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Anisotropic effect of the nitrate anion—manifestation of diamagnetic proton chemical shifts in the ^{1}H NMR spectra of NO_3^- coordinated complexes

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ABSTRACT

The anisotropic effect of the planar nitrate anion NO_3^- has been ab initio calculated employing the *Nucleus-Independent Chemical Shift (NICS)* concept of von Ragué Schleyer and visualized as *Iso-Chemical-Shielding Surfaces (ICSSs)* of various (de)shieldings. Complexation-induced shifts in the ^{1}H NMR spectra of nitrate/metal complexes or nitrate/receptor supramolecules can be separated now into anisotropic influences of the suitably coordinated nitrate anions and effects originating from differential sources.

1. Introduction

Wolinski, already in 1997,[1] calculated the magnetic shielding surfaces by point shielding calculations in order to better understand the influence of adjacent nuclei, lone pairs, and bonds on the magnetic shielding of certain nuclei. Von Ragué Schleyer et al.[2] not only used the *Nucleus-Independent Chemical Shift (NICS)* at the center of aromatic ring systems to quantify aromaticity, he and his co-workers[3] studied also the NICS values on a grid around the aromatic compounds to provide insight into diatropic and paratropic regions of the molecules.[3]

At about the same time, Klod and Kleinpeter[4] visualized the *Through Space NMR Shieldings (TSNMRSs)* of the double bond, the triple bond, and analogous heterocyclic functional groups as well as of benzene as *Iso-Chemical-Shielding Surfaces (ICSSs)*, which were calculated employing the NICS concept of von Ragué Schleyer:[5] A lattice of 'ghost atoms' surrounding the π electron system located at the center of a virtual cube (10×10×10 Å) is ab initio MO calculated employing the GIAO perturbation method[6] and the resulting data set is transformed into a contour file of ICSS of different intensity and direction.[4] By this procedure, the TSNMRSs of the functional group/aromatic moiety can be specified and employed to quantitatively determine the stereochemistry of potential proximal nuclei; a number of example applications have been published.[4,7–24] Additionally to stereochemical applications, prevalent assertions in prescribed NMR textbooks that are in fact incorrect have also been addressed, e.g., the ^{1}H chemical shift difference between the *axial* and *equatorial* protons in cyclohexane *is not due to the anisotropic effect of the C–C single bond*[10] and the deshielding by 1.57 ppm of H-4 in 11-ethynylphenanthrene relative to the corresponding δ value in phenanthrene *does not arise from the anisotropic effect of the C≡C triple bond.*[15] Finally this method[4] was successfully employed to visualize and quantify (anti)aromaticity,[25] the endo- and exohedral aromaticity of fullerenes,[26] and also partial (anti)aromaticity of fulvalenes[27] and fulvenes.[28]

Similar approaches to calculate TSNMRSs have been published by Alkorta and Elguero (to probe the anisotropic effect of the C–C single bond)[29] and Martin et al.[30] (to study through space NMR shielding effects of aromatic molecules and of a number of functional groups), however, supramolecules including one distance-dependent hydrogen of H_2 or methane were applied to probe the anisotropic shielding surfaces. In the two cases, shieldings of similar size and direction, comparable with the results of our model, were obtained.

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The TSNMRSs obtained were in excellent accordance with data obtained by application of the classical model of Bovey and Johnson[31] and Haigh and Mallion[32] if the distances were more than 2.5–3 Å from the anisotropic functional group. This provided us with a new method to quantitatively ab initio MO calculate both the through space effects of certain bonds and functional groups and of aromatic moieties as well on proximal nuclei. The major aim of the present paper is to extend the application of this method[4] to the nitrate anion in order to visualize and quantify the anisotropic effect of this functional group and to apply this effect to manifest unexpected diamagnetic chemical shift effects in a series of palladium(II) complexes.

2. Computational details

Ab initio calculations were performed on SGI Octane and SGI Origin 2000 workstations and a Linux cluster using the *Gaussian 03* program package.[33] Geometry optimizations were performed at various levels of theory[34] [B3LYP/3-21G*, B3LYP/MWB, B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd); MP2/6-31G**] without restrictions; due to available computer facility and nearest results to MP2 calculations, the mixed level [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] was employed for the theoretical calculation of the compounds studied (**1**–**10**). The chemical shieldings in the surroundings of the molecules were calculated based on the NICS concept[5] whereby the molecule was placed at the center of a grid of ghost atoms ranging from −10.0 to +10.0 Å in all three dimensions with a step width of 0.5 Å, resulting in a cube of 68,921 ghost atoms. The chemical shielding calculations were performed using the GIAO[6] method at the same levels of theory (the effect of the basis sets was also tested but significant size deviations in TSNMRSs were not recorded). Since GIAO is a coupled HF method that uses gage-independent atomic orbitals for the calculation of shielding values, it can be applied to the calculation of NICS.

From the GIAO calculations, the coordinates and isotropic shielding values of the 'ghost atoms' were extracted. After transformation of the tabulated chemical shieldings into a *SYBYL*[35] contour file, the TSNMRSs of the molecules were visualized as ICSS of different shielding or deshielding.

3. Results and discussion

3.1. The anisotropic effect of the nitrate anion

The anisotropy of the magnetic susceptibility of the nitro group and of the nitrate anion has been determined by measuring the Cotton–Mouton effect[36] and the nitrate anisotropy was quantified by both the ^{15}N shielding tensor and the ^{14}N quadrupole coupling constant.[37] The anisotropic shielding surface of HNO_2 was first studied by Martin et al.:[38,30g] Deshielding in-plane and shielding above nitrogen was calculated in good agreement with the experiment.[39] The shielding surface of the nitrate ion was calculated by Mahoney at al.[40] employing the same method;[38,30g] quantitative

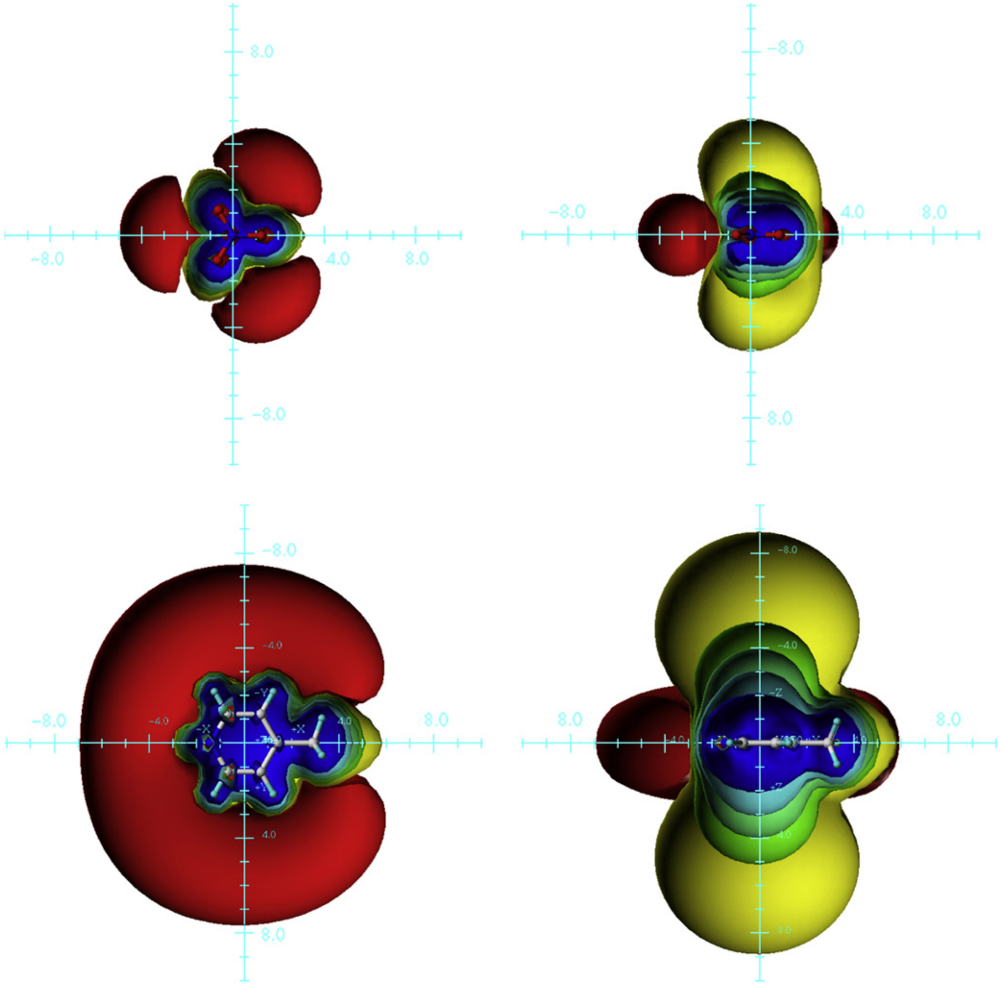


Figure 1. Visualization of TSNMRS of the nitrate anion and of 4-methylpyridine **4** by ICSS of different direction and size (blue represents −5 ppm shielding; cyan, −2 ppm shielding; greenblue, −1 ppm shielding; green, −0.5 ppm shielding; yellow, −0.1 ppm shielding; red, 0.1 ppm deshielding), orthographic view.

dependences in the vicinity of the nitrate anion [deshielding in-plane (from nitrogen crossing N–O bonds much less than along O–N–O bisector crossing), directly above nitrogen shielding] are given.

The results are corroborated by the results of the present TSNMRS calculations of the nitrate anion, which are visualized in Figure 1. Above and below the plane of the planar nitrate anion proves to be the highfield shift region [ICSS (−0.1 ppm), yellow, at 5.1 Å from the central nitrogen of the molecule]; the plane of the nitrate anion reveals the deshielding region of the anisotropic effect, however, only along the O–N–O bisector [ICSS (+0.1 ppm), red, at 5.0 Å from nitrogen center]; the effect toward the oxygens along the N–O bonds is negligible only. The ICSSs of ±0.1 ppm (yellow and red, respectively, cf. Fig. 1) have been calculated and were employed to visualize the anisotropic effect of the nitrate anion, however, the complete grid of ghost atoms ranging from −10.0 to +10.0 Å in all three dimensions resulting in a cube of 68,921 ghost atoms is available and can be employed to determine quantitatively this effect in complexes and supramolecules including nitrate anions.

In addition to the nitrate anion anisotropy effect, in Figure 1, the ring current effect of 4-methylpyridine is given [TSNMRS values are identically visualized as ICSSs of different (de)shielding]; readily to see, the ring current effect of the aromatic moiety is stronger in the two directions than the anisotropic effect of the nitrate anion [in-plane ICSS (0.1 ppm)=6.9 Å; perpendicular to center ICSS (−0.1 ppm)=8.9 Å] but sizes of different regions are identical (deshielding in-plane but shielding above/below the plane of the molecules). The ring current effect of 4-methylpyridine was employed to calculate the combined effect (together with the nitrate anisotropic effect) in **5** and **9**; results will be discussed along the corresponding paragraphs (vide infra).

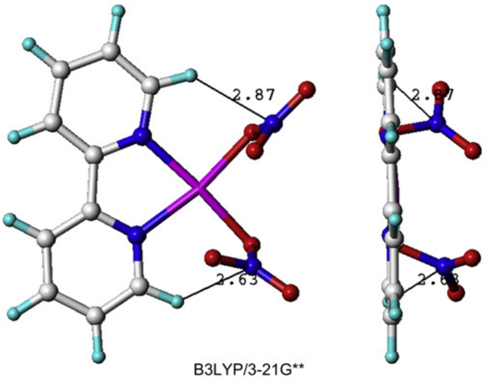
3.2. Ab initio calculation of the structure of a series of Pd(II) complexes 2b, 3, 5, 7b, and 8–10[41]

First, for finding out the best level of theory, the bipyridine (bpy) complex **2b** was studied. In Figure 2, the corresponding structures as obtained at different levels of theory are given; differences are small, but only in case of the mixed level [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] (largest one available employing Gaussian 03), results similar to the MP2 level were obtained, which, to apply generally for the larger complexes, was out of the possibilities of the available computer facility. Thus, the [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] mixed level of theory was selected as the method of choice and the remaining complexes **3**, **5**, **7b**, and **8**–**10**[41] (cf. Scheme 1) were calculated at this theoretical level.

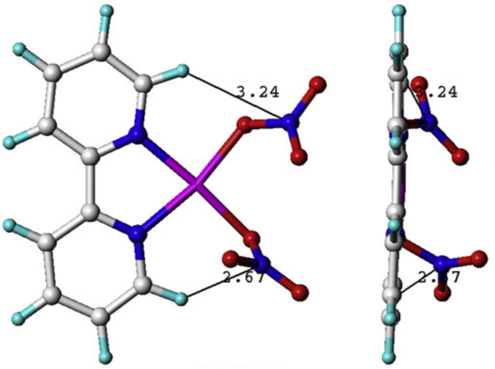
3.3. [*cis*-Pd(bpy)(NO_3)$_2$] 2b, [Pd(bpy)$_2$](NO_3)$_2$ 3, and [*cis*-Pd(bpy)(4-methylpyridine)$_2$](NO_3)$_2$ 5

In Figure 3, the structure of the *bpy* complex **2b** is given and the anisotropic effect of one nitrate ligand is visualized; in addition (right) the anisotropic effects of the two nitrate ligands on the *bpy* protons are notified. The bpy$_\alpha$ protons are shielded by −0.32 ppm, the other *bpy* protons are much less influenced by the anisotropic effects of nitrate anions in **2b**. In agreement with the experimental ^{1}H NMR spectra, the bpy$_\alpha$ protons ($\Delta\delta$=−0.41 ppm) are shielded; the effect ($\Delta\delta$=−0.32 ppm), however, proved to be something smaller than experimentally obtained but in correct direction (cf. Table 1). The anisotropic effects on bpy$_\beta$ to bpy$_\delta$ protons are much smaller (<0.1 ppm).

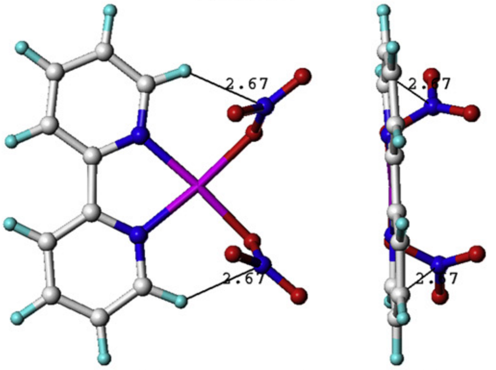
In [Pd(bpy)$_2$](NO_3)$_2$ **3** the same effect on bpy$_\alpha$ protons is almost negligible ($\Delta\delta$=−0.02 ppm); the same anisotropic effect on the other protons proves to be between 0.0 and −0.09 ppm and also shielding. Thus, the anisotropic effect of the nitrate anions in **3** proves to be negligible only, obviously due to the position of the bpy$_\alpha$ protons in-between the shielding/deshielding regions of the nitrate anion anisotropic effect. The effect of the second bpy ligand was not considered; thus, deshielding of bpy$_\alpha$ to bpy$_\delta$ in **3** with respect to **1** should be of this origin.



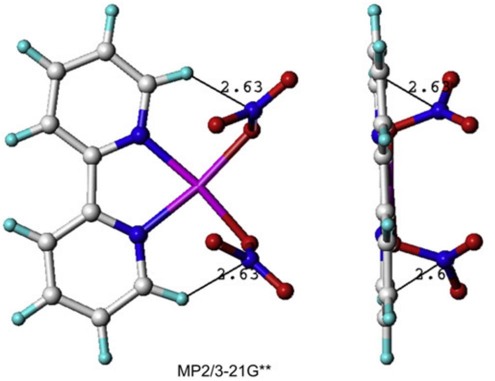
B3LYP/3-21G**



B3LYP/MWB



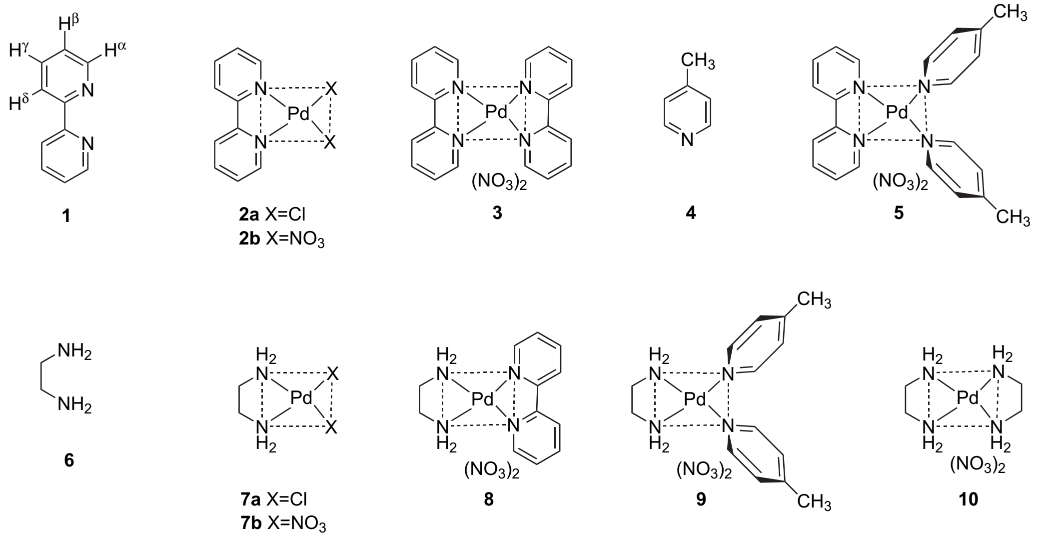
B3LYP/6-311G** (for C,H,O,N); B3LYP/3-21G** (for Pd)



MP2/3-21G**

Figure 2. Structure of [*cis*-Pd(bpy)(NO_3)$_2$] **2b** at various levels of theory, orthographic view.

In [*cis*-Pd(bpy)-(4-methylpyridine)$_2$](NO_3)$_2$ **5**, however, especially due to additional anisotropic ligands (two 4-methylpyridyls), the effects are remarkable. In this case, the anisotropic effects of the



Scheme 1. Compounds studied.

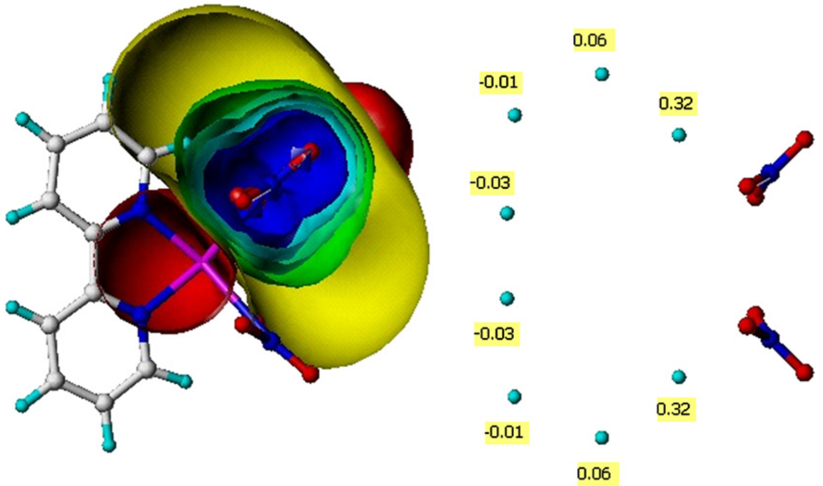


Figure 3. Structure of [*cis*-Pd(bpy)(NO$_3$)$_2$] **2b** calculated at the [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] mixed level of theory together with TSNMRS of one nitrate anion (left) and anisotropic effects of both nitrate anions on the bipyridine protons H^{α}–H^{δ} (right).

nitrate ligands and of the ring current effects of the 4-methylpyridyl ligands, calculated by the same method,[4,25] were evaluated (cf. Fig. 4). The best agreement with proton NMR spectroscopy is obtained for bpy$_{\alpha}$ protons [−1.37 ppm (calcd), −1.29 ppm (exp.)]. The bpy$_{\beta}$ protons, due to the ring current effect of the additional aromatic moieties, should be still shielded [−0.24 ppm (calcd)] but are actually deshielded by about the same amount as in **2b** and **3**. The protons bpy$_{\gamma}$ to bpy$_{\delta}$ are deshielded up to ca. 0.1 ppm by the combined anisotropic/ring current effects and are similar as in **1** and **3** and are thus not characteristically influenced.

As a first resume, the anisotropic effects of nitrate anions in **2b**, **3**, and **5** (and additionally the ring current effect of the 4-methylpyridyl ligand in **5**) are only for the bpy$_{\alpha}$ protons in excellent agreement with the experiment; in case of bpy$_{\beta}$ to bpy$_{\delta}$ protons the corresponding effects are much smaller (±0.1 ppm or smaller) and are masked obviously by the coordination induced shifts of the Pd(II) ion.[41]

Table 1
^{1}H NMR chemical shifts δ/ppm of bipyridine (bpy) **1** and of various complexes **2**, **3**, and **5**[41]

No.	H^{α}	H^{δ}	H^{γ}	H^{β}	H_{arom}
1	9.22	7.99	8.49	8.92	
2a	9.67	8.35	8.89	9.11	
$\Delta\delta$[a]	+0.45	+0.36	+0.40	+0.19	
2b	8.81	8.36	8.99	9.13	
$\Delta\delta$[a]	−0.41 (−0.32)[b]	+0.37 (−0.06)	+0.50 (+0.01)	+0.21 (+0.03)	
3	9.35	8.50	9.06	9.26	
$\Delta\delta$	+0.13 (−0.02)	+0.51 (0.0)	+0.57 (−0.04)	+0.34(−0.09)	
4	—	—	—	—	8.95
5	7.93	8.26	9.03	9.31	9.59
$\Delta\delta$	−1.29 (−1.37)	+0.27 (−0.24)	+0.54 (+0.01)	+0.39 (+0.10)	+0.64

[a] $\Delta\delta$=chemical shift difference to noncomplexed ligand.
[b] In brackets are the calculated values.

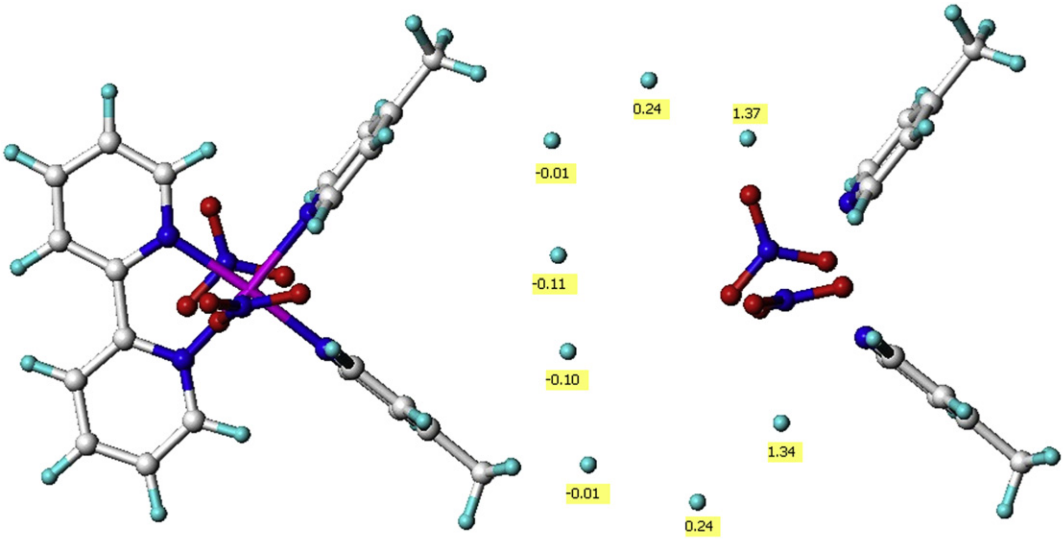


Figure 4. Structure of [*cis*-Pd(bpy)(4-methylpyridine)$_2$](NO$_3$)$_2$ **5** calculated at the [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] mixed level of theory (left) and anisotropic effects of both nitrate anions on the bipyridine protons H$^\alpha$–H$^\delta$ (right).

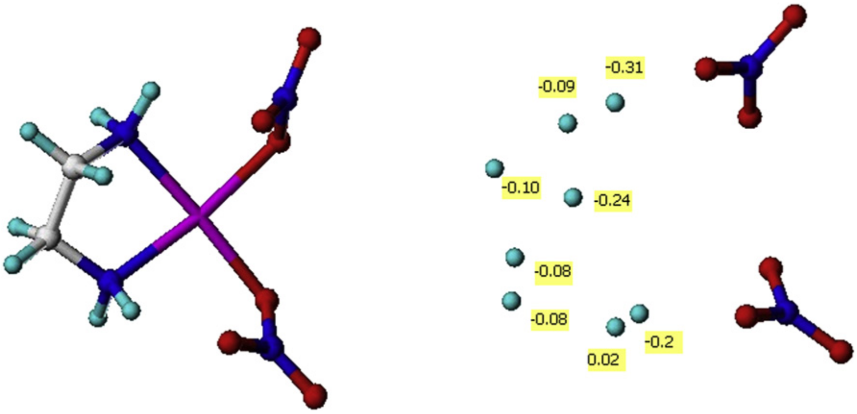


Figure 5. Structure of [*cis*-Pd(en)(NO$_3$)$_2$] **7b** calculated at the [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] mixed level of theory (left) and anisotropic effects of both nitrate anions on the ethylene diamine protons (right).

3.4. [*cis*-Pd(en)(NO$_3$)$_2$] 7b, [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

Next, the corresponding ethylene diamine (*en*) complexes have been studied by the same method. In **7b**, the anisotropic effect of nitrate anion on the ^{1}H chemical shift of the amino protons proved to be different from **2b**; actually, it is deshielding ($\Delta\delta$=+0.15 ppm) resulting from the position of these protons near to the plane of the nitrate anion (cf. Fig. 5). The orientations of the bound nitrate anions are different in **7b** compared with **2b** due to the smaller size of the *en* ligand and, in addition, intramolecular hydrogen bonding of nitrate anion oxygens and suitably positioned amino hydrogen atoms is possible. The existence of these H bonds was proved by a low temperature ^{1}H NMR study (showing a number of signals for the amino protons at −5 °C)[42] and the X-ray study of **7b** in the solid state.[42] The deshielding effect of the nitrate anions in the proton NMR spectrum of **7b** is much larger than theoretically calculated (cf. Table 2) and the intramolecular hydrogen bonding might be responsible for the larger deshielding of the amino protons in the ^{1}H NMR spectrum of **7b**. The anisotropic effect of nitrate anion is stronger in the mixed *bpy*/*en* complex **8** ($\Delta\delta$=+0.35 ppm), the direction in agreement with the experimental value (cf. Table 2); in addition to intramolecular hydrogen bonding (vide supra) deshielding from the ring current effect of the *bpy* moiety on the amino protons will participate in the overall lowest field position of the NH$_2$ protons in **8** (cf. Fig. 6 and Table 2).

With respect to the anisotropic effect of nitrate in **9** and **10** (and in combination with the ring current effect of 4-methylpyridinyl in **9**) no remarkable influences on the chemical shifts of the amino protons were found (cf. Table 2). In the structures obtained (cf. Fig. 7) the two anisotropic effects are less than ±0.1 ppm. Experimental NH$_2$ proton chemical shifts are less deshielded than in **7b** and **8** (and thereby in agreement with the calculations of both anisotropic effect of nitrate anion and ring current effect of 4-methylpyridyl) but lowfield shifted compared with the free *en* (**6**); thus, the lowfield position of the amino protons in the ^{1}H NMR spectra of **9** and **10** with respect to **6** is an interplay of Pd(II) coordination induced shifts and effect of hydrogen bonding of the

Table 2
^{1}H NMR chemical shifts δ/ppm of ethylene diamine NH$_2$ protons in **6**–**10**[41]

No.	δ	$\Delta\delta$ (NH$_2$), exp.	$\Delta\delta$ (NH$_2$), calcd
6	3.91	—	—
7a	—	+1.63	—
7b	—	+2.45	+0.15
8	—	+2.87	+0.35
9	—	+2.31	+0.06
10	—	+1.63	−0.07

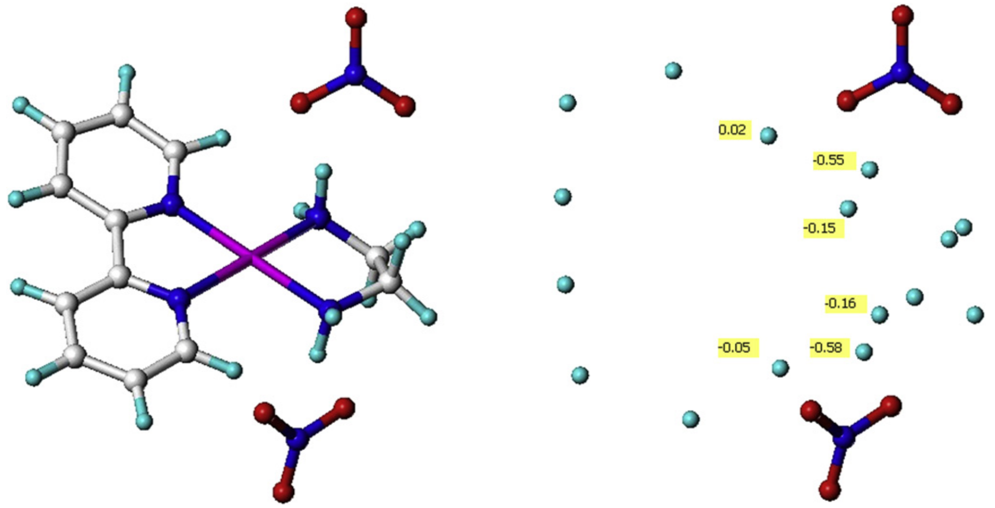


Figure 6. Structure of mixed [Pd(en)(bpy)](NO$_3$)$_2$ **8** calculated at the [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] mixed level of theory (left) and anisotropic effects of both nitrate anions on the ethylene diamine protons (right).

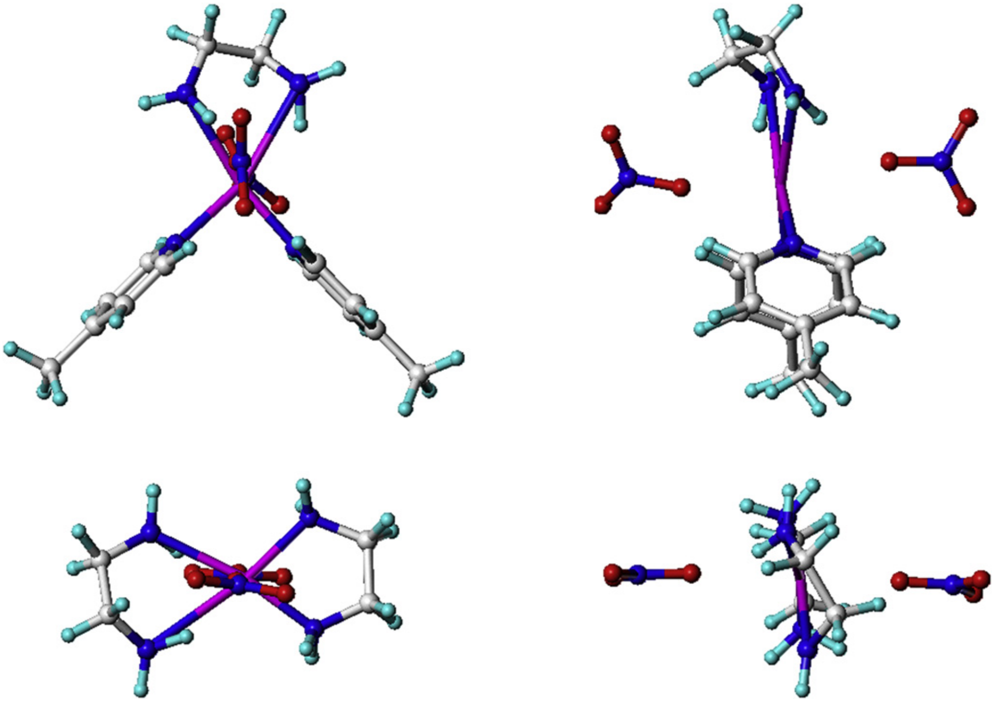


Figure 7. Structures of [*cis*-Pd(en)(4-methylpyridine)$_2$](NO$_3$)$_2$] **9** (above) and [Pd(en)$_2$](NO$_3$)$_2$ **10** (below) calculated at the [B3LYP/6-311G** (for C, H, O, N); B3LYP/3-21G** (for Pd)] mixed level of theory (left) and anisotropic effects of both nitrate anions on the ethylene diamine protons (right) mixed level of theory—orthographic view.

amino protons to nitrate anion oxygen atoms, but not of the anisotropic effect/ring current effects of nitrate anion and the 4-methylpyridyl aromatic moiety, respectively.

4. Conclusion

The anisotropic effect of the nitrate anion on proximal nuclei has been ab initio MO calculated employing the GIAO distortion method. In agreement with previous efforts,[38,30g,40] this effect is shielding above and below the plane of this planar molecule but deshielding in this plane (from nitrogen crossing the O–N–O bisector). This anisotropic effect (and the ring current effect of the 4-methylpyridyl aromatic moiety, calculated by the same method) was employed to manifest the different chemical shifts of bpy$_\alpha$ protons in the palladium complexes **2b**, **3**, and **5** and of the amino protons of the *en* complexes **7b** and **8**–**10**. The calculated chemical shift sequences (due to anisotropic effects of nitrate and 4-methylpyridyl, respectively) of both classes of protons are in agreement with experimental differences; however, in addition to the anisotropic effects, in **7b**–**10**, intramolecular hydrogen bonding N–H···O–N, as the dominating effect, must be taken into account. But, due to the theoretical quantification of the anisotropic effects, both influences on the chemical shifts of the amino protons can be separated.

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