interesting to see whether $[FeH_6]^{4-}$ and other binary hydrido anions might prove useful as precursor species for the synthesis of ternary or intermetallic hydrides under mild conditions. We note, for example, that the preparation of the latter ternary hydrides currently employs a high-temperature process, while the former binary hydrido anions can, in contrast, be obtained under ambient temperatures.

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Supplementary Material Available: Listings of thermal parameters and the observed and calculated structure factors for both the X-ray and neutron analysis of $FeH_6Mg_4X_4(THF)_8$ (44 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Generale ed Inorganica, Università di Venezia, 30100 Venice, Italy, and Christopher Ingold and Ralph Forster Laboratories, Chemistry Department, University College, London WC1H OAJ, England

Displacement of Ammonia from *cis*-Diamminebis(dimethyl sulfide)platinum(II) Perchlorate in Basic Aqueous Solution. First- and Second-Order Dependences of Rate on Hydroxide Concentration

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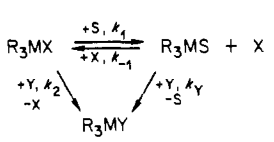
In basic aqueous solution, the ammonias in *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ are displaced by hydroxide in two consecutive stages. The first follows the rate law $-d \ln [\text{complex}]/dt = k_1^{\circ} + k_a[OH^-] + k_b[OH^-]^2$, with $k_1^{\circ} = 6.5 \times 10^{-5}$ s^{-1}, $k_a = 4.4 \times 10^{-3}$ M^{-1} s^{-1}, and $k_b = 4.6 \times 10^{-3}$ M^{-2} s^{-1}, all at 25.0 °C and $\mu = 0.1$. The displacement of the second ammonia follows the simpler rate law $-d \ln [\text{complex}]/dt = k_1^{\circ\prime} + k_a'[OH^-]$, with $k_1^{\circ\prime} = 3.6 \times 10^{-6}$ s^{-1} and $k_a' = 7.8 \times 10^{-4}$ M^{-1} s^{-1} at 50.0 °C and $\mu = 0.1$. The nature of the $[OH^-]$ dependence is discussed, and it is suggested that direct nucleophilic substitution and/or ion association provides a better explanation of the observations than base catalysis resulting from the deprotonation of the ammonia.

Introduction

The rate law for ligand-substitution reactions in four-coordinate planar d^8 metal complexes carried out under pseudo-first-order conditions (a sufficient excess of entering and leaving groups) takes the form $k_{obsd} = k_1k_Y(k_{-1}[X] + k_Y[Y])^{-1} + k_2[Y]$, which reduces to the usual form, $k_{obsd} = k_1 + k_2[Y]$ when $k_Y[Y] \gg k_{-1}[X]$. This is consistent with the mechanism in which associative displacement of S by Y in the reaction $R_3MX + Y = R_3MY + X$ is paralleled by associative solvolysis and competition for the solvento intermediate, R_3MS, which must be labile and only present in very low concentration if the relationship is to hold.[1]



Frequently, the contribution from the solvolytic path is small, and studies of the reaction with relatively low concentrations of weak nucleophiles in order to obtain precise values for k_1 may be complicated by the reversibility of the solvolytic pathway (i.e., $k_Y[Y] \gg k_{-1}[X]$).[2] A common way of avoiding this problem is to study the solvolytic reaction alone, but this is generally reversible. When the leaving group, Y, is basic, it might be possible to force the solvolysis to completion by adding an acid, care being taken to ensure that the solvolytic process was not subject to acid catalysis.[3] If the solvent is protonic, use can be made of the fact that a lyate ion (deprotonated neutral ligand) generally forms much stronger complexes than the ligand itself. A much used system is the aquo–hydroxo acid–base pair in aqueous solution (or methanol–methoxide in methanol). Coupled with the fact that hydroxide and methoxide have been shown, in the past, to be poor nucleophiles,[4] it has frequently been a practice to add excess hydroxide to an aqueous or methanolic solution in order to obtain a precise measurement of k_1.

As part of our studies of the ways in which the charge of the substrate affected its reactivity and nucleophilic discrimination properties, we recently examined the reactions of *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ with anionic nucleophiles.[5] The reactions occurred in two stages, stopping at the neutral product. The first step was always the displacement of ammonia while the second depended upon the nature (mainly the trans effect) of the entering group. With NH_3 as the leaving group it was convenient to determine k_1 in the presence of perchloric acid, but as a cross-check, we also looked at the solvolysis in the presence of excess hydroxide. Thus

$$cis\text{-}[Pt(Me_2S)_2(NH_3)_2]^{2+} + H_2O \rightarrow cis\text{-}[Pt(Me_2S)_2(NH_3)(H_2O)]^{2+} + NH_3$$

$$cis\text{-}[Pt(Me_2S)_2(NH_3)(H_2O)]^{2+} + NH_3 \xrightarrow{+H^+,\ \text{fast}}$$

$$cis\text{-}[Pt(Me_2S)_2(NH_3)(H_2O)]^{2+} + NH_4^+ \xrightarrow{+OH^-,\ \text{fast}} cis\text{-}[Pt(Me_2S)_2(NH_3)(OH)]^{+} + NH_3 + H_2O$$

The values of k_1 obtained with excess acid or with low concentrations (<0.001 M) of hydroxide were in good agreement,

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[†] Università di Venezia.

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(1) Gosling, R.; Tobe, M. L. *Inorg. Chem.* **1983**, *22*, 1239.

(2) Kennedy, B. P.; Gosling, R.; Tobe, M. L. *Inorg. Chem.* **1977**, *16*, 1744.

(3) Cusumano, M.; Guglielmo, G.; Ricevuto, V.; Romeo, R.; Trozzi, M. *Inorg. Chim. Acta* **1976**, *16*, 135.

(4) Belluco, U.; Cattalini, L.; Basolo, F.; Pearson, R. G.; Turco, A. *J. Am. Chem. Soc.* **1965**, *87*, 241.

(5) Annibale, G.; Canovese, L.; Cattalini, L.; Marangoni, G.; Michelon, G.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.*, in press.

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but we noticed a significant dependence of the rate on [OH$^-$] at higher concentrations. In view of the rarity of examples where substitution at Pt(II) has a rate that is sensitive to [OH$^-$],[6] we have examined this phenomenon more closely. This paper reports the general features of the reaction and its kinetics.

Experimental Section

cis-[Pt(Me$_2$S)$_2$(NH$_3$)$_2$](ClO$_4$)$_2$ was part of the sample described and used in the previous work.[5] All other reagents were analytical grade and were used without further purification. ^{1}H NMR spectra were measured with an EM 390 Varian spectrometer.

Kinetics. The reactions were started by adding the complex to a prethermostated solution of base of known ionic strength (NaClO$_4$) in the thermostated cell of a Varian Cary 219 spectrophotometer. The variation of optical density with time was followed by scanning the spectrum within the range 230–250 nm at appropriate timer and/or measuring the changing absorbance at 236 nm (the isosbestic point for the second change). This allowed a study of the first stage without interference from the second.

Numerical Treatment of Data. The kinetic data for the first stage, measured at the isosbestic point for the second, were processed by a nonlinear regression program following the Gauss–Newton algorithm, with three optimized parameters, D_0, D_∞, and k_{obsd}, where D_0 is the absorbance at zero time, D_∞ the absorbance at the end of the reaction(the absorbance of the isosbestic point), and k_{obsd} is the first-order rate constant. The convenience of working at the isosbestic point was countered by the relatively small change in absorbance, and so the kinetics were analyzed at other wavelengths where the absorbance changes are larger but the second step interferes. There, the data were processed by using a nonlinear regression program with five optimized parameters in the Gauss–Newton algorithm, D_0, D_1, D_2, k_{obsd}(I), and k_{obsd}(II), where D_0 is the absorbance at zero time, D_1 is the absorbance of the pure intermediate species at the wavelength of measurement, D_2 is the absorbance at the end of the second stage, and k_{obsd}(I) and k_{obsd}(II) are the first-order rate constants for the first and second stages, respectively. The experimentally determined rate constants are reported in Table I. Because the rates were so slow and because it was important to study the dependence of k_{obsd}(II) on [OH$^-$], the latter was studied in detail at 50.0 °C. Under these conditions, especially at the higher base concentrations, the first stage was virtually complete before the first measurement was taken. The kinetic data could then be processed by the three-parameter program.

Results

The spectrum of a solution of *cis*-[Pt(Me$_2$S)$_2$(NH$_3$)$_2$]-(ClO$_4$)$_2$ in dilute aqueous acid changes with time and is characterized by a general increase in absorbance over the range 230–250 nm. A kinetic analysis of the change of absorbance with time at any wavelength in this region clearly indicates a two-exponential relationship that analyzes as two consecutive first-order processes. The two rate constants, k_{obsd}(I,H) and k_{obsd}(II,H) (it is confirmed below that the assignment is valid because the second stage is the slower) are collected in Table I. When the complex is dissolved in 0.2 M NaOH, the spectral changes over the range 230–250 nm are more directly informative. A relatively rapid change corresponding to a general rise in absorbance is followed by the development of an isosbestic point at 236 nm with a decrease of absorbance at lower wavelengths and an increase at higher ones. At the end of the reaction there is a peak at 241 nm and a minimum at 234 nm. The change at the wavelength at which the isosbestic point develops follows a first-order rate law and the rate constant, k_{obsd}(I,OH), was obtained as described above. Analysis of the biphasic curve at 241 nm with k_{obsd}(I,OH), thus determined, inserted as a constant gave values for k_{obsd}(II,OH). These are also collected in Table I. A set of values for k_{obsd}(II,OH) measured at 50.0 °C are also included in the table. Acidification of the solution at the end of the second stage of the reaction caused the spectrum to change instantaneously to one identical with that found at the end of the reaction in acid solution.

Table I. First-Order Rate Constants for the First (I) and Second (II) Stages of the Reactions of *cis*-[Pt(Me$_2$S)$_2$(NH$_3$)$_2$]$^{2+}$ in Water[a]

OH$^-$	H$^+$	Br$^-$	temp, °C	μ, M	$10^5 \times k_{obsd}$(I), s^{-1}	$10^5 \times k_{obsd}$(II), s^{-1}
1.0	···	···	25	1.0	920	6.3
0.95	···	···	25	1.0	850	···
0.9	···	···	25	1.0	770	···
0.85	···	···	25	1.0	695	···
0.8	···	···	25	1.0	640	4.7
0.75	···	···	25	1.0	580	···
0.7	···	···	25	1.0	543	···
0.6	···	···	25	1.0	440	···
0.55	···	···	25	1.0	410	···
0.5	···	···	25	1.0	340	···
0.45	···	···	25	1.0	310	···
0.4	···	···	25	1.0	250	···
0.35	···	···	25	1.0	235	···
0.3	···	···	25	1.0	180	···
0.25	···	···	25	1.0	155	···
0.2	···	···	25	1.0	115	···
0.18	···	···	25	1.0	95	···
0.16	···	···	25	1.0	80	···
0.15	···	···	25	1.0	85	···
0.14	···	···	25	1.0	75	···
0.12	···	···	25	1.0	65	···
0.1	···	···	25	1.0	60	···
0.09	···	···	25	1.0	50.5	···
0.08	···	···	25	1.0	48	···
0.075	···	···	25	1.0	43	···
0.07	···	···	25	1.0	38	···
0.06	···	···	25	1.0	35	···
0.05	···	···	25	1.0	28	···
0.04	···	···	25	1.0	26.5	···
0.03	···	···	25	1.0	19	···
0.02	···	···	25	1.0	15.5	···
0.01	···	···	25	1.0	10.5	···
0.008	···	···	25	1.0	11	···
0.006	···	···	25	1.0	9.5	···
0.004	···	···	25	1.0	9.0	···
0.002	···	···	25	1.0	7.0	···
0.001	···	···	25	1.0	6.7	···
0.0001	···	···	25	1.0	6.3	···
0.2	···	···	25	0.2	350	2.15
0.1	···	···	25	0.1	230	1.45
0.01	···	···	25	0.01	45.2	0.68
0.001	···	···	25	0.001	13	···
···	0.01	···	25	1.0	5.5	1
···	0.005	···	25	0.005	6.9	1
···	0.001	···	25	1.0	6.3	1
0.2	···	···	50	1.0	···	14.4
0.3	···	···	50	1.0	···	19.3
0.5	···	···	50	1.0	···	32.8
0.6	···	···	50	1.0	···	40.2
0.8	···	···	50	1.0		53.3
0.1	···	0.1	25	1.0	530[b]	
0.1	···	0.08	25	1.0	420[b]	
0.1	···	0.06	25	1.0	350[b]	
0.1	···	0.04	25	1.0	240[b]	
0.1	···	0.02	25	1.0	155[b]	
0.1	···	0.01	25	1.0	110[b]	
0.1	···	0.008	25	1.0	95[b]	
0.1	···	0.006	25	1.0	91[b]	

[a] The substrate concentration was always less than 10^{-4} mol dm^{-3}. The standard errors in the rate constants are generally less than 5%. [b] Measured at 265 nm; gives $k_{obsd} = k_1 + k_2[\mathrm{Br}]$, with $k_1 = 6 \times 10^{-4}$ s^{-1} and $k_2 = 4.6 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}.

The nature of these spectroscopic changes were established by ^{1}H NMR (Figure 1). The spectrum of *cis*-[Pt(Me$_2$S)$_2$-(NH$_3$)$_2$](ClO$_4$)$_2$ in D$_2$O (0.02 M solution) consists of a peak at δ 2.56 with ^{195}Pt satellites ($J_{^{195}\mathrm{Pt}-^{1}\mathrm{H}}$ = 46.5 Hz) assigned to the coordinated Me$_2$S and one at δ 4.60 assigned to HOD. The peaks assignable to the NH$_3$ protons are absent, and it is assumed that proton exchange with the coordinated ammines

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[6] Baddley, W. H.; Basolo, F. *J. Am. Chem. Soc.* **1964**, *86*, 2075.

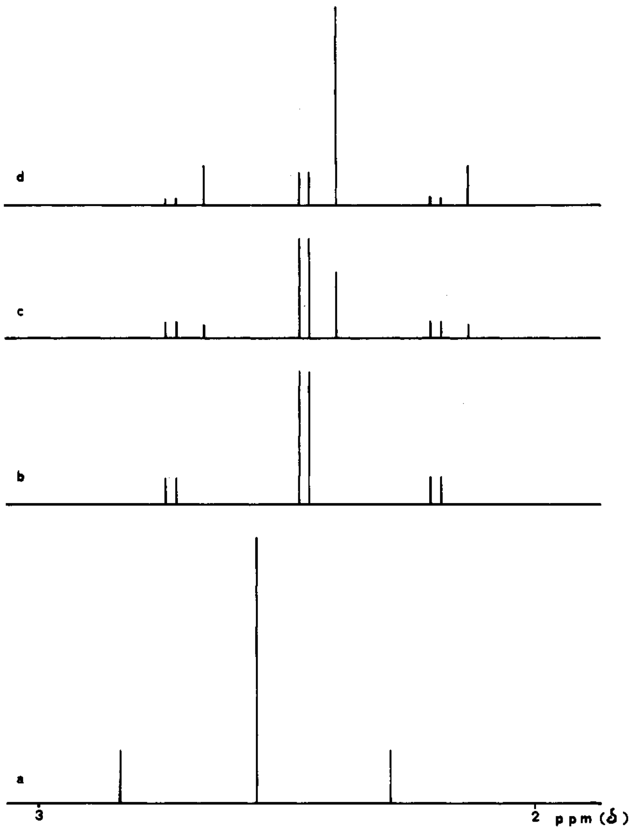
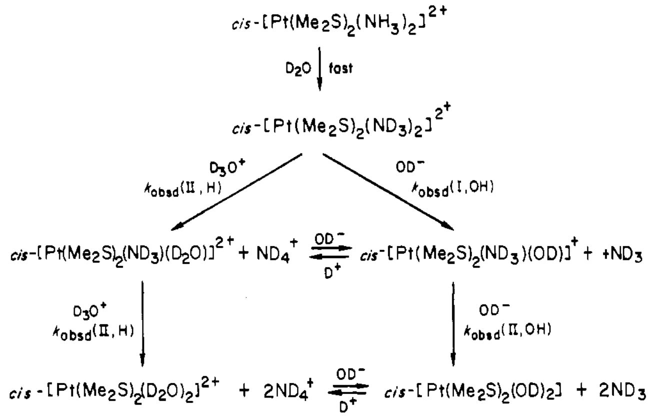


Figure 1. ^1H NMR changes in a solution of *cis*-$[Pt(Me_2S)_2(NH_3)_2](ClO_4)_2$ (0.02 mol dm^{-3}) in D_2O at 34 °C: complex alone (a); complex in the presence of OD^- (0.5 mol dm^{-3}) after 10 min (b), after 2 h (c), and after 100 h (d).

Scheme I



is fast. On acidification with $HClO_4$ there is a slow change in which the original "triplet" decreases and a new signal at δ 2.52 with ^{195}Pt satellites ($J_{^{195}Pt-^{1}H}$ = 45 Hz) grows. The three new peaks are split, but the separation is very small. A slower subsequent stage results in the disappearance of this set and the appearance of a new sharp peak at δ 2.45 with ^{195}Pt satellites ($J_{^{195}Pt-^{1}H}$ = 55 Hz). The two NMR changes correspond to the two spectrophotometric changes used to analyze the kinetics and can be identified as the successive loss of the ammonias, the three species being *cis*-$[Pt(Me_2S)_2(NH_3)_2]^+$, *cis*-$[Pt(Me_2S)_2(NH_3)(H_2O)]^{2+}$ (the splitting of the methyl signal is caused by the two Me_2S ligands being in different environments), and *cis*-$[Pt(Me_2S)_2(H_2O)_2]^{2+}$. At no time is any signal due to free Me_2S seen at δ 2.11.

The ^1H NMR spectrum of a solution of *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ in D_2O to which base has been added changes in much the same way. The signal at δ 2.56 ($J_{^{195}Pt-^{1}H}$ = 46.5 Hz) is replaced by two peaks at δ 2.475 and 2.455, both with ^{195}Pt satellites ($J_{^{195}Pt-^{1}H}$ = 45 Hz in both cases). The splitting is more pronounced here since the difference between NH_3 and OH as trans partners is greater than the difference between NH_3 and H_2O. The slower second stage leads to a sharp peak at δ 2.40 with ^{195}Pt satellites ($J_{^{195}Pt-^{1}H}$ = 45 Hz). Once again no signal is observed at any stage that can be assigned to uncoordinated Me_2S. An example of the ^1H NMR spectrum changing with time is given in Figure 1. The general reaction path is shown in Scheme I.

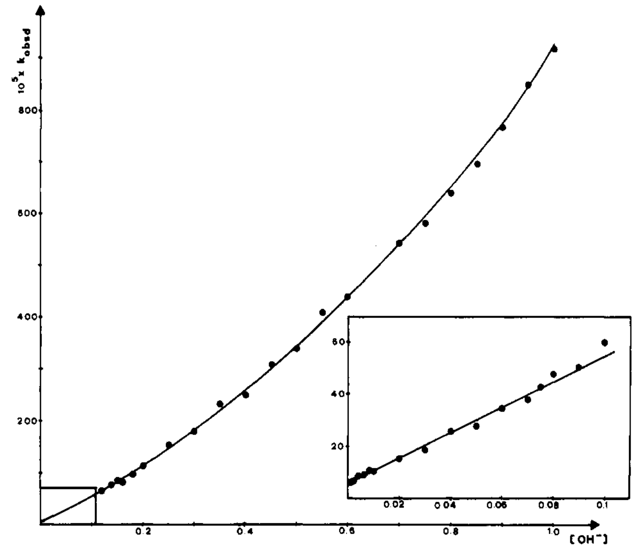


Figure 2. Plot of $k_{obsd}(I,OH)$ vs. $[OH^-]$.

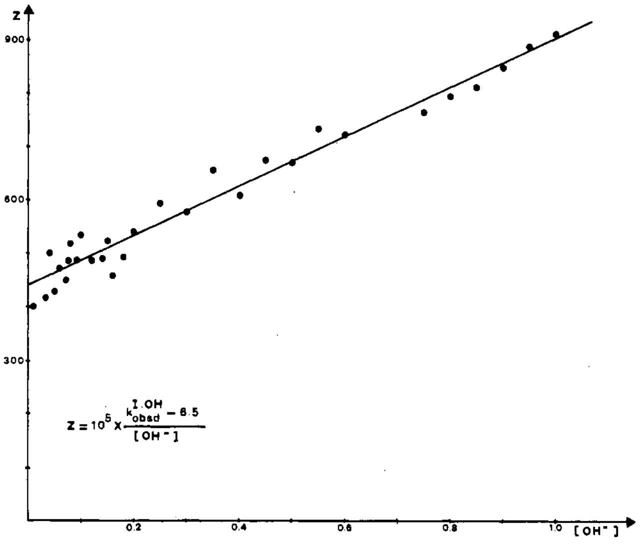
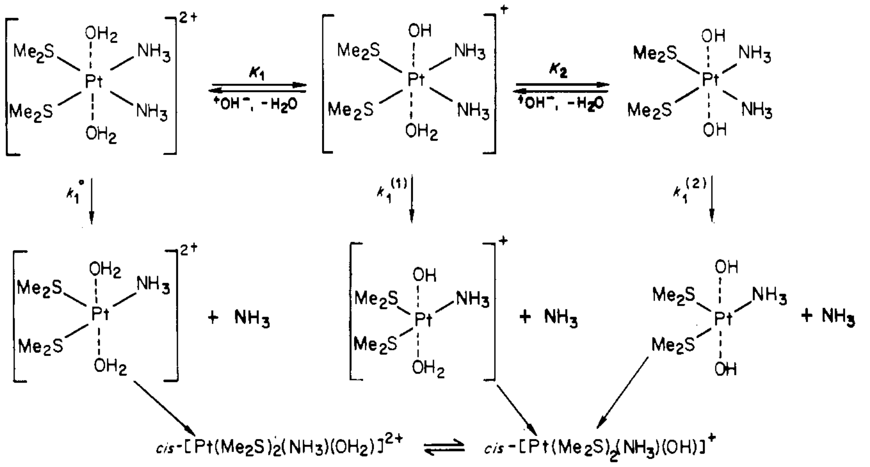


Figure 3. Plot of $10^5(k_{obsd}(I,OH) - k_1{}^0)/[OH^-]$ vs. $[OH^-]$.

It will be seen that the values of $k_{obsd}(I,H)$ and $k_{obsd}(II,H)$ are independent of acid concentration and ionic strength, consistent with their identification as rate constants for the reaction of the unprotonated complex with H_2O. There is a close agreement with the values of k_1 obtained in the first stage of the reaction between *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ and Br^- (from the previous work[5]) and also for the reaction in very weak basic solution (Table I).

The significant observation in this work is that the rate constants in basic solution are affected by $[OH^-]$. Analysis of the data shows that, while at low $[OH^-]$ the value of $k_{obsd}(I,OH)$ agrees closely with that of $k_{obsd}(I,H)$, it increases when $[OH^-]$ is increased beyond 0.001 M and also decreases with increasing ionic strength (Table I; Figure 2). A plot of $k_{obsd}(I,OH)$ against $[OH^-]$ is linear at first (intercept $k_1{}^0 = 6.5 \times 10^{-5}\ s^{-1}$), but at high enough $[OH^-]$, the curve slopes upward. A plot of $(k_{obsd}(I,OH) - k_1{}^0)/[OH^-]$ against $[OH^-]$

Scheme II



is linear with random scatter of the points (Figure 3). Small curvatures would not be detected. The rate law thus takes the form $k_{obsd}(I,OH) = k_1° + k_a[OH^-] + k_b[OH^-]^2$, with k_a = intercept of the above plot (or initial slope of the plot of $k_{obsd}(I,OH)$ against $[OH^-]$ = 4.4×10^{-3} M^{-1} s^{-1} and k_b = slope = 4.6×10^{-3} M^{-2} s^{-1}.

A plot of $k_{obsd}(II,OH)$, measured at 50.0 °C, is linear with a finite intercept, so that $k_{obsd}(II,OH) = k_1°' + k_a'[OH^-]$, where $k_1°' = 3.6 \times 10^{-6}$ s^{-1} and $k_a' = 7.6 \times 10^{-4}$ M^{-1} s^{-1}. There is no indication, even at the highest $[OH^-]$ used (0.8 M), of any departure from this first-order dependence.

The problem of understanding the dependence of the rate constant on $[OH^-]$, which is a proton base as well as a nucleophile, requires a consideration of its two roles. This has been the subject of much study over many years in the base-catalyzed substitution reactions of octahedral cobalt(III) and other transition-metal complexes[7] but is rare in platinum(II) chemistry. The role of hydroxide as a base will be considered first. Any scheme involving deprotonation of dimethyl sulfide can be ruled out immediately because at no stage of the reaction is there any exchange of the methyl protons with D. Proton exchange in NH_3 being fast in this system, it is possible that deprotonation of nitrogen is involved. One can rule out the highly unlikely possibility that the amido ($-NH_2^-$) ligand is a better leaving group than NH_3 by making comparison with the parallel acid–base ligand pair OH^- and OH_2, where the neutral member is by far the more labile. On the other hand, serious consideration must be given to the possibility that the amido group might labilize the second ammonia. Labilization of the substitution of a ligand by deprotonation of a coordinated amine is well-known in cobalt(III) chemistry (D_{cb} mechanism)[7] and has indeed been proposed to account for the $[OH^-]$-dependent displacement of chloride from $[Pd(Et_4dien)Cl]^+$ (Et_4dien = 1,5-bis(diethylamino)-3-azapentane), when all other nucleophile-dependent pathways have been suppressed by steric hindrance.[6] In that system, the alternative direct nucleophilic attack by hydroxide mechanism has been ruled out because this dependence is not present in the reactions of the complex where the secondary nitrogen has been methylated. A dissociative conjugate base mechanism of this sort seems to be ruled out for the system studied here by the fact that the rate of displacement of NH_3 from *cis*-$[Pt(Me_2S)_2(OH)(NH_3)]^+$ is also dependent upon $[OH^-]$. One might invoke a mechanism in which the amido group promoted an associative attack by hydroxide. This could only occur in the first stage and would account for the contribution from the second-order $[OH^-]$ dependence. Since the displacement of the second ammonia could not be base catalyzed in this way, only the first-order $[OH^-]$ dependence would remain. However, it is not immediately obvious how an amido ligand would facilitate an associative attack, and in any case, the reaction between *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ and bromide is not catalyzed by hydroxide; only the nucleophile-independent pathway is affected. The role of OH^- does not, therefore, seem to be that of a protonic base in this reaction.

In its role as a nucleophile and Lewis base, one might distinguish between some form of preequilibrium leading to an increase in coordination number (or axial ion association) and a direct nucleophilic attack by means of an A mechanism. If, indeed, this is the first example of direct nucleophilic attack by hydroxide in a platinum(II) complex in the way other nucleophiles, e.g. Cl^-, Br^-, etc., enter, k_a can be identified as k_2 for hydroxide, $=4.4 \times 10^{-3}$ M^{-1} s^{-1} for the displacement of the first ammonia, and is of a similar magnitude to that of Cl^- (8.3×10^{-3} M^{-1} s^{-1}).[5] It has never been clear why OH^- should have no direct nucleophilic pathway in other platinum(II) substrates, and it is likely that $k_2[OH^-]$ was never large enough compared to k_1 in water (both pathways leading to the same product) for its contribution to be measurable. Since it is now clear that the charge of the complex, contrary to what was said many years ago,[8] does play a significant role, the reactions of the dicationic substrate with the anionic hydroxide might be enhanced with respect to the solvolysis. An examination of other dicationic substrates in this context is called for. However, although this is sufficient to account for the kinetics of the displacement of the second ammonia, albeit from a 1+-charged substrate, it cannot account for the $[OH^-]^2$ term in the first stage, which becomes quite significant at high $[OH^-]$ (>0.1 M). It is therefore necessary to require that at least one of the two hydroxides that has to be involved in the transition state must also be present in a preequilibrium modification of the substrate. A mechanism whereby the hydroxide ion pair was much more sensitive to associative attack by other nucleophiles can be ruled out for the same reason that the A_{cb} mechanism was discarded, namely the lack of base catalysis of substitution by other nucleophiles.

Formation of five-coordinate (and even six-coordinate) species in platinum(II) chemistry is quite well-known. Addition of anions in the axial positions (the rest of the complex remaining in the square-planar arrangement) is well-known in dicationic complexes, but mainly those with "soft" donor atoms. For example, $[Pt(diars)_2]^{2+}$ [diars = *o*-phenylene-

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[7] Tobe, M. L. "The Mechanism of Base Catalyzed Substitution"; Sykes, A. G., Ed.; Academic Press: London, 1983; Adv. Inorg. Bioinorg. Mech. Vol. 2, in press.

[8] Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 385.

bis(dimethylarsine)] associates strongly with halide and thiocyanate ions in solution,[9] and halide ions occupy axial positions in the crystalline solid.[10] No reports have been published of any interaction of such complexes with hydroxide, but it is not known whether this is because no such interaction takes place or just that the experiment has never been carried out.

It is of interest to note that, while there is considerable evidence for the interaction of hydroxide (and cyanide) ions with $[Pt(bpy)_2]^{2+}$, $[Pt(phen)_2]^{2+}$, and similar species (bpy = 2,2′-bipyridyl; phen = 1,10-phenanthroline), there is no evidence for interaction with chloride. This was interpreted in terms of addition of OH^- or CN^- to the heterocyclic base rather than to the metal,[11] but a recent critical review of the evidence[12] argues convincingly that both in the solid and in solution the hydroxide is bound to the metal. X-ray diffraction studies prove that, in $[Pt(phen)_2CN]^+$, the metal is square pyramidal with the cyanide in the basal plane.[13] Whether this can be taken as a precedent for the *cis*-$[Pt(Me_2S)_2(NH_3)_2]^{2+}$ system or whether its driving force is the provision of a means whereby the strong distortions due to the nonbonding repulsive interactions between the hydrogens on the phenanthrolines in the square-planar complex are regularized remains to be examined.

A mechanism reminiscent of that invoked to account for a similar higher order nucleophilic dependence in the displacement, by chloride, of 5-NO_2-phen from $[Au(5\text{-}NO_2\text{-}phen)Cl_2]^+$ is[14] shown in Scheme II. No attempt is made to distinguish between coordination and ion association, and the involvement of water in these axial positions is possible (in which case it is reminiscent of the early Basolo and Pearson mechanism for square planar substitution[15]). Likewise, no commitment is made as to the geometry of these five-coordinate species, or the location of the ligands within them. A square pyramid is just easier to draw.

Provided the reaction involving the association of OH^- and the subsequent proton-transfer processes are fast, the kinetics will be first order in [complex] and the observed first-order rate constants will be related to $[OH^-]$ by expressions of the sort

$$k_{obsd}(I,OH) = (k_1^\circ + k_1^{(1)}K_1[OH^-] + k_1^{(2)}K_1K_2[OH^-]^2)/(1 + K_1[OH^-] + K_1K_2[OH^-]^2)$$

This will reduce to the form $k_{obsd}(I,OH) = k_1^\circ + k_1^{(1)}[OH^-] + k_1^{(2)}K_1K_2[OH^-]^2$ provided $K_1[OH^-]$ and $K_1K_2[OH^-]^2$ are much less than unity. The scatter of the data does not allow us to detect the departures from the simplified relationship for $K_1 < 0.1$ although it is possible that the reduction in $k_{obsd}(I,OH)$ due to $K_1[OH^-]$ becoming significant compared to 1 is fortuitously compensated by a contribution from $k_1^{(2)}K_1K_2[OH^-]^2$, but this cannot allow for much larger values of K_1 and K_2. Comparison with the empirical rate law would make $k_1^{(1)}K_1 = k_a$ and $k_1^{(2)}K_1K_2 = k_b$. The smaller the values of K_1 and K_2, the larger will $k_1^{(1)}$ and $k_1^{(2)}$ have to be in order to compensate, and it remains necessary to explain why such new facile paths are available for entry of hydroxide alone. The lack of a second-order $[OH^-]$ dependence of the second stage of the reaction is perhaps consistent with the lower charge of the substrate and the small size of K_2 when OH^- is attached to an uncharged aggregate.

At this stage it is only possible to demonstrate the phenomenon of multiorder hydroxide dependence and to rule out certain of the possible explanations. We are now studying the factors that relate to the occurrence of this phenomenon and hope thereby to elucidate the cause.

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Bridged or Nonbridged Structures for Dinuclear Metal Complexes. The Case of Tetrakis(methyl isocyanide)dipalladium(I) Iodide: An Unbridged Compound

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The structure of $(CH_3NC)_4Pd_2I_2$ has been determined by X-ray diffraction. Molecules of the type $(RNC)_4Pd_2X_2$ were originally assigned a halide-bridged structure largely on the basis of infrared data. $(CH_3NC)_4Pd_2I_2$ crystallizes in the space group $P\bar{1}$ with cell dimensions (determined at 140 K) of $a = 7.188$ (2) Å, $b = 10.933$ (2) Å, $c = 12.803$ (4) Å, $\alpha = 80.58$ (2)°, $\beta = 75.45$ (2)°, $\gamma = 81.22$ (2)°, $Z = 2$, and $V = 954.3$ (4) Å^3. The structure was refined to a conventional R value of 0.039 from 2489 significant reflections. It has an unbridged structure with a linear I–Pd–Pd–I unit and two terminal isocyanide ligands on each palladium. The Pd–Pd and average Pd–I distances are 2.533 (1) and 2.698 (1) Å. The low-energy metal–halogen stretching vibrations, which caused the original structure misidentification, are discussed in the context of other compounds with linear X–M–M–X units.

Introduction

Polynuclear metal complexes continue to attract considerable attention both as models for catalysts and as actual catalyst precursors.[1] Binuclear complexes offer the simplest unit in which the important metal–metal interactions can be studied. Here, the relative energies of structural alternatives such as bridged vs. unbridged structures and the choice of bridging ligands are not readily predicted. Several theoretical articles dealing with the question of bridged vs. unbridged structures have appeared recently, and these articles recount the results of numerous experimental observations.[2–4]

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