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Manifestation of diamagnetic chemical shifts of proton NMR signals by an anisotropic shielding effect of nitrate anions

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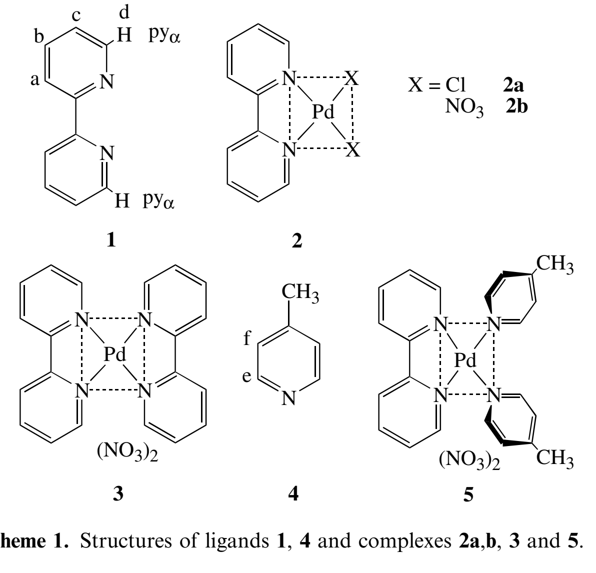
Abstract—A remarkable upfield shift of the py$_\alpha$ protons of complexed 2,2′-bipyridine in [*cis*-Pd(bpy)$(NO_3)_2$] is observed which is considered to originate from the anisotropic influence of suitably positioned coordinated nitrate anions around the Pd(II) centre of the molecule. A typical complexation-induced downfield shift is observed for the NH_2 protons in [*cis*-Pd(en)$(NO_3)_2$] where 'en' stands for ethylenediamine.

Proton NMR spectrometry has become one of the paramount techniques for characterisation of organic molecules.[1] Various factors are known to influence chemical shifts of the protons present in a molecule. One of these factors is the anisotropic effect notably observed in alkenes, ketones/aldehydes, alkynes and aromatic compounds. The effect is also seen in alkanes, for example, the axial protons of cyclohexane are subject to a diamagnetic shift (upfield) while the equatorial protons show a paramagnetic shift (downfield). Although the origin of anisotropy shielding effects is still under debate,[2] the utility of the effect is well accepted. In general, the signals of ligand-based protons which are close to the metal binding sites, upon complexation, undergo a downfield shift. The downfield shift is due to the electron-withdrawing effect of the metal ion. We report here a remarkable upfield shift of the py$_\alpha$ protons of complexed 2,2′-bipyridine in a square planar mononuclear Pd(II) complex, that is, [*cis*-Pd(bpy)$(NO_3)_2$]. However, a typical downfield shift was observed for the NH_2 protons in [*cis*-Pd(en)$(NO_3)_2$] where 'en' stands for ethylenediamine. The upfield shift of the py$_\alpha$ protons is considered to originate from the anisotropic influence[3] of suitably positioned, coordinated nitrate anions around the Pd(II) centre. The downfield shift of the NH_2 protons is attributed to a metal ion complexation and possible H-bonding with the coordinated anion and solvents. The relative magnitude of the change in chemical shift observed due to the effect of the coordinated nitrate ion is compared qualitatively with that of a chloride ion, and pyridine based ligands. Compounds **1**–**10** used in this study were carefully chosen ligands and Pd(II)-based complexes (Schemes 1 and 2).

The observation of a nitrate-induced diamagnetic shift arose during our work on metal-driven self-assembly. Some of the molecules of interest were generated from



Scheme 1. Structures of ligands **1**, **4** and complexes **2a**,**b**, **3** and **5**.

Keywords: NMR spectroscopy; Nitrate anion; Diamagnetic shift; Anisotropy shielding; Pd(II) complex.

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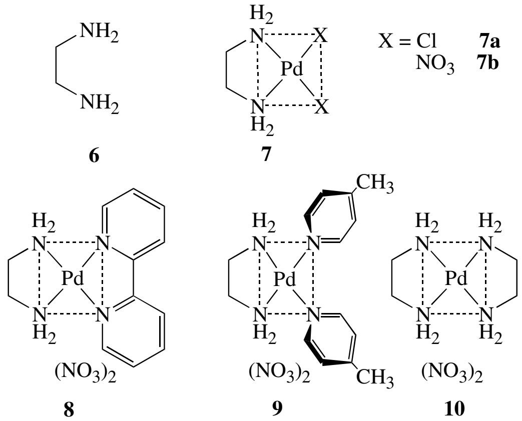

Scheme 2. Structures of ligand **6** and complexes **7a**,**b**–**10**.

cis-protected Pd(II) and pyridine appended non-chelating multidentate ligands. 2,2′-Bipyridine, **1** is a cis-protective group for Pd(II) and has been utilised by Kusukawa and Fujita[4] to construct self-assembly molecules. Starting from compound **1** and $PdCl_2$ the square planar complex [*cis*-Pd(bpy)Cl_2], **2a** can be obtained[5] which, upon anion exchange with $AgNO_3$, gives [*cis*-Pd(bpy)$(NO_3)_2$], **2b**.[5] Suitable ligands can replace the nitrate anions in **2b** to form molecules of the general formula $[\{cis\text{-Pd(bpy)}\}_x(\text{ligand})_y](NO_3)_{2x}$. The simple mononuclear complexes [Pd(bpy)$_2$$(NO_3)_2$], **3**, [*cis*-Pd(bpy)(4-methylpyridine)$_2$]$(NO_3)_2$, **5** and [Pd(en)(bpy)]$(NO_3)_2$, **8**, considered in this work, belong to the general formula $[\{cis\text{-Pd(bpy)}\}_x(\text{ligand})_y](NO_3)_{2x}$. 4-Methylpyridine, **4** was used as a unidentate pyridine-ligand for the synthesis of **5** and other related compounds. Complex [*cis*-Pd(en)Cl_2], **7a**[6] where ethylenediamine, **6** is the cis-protective group, undergoes anion exchange with $AgNO_3$ to yield the square planar [*cis*-Pd(en)$(NO_3)_2$], **7b**.[7] We also found that a DMSO-d_6 solution of complexes **2a** or **7a** undergo in situ anion exchange with $AgNO_3$ to give **2b** and **7b**, quantitatively. Many compounds of the general formula $[\{cis\text{-Pd(en)}\}_x(\text{ligand})_y](NO_3)_{2x}$ have been prepared from **7b** and suitable ligands,[8] hence **7b** is a useful synthon in Pd(II)-based coordination chemistry. The simple mononuclear complexes [Pd(en)(bpy)]$(NO_3)_2$, **8**, [*cis*-Pd(en)(4-methylpyridine)$_2$]$(NO_3)_2$, **9** and [Pd(en)$_2$$(NO_3)_2$], **10** belong to this general formula. We have exploited **1** and **6** as cis-protecting groups for our research work on Pd(II)-driven self-assembly chemistry.[9,10] The synthesis and reactivity of Pd(II) and Pt(II) complexes in DMSO solutions is one of our research interests,[9–11] thus, it was important to obtain NMR spectral data for allied compounds in DMSO-d_6 for comparison.

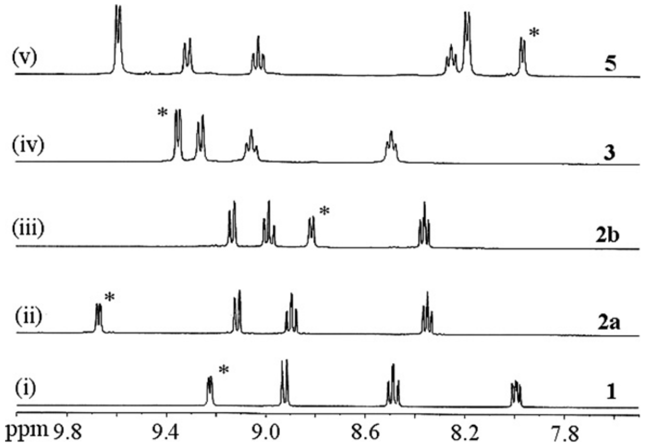

Figure 1. ^1H NMR spectra (400 MHz) of (i) 2,2′-bipyridine **1**, (ii) [*cis*-Pd(bpy)Cl_2] **2a**, (iii) [*cis*-Pd(bpy)$(NO_3)_2$] **2b**, (iv) [Pd(bpy)$_2$]$(NO_3)_2$, **3** and (v) [*cis*-Pd(bpy)(4-methylpyridine)$_2$]$(NO_3)_2$, **5** in DMSO-d_6 using external TMS in $CDCl_3$ in a sealed capillary as the standard. The signals due to the py$_\alpha$ protons, that is, H_d of the bpy fragment, are marked with asterisks.

Initially, the ^1H NMR spectra of **1**, **2a** and **2b** (Scheme 1, Fig. 1) were recorded in DMSO-d_6, using external TMS in $CDCl_3$ as the reference. All four types of proton present in **1** appeared at distinctly different chemical shifts[12] (Table 1). In the case of complex **2a** the square planar geometry around Pd(II) involves two pyridyl-*N* centres of ligated **1** and two chloride counteranions.[13] The downfield shift is due to the electron-withdrawing effect of the metal ion. Thus, as may be expected for a metal complex, all the signals in compound **2a** were found to be shifted downfield with respect to **1** (Table 1) with a $\Delta\delta$ of +0.45 ppm for the H_d (py$_\alpha$) protons.[12] Compound **2b** also contains a square planar Pd(II) centre,[5] however, there are two bound nitrate ions instead of chlorides. In the solid state a compound very similar to **2b**, which is in fact a dimer, shows self-stacking in a zig–zag manner in one dimension.[14] In the case of **2b**, once again a downfield shift with respect to **1** was observed for all the protons except the py$_\alpha$ protons. There was a remarkable upfield shift of the py$_\alpha$ signal of **2b** where $\Delta\delta = -0.86$ and -0.41 ppm, with respect to compounds **2a** and **1**, respectively. Since the metal centre can withdraw electron density from the ligand to make py$_\alpha$ downfield shifted, the observed upfield shift in **2b** is attributed to an anisotropy effect of the nitrate groups. A recent report[15] by Smith and co-workers illustrates the anisotropic effect exhibited by an encapsulated nitrate anion of a cryptate which was generated by the addition of 15 equiv of a nitrate salt to a cryptand. The shift of $\Delta\delta = -0.20$ ppm for a suitably positioned endohedral proton in one of the nitrate-bound cryptands was the largest upfield shift observed in these systems. The comprehensive shielding surface of an encapsulated nitrate ion may differ from that of a free one. Theoretical calculations on a free trigonal planar nitrate anion were performed[15] and it was shown that the shielding zone of the anion was at a maximum above the central N atom of the anion and deshielding was predicted around the peripheral plane. Therefore, the upfield shifted py$_\alpha$ protons in **2b** which are located above the plane of the nitrate ions, as seen from its energy minimised structure and discussed later in this report, are certainly under the influence of the shielding zone of the anion.

The chemical shifts of the signals in the ^1H NMR spectrum of [*cis*-Pd(bpy)Cl_2], **2a** were not changed upon the addition of 1 or 2 equiv of a solution of tetrapropylammonium nitrate. In this situation nitrate ions, which cannot replace the strongly bound chloride ions, are available as free ions and are not coordinated to the

Table 1. Proton NMR spectral data (400 MHz, TMS in $CDCl_3$ in a sealed capillary) of the ligands, and complexes **1**–**5** showing the chemical shifts δ in ppm and coupling constants J in Hz. The value of $\Delta\delta$ is with respect to uncomplexed ligands **4** and/or **1**

	H_d (py_α)	H_a	H_b	H_c	H_e
1	δ: 9.22 (d)	8.92 (d)	8.49 (dt)	7.99 (m)	
	J: 4.28	7.84	7.46, 1.82	Multiplet	
	$\Delta\delta$: 0.00	0.00	0.00	0.00	
2a	δ: 9.67 (d)	9.11 (dd)	8.89 (dt)	8.35 (m)	
	J: 5.67	8.08, 0.78	7.77, 1.50	Multiplet	
	$\Delta\delta$: +0.45	+0.19	+0.40	+0.36	
2b	δ: **8.81** (d)	9.13 (d)	8.99 (dt)	8.36 (m)	
	J: 5.35	7.41	7.70, 1.34	Multiplet	
	$\Delta\delta$: **−0.41**	+0.21	+0.50	+0.37	
3	δ: 9.35 (d)	9.26 (d)	9.06 (t)	8.50 (t)	
	J: 5.40	7.92	7.69	6.47	
	$\Delta\delta$: +0.13	+0.34	+0.57	+0.51	
4	δ:				8.95 (d)
	J:				5.48
5	δ: 7.93 (d)	9.31 (d)	9.03 (t)	8.26 (t)	9.59 (d)
	J: 5.32	8.03	7.89	5.31	6.29
	$\Delta\delta$: **−1.29**	+0.39	+0.54	+0.27	+0.64

metal centre. Thus, it was established that the uncoordinated nitrate ions have no influence on the shift of the py_α protons. However, the addition of 2 equiv of $AgNO_3$ to **2a** results in the formation of **2b** due to the precipitation of the insoluble AgCl. Here the nitrate anions are not free but are bound to the metal centre and thus the upfield shift is observed. This study indicates that the anion needs to be bound to the metal centre and only then does it have the opportunity to properly orient itself to display the anisotropy effect.

In order to obtain added support for this interpretation we examined two more compounds, **3**[16] and **5**. The choice of these two compounds was based on the following considerations. It is well known that aromatic rings exhibit a ring current effect which has a remarkable effect on the chemical shift positions of the related protons in their ^1H NMR spectra. Protons situated above or below the molecular plane are upfield shifted and the effect diminishes upon moving towards the periphery of the ring. The protons situated around the plane (up to 54.7°) and close to the periphery of the ring are downfield shifted. Keeping the effect of the aromatic ring current in mind we chose compounds **3** and **5**, where additional ligands having aromatic rings are disposed in two different manners around the *cis*-$Pd(bpy)^{2+}$ moiety via complexation, by replacing the bound counter anions of **2b**. The two different dispositions are such that the molecular plane of the new aromatic ligands results in minimum/maximum possible dihedral angles with the $Pd(bpy)^{2+}$ moiety, that is, the molecular plane of the new aromatic ligands remain either closely parallel, or perpendicular, to the molecular plane of the *cis*-$Pd(bpy)^{2+}$ moiety. Such an arrangement would bring the ring current effect of the aromatic rings to bear on the py_α protons of interest. The synthesis of **3** and **5** was achieved by replacement of the nitrate anions of **2b** by one bpy unit in the case of **3**, or 2 equiv of 4-methylpyridine, **4** in the case of **5** (Scheme 1).

In the case of compound **3**, the additional bpy unit is not exactly in the same plane as the other being twisted with a dihedral angle of about 33° due to steric repulsion.[16] With respect to compound **1** (Fig. 1), the $\Delta\delta$ for **3** was found to be only +0.13 ppm in contrast to +0.45 ppm as observed in the chloride-bound complex [*cis*-$Pd(bpy)Cl_2$], **2a**. In the complexes of non-chelating pyridine rings and Pd(II), the ligands are known to orient perpendicular to the plane of the square planar coordination geometry of the metal ion, in a propeller shape.[17] In this type of orientation, the py_α protons of the bpy moiety in **5** are above the molecular plane of the coordinated aromatic ligand **4**. In line with expectation, compound **5** shows $\Delta\delta$ of the bpy based py_α as −1.29 ppm with respect to compound **1** (Fig. 1), the upfield shift being due to the dominating ring current effect. Therefore, in [*cis*-$Pd(bpy)(NO_3)_2$], **2b** the H_d protons must be influenced by a shielding zone which is attributed to the adjacent nitrate ions.

Ethylenediamine, **6** is well known as a cis-protecting group for Pd(II) where the other two coordination sites are occupied with monoanions. The orientations of the bound nitrate anions in **7b** are likely to be different from their orientations in **2b** on account of the smaller size of **6**. The NH_2 protons in **7a**,**b** were found to be shifted downfield irrespective of the anions (Fig. 2) as compared to free ethylenediamine **6**. The shift of the NH_2 signals of **7a**,**b** as compared to **6** were $\Delta\delta = +1.63$ (for **7a**) and +2.45 (for **7b**) ppm. More interestingly the magnitude of the downfield shift of the NH_2 signals due to the influence of nitrate anions, that is, in **7b** was higher than that due to the chloride anions in **7a**. Therefore, the NH_2 protons are probably located outside the shielding zone of the bound nitrate anions which could also be a deshielding zone. An intramolecular H-bond between

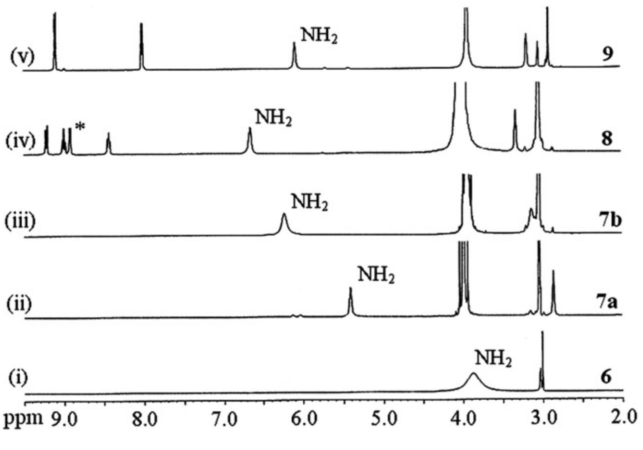

Figure 2. ^1H NMR spectra (400 MHz) of (i) ethylenediamine **6**, (ii) [*cis*-$Pd(en)Cl_2$] **7a**, (iii) [*cis*-$Pd(en)(NO_3)_2$] **7b**, (iv) $[Pd(en)(bpy)](NO_3)_2$ **8** and (v) [*cis*-$Pd(en)(4\text{-methylpyridine})_2](NO_3)_2$, **9** in DMSO-$d_6$ using external TMS in $CDCl_3$ in a sealed capillary as the standard. The signal due to the py_α protons, that is, H_d of the bpy fragment is marked with an asterisk.

suitably positioned oxygens of the anions and H of NH_2 is possible[18] which might also be responsible for the downfield shift. In the energy minimised structure of **7b**, the position of the two protons of the NH_2 groups are not symmetrical with respect to the coordinated nitrate anion. However, both protons appear as a single but broad signal in the ^1H NMR spectrum. In fact **7b** can show as many as four signals[7] for the NH_2 protons at −5 °C in DMF-d_7. The effect of the nitrate anions as evidenced in the ^1H NMR spectra of **2b** and **7b** indicates that in compound **2b** with bpy as a cis-protecting group, a suitable situation arises where the nitrate anions can manifest a diamagnetic anisotropic shielding effect.

In order to check the effect of the aromatic ring current we chose compounds [Pd(en)(bpy)]$(NO_3)_2$, **8**[10] and [*cis*-Pd(en)(4-methylpyridine)$_2$]$(NO_3)_2$, **9** where additional ligands having aromatic rings are disposed in two different manners around the *cis*-Pd(en)$^{2+}$ moiety via complexation through the replacement of the bound counteranions of **7b**. In fact the $\Delta\delta$ for the NH_2 signal in **8** was found to be +2.87 ppm with respect to compound **6** (Fig. 2). The NH_2 protons are shifted downfield due to the inductive effect of this typical ligand environment and also possibly by the deshielding zone of the coplanar bpy unit. The $\Delta\delta$ for the NH_2 signal in **9** was found to be +2.31 ppm with respect to compound **6** (Fig. 2). The NH_2 protons in **9** are in almost the same environment as in **8** so far as an inductive effect is concerned. Further, the 4-methylpyridine ligand is not coplanar to the en moiety, rather it is almost perpendicular to the square plane of the complex, hence a deshielding effect is ruled out. Also the shielding influence due to the ring current from the 4-methylpyridine units may not be enough in **9** because the NH_2 protons are not directly above the plane of the aromatic ligands. Probably, this is due to the small size of the en unit compared to bpy. Further, the small size is responsible for the almost coplanar orientation of the nitrate anions in **7b**, which may allow H-bonding.

The shifts of the ethylenediamine methylenes, when complexed with Pd(II) forming a five-membered ring, is of interest, being only slightly downfield shifted compared to free **6**, even though they are very close to the metal. Thus, there may be a slight local anisotropic effect of the bound ethylenediamine on itself, and also on the bpy unit (Fig. 3), with the py$_\alpha$ protons showing a $\Delta\delta$ of −0.30 ppm compared to free bpy. Finally, the spectrum of [Pd(en)$_2$]$(NO_3)_2$, **10**[19] was also recorded to complete the observations (Fig. 3). The $\Delta\delta$ of the NH_2 protons in **10** was +1.63 ppm compared to free **6** in contrast to +2.45 ppm (for **7b**) and +2.31 ppm (for **9**). This data indicates that the nitrate anion induces a paramagnetic environment.

DFT quantum computational studies on [*cis*-Pd(bpy)$(NO_3)_2$], **2b** and [*cis*-Pd(en)$(NO_3)_2$], **7b** were undertaken using the GAUSSIAN 03 set of algorithms.[20] The hybrid Becke-3–Lee–Yang–Parr (B3LYP) exchange correlation functional was applied for DFT calculations.[21] Geometries were fully optimised at the B3LYP level of theory using 6-311G(d,p) basis sets for all the atoms except Pd, for Pd, the MWB basis set was used. The energy optimised structures found on the stationary points are represented as models in Figures 4 and 5. It was observed that in the case of complex **2b**, the H$_d$ protons (py$_\alpha$ of bpy) were located above the molecular plane of the adjacent planar nitrate moiety at a distance of 2.37 Å from the oxygen coordinated to the Pd(II) centre. This is the shortest distance between this proton and any of the three oxygen atoms of the nitrate. The distance of the H$_d$ proton from the central nitrogen of the coordinated nitrate is 2.94 Å. Also, the planes of the nitrates were almost perpendicular to the square plane of the coordinated Pd(II) where the dihedral angle between the plane of the nitrate ion and the coordination square plane was about 95°. In the case of **7b** the situation was different and the nitrate and the square plane were almost co-planar with a dihedral angle of about 157°. The two NH_2 protons in **7b** were not equivalent, however, a single downfield shifted broad peak was observed in the NMR spectrum. The distance of one of the NH_2 protons which is almost coplanar to the coordinated nitrate is described here. The distance of this selected NH_2 proton from the oxygen coordinated to the Pd(II) centre is 2.92 Å; however, the shortest distance between the

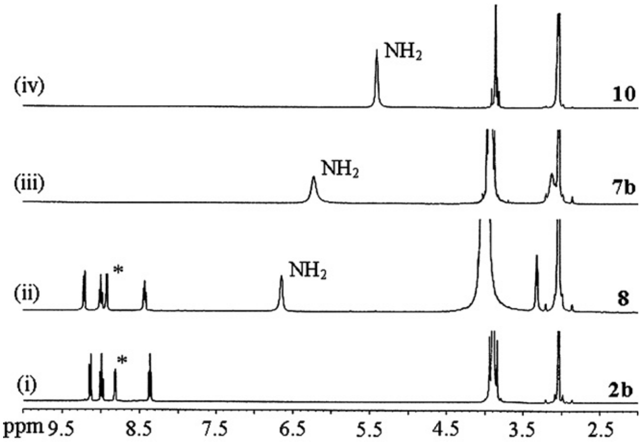

Figure 3. ^1H NMR spectra (400 MHz) of [*cis*-Pd(bpy)$(NO_3)_2$], **2b**, [Pd(en)(bpy)]$(NO_3)_2$, **8**, Pd(en)$(NO_3)_2$, **7b** and [Pd(en)$_2$]$(NO_3)_2$, **10** in DMSO-d_6 using external TMS in $CDCl_3$ in a sealed capillary as the standard. The signals due to the py$_\alpha$ protons, that is, H$_d$ of the bpy fragment are marked with asterisks.

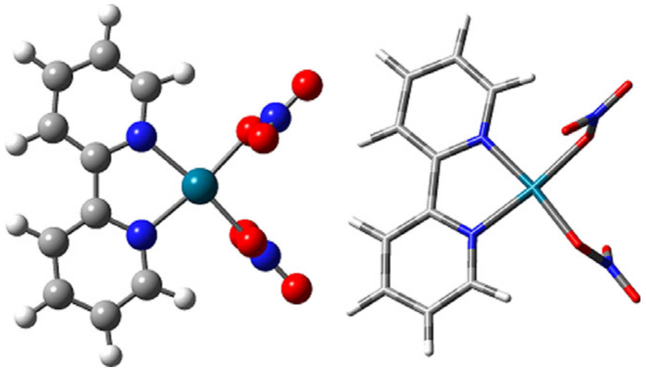

Figure 4. Energy minimised structure of [*cis*-Pd(bpy)$(NO_3)_2$], **2b** showing the position of H$_d$ (py$_\alpha$) with respect to the plane of the bound nitrate ion. Ball and stick as well as tubular models are shown.

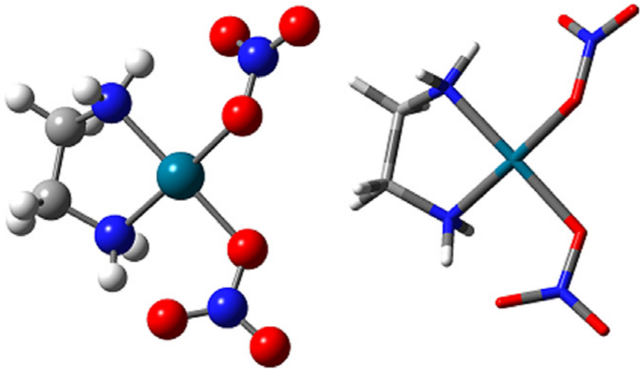

Figure 5. Energy minimised structure of [*cis*-Pd(en)$(NO_3)_2$], **7b** showing the position of NH_2 with respect to the plane of the bound nitrate ion. Ball and stick as well as tubular models are shown.

proton and any of the three oxygen atoms of the nitrate is 1.93 Å. The py$_\alpha$ protons in **2b** are positioned above the plane of the trigonal planar nitrate anion and are shifted upfield in line with the finding of Smith and co-workers,[15] whereas the NH_2 protons of **7b** undergo a downfield shift which may be a combination of several effects, for example, paramagnetic anisotropy, inductive, perturbation of the charge and possible H-bonding.

The calculated[22] $\Delta\delta$ values of the py$_\alpha$ signal of **2b** with respect to **1** was +0.15 ppm which, although a downfield shift, is not very significant. This is in contrast to the experimentally obtained value of −0.41 ppm. The calculated shift of the averaged NH_2 signals of **7b** with respect to **6** was found to be about +2.0 ppm, which is in line with the experimentally obtained value of +2.45 ppm.

In conclusion we have demonstrated the diamagnetic shielding effect of nitrate ions towards suitably positioned protons in a Pd(II)-based complex.

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