.

The halide complexes and SCN^- complexes have been identified by elemental and IR analysis. According to what is already known [7], $(M2)OH_2$ and $(M3)OH_2$ give, with SCN^-, precipitates which correspond with isothiocyanate complexes, while the isomer thiocyanate is obtained from $(M1)OH_2$.

The ^{13}C NMR spectra were recorded using a Varian XL100 instrument.

Method and Results

The Titrations with NaOH

The titration curves of the MOH_2 complexes with NaOH resemble, at first sight, those of the usual weak monoprotic acids. The half-titration p[H] values, $p[H]_{0.5}$, are independent (within ±0.006) of the concentration in the experimental range. They satisfactorily agree with the pK_a quoted in the literature (7.1 [8] or 7.5 [9] for $(M1)OH_2$, 7.5 [10] for $(M2)OH_2$), considering the different experimental conditions. However, the titration curves have a greater slope than one expects, as though the value of pK_a were to increase during the titration. This behaviour is particularly evident for $(M1)OH_2$, but can also be observed for $(M2)OH_2$ and $(M3)OH_2$. In Fig. 1 we have reported the differences, $\Delta p[H]$, between experimental p[H] and p[H] values

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*The 1.9×10^{-14} value was evaluated on the grounds of: i) the K_w values in KCl and NaCl solutions [5], which are near each other in a wide range of I; ii) the mean activity coefficients of $NaClO_4$, which are, in turn, very near to those of KCl and NaCl [5, 6]. Very similar ion–ion and ion–solvent interactions occur, reasonably, in $NaClO_4$, NaCl and KCl solutions, and therefore the stoicheiometric K_w value must be very similar. The mean activity coefficients in $NaNO_3$ solutions are appreciably lower than the others [5] and a K_w value of 2.1×10^{-14} is evaluated, if one accounts for a corresponding decrease in the H^+ and OH^- activity coefficients.

TABLE I. pK_a and K_D Values of $(M1)OH_2$, $(M2)OH_2$ and $(M3)OH_2$ at 25 °C and $I = 0.5\ M$, in $NaClO_4$ (a) and $NaNO_3$ (b).

	$M(1)OH_2$	$(M2)OH_2$	$(M3)OH_2$
pK_a	7.589 ± 0.006 (a) 7.543 ± 0.006 (b)	7.688 ± 0.007 (a) 7.677 ± 0.007 (b)	7.293 ± 0.006 (a) 7.241 ± 0.006 (b)
K_D	156 ± 8 (a) 125 ± 5 (b)	8 ± 2 (a) 3 ± 1 (b)	12 ± 3 (a) 5 ± 1 (b)

one calculates for a monoprotic acid having the same $p[H]_{0.5}$ and the same concentration. Such differences are an approximately linear, S-shaped function of the titrated fraction (α_b), and they increase as the concentration increases. In our opinion, the only reasonable explanation is the occurrence of a further equilibrium, $MOH_2 + MOH \rightleftarrows M_2OH + H_2O$, according to the suggestions of Martin and Lim [9]. On the grounds of this equilibrium, the value of $p[H]_{0.5}$ does not change. The slope of the $\Delta p[H]$ curves must depend on the concentration and the K_D value (where $K_D = [M_2OH][MOH_2]^{-1}[MOH]^{-1}$), but it must be practically independent of pK_a.

The K_D value is easily calculated from each experimental p[H] (except very near to the half-titration or to the equivalent points) after assuming $pK_a = p[H]_{0.5}$ (Fig. 1, lower section). It can also be sought after by attempts, so as to reproduce the experimental $\Delta p[H]$ slopes. A K_D value of 156 ± 8 M^{-1}, together with a pK_a value of 7.589 ± 0.006, allows the reproduction of the $(M1)OH_2$ titration curves in $NaClO_4$ solutions (Fig. 1, upper section). Errors in concentrations and in equivalent points are the main reasons of the deviations observed; they are also responsible for the small discrepancies in $p[H]_{0.5}$ (Gran's method [11] was used to identify the equivalent points, but it was rather unsatisfactory, due perhaps to the dimerization reaction).

The pK_a and K_D values of $(M1)OH_2$, $(M2)OH_2$ and $(M3)OH_2$ in both $NaClO_4$ and $NaNO_3$ solutions are reported in Table I. In the dimerization equilibria, we assume that the M_2OH species contains a metal–hydroxide–metal bridge. For $(M2)OH_2$ and $(M3)OH_2$ the K_D values are considerably less than for $(M1)OH_2$, in agreement with the greater steric hindrance.

Another, very different justification had been suggested for the anomalous curves of $(M1)OH_2$, *i.e.*, it would exist, in the aqueous solutions, as a dimeric, diprotic $(MOH_2)_2$ (instead of monomeric MOH_2), having pK_1 and pK_2 near each other [12]. However, this does not explain why the $\Delta p[H]$ also depends on the concentration (pK_1 and pK_2 should be changed for each concentration). As further evidence, two (very sharp) peaks are observed in the ^{13}C NMR spectra of aqueous concentrated solutions of $(M1)OH_2(ClO_4)_2$, at 106 and 113 ppm, and this only agrees with the monomeric structure. When two diethylenetriamines connect two palladium atoms, as in the hypothetic dimeric structure $(MOH_2)_2$, four non equivalent carbon atoms should result, instead of two.

As for $(M1)OH_2$, some studies were also made through UV spectra at different pH. An apparent isosbestic point occurs at about 292–295 nm, however it is rather undefined and may agree with the presence of the three species $(M1)OH_2$, $(M1)OH$ and $(M1)_2OH$. The molar absorptivities of $(M1)OH_2$ and $(M1)OH$ are, respectively, $\epsilon_1 = 523 \pm 2$ and $\epsilon_2 = 410 \pm 2$ at 315 nm, and an approximate pK_a value, 7.64 ± 0.09, may be evaluated disregarding the $(M1)_2OH$ dimer. It has not been possible to confirm, in this way, the $(M1)_2OH$ dimer, may be because of the insufficient accuracy of the measurements, or because its extinction coefficient, ϵ_3, is near the sum $\epsilon_1 + \epsilon_2$. As a matter of fact, the experimental absorbances are slightly better interpreted if one assumes that $(M1)_2OH$ is present. A molar absorptivitiy, $\epsilon_3 \cong 960$, may be evaluated for $(M1)_2OH$ by least squares methods, using the potentiometric pK_a and K_D values.

The Titrations with NaX

When MOH_2 solutions are titrated with NaX, an increasing amount of MOH_2 becomes the non-acid MX species and the pH increases. The concentrations of MOH_2, MOH and M_2OH are correlated to the H^+ concentration and are easily calculated once the pK_a and K_D are known. [MX] and [X] are then calculated by subtraction, knowing the analytical concentration of $X(C_X)$ and of the complexes (C_M). One can therefore calculate the stability quotient, $K_f = [MX][MOH]^{-1}[X]^{-1}$, from each experimental p[H] value.

A known NaOH amount was always added to the solutions before titrating with NaX (the analytical concentration of NaOH, C_b, was usually set at 10–20% of C_M). That is a rather important device since, in this way, MOH does not vanish during the titration. Reliable K_f values are only obtained at non vanishing [X], since [X] is to be calculated by subtraction; in correspondence, $[MOH_2]$ is usually very slight. The added NaOH allows to calculate

TABLE II. K_f and K_{DX} Values of $(M1)OH_2$, $(M2)OH_2$ and $(M3)OH_2$ at 25 °C and I = 0.5 *M* in $NaClO_4$ (a) and $NaNO_3$ (b).

X	K_f/M^{-1}		
	$(M1)OH_2$	$(M2)OH_2$	$(M3)OH_2$
Cl^-	$[5.3 \pm 0.1] \times 10^2$ (a)	$[1.2 \pm 0.1] \times 10^3$ (a)	$[1.4 \pm 0.1] \times 10^3$ (a)
	$[5.10 \pm 0.05] \times 10^2$ (b)	$[1.10 \pm 0.07] \times 10^3$ (b)	$[1.34 \pm 0.08] \times 10^3$ (b)
Br^-	$[2.3 \pm 0.1] \times 10^3$ (a)	$[1.76 \pm 0.08] \times 10^3$ (b)	$[1.8 \pm 0.1] \times 10^3$ (a)
			$[1.94 \pm 0.03] \times 10^3$ (b)
I^-	$[7.3 \pm 0.3] \times 10^4$ (a)	$[7.0 \pm 0.5] \times 10^3$ (b)	$[7.6 \pm 0.4] \times 10^3$ (b)
SCN^-	$[5.5 \pm 0.2] \times 10^5$ (a)	$[1.2 \pm 0.1] \times 10^5$ (b)	$[1.4 \pm 0.1] \times 10^5$ (b)
	K_{DX}/M^{-1}		
$M1^+$	5 ± 3 (a)		
$MSCN^+$	650 ± 20 (a)	50 (b)	64 ± 5 (b)

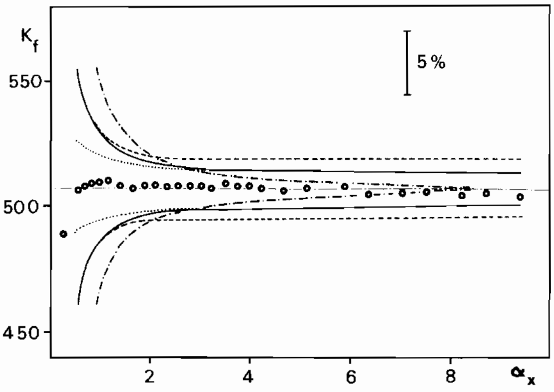

Fig. 2. Circles: K_f values from a titration of $(M1)OH_2$ with 0.5 *M* Cl in $NaNO_3$ solution. Lines: systematic deviations which arise from errors: ±1% in C_M (full lines); ±2% in C_b, or ±0.01 in p[H], or ±0.01 in pK_a (dashed lines); ±1% in C_X (dotted lines); ±20% in K_D (dash-and-dot lines).

$[MOH_2]$ as a ratio, with a practically constant relative error, from [MOH], $[H^+]$ and K_a*.

As further advantages, the addition of NaOH improves the sensitivity ($[H^+]$ becomes a practically linear function of $[MOH_2]$ instead of $[MOH_2]^{1/2}$), increases the pH range and lessens the effects of CO_2 or free amine traces. If, instead, one titrates a solution of MOH_2 alone, the pH shifts towards that of the solvent, and becomes too dependent on the impurities.

The K_f values in Table II are an average of the values obtained at various $\alpha_X = C_X/C_M$ ratios, in several titrations. The titrations were generally carried on to a ratio 3–10. Depending on α_X, the K_f are differently affected by errors in p[H], in reagent amounts, in pK_a, K_D and K_w. However, a rather incorrect K_w value does not influence the results in the case of weak ligands (Cl^-, Br^-); it only becomes important with stronger ligands, at rather high α_X values (for instance, in the case of SCN^- an error of 20% in K_w causes an error of 8% in K_f when α_X = 10, but only 2% when α_X = 3). The effect of reasonable, indicative errors in the other parameters is shown in Fig. 2, together with the K_f values obtained in a titration of $(M1)OH_2$ with Cl^-, in $NaNO_3$ solution. The behaviour one observes at low α_X is particularly interesting, since the deviations must increase just in these cases if an appreciable systematic error occurs. That could supply a critical test for the reliability of the results. The K_f quoted in Fig. 2, for instance, cannot be affected by appreciable errors. It is significant that the best K_D value to use, to obtain such results, is exactly that of the titrations with NaOH.

With stronger ligands, the errors qualitatively propagate in the same way, but not so favourably. For SCN^- it is quite impossible to diagnose a systematic deviation by inspection of a K_f graph as in Fig. 2. The errors are critically dependent on the slightest parameter variation up to $C_X \cong C_M$, whereas they become constant in every case at slightly higher C_X. However, we believe that the K_f uncertainty

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*As a matter of fact, one also accounts for K_D; *i.e.*, one calculates $[MOH_2]$, together with [MOH] and $[M_2OH]$, resolving the equations $[MOH] + [OH^-] + [M_2OH] = C_b + [H^+]$, $[M_2OH] = [MOH][MOH_2]K_D^{-1}$, $[MOH_2] = [MOH][H^+]K_a^{-1}$, where K_a, K_D, C_b and $[H^+]$ are known. The [MX] value is then calculated ($[MX] = C_M - [MOH_2] - [MOH] - 2[M_2OH]$), and the [X] value is calculated as $[X] = C_X - [MX]$. The errors decrease when $[MOH_2]$ decreases and [X] increases.

does not exceed ±10%, on the grounds of repeated tests.

The occurrence of some M_2X dimers in the reactins involving the halides and, in particular, SCN^-, appeared very probable, considering the similar dimer formation with OH^-. A dimerization reaction does not invalidate the K_f values one calculates at sufficiently high α_X values, where the dimers must disappear, but the deviations can be very high if $\alpha_X < 1$. As a first test for dimerization, one may check several, tentative values of the dimerization constant, $K_{DX} = [M_2X][MX]^{-1}[MOH_2]^{-1}$, up to reaching a better K_f constancy (a slight improvement in the 0.7–1.1 range of α_X, was only observed for the reaction between $(M1)OH_2$ and SCN^-, using K_{DX} from about 10^2 to 10^3). However, this is not reliable proof for dimerization since, at low α_X, fictitious improvements may arise from casual compensation of errors. Another method is to be used, which allows to evidence a dimerization and to reliably calculate K_{DX} provided rather strong ligands are in cause. The first amounts of X one adds must react, quantitatively, with the exceeding MOH_2, so as to give, if M_2X is also formed, higher p[H] than one expects even assuming an infinite K_f value. This was always verified when titrating with SCN^-. Physically inconsistent, negative K_f are calculated in correspondence if, as in the usual calculations, the [X] value is equated to the algebraic sum $S = C_X - C_M + [MOH] + [MOH_2] + 2[M_2OH]$, disregarding $[M_2X]$ (this sum strictly corresponds to $[X] - [M_2X]$, and becomes negative). On the contrary, at sufficiently low α_X one may equate the negative S to $-[M_2X]$, disregarding [X]. One may thus calculate [MX] (we say $[MX] + 2[M_2X] = C_M - [MOH_2] - [MOH] - 2[M_2OH]$).

A constant value of the ratio $-S/([MOH_2][MX])$, *i.e.* of K_{DX}, is to be obtained if dimerization occurs.

The results of such calculations are shown in Fig. 3 for two titrations of $(M1)OH_2$ with SCN^- in $NaClO_4$ solution (the approximation $S = -[M_2X]$ fails when α_X approaches 0.9, instead of 1.0, because of the added NaOH amount). Similar results have been obtained for $(M3)OH_2 + SCN^-$ ($K_{DX} = 64 \pm 5\ M^{-1}$) and $(M2)OH_2 + SCN^-$ ($K_{DX} \cong 50\ M^{-1}$: the latter is a rather uncertain value, since the reaction was slow and the equilibrium values of the p[H] were reached with some doubt). A weak dimerization, $K_{DX} = 5 \pm 3$, also seems to occur in the reaction between $(M1)OH_2$ and I^-. No dimerization was identified in any of the other cases.

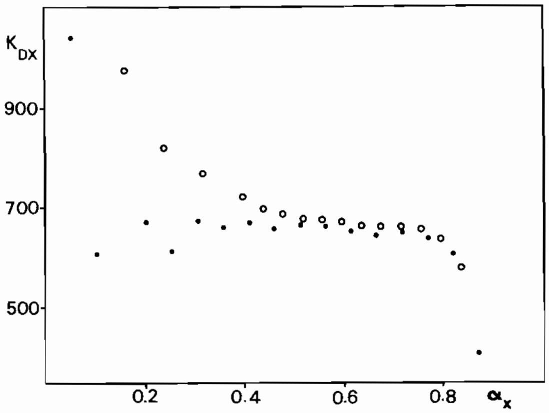

Fig. 3. Values of the ratio $-S/([MOH_2][MX])$ for two titrations of $(M1)OH_2$ with SCN^- in $NaClO_4$ solutions, as a function of the titrated fraction α_X.

Discussion

No literature data is available for K_D and K_{DX}; a dimerization was only hypothesized in the reactions involving $(M1)OH_2$ and OH^- [9], but no attempt was made to obtain the corresponding constant.

The K_f values may be compared, in some cases, with literature data. For the reaction of $(M2)OH_2$ and Cl^-, a value of 1400 M^{-1} (as compared with our 1200 ± 100) is obtained as a ratio between the specific anation rate (2.4 $sec^{-1}\ M^{-1}$) [10] and the specific aquation rate ($1.7 \times 10^{-3}\ sec^{-1}$, by interpolation at I = 0.5) [13, 14]. Other authors report some K_f values for the reactions between $(M2)OH_2$ and halides, which strongly disagree with ours and among them [7, 15]. However, in ref. 15 the K_fs are calculated by a rather unreliable ratio of kinetic constants which do not refer to the same ionic strength and composition, whereas in ref. 7 some anation rate constants are used, which do not agree with the subsequent values obtained by Goddard and Basolo [10].

Hewkin and Poë relate some interchange constants, K_{XY}, for reactions $MX + Y \rightleftarrows MY + X$ of (M1) and (M2) complexes with halides and thiocyanate [7]. They agree, within at least 35%, with the corresponding values one can calculate from Table II. Their measurements were carried out by spectrophotometric methods, and some extinction coefficients were rather uncertain; furthermore, despite the ionic strength was always 0.5 *M*, their solutions were very different from time to time.

Other interchange constants may be calculated from kinetic data. It is well known that these equilibria follow a mechanism [14]

$$MX + H_2O + Y \underset{k_X}{\overset{k'_X}{\rightleftarrows}} MOH_2 + X + Y \underset{k'_Y}{\overset{k_Y}{\rightleftarrows}} MY + X + H_2O$$

so that $K_{XY} = k'_X k_Y / k'_Y k_X$. All four rate constants are available for the reactions of the (M2) complexes and the halides [10, 13], but unfortunately only k'_X and k'_Y are given at I = 0.5 *M* [13], while k_X and k_Y are given at I = 0.02 *M* [10]. However, if one assumes that the k_Y/k_X ratio does not change appreciably when changing the ionic strength, one calculates 1.3, 3.8 and 3.0 for K_{ClBr}, K_{ClI} and K_{BrI} respectively, which acceptably agree with the corresponding values 1.6, 6.4 and 4.0 obtained from Table II. Quite suprisingly, our K_{XY} values 1.6, 6.4 and 4.0 are almost undistinguishable from the k'_X/k'_Y ratios (1.57, 6.25 and 3.97), as though the exchange equilibria occurred without involving MOH_2. This stresses the fact that comparisons between equilibrium constants and kinetic data may provide, in some cases, a misleading idea of the reaction mechanisms.

Hewkin and Poë [7] have widely discussed the relative stabilities of the halide and the thiocyanate complexes (M1)X and (M2)X in terms of inductive and steric effects. The discussion may now be extended to include the (M3)X complexes (for which no literature data is available) and the protonic and dimerization equilibria. The K_a values increase in the rather unexpected order $(M3)OH_2 > (M1)OH_2 > (M2)OH_2$. The higher acidity of $(M3)OH_2$ is, probably, a consequence of: i) the lower inductive effect of the methyl groups (as compared with the ethyl groups of $(M2)OH_2$); ii) the presence of the ternary nitrogen atoms alone, which usually are not so basic as the primary and secondary nitrogen atoms. The effective positive charge of the central Pd atom would be higher than in $(M1)OH_2$ and $(M2)OH_2$. However, these effects cannot account for the greater acidity of $(M1)OH_2$ *vs.* $(M2)OH_2$. As for $(M1)OH_2$ one should consider, perhaps, additional contributions coming from tautomeric equilibria between O-bonded and N-bonded hydrogen, or from intramolecular hydrogen bond, which might favour the deprotonated species. However, further, hardly evaluable, effects must arise from the different solvation around the Pd-bonded water molecule, due to the hydrophobic action of the alkyl groups.

Another, rather unexpected, result is the relative stability sequence of the chlorocomplexes, $(M3)Cl \geqslant (M2)Cl > (M1)Cl$, which does not confirm the evaluation of Hewkin and Poë, $(M1)Cl > (M2)Cl$, and which disagrees with the observed stability sequence of Br^-, I^-, SCN^- and of the dimers. Once again these results could be related to the lower positive charge of the metal center in (M1)X, due to the presence of primary nitrogen atoms.

The steric effects become, clearly, the prevalent ones for more encumbering ligands, as well as in dimerization reactions.

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