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Interactions of 1,5-naphthyridine with Pd(en)Cl₂ or [Pd(en)(H₂O)₂](NO₃)₂ in aqueous solution†

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Abstract

The nature of the complexes formed in aqueous solution between either Pd(en)Cl₂ or [Pd(en)(H₂O)₂](NO₃)₂ and 1,5-naphthyridine (1,5-NAP), where en is ethylenediamine, have been investigated by 1-D and 2-D ¹H NMR spectroscopy and potentiometric titration. Above pH 5.0, two major complexes have been identified with the stoichiometries of 2:1 and 1:1 (M:L ratio) as well as small amounts of a 1:2 complex and/or oligomer. The 2:1 complex consisted of a Pd(en)²⁺ moiety symmetrically bonded to each of the nitrogen atoms of the 1,5-NAP, as indicated by the presence of just three ¹H NMR resonances in the aromatic region. The 1:1 complex had six resonances as a result of only one 1,5-NAP nitrogen atom being bonded to a Pd(en)²⁺ group. At pH <5, the uncomplexed nitrogen of the 1:1 and other singly bonded 1,5-NAP species became protonated and resulted in the formation of a large number of complexes. Job's method plots at pH 6 showed that the 1:1 complex is stable over a large concentration range. Above pH ~6 the 1:1 complex can dimerize *via* deprotonation of a water ligand on the Pd(en)²⁺ to form an hydroxo-bridged or oxo-bridged species. Evidence for this was observed in the upfield shifts of the resonances as the pH increased. The species distribution curve from potentiometric titrations and the NMR data were in good agreement at concentrations of 1–4 mM. NOESY data indicated that free 1,5-NAP ligand was exchanging with that in the 1:1 complex. In order to interpret the en region of the ¹H NMR spectra, the spectra of [Pd(en)(H₂O)₂](NO₃)₂ in D₂O at various pD were obtained.

Introduction

The coordination chemistry of 1,5-naphthyridine (1,5-NAP)^{1–6} has not been as thoroughly investigated as that of 1,8-naphthyridine, which can form dinuclear metal complexes by bridging across two metal centers^{7–15} as well as monomeric compounds. However, as a result of the geometrical location of the two nitrogen atoms, 1,5-NAP has the potential to

†Electronic supplementary information (ESI) available: ¹H NMR spectra of 2:1, 1:1, and 1:2 mole ratio of Pd(en)Cl₂:1,5-NAP and pure 1,5-NAP; pH titration plot. See DOI: 10.1039/b810487e

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serve as a bridging or linker ligand between multiple metal centers to form larger metallacycles.

Frequently nucleobases, nucleosides, nucleotides^{16–18} and other bis(amine) ligands, such as 4,4'-bipyridine,^{19–25} have been used as bridging ligands, especially with Pd(II) and Pt(II) complexes. In studies of the interaction of either Pd(en)Cl₂ or [Pd(en)(H₂O)₂](NO₃)₂ with nucleotides, it was found that a cyclic tetramer of [Pd(en)(μ-N7,N1-5'-GMP)]₄, where 5'-GMP = guanosine 5'-monophosphate, forms in aqueous solution.^{26–30} This structure expands to a hexamer upon introduction of a variety of organic molecules,³⁰ resulting in the formation of very strong host–guest interactions. Although the ligand 4,4'-bipyridine, like bridging 5'-GMP, bonds to Pd(en)²⁺ to form cyclic tetramers or polymers *via* the two nitrogens, [Pd(en)(4,4'-bipyridine)]₄⁸⁺ typically forms weak host–guest complexes and remains tetrameric.²⁵ However, Fujita has reported what appears to be a strong host–guest interaction between [Pd(en)(4,4'-bipyridine)]₄⁸⁺ and 1,3,5-trimethoxybenzene.²³ Since one cause for the difference between the two bridging ligands could be flexibility in the 4,4'-bipyridine ligand, it was thought that 1,5-naphthyridine, with its fused aromatic ring system and two nitrogen atoms *trans* to each other, might form good host–guest complexes analogous to the Pd(en)-5'-GMP system. Another cause for the difference in the behavior of the two ligands is the presence of ionizable protons on 5'-GMP which allows a reduction in the positive charge on [Pd(en)(N7,N1-5'-GMP)]₄.

We report herein that the Pd(en)-1,5-NAP system in aqueous solution formed two major complexes: 2:1 (metal to 1,5-NAP); 1:1 with several possible related structures, depending on the pH. Small amounts of species believed to be a 1:2 complex or an oligomer, or possibly both, were also observed. However, cyclic species were not observed, as evidenced by the lack of any host–guest behavior. The stoichiometry of the various reaction products and their structures were proposed for the Pd(en)Cl₂–1,5-NAP or [Pd(en)(H₂O)₂](NO₃)₂–1,5-NAP complexes based on ¹H NMR spectroscopy and pH titration data. To date it has not been possible to isolate any crystalline compounds for X-ray structure determination. Mass spectrometric analysis of this system was not attempted because our experience and that of others has shown that the ESI-MS of aqueous solutions of Pd(II) and Pt(II) complexes results in ligand exchange and unusual multimers, some of which are believed to be formed during the ESI process.^{31,32} Even the simple compound Pd(en)Cl₂, whose solution chemistry has been well studied, has a very complicated mass spectrum.³²

Results and discussion

Free 1,5-NAP has C_{2h} symmetry and, therefore, has only three different protons labeled α, β, and γ, as shown in Fig. 1. The proton chemical shifts for a 10 mM solution of 1,5-NAP in D₂O were: α, 8.96 ppm (dd, J_{αβ} = 4.2, J_{αγ} = 1.7 Hz); γ, 8.46 ppm (complex d, J_{βγ} = 8.5 Hz); β, 7.84 ppm (dd, J_{βγ} = 8.5, J_{αβ} = 4.2 Hz). A solution of pure Pd(en)Cl₂ exhibited resonances at 2.72 and 2.76 ppm, where the more upfield signal was a hydrolysis product of Pd(en)Cl₂.

Pd(en)Cl₂–1,5-NAP

The ¹H NMR spectra in D₂O at 10 mM total concentration are shown in Fig. 1. At very high Pd(en)Cl₂ relative concentration (9:1, M:L), three 1,5-NAP resonances were observed at

10.18 (γ), 9.59 (α) and 8.26 (β) ppm. All of the resonances shifted significantly downfield from their positions in free 1,5-NAP, which indicated that the 1,5-NAP was coordinated to the Pd(II) ion. It is noteworthy that the γ proton had become the most downfield. The presence of only three lines in the spectrum of this complex indicated that the 1,5-NAP was in a symmetric environment and thus the two nitrogens were both coordinated to a metal ion, giving a 2:1 complex (210 in Scheme 1). The three lines had the same integrated intensities, but with the gradual increase in 1,5-NAP concentration their relative intensities decreased with respect to the total 1,5-NAP integrated intensity, and they disappeared entirely at the ratio of 4:6 Pd(en)Cl₂:1,5-NAP. Like the 1,5-NAP signals, the en resonance in the 2:1 complex was located downfield of that in Pd(en)Cl₂ (Fig. 1(b))

As the relative concentration of 1,5-NAP increased to 8:2, a new species with six multiplets, each integrating as 1.0 proton, appeared at 9.94, 9.39, 9.15, 8.73, 8.13, and 8.00 ppm. These gradually increased in relative intensity to a maximum at a 5:5 reaction ratio and then their intensities began to decrease, disappearing at a mole ratio between 1:9 and 0:10 (Fig. 1). A Job's plot of the data showed that the stoichiometry of this complex was 1:1 (Fig. 2). The six lines indicated that only one nitrogen of the 1,5-NAP was coordinated to a Pd(II), which removed the symmetry in the 1,5-NAP moiety. Other evidence for the formation of a 1:1 complex was that the integrated intensity of the six lines from 1,5-NAP (6 H) was always 1.5 times that of the reacted en (4 H) intensity, irrespective of concentration. The en in the 1:1 complex was located just slightly downfield (2.88 ppm) from that of the 2:1 (2.87 ppm) complex.

At high 1,5-NAP concentrations (M:L of 4:6 or higher), another new species appeared with at least six very broad lines at 10.25, 9.67, 9.46, 9.18, 8.64, and 8.26 ppm, which were assigned to a probable mixture of 1:2 complex and an oligomeric species, the latter based on the broadness of the resonances. This complex (or complexes) had the largest downfield chemical shift for en, as expected due to electronic effects (two neutral 1,5-NAP substituted for the negatively charged Cl⁻ ions). The chemical shifts of the free 1,5-NAP shifted slightly upfield with increasing concentration, which is most likely an indication of π - π stacking between the 1,5-NAP aromatic rings in the free ligand.

[Pd(en)(H₂O)₂](NO₃)₂-1,5-NAP

The ¹H NMR spectral changes and chemical shifts in the aromatic region were essentially the same for the different ratios of 1,5-NAP to [Pd(en)(H₂O)₂](NO₃)₂ (Fig. 3(a)) as for the Pd(en)Cl₂-1,5-NAP system. From the NMR spectra in Fig. 1 and 3, it is observed that the 2:1 and 1:1 (M:L) complexes in aqueous solution existed in equilibrium with each other at high M:L mole ratios, while the 1:1 and 1:2 and/or oligomeric complexes existed in equilibrium at low M:L more ratios. At the 1:1 mole ratio, the 1:1 complex was the most abundant along with smaller amounts of the 2:1 complex and unreacted 1,5-NAP.

Analysis of the en region

The en region of the ¹H NMR of the [Pd(en)(H₂O)₂](NO₃)₂-1,5-NAP system reflected not only the presence of the various Pd(en)-1,5-NAP complexes, but also a number of Pd(en)²⁺ species not complexed to 1,5-NAP (Table 1). In order to identify the latter species, a study

of the pH dependence of the proton NMR spectrum of $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ was performed and the results are included in Table 1. In addition to the $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2]^{2+}$ ion, the hydrolysis products, $[\text{Pd}(\text{en})(\text{OH})_2]$ and the dimer $[(\text{Pd}(\text{en}))_2(\mu_2\text{-OH})_2]^{2+}$ as well as another hydrolysis complex reported in potentiometric titrations,^{26,33,34} which could be either $[\text{Pd}(\text{en})(\text{H}_2\text{O})(\text{OH})]^+$ or $[(\text{Pd}(\text{en})(\text{H}_2\text{O}))_2(\mu\text{-OH})]^{3+}$, were observed as the pD increased. Anywhere from one to three of these species were observed in a solution, depending on the pH. The di- $\mu\text{-OH}$ bridged complex at 2.55 ppm was observed in all of the solutions in the pD = 5–10 range, although little or none was present in the $\text{Pd}(\text{en})\text{Cl}_2$ –1,5-NAP solutions.

There was a marked difference in the en resonance of the 1:1 complex, depending on whether the anion was Cl^- or NO_3^- (Fig. 1(b) and 3(b)). The 1:1 complex with Cl^- anion was located downfield at 2.88 ppm compared to 2.83 ppm with NO_3^- anion. However, the more significant difference was that the Cl^- -containing system was a singlet and the NO_3^- -containing system was an AA'BB' multiplet. A similar multiplet has been observed previously in cyclic $[\text{Pd}(\text{en})(\mu\text{-}N1,N7\text{-}5'\text{-GMP})]_n$ ($n = 4$ or 6) and was the result of rigidity in the en moiety due to the steric crowding around the Pd(II).³⁰ Since the 1:1 Pd(en)- 1,5-NAP complex is clearly monomeric, the reason for any steric crowding is unknown at this time. However, it is apparent that NO_3^- involvement must be important because it was not present when $\text{Pd}(\text{en})\text{Cl}_2$ was used. Efforts to obtain crystals for X-ray structure analysis are continuing.

2-D NMR spectra

The COSY spectrum of the $\text{Pd}(\text{en})\text{Cl}_2$ -1,5-NAP (1:1) system at a concentration of 9 mM and pD 6.8 in D_2O is shown in Fig. 4. The more intense set of six sharp resonances corresponding to the 1:1 complex can be separated into two sets of three multiplets. The one set (A) had resonances at 9.94 ppm (γ), 9.15 ppm (α), and 8.13 ppm (β). The other set (B) occurred at 9.39 ppm (α), 8.73 ppm (γ), and 8.00 ppm (β), in which the order of the α and γ protons is the same as in free 1,5-NAP, but shifted downfield from free 1,5-NAP. These data suggested that the A set of resonances were those from the protons in the 1,5-NAP ring containing the nitrogen to which the $\text{Pd}(\text{en})^{2+}$ was bonded and the B set was from the other ring. The resonances from the 2:1 complex are also present in the COSY (10.18, 9.59, and 8.26, ppm) as well as some free 1,5-NAP (α , 8.96; γ , 8.46; β , 7.84 ppm).

To further understand the solution structure of the 1:1 complex, a phase sensitive NOESY experiment was performed with solvent suppression. From examination of the positive phase of this spectrum, which shows only the diagonals and exchange crosspeaks, it was observed that there was exchange of the 1,5-NAP ligand between the various complexes and also with free 1,5-NAP. This was especially noticeable in the β proton region (Fig. 5). Exchange crosspeaks were observed between the 2:1 complex and both the 1:1 (A) and 1:1 (B), between the 1:1 (A) and the 1:1 (B), and between the free 1,5-NAP and the 1:1. Similar exchange crosspeaks were present throughout the spectrum.

pH titration experiment

pH titrations were employed to further identify the possible species present in aqueous solution (Fig. 6). Table 2 lists all of the possible Pd(en)-1,5-NAP species that were identified in aqueous solution with their stability constants at 1.00 mM concentration, 298 K, and $I = 0.1$ M NaNO₃. Free 1,5-NAP has a pK_a of 3.05 at 298 K ($I=0.1$).^{35,36} In the absence of ligand, [Pd(en)(H₂O)₂](NO₃)₂ can hydrolyze to give species (2–1), (2–2), (3–3) and (1–2) with log K of –3.34, –8.49, –10.89 and –15.01, respectively, as reported previously.²⁶ The species [Pd(en)(H₂O)(OH)]⁺ (1–1) might be expected to form, but pH titrations at 1–4 mM did not show its presence. Instead the monohydroxo-bridged dimer, [Pd(en)(H₂O)]₂(μ-OH)³⁺, (2–1) appeared to form preferentially upon mono-deprotonation.

The distribution curve based on the pH titration data and a monomer–dimer model for all of the species is shown in Fig. 6. From this and Scheme 1, it can be seen that the 1:1 complexes, namely, (110), (22–1) and (22–2) were the main species at pH 3–9.5. As the pH increased, the 22–1 and 22–2 species were formed by the stepwise deprotonation of a H₂O molecule complexed to the Pd(en)²⁺. These are proposed to be the hydroxo and oxo-bridged dinuclear complexes, respectively. The 2:1 complexes, (210, pH range 3–7) and (21–2, pH range 7–10) made up ~10% of the 1,5-NAP concentration, and the latter of these was formed by the dissociation of a proton from a coordinated H₂O ligand on each of the Pd(en)²⁺ centers. A 1:2 complex, (120) was less abundant than the other complexes.

Concentration and pH dependence

As shown in Fig. 6, the relative concentration of a given species in a solution depends on the pH of the solution. Fig. 7 shows the NMR spectra of 4.0 mM [Pd(en)(H₂O)₂](NO₃)₂-1,5-NAP (1:1) at various pD. This concentration was chosen to approximate the concentration of the pH titration experiment. Remembering that $pD = pH \text{ meter} + 0.4$, there is generally good agreement between the spectrum at pD 6.3 in Fig. 7 and the species distribution plot (Fig. 6). By comparing the spectra of the 1:1 complex at pD 6.1–6.3 in Figs. 3(a) and Figs. 7(a), the effect of concentration on the species distribution can be observed.

At 4.0 mM the 1:1 complex was always the main species at pD 3.1–10.0, either in the form of a monomer or a dimer. At pH 2.7–5.2 the spectra contained a number of weak signals from species present in small amounts in addition to the major 1:1 species. Some of these were assigned to the 2:1 and 1:2 complexes, but complexes protonated at the non-Pd bonded 1,5-NAP nitrogen and/or protonated free 1,5-NAP are possibilities for the additional resonances at low pD. Broad resonances that might be indicative of oligomer formation were not observed in this pD range. Above pD 6.3, the resonances of the 1:1 complex (110) gradually shifted upfield with increasing pD as deprotonation of the aqua ligand proceeded to form sequentially the 22–1 and 22–2 species. Considerable dissociation occurred beginning at a pD of 8.6, which resulted in the formation of free 1,5-NAP and Pd(en)(OH)₂. A small amount of the 2:1 complex, existed throughout the entire pD range.

A ¹H NMR spectrum of 20 mM [Pd(en)(H₂O)₂](NO₃)₂-1,5-NAP (1:1) at pD 4.3 (Fig. 8) permitted an examination of the species formed at higher concentration and at acidic pD. This spectrum contained the same resonances as that of the 4.0 mM solution shown in Fig.

7, except that the resonances were much more intense at 20 mM. There are at least 26 multiplets in the 1,5-NAP region of the spectrum. It is clear that the increased concentration at acid pH had caused a major change in the nature and distribution of the various species. The 2:1 (210) complex was found to be the most abundant complex by integrated intensity, while the amount of unprotonated 1:1 (110) complex was relatively much less (approximately one-third that of the 2:1). The relative increase in the 2:1 complex is attributed to the fact that there are no available protonation sites on the 1,5-NAP whereas in the 1:1 complex the 1,5-NAP has one uncoordinated nitrogen available for protonation. Resonances that were thought to be either a 1:2 complex or oligomer at higher pD have sharpened and shifted slightly downfield, although it is difficult to be certain of assignments in the crowded regions of the spectrum. Therefore, it was concluded that this species is a more likely a small amount of 1:2 complex at pD 4.3 and lower. At pD > 7 the spectrum reverted to the same as that for the 1:1 stoichiometry shown in Fig. 3(a). It is concluded that the new lines in the spectrum at acidic pH arose from protonated 1:1 and 1:2 complexes (110, 22-1, 120) and possibly some free 1,5-NAP. Although the presence of a protonated 2:3 or other higher multinuclear complex is possible, it was not observed at higher pH and could not be identified if present at acid pH.

Conclusions

1,5-Naphthyridine acts as a ligand coordinating to Pd(II) in either $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ or $\text{Pd}(\text{en})\text{Cl}_2$ in aqueous solutions, forming the 2:1 and 1:1 complexes, as well as a 1:2 or oligomeric species. The ^1H NMR spectra and Job's plots indicated that the 1:1 species in its various protonated or unprotonated monomeric and dimeric forms was the major species in most solutions between pD 3–10, irrespective of concentration. The 2:1 complex also existed over a large pD range.

Since the 1,5-NAP in the 1:1 complex showed the presence of six different protons (unsymmetrical), only one of the 1,5-NAP nitrogen atoms was bonded to the $\text{Pd}(\text{en})^{2+}$ moiety, eliminating the possibility of a cyclic or polymeric structure. No evidence for a cyclic structure was observed in any of the solutions and this was supported by the exchange of the 1,5-NAP ligands observed for the 1:1 complex and by the lack of host–guest behavior. The ready formation of the 2:1 complex (210) indicates that the basicity of the uncomplexed nitrogen in the 1:1 complex is sufficient to bond an additional $\text{Pd}(\text{en})^{2+}$ moiety. Therefore, the lack of cyclization might reside in the $\text{Pd}(\text{en})^{2+}$ center. The 1:2 complex and/or oligomer is clearly less stable (Fig. 1, 3 and 6) than the 1:1 and 2:1 species and the lines were always broad at the higher pD values.

The formation of a 2:3 complex can also be postulated to be formed by the bonding of the monomeric complexes (110 and 120) to each other in acidic solution at the higher concentrations. The ^1H NMR spectrum of this type of species would have a six line group from the terminal 1,5-NAP ligands and a three line pattern from the central 1,5-NAP and the two groups would have a 2:1 intensity ratio, respectively. However, due to the complexity of the spectra of the 20 mM $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ –1,5-NAP system at low pH, it was impossible to determine whether or not this was formed.

Experimental

Materials

Pd(en)Cl_2 , HNO_3 , NaOH , NaOD , NaNO_3 , DCl , and D_2O were purchased from Sigma-Aldrich, AgNO_3 was purchased from Fischer Scientific, and the 1,5-naphthyridine was purchased from TCI-EP Japan. All chemicals were used as received. Deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$) was obtained by passage of water through a Barnsted Nanopure system. A Fisher Accumet 925 pH meter was used for the pH titrations and for adjustments of the pD of NMR samples.

Preparation of 20 mM $[\text{Pd(en)(H}_2\text{O)}_2](\text{NO}_3)_2$

Pd(en)Cl_2 (95.0 mg, 0.400 mmol) was placed in a beaker and deionized water (20 mL) was added using a volumetric pipette. The beaker was covered and heated in a water bath until a suspension formed. Two equivalents of AgNO_3 (135.9 mg, 0.800 mmol) were added to the suspension with stirring. The mixture was allowed to stand for 2 hours at room temperature and then was filtered through a Millex SLAA syringe filter unit (0.8 μm , Millipore Inc.) to remove AgCl .

Stock solutions of Pd(en)Cl_2 were prepared by weighing exact amounts of Pd(en)Cl_2 and dissolving it in a D_2O solution of 1,5-naphthyridine. The concentration varied from $4.0\text{--}20 \times 10^{-3} \text{ M}$, depending on the experiment. The pD of the solution was adjusted to a pD range of 5.4–7.4 with 0.1 M DCl or 0.1 M NaOD (D_2O solutions). The pD values were determined by adding 0.4 units to the pH meter readings.

NMR measurements

Solutions with various ratios of either Pd(en)Cl_2 or $[\text{Pd(en)-(D}_2\text{O)}_2](\text{NO}_3)_2$ and 1,5-NAP were prepared and the solutions were allowed to equilibrate for ~2 hrs before the spectra were obtained. ^1H NMR spectra (1D and 2D) of all samples were recorded on a Varian INOVA spectrometer at 499.77 MHz in D_2O at 26 °C using HOD at 4.800 ppm as the internal reference. Coupling constants (J) are given in Hz.

Job's method (continuous variations) experiments were performed using 20 mM stock solutions of $[\text{Pd(en)(D}_2\text{O)}_2](\text{NO}_3)_2$ and 1,5-naphthyridine at pD 6.1, and 10 mM stock solutions of Pd(en)Cl_2 and 1,5-NAP at pD 6.3. Ten samples with a total concentration of 10 or 20 mM (10:0, 9:1, 8:2...0:10 mole ratios) ranging from pure ligand (1,5-NAP) to pure $[\text{Pd(en)(D}_2\text{O)}_2](\text{NO}_3)_2$ or Pd(en)Cl_2 were prepared. The percentages of the various species were determined based on the relative integrated proton intensities of the individual species with respect to the total integrated intensity for the 1,5-NAP or en regions, as appropriate.

Potentiometric titrations

The stability constants of the ternary (pseudo-binary) complexes were determined by pH titrations, as previously described.²⁶ Samples containing 1.00 mM $[\text{Pd(en)(H}_2\text{O)}_2](\text{NO}_3)_2$ and 1.00 mM 1,5-NAP were used. Pure moist N_2 was bubbled through the samples to ensure the absence of oxygen and carbon dioxide during stirring of the solutions. All pH titrations were performed on 20 mL samples at $298 \pm 0.1 \text{ K}$ at a constant ionic strength of 0.10 M

NaNO₃. Experiments were carried out in duplicate to assure data reliability. The stability constants were defined by:

$$pM + qL + rH = M_pL_qH_r; \log \beta = [M_pL_qH_r]/[M]^p[L]^q[H]^r,$$

where M is Pd(en), L is 1,5-NAP, and H is the proton.

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Fig. 1.

^1H NMR spectra of $\text{Pd}(\text{en})\text{Cl}_2\text{-1,5-NAP}$ in D_2O at different M:L ratios, 10 mM total conc., pD 6.3, 26 °C.; 11 = 1:1 complex; 21 = 2:1 complex; * = 1:2 complex or oligomer.

Fig. 2.
Job's plot from the aromatic region of Pd(en)Cl₂-1,5-NAP in D₂O, 10 mM total conc, pD 6.3.

Fig. 3.

^1H NMR spectra of $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ -1,5-NAP at different M:L ratios at total concentration of 20 mM, D_2O , pH 6.1, 26 °C; 11 = 1:1 complex; 21 = 2:1 complex; * = 1:2 complex or oligomer; ** = $[(\text{Pd}(\text{en}))_2(\mu\text{-OH})_2]^{2+}$.

Fig. 4.
COSY spectrum of 9 mM Pd(en)Cl₂-1,5-NAP (1:1) in D₂O, pD 6.8.

Fig. 5.
Partial NOESY spectrum showing exchange crosspeaks in β proton region; 9 mM
Pd(en)Cl₂-1,5-NAP (1:1) in D₂O, pD 6.8.

Fig. 6.
Species distribution curve of 1.00 mM $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2-1$, 5-NAP, 298 K, $I = 0.1$ M NaNO_3 .

Fig. 7.
 ^1H NMR spectra of 4 mM $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ -1,5-NAP (1:1) as a function of pD, D_2O ,
 26 °C; * = 1:2 complex or oligomer; ** = $[(\text{Pd}(\text{en}))_2(\mu\text{-OH})_2]^{2+}$.

Fig. 8.

^1H NMR spectrum of 20 mM $[\text{Pd}(\text{en})(\text{H}_2\text{O})_2](\text{NO}_3)_2$ -1,5-NAP (1:1) at pD 4.3, 26 °C.

Scheme 1.

Observed and proposed formulae for Pd(en)-1,5-NAP complexes.

Table 1

¹H NMR assignments for en in Pd(en)(NO₃)₂ and Pd(en)-1,5-NAP in D₂O at 25 ° C^a

Assignment	Pd(en)(NO ₃) ₂ , 5, 25 mM ^b	Pd(en)Cl ₂ -1,5- NAP, 10 mM total conc., pD 6.3 ^c	Pd(en)(NO ₃) ₂ -1,5- NAP, 20 mM total conc., pD 6.1 ^c	Pd(en)(NO ₃) ₂ -1,5-NAP, 4mM ^b (1:1)	Pd(en)(NO ₃) ₂ -1,5-NAP, 20 mM ^b (1:1)
2:1		2.87	2.87	Obscured by 1:1	Obscured by 1:1
1:1		2.88	2.83 AA'/BB'	2.83-2.86, AA'/BB' ^d	2.83-2.87, AA'/BB' ^d
1:2/oligomer		3.05	3.05	3.05 (pD 3.1-7.2)	3.05 (pD 6.6-8.4) weak
[Pd(en)(H ₂ O) ₂] ²⁺	2.66, 2.68 (pD 2.5-5.5)	Not observed	2.66	2.64 (pD 3.1-6.3)	2.67 (pD 2.7-5.6)
[(Pd(en)(H ₂ O) ₂ (μ-OH)] ³⁺ or [Pd(en)(H ₂ O)(OH)] ⁺	2.64, 2.66 (pD 5.5-8.5)	2.66-2.67	2.67	Not observed	Not observed
[(Pd(en) ₂ (μ-OH) ₂] ²⁺	2.54, 2.56 (pD 5.5-9.5)	2.54 vw	2.54 strong	2.55 (pD 5.6-10.0)	2.55 (pD 6.6-8.4)
Pd(en)(OH) ₂	2.64 (pD >9.0)	Not observed	Not observed	2.63 (pD 10.0-11.6)	Not observed
Other ^e		2.72 ^f		2.97 several lines	2.97 several lines

^aChemical shifts in ppm.

^bpD dependent studies; 1st number at 5 mM, 2nd at 25 mM.

^cJob's study data.

^dUpfield at higher pD.

^eUnknown origin.

^fChloro species.

Table 2

Complex species and stability constants of [Pd(en)(H₂O)₂](NO₃)₂–1,5-NAP system at 1.00 mM, 298 K, I = 0.1 M NaNO₃

Species	Free 1,5-NAP	120	210	21–2	110	22–1	22–2
p <i>K</i> _a	3.05						
log K		8.18 ± 53	8.97 ± 21	–4.27 ± 21	5.21 ± 11	7.04 ± 12	3.83 ± 07