Aqueous Chemistry of Pt(II) and Pd(II) Complexes of 2,2′-Bipyridine and 1,10-Phenanthroline: pH Dependence

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Amongst the most studied coordination compounds are those involving heterocyclic bases such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen). However, the aqueous chemistry of the most readily available Pt(II) and Pd(II) complexes, *viz.* [$MLCl_2$] (L = bpy, phen) has been rather limited due to their lack of solubility. The addition of nucleophiles (OH^-, CN^-) has been studied for the more soluble bis-complexes, $[M(L)_2]^{2+}$ [1].

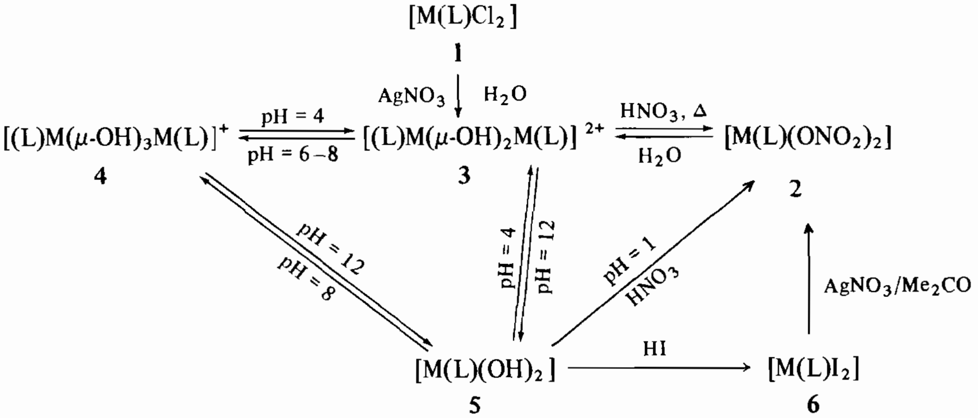
As part of a study to synthesize water soluble Pt(II) and Pd(II) complexes for pharmacological studies, we have studied the halide abstraction from bpy and phen complexes using silver nitrate. With water as a solvent, it is generally assumed that this will result in the formation of the corresponding diaquo complex. This communication demonstrates that this is not always the case.

Results and Discussion

[$M(L)Cl_2$] (**1**; M = Pd, Pt; L = bpy, phen) reacts with silver nitrate (2 mol) fairly rapidly in hot water (M = Pt, 30 min; M = Pd, 10 min). Removal of the precipitate of AgCl from the hot solution and cooling the filtrate separates the appropriate hydroxy-bridged dimer $[M(L)(\mu\text{-}OH)]_2(NO_3)_2$ (**3**) as very fine needles. The reaction of $AgNO_3$ with [Pt(bpy)-Cl_2] was first carried out by Morgan and Burstall [2] who suggested that the product was [Pt(bpy)-$(NO_3)_2$]. However, their elemental analyses (Pt,N) are not very convincing.

The Pt(II) dimeric complexes (**3**) are deep yellow–orange in colour and are fairly resistant to substitution. Thus, there is no reaction with LiCl in water at 100 °C and the compounds can be recrystallized from dilute nitric acid. Boiling in dilute nitric acid for 30 min is required to cleave the dimer, giving yellow [$Pt(L)(ONO_2)_2$] (**2**). This dinitrato complex can also be prepared by halide abstraction of [Pt(L)-I_2] (**6**)* using $AgNO_3$ in acetone (these reactions are summarized in Scheme 1). The Pd(II) dimeric complexes (**3**) are fawny yellow and only slight heating in dilute nitric acid is required to form the dinitrato complex, [$Pd(L)(ONO_2)_2$] (**2**). Dissolution of both the Pt(II) and Pd(II) dinitrato compounds (**2**) in warm water results in spontaneous dimerization to the hydroxy-bridged complexes (**3**).

Infra-red spectroscopy is a useful technique to distinguish between the dinitrato complexes (covalent nitrate, point group C_{2v}) and the hydroxy-bridged dimers (ionic nitrate, point group D_{3h}). The infra-red spectra of the dinitrato complexes were found to be very similar to that published by Livingstone [3] for [$Pd(bpy)(ONO_2)_2$]. Thus, the asymmetric NO_2 stretch (ν_4) occurs in the range 1550–1510 cm^{-1} for the Pt compounds and in the range 1510–



Scheme 1.

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*[$Pt(L)I_2$] (**6**) can be readily synthesized by base hydrolysis of [$Pt(L)Cl_2$] (**1**) and acidifying the resulting deep orange solution, in the presence of excess KI, to pH 2 using HNO_3.

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1490 cm^{-1} for the Pd compounds. The NO_2 symmetric stretch (ν_1) was found to be fairly independent of the metal and ligand and is in the range 1285–1255 cm^{-1}. The NO stretching vibration (ν_2) lies in the range 990–933 cm^{-1}, with the Pd complexes having a slightly higher wavenumber than the Pt complexes. The non-planar rocking vibration (ν_6) appears as a weak to medium band at 800 cm^{-1}. The ν_4, ν_2 and ν_1 bands were split probably due to the *cis* disposition of the two nitrato groups.

For the dimers, the strong band in the region 1370–1360 cm^{-1} was assigned to the NO_2 asymmetric stretch and the band at 835 cm^{-1} to the NO_2 deformation, indicating ionic nitrate [3]. Additional bands were observed at ≈1040 cm^{-1} and in the range 500–600 cm^{-1} which were not present in the nitrato or the chloro complexes: these bands have been assigned [4] to the MOH bending and the MO stretching vibration respectively.

The dimers (3) can also be separated as the ClO_4^- and BF_4^- salts by adding the appropriate anion to a hot concentrated solution of the nitrate salt.

Reaction of the Dimers with Base

Addition of hydroxide to the Pt(II) dimers (3) results in the formation of a deep red solution from which maroon–red solids were isolated as the nitrate, perchlorate and tetrafluoroborate salts. All these compounds analyse for one equivalent of the anion to two metal atoms.

UV–Vis spectroscopy and conductimetric titrations indicate that the red complex is formed on reaction of one mole of the Pt(II) dimer (3) with one mole of hydroxide. A concentrated solution of the red compound can be heated in a 2 M NaOH solution without any change, whereas a dilute solution reacts more readily (~12 h at 25 °C) with base to form the dihydroxy complex, $[Pt(L)(OH)_2]$ (5). By contrast, the red complex reacts with acid instantaneously to form the hydroxy-bridged dimer.

The ^{195}Pt NMR spectra of $[Pt(bpy)(OH)_2]$, $[Pt(bpy)(\mu\text{-}OH)]_2^{2+}$ and the red complex each show a singlet at −1776, −1340 and −1318 respectively (ref. = Na_2PtCl_6). The red complex is clearly not a mixture of the dimer and the dihydroxy complexes but seems to be the intermediate between the two. We therefore propose the formulation $[Pt_2(L)_2(OH)_3]^+$ (4) for the red complex.

For this formulation three structures are possible: (a) $[\{Pt(L)(OH)\}_2(\mu\text{-}OH)]^+$ with a single hydroxy-bridge, (b) the asymmetric complex, $[(L)Pt(OH)(\mu\text{-}OH)_2Pt(L)]^+$, in which one platinum is five coordinate and (c) the triply-bridged species $[(L)Pt(\mu\text{-}OH)_3Pt(L)]^+$. A complex of type (a), $[\{Pt(NH_3)_2(OH)\}_2(\mu\text{-}OH)]^+$, has been proposed as an intermediate by Appleton *et al.* [5] in the NMR study of reaction of hydroxide with $[Pt(NH_3)_2(OH_2)_2]^{2+}$, although the complex has not been isolated. The red colour of the bpy and phen complexes (4) is in line with the intense colour usually found for five coordinate Pt(II) compounds [1b, 6]. However, an asymmetric structure where only one of the metals in the dimer is five coordinate seems unlikely. We therefore favour the triply-bridged structure (c), which is consistent with the ^{195}Pt NMR spectrum. All attempts to grow crystals for an X-ray structure determination gave only fine needles.

The addition of base to a dilute solution of $[Pd(L)(\mu\text{-}OH)]_2^{2+}$ results in the formation of an initial intense yellow solution which rapidly fades to an almost clear solution, the UV spectrum of which corresponds to $[Pd(L)(OH)_2]$. The yellow complex $[Pd_2(L)_2(OH)_3]^+$ can be isolated as the nitrate or perchlorate salt when concentrated solutions are used. Dissolution of these compounds in water results in very rapid decoloration. Surprisingly, addition of an equimolar quantity of NaOH to $[Pd(L)(\mu\text{-}OH)]_2^{2+}$ gives rapid formation of $[Pd(L)(OH)_2]$ (5), whereas excess NaOH stabilizes the intermediate deep yellow colour which is transformed during 20 min at room temperature to $[Pd(L)(OH)_2]$. There are several isosbestic points for both L = bpy and phen.

Addition of Acid to $[Pt(L)(OH)_2]$

$[Pt(bpy)(OH)_2]$ (5) was first prepared and characterized by Gillard *et al.* [7] and is one of the first Pt(II) complexes with hydroxy ligands to be isolated. The nature of the species formed when HNO_3 is added to $[Pt(L)(OH)_2]$ is strongly dependent on the pH.

There is no immediate change in colour when the pH of the deep orange solution of $[Pt(L)(OH)_2]$ is lowered to ~8. However, when this solution is allowed to stand at room temperature for 12 h, a fine red precipitate is deposited, the analysis and IR spectrum of which corresponds to the product 4.

The hydroxy-bridged dimer (3) (as the perchlorate (a) or the nitrate salt (b)) is obtained if the pH of a solution of $[Pt(L)(OH)_2]$ is lowered to 4 using $HClO_4$ or HNO_3, Gillard *et al* [7] characterized the complexes obtained by this method (L = bpy) as $[Pt(bpy)(OH)(NO_3)]$ and $[Pt(bpy)(H_2O)(OH)](ClO_4)$ respectively. Both of these formulations are unlikely as the IR spectrum of (a) does not show the presence of coordinated nitrate and the IR spectrum of (b) shows an absorption at 3450 cm^{-1} but no absorption at 1630 cm^{-1}, which is the criterion for the presence of only a hydroxyl group.

When the pH of the solution of $[Pt(L)(OH)_2]$ is lowered very quickly to 1 using HNO_3, a bright yellow solution is obtained from which the crystalline substance $[Pt(L)(ONO_2)_2]$ (2) is obtained on removal of the solvent. However, if the pH is lowered slowly (over a period of 10 min), the compound obtained on evaporation of the solvent is a mixture of the hydroxy-bridged dimer (**3**) and the dinitrato complex (**2**) (the two compounds can be easily separated by extraction with hot acetone in which the dinitrato complex dissolves). Gillard *et al.* [7] have also prepared the dinitrato complex by this route.

Conclusions

In conclusion, our results demonstrate for the ligands bpy and phen the non-existence of the diaquo or aquo-hydroxy complex in normal aqueous solutions. Instead the dimer is formed exclusively and this is resistant to reaction with nucleophiles other than hydroxide. The formation of a diaquo species requires highly acidic conditions, at which point acid hydrolysis of the ligand may occur. In addition, our results call for a reinterpretation of the studies that have been reported [9] for the reactions of '$[M(L)(H_2O)_2]^{2+}$'.

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