Nitrogen-14 Nuclear Quadrupole Resonance Spectra in Palladium(II) Complexes of 1,10-Phenanthroline[1]

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Abstract: Nitrogen-14 NQR spectra have been measured for solid samples of 13 1,10-phenanthroline (phen) complexes of Pd(II) at 77 K, using the double resonance, level-crossing technique. The field gradient parameters for coordinated phen can be related to the effective occupancy of the nitrogen orbital in the bond to the metal. The model employed for coordinated nitrogen is based on the Townes–Dailey model. The same parameters employed in earlier work to account for the field gradient in coordinated pyridine account very well for coordinated phen data. The ^{14}N NQR data can be utilized to order the monodentate X ligands in (phen)PdX$_2$ or the bidentate ligand Y in (phen)PdY in terms of electron donation toward Pd(II). The order obtained is fumaronitrile > η-allyl > *N*-cyanocarbimato > $CN^- = I^- > SCN^- = NO_2^- > Br^-$ = *o*-phthalato > Cl^- = oxalato > $NO_3^- \sim$ phen. The position of phen at the end of the series is anomalous. The ^{14}N NQR spectra of other functional groups, including CN, SCN, NO_3, and NO_2, are also observed.

The recent development of double resonance techniques for the detection of ^{14}N pure nuclear quadrupole (NQR) spectra opens interesting new possibilities for application of this technique to the study of metal complexes containing nitrogen ligands. The method employed, involving adiabatic demagnetization in the laboratory frame, permits several types of double resonance experiments.[3-8] The particular technique involved in detection of ^{14}N resonances involves transfer of energy between ^1H and ^{14}N spin systems via level crossing (double resonance via level crossing, drlc). This technique has been applied successfully to the detection of ^{14}N resonances in glyoximato complexes of Pt, Pd, and Ni.[7] A marked change in the field gradient tensor at nitrogen from the parameters which characterize the free ligand is evident. More recently we have studied several compounds in which pyridine is coordinated to a variety of Lewis acids.[8] Application of a modification of the Townes–Dailey model[9,10] leads to a satisfying correlation between the field gradient tensor parameters and the extent of charge removal from the nitrogen lone pair orbital by the Lewis acid.

In the present contribution, we report the ^{14}N NQR spectra for 1,10-phenanthroline (phen) and complexes of this ligand with palladium(II), (phen)PdX$_2$, or (phen)PdY, in which X and Y represent monodentate and bidentate ligands, respectively. These complexes present examples of approximately square-planar geometry about the central metal. They provide an opportunity to observe the effect of ligands trans to the coordinated nitrogen on the effective charge of the metal, as experienced by phenanthroline.

Experimental Section

Samples. Dichloro(1,10-phenanthroline)palladium(II), Pd(phen)Cl$_2$, was prepared by an adaptation of the method of Livingstone.[11] The K_2PdCl_4 (5.00 g) was dissolved in dilute hydrochloric acid (3 L of water + 10 mL of concentrated hydrochloric acid) before being added to the phenanthroline (3.20 g) solution. The golden yellow product was heated with stirring at 80 °C for 24 h before being isolated, yield 5.4 g (98%). Anal. Calcd for Pd(phen)Cl$_2$: N, 7.82; Cl, 19.82. Found: N, 8.04; Cl, 19.64.

Dibromo(1,10-phenanthroline)palladium(II), Pd(phen)Br$_2$, was prepared by the method of Livingstone[11] with the modification of adding hydrobromic acid (10 drops) and KBr (10 g) to the K_2PdBr_4 solution, yield 1.09 g (98%). Anal. Calcd for Pd(phen)Br$_2$: Pd, 35.8. Found: Pd, 36.1.

Diiodo(1,10-phenanthroline)palladium(II), Pd(phen)I$_2$, was prepared by the method of Livingstone[11] except that K_2PdI_4 was prepared from K_2PdCl_4 (4.1 g) dissolved in water (2 L) by adding HI (1 mL) and KI (300 g) and allowing the solution to stand overnight. Phenanthroline (2.50 g) dissolved in water (2 L) was then added to the solution, yield 6.7 g (98%). Anal. Calcd for Pd(phen)I$_2$: C, 26.7; H, 1.5; N, 5.2; I, 47.6. Found: C, 26.6; H, 1.5; N, 5.0; I, 47.4.

Dithiocyanato(1,10-phenanthroline)palladium(II), Pd(phen)(SCN)$_2$, was prepared by an adaptation of the method of Livingstone[11] using 1.00 g of K_2PdCl_4 and 1.60 g of KSCN, and filtering the $K_2Pd(SCN)_4$ solution prior to use. Anal. Calcd for Pd(phen)(SCN)$_2$: Pd, 26.3. Found: Pd, 26.1.

The next eight compounds were prepared from a solution of water-soluble dinitrato(1,10-phenanthroline)palladium(II) presumably containing the ion Pd(phen)$(H_2O)_2^{2+}$ in solution. This lemon-yellow solution was prepared by grinding Pd(phen)Cl$_2$ (4.00 g, 11.2 mmol) in a mortar with $AgNO_3$ (3.00 g, 22.4 mmol) and a small amount of water (5 mL) until a homogeneous paste was obtained. Water (100 mL) was added, and the mixture was allowed to stand in the dark. After 48 h the mixture was added to 3.5 L of water and heated to 80 °C with stirring. It was filtered to remove the bulk of the silver chloride and filtered twice more through Celite to give a clear solution containing approximately 2.8 mmol of Pd(phen)$(H_2O)_2^{2+}$ per liter.

Dinitrato(1,10-phenanthroline)palladium(II), Pd(phen)$(NO_3)_2$. Two liters of concentrated nitric acid was added to 4 L of the Pd(phen)$(H_2O)_2^{2+}$ solution. After being stirred overnight the resulting yellow precipitate was filtered out, washed with acetone, and dried under vacuum, yield 4.17 g (91%) of a light yellow powder. Anal. Calcd for Pd(phen)$(NO_3)_2$: Pd, 25.9; C, 35.12; H, 1.95. Found: Pd, 25.9; C, 35.25; H, 2.04.

***N*-Cyanocarbimato(1,10-phenanthroline)palladium(II), Pd(phen)$S_2C_2N_2$.** Dipotassium *N*-cyanocarbimate, $K_2S_2C_2N_2$[12] (3.00 g, 15.5 mmol) was dissolved in water (100 mL) and the solution added with stirring to 4 L (11.2 mmol) of the Pd(phen)$(H_2O)_2^{2+}$ solution. Stirring was continued for 3 h, and the yellow precipitate was filtered out, reslurried in water (2 L), and allowed to stand overnight. The precipitate was filtered out, washed with water and acetone until the acetone wash was colorless, and dried under vacuum, yield 3.39 g (75%) of a yellow powder. Anal. Calcd for Pd(phen)$S_2C_2N_2$: Pd, 26.4; C, 41.79; H, 1.99. Found: Pd, 26.7; C, 41.87; H, 2.06.

Dicyano(1,10-phenanthroline)palladium(II), Pd(phen)$(CN)_2$. NaCN (0.60 g) in water (200 mL) was added to 2 L of the Pd(phen)$(H_2O)_2^{2+}$ solution with stirring. The white precipitate was filtered out, washed with water, and dried under vacuum. Anal. Calcd for Pd(phen)$(CN)_2$: Pd, 31.4. Found: Pd, 31.5.

Oxalato(1,10-phenanthroline)palladium(II), Pd(phen)C_2O_4. Potassium oxalate monohydrate (3.00 g) in water (100 mL) was added to 4 L of the Pd(phen)$(H_2O)_2^{2+}$ solution in the dark. After 3 h of stirring, the precipitate was filtered out, washed with water and acetone, and dried under vacuum, all in the dark; yield 3.63 g (87%) of very pale yellow plates. This compound had been prepared previously by a different method.[11] Anal. Calcd for Pd(phen)C_2O_4: Pd, 28.3; C, 44.92; H, 2.14. Found: Pd, 28.6; C, 44.74; H, 2.24.

Table I. ^{14}N NQR Parameters for *o*-Phenanthroline in Palladium(II) Complexes

Compd	$\nu_+{}^a$	$\nu_-{}^a$	$\nu_0{}^a$	e^2Qq/h^a	η
phen	3984	3148	836	4755	0.352
	3854	3096	758	4633	0.327
1. Pd(phen^b)FMN	2497	2170	328	3111	0.211
2. [Pd(phen)(η-allyl)]Cl	2098	1916	182	2676	0.136
3. Pd(phen)$S_2C{=}NCN$	1969	1803		2515	0.132
	1878	1754		2421	0.102
4. Pd(phen)$(CN)_2$	1744	1651		2263	0.082
5. Pd(phen)I_2	1715	1620		2224	0.086
	1573	1573		2097	0.00
6. Pd(phen)$(SCN)_2$	1585	1585		2113	0.0
7. Pd(phen)$(NO_2)_2$	1585	1546		2087	0.037
8. Pd(phen)Br_2	1540	1460		2000	0.080
9. Pd(phen)(*o*-phthalate)	1535	1456		1994	0.079
10. Pd(phen)Cl_2	1500	1422		1948	0.080
11. Pd(phen)C_2O_4	1475	1388		1909	0.091
12. Pd(phen)$(NO_3)_2$	1334	1181	153	1677	0.182
	1280			?	?
13. Pd$(phen)_2(ClO_4)_2$	1329	1169	160	1665	0.092
	1266	1031	235	1531	0.307

^{a} kHz. ^{b} FMN = *trans*-1,2-dicyanoethylene, fumaronitrile.

Table II. ^{14}N NQR Parameters in Palladium(II) Complexes

Compd	Functional group	$\nu_+{}^a$	$\nu_-{}^a$	$\nu_0{}^a$	e^2Qq/h^a	ν
Pd(phen)FMN	CN	2942	2418	524	3573	0.293
		2913	2418	494	3555	0.278
		2497	2169	328	3111	0.211
Pd(phen)$(CN)_2$	CN	2910	2864		3849	0.024
Pd(phen)$S_2C{=}NCN$	CN	2749			3665	0.00
	=N	2121			4240 (?)	1 (?)
Pd(phen)$(SCN)_2$	SCN	2770		562	3319	0.34
Pd(phen)$(NO_3)_2$	NO_3	548	413	135	641	0.421
Pd(phen)$(NO_2)_2$	NO_2	2680		580	3190	0.364

^{a} kHz.

Phthalato(1,10-phenanthroline)palladium(II), Pd(phen)$C_4H_4O_4$. Potassium acid phthalate (1.25 g) dissolved in water (100 mL) was added to 2 L of Pd(phen)$(H_2O)_2{}^{2+}$ solution and stirred for 2 h in the dark. The pale yellow precipitate was filtered out, washed with water and acetone, and dried under vacuum, all in the dark; yield 2.35 g (93%). Anal. Calcd for Pd(phen)$C_8H_4O_4$: Pd, 23.6; C, 53.33; H, 2.67. Found: Pd, 23.5; C, 53.06; H, 2.88

Dinitro(1,10-phenanthroline)palladium(II), Pd(phen)$(NO_2)_2$. Sodium nitrite (1.00 g) in water (50 mL) was added to 2 L of the Pd(phen)$(H_2O)_2{}^{2+}$ solution with stirring for 3 h. A yellow suspension resulted which could not be filtered and would not settle. It was heated to boiling and cooled to room temperature giving a yellow precipitate which was filtered out, washed with water and acetone, and dried under vacuum, yield 1.20 g (57%) of fine yellow crystals. This compound had been prepared previously by a different method.[11] Anal. Calcd for Pd(phen)$(NO_2)_2$: Pd, 28.0; C, 38.10; H, 2.12. Found: Pd, 27.9; C, 38.38; H, 2.36.

Allyl(1,10-phenanthroline)palladium(II) chloride, η-C_3H_5Pd(phen)Cl. $[\eta\text{-}C_3H_5PdCl]_2$[13] (1.95 g, 5.3 mmol) was dissolved in chloroform (50 mL) and added to a solution of anhydrous phenanthroline (2.07 g, 11.5 mmol) in chloroform (50 mL) with stirring. The resulting white precipitate was collected by filtration, recrystallized from methanol, washed with chloroform, and dried under vacuum at 65 °C for 24 h, yield 2.70 g (70%) of an off-white powder. Anal. Calcd for η-C_3H_5Pd(phen)Cl: Pd, 29.1. Found: Pd, 28.9.

Bis(1,10-phenanthroline)palladium(II) perchlorate, [Pd$(phen)_2$]$(ClO_4)_2$, was prepared as in the literature.[11]

Fumaronitrile(1,10-phenanthroline)palladium(0), Pd(phen)$C_4H_2N_2$, was prepared as in the literature.[14] It proved to be impure and was recrystallized twice by dissolving in boiling chlorobenzene, filtering, and cooling slowly to 0 °C.

NQR Measurements. The ^{14}N NQR measurements were carried out as previously described.[6-8] Sample temperature in all cases was 77 K. Several complexes that appeared to be pure neveretheless exhibited proton T_1 times too short to permit carrying out the experiment. These compounds included the malonato, sulfito, and acetato.

Results and Discussion

Table I lists the observed ^{14}N transition frequencies in 1,10-phenanthroline (phen) and several of its complexes with palladium. In several of the compounds, in which the ligands trans to the phen contain nitrogen, the ^{14}N transitions due to these nitrogens were observed as well. These are listed in Table II. In all instances all of the transition frequencies listed were actually observed. The precision with which frequencies are determined is in the range of 2-3 kHz.

We are not aware of crystal structure determinations for any of the specific substances reported on herein. The crystal structure for 2,9-dimethyl-1,10-phenanthroline Pd$(NO_2)_2$[15] is the only example of a palladium(II) complex of 1,10-phenanthroline. However, in this case there is presumably some steric crowding due to methyl groups in the 2 and 9 positions. This may cause some slight increase in the Pd-phenanthroline nitrogen bond distances, but such increase should be small. The Zn-N distances in dichloro(2,9-dimethyl-1,10-phenanthroline)zinc(II) are 2.06 and 2.07 Å,[16] as compared with corresponding distances of 2.05 and 2.07 Å in dichloro(1,10-phenanthroline)zinc(II).[17] In this comparison, involving a tetrahedral geometry around the metal, no lengthening resulting from the presence of the 2,9-methyl groups is apparent.

In the palladium structure the N-Pd-N bond angle is observed to be 83°. In light of the limited structural evidences, we assume that all of the complexes studied herein possess an essentially planar four-coordinate geometry, with the central

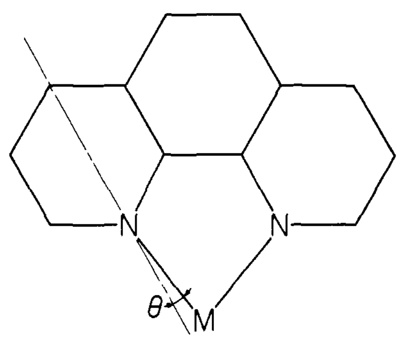


Figure 1. Geometry of 1,10-phenanthroline-metal interaction.

Pd located approximately equidistant from the two nitrogens of the phenanthroline ligand, and with an N-Pd-N internal bond angle of about 83°, as illustrated in Figure 1.

Since phenanthroline closely resembles pyridine in chemical and structural characteristics, it is reasonable to expect that the charge distribution about the nitrogens of phenanthroline should correspond closely to that in pyridine. In accordance with this, the averaged ^{14}N field gradient parameters in 1,10-phenanthroline (e^2Qq/h = 4.75 MHz, η = 0.35), correspond closely to the averaged values for pyridine (e^2Qq/h = 4.58 MHz, η = 0.396). Given this similarity, it is also reasonable to assume that the formation of a Lewis acid-base adduct should result in changes in the field gradient tensor at the phenanthroline nitrogen atoms similar to the changes which occur upon adduct formation at pyridine. We have recently shown[8] that the changes in the ^{14}N field gradient tensor in pyridine upon interaction with a Lewis acid can be well accounted for in terms of a modified Townes-Dailey model. In the model for coordinated nitrogen the effective occupancy of the donor orbital (formerly the lone pair orbital) is assumed to decrease upon interaction with the Lewis acid. Correspondingly, through inductive effects and polarization of the π charge distribution, the populations of the nitrogen sp^2 hybrid orbitals directed toward carbon, and the p_π orbital centered on nitrogen increase upon adduct formation.

In phenanthroline, the lower symmetry of the ligand itself, and placement of the Lewis acid away from the pseudo-twofold axis through the nitrogen, complicate interpretation of the NQR data for the coordinated ligand. However, if it is assumed that the field gradient tensor at each nitrogen in 1,10-phenanthroline has its major axis along the axis which passes through nitrogen and the carbon atom located opposite it in the six-membered ring, then the model employed to interpret the pyridine ^{14}N NQR results should be applicable as well to phenanthroline. In metal complexes of phenanthroline the metal-nitrogen axis is displaced from the pseudo-twofold axis just mentioned by about 8-10° (Figure 1). This displacement should result in a loss in symmetry of charge distribution around nitrogen, and may affect both e^2Qq/h and η. However, since the mixing of contributions of the p orbitals in the electron density distribution varies as $\sin^2\theta$ and $\cos^2\theta$, where θ is the angle between the N-M bond axis and the pseudo-twofold axis, a displacement of about 10° from the axis results in a mixing of p orbital contributions to the extent of only about 3%.

The results of a series of molecular orbital calculations support this conclusion.[18] A molecular orbital calculation and Mulliken population analysis for pyridinium ion was carried out using the parameter-free Fenske-Hall approximate MO method.[19] The proton was displaced by an angle θ from the twofold axis of the pyridine, in the plane of the ring, maintaining constant H-N distance. The calculation was repeated at 1° intervals of θ in the range 0-10°. The calculated quadrupole coupling constant, e^2Qq/h, varied in this range by only 1.6%. The calculated asymmetry parameter η is varied to a somewhat larger extent, from 0.45 to 0.60. These and related calculations, to be reported elsewhere,[18] support the idea that in-plane angular displacements of up to about 10° of the Lewis acid from the axis along which the lone pair orbital is directed in the free base do not substantially alter the nitrogen field gradient parameters.

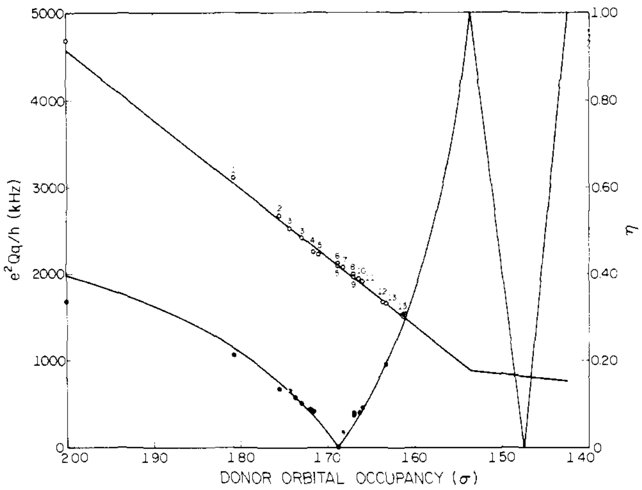


Figure 2. Quadrupole coupling constant, e^2Qq/h (kHz), open circles, and asymmetry parameter η, closed circles, for 1,10-phenanthroline complexes of Pd(II), as a function of donor orbital occupancy. The lines represent the variations in e^2Qq/h and η with donor orbital occupancy for coordinated pyridine. The numbers refer to the numbering of compounds given in Table I.

Accordingly, it seems reasonable to suppose that the field gradient model developed for pyridine might be applicable to phenanthroline as well. The two lines in Figure 2 show the variations in e^2Qq/h and η vs. donor orbital occupancy, σ, based on the model developed for pyridine complexes, and assuming, as before, that e^2Qq_0/h = 9.0 MHz.[8] The data for phenanthroline and its palladium(II) complexes are shown on this graph. For each compound the open circle represents e^2Qq/h, and, on a vertical line with it, the closed circle represents η. (Note that e^2Qq/h and η accidentally fall at the same point on the graph for one of the ^{14}N signals of $[Pd(phen)_2](ClO_4)_2$, point 13.)

The value of e^2Qq/h for phenanthroline itself (the average of the two observed signals is used) is slightly larger than the average value for pyridine. On the other hand, the η value is somewhat smaller. In fitting the NQR parameters for each compound to the two pyridine curves, the value of σ was chosen to give the best fit for both e^2Qq/h and η. However, since the e^2Qq/h value for free phenanthroline is a better fit to the pyridine value than η for free phenanthroline, a greater emphasis was placed on fitting the e^2Qq/h value. Secondly, since e^2Qq/h for free phenanthroline lies above the value for free pyridine, the e^2Qq/h values for the phenanthroline complexes were placed in most cases just above the pyridine line. As is evident from Figure 2, the fits of both e^2Qq/h and η for each compound to the pyridine lines are remarkably good.

Table III lists the estimated nitrogen donor orbital occupancy for the phenanthroline complexes, based on the fits of e^2Qq/h and η to the working curves, as illustrated in Figure 2. There are several interesting aspects to these data. The donor orbital occupancy is largest in the FMN complex, in which the phenanthroline is trans to a *trans*-1,2-dicyanoethylene ligand. This complex may be viewed as an olefin complex of palladium(0), or as a metallocycle, formally of palladium(II).[20,21] The NQR results show that the metal atom in this complex is a considerably weaker Lewis acid toward phenanthroline than in complexes such as the dihalo or dicyano, in which the palladium is more obviously in the +2 oxidation state.

Table III. Estimated Donor Occupancies in 1,10-Phenanthroline Complexes

Compd	σ	Compd	σ
phen	2.00	Pd(phen)(NO_2)$_2$	1.68
Pd(phen)FMN	1.81	Pd(phen)Br_2	1.67
[Pd(phen)η-allyl]Cl	1.76	Pd(phen)(o-phthalato)	1.67
Pd(phen)$S_2C{=}NCN$	1.75, 1.74	Pd(phen)Cl_2	1.66
Pd(phen)(CN)$_2$	1.72	Pd(phen)C_2O_4	1.66
Pd(phen)I_2	1.72, 1.69	Pd(phen)(NO_3)$_2$	1.64
Pd(phen)(SCN)$_2$	1.69	[Pd(phen)$_2$]ClO_4	1.63, 1.61

The strongly donor characteristic of the trihaptoallyl group is evident in the relatively large value for σ in the [Pd(phen)-(η-allyl)]$^+$ complex, as compared with values for complexes involving two monoanionic monodentate ligands, or a single dianionic bidentate ligand. It is noteworthy that the palladium also exhibits a relatively low apparent effective charge in the complexes involving bonding of sulfur to the metal, such as the S_2CNCN complex.

The donor orbital occupancy in phenanthroline PdX_2 complexes is significantly lower than in the corresponding bis(pyridine)ZnX_2 complexes,[8] indicating that the palladium is a substantially stronger Lewis acid site. The metal-nitrogen distances are not greatly different in the two series; for example, the Zn-N distances in $Zn(NO_3)_2(py)_2$ are 2.016 and 2.048 Å, respectively.[17] Thus, the Zn-N distances average about 0.06 Å shorter than in the phenanthroline-palladium complex. The fact that the donor orbital occupancy of the nitrogens is lower in the palladium complexes, despite the slightly longer metal-nitrogen distances, suggests that the covalency of the metal-nitrogen bond is higher in the palladium compounds, consistent with the higher electronegativity expected for Pd(II) as compared with Zn(II).[22]

Strong interaction of a given ligand with Pd(II), leading to charge transfer to the metal, should result in a lower effective nuclear charge at the metal, and a resulting larger value for σ. The order of σ values for the complexes is not in accord with the usual spectrochemical series order.[23] In particular, the halide ion order is inverted, the complexes containing dianionic ligands involving coordinated oxygen have comparatively low σ values, and the σ values for $[Pd(phen)_2]^{2+}$ lie lowest in the series. It should be kept in mind, however, that the effective charge on the central metal, which is the quantity reflected in the ^{14}N NQR parameters of the phenanthroline, is reduced more by the covalent components of the interaction between Pd and the trans ligand(s) than by the electrostatic interaction. The covalent component is likely to be more important for the softer, or more polarizable, bases such as 1,2-*trans*-dicyanoethylene, allyl anion, or a sulfur ligand.

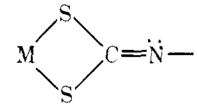
The same considerations help to explain the observation that the one neutral ligand studied, phen itself, is apparently less effective in reducing the effective charge on the metal than *all* of the anionic ligands studied. (Simple point charge calculations demonstrate conclusively that the field gradient difference between neutral and anionic ligands trans to the nitrogen atoms cannot be due to contributions from point charges located at the anionic ligands.)

^{14}N Spectra of Other Ligands. The power of the double resonance NQR technique for detection of ^{14}N signals is evidenced dramatically in the results obtained on complexes containing nitrogens other than those in the phenanthroline ligand. Many of the transitions observed are so low in frequency as to be essentially unobservable by any other technique. The ^{14}N NQR data pertaining to other than the phenanthroline signals in the complexes studied are listed in Table II.

The ^{14}N field gradient parameters in Pd(phen)(NO_3)$_2$ complex are similar to those observed in the pyridinium nitrate complex, $H(py)^+NO_3^-$.[8] In the phenanthroline complex the nitrate groups are presumed to be coordinated to the divalent metal ion as monodentate ligands; in the pyridinium salt the nitrate group appears to be hydrogen bonded through one of the NO bonds to an adjacent Hpy^+ ion.[24]

The ^{14}N NQR parameters of the thiocyanato nitrogens in Pd(phen)(SCN)$_2$ strongly suggest that the SCN^- ligand is S-coordinated. The observed value of e^2Qq/h is characteristic of a terminal C≡N type unit.[8,10,25] The substantial departure of η from zero in S-coordinated SCN^- is to be expected in light of the values observed, $\eta \sim 0.45$–0.50, for ^{14}N in organic thiocyanates and S-bonded complexes.[10,25] In both cases, the SCN ligand is nonlinear. The values for the ^{14}N field gradient parameters in Pd(phen)(SCN)$_2$, in which S-coordination seems assured, contrast greatly with those observed in $Zn(NCS)_2(py)_2$, in which N-coordination apparently occurs.[8,26]

The nitrogen resonances characteristic of $S_2C{=}NCN$ ligand indicate the presence of a C≡N grouping. In addition, there is a lower frequency resonance resonance which may be ascribed to the central nitrogen of this ligand. The predominant Lewis structure for this coordinated ligand is



Since the structure of the complex containing the $S_2C{=}NCN$ ligand is not available, the geometry about the central nitrogen atom is not known. However, it seems unlikely that the bonds at this atom would be linear. The observation of only one signal that can reasonably be assigned to this nitrogen, thus suggesting $\eta \sim 0$, is not readily rationalized. In oximes, in which the bonding is roughly similar, field gradients tend to be quite large, in the vicinity of 4800–5000 kHz, with η values in the range of 0.5–0.6.[7] As another comparison, in azoxybenzene, containing an ON=N- bonding arrangement, e^2Qq/h and η for the imine nitrogen are 4430 kHz and 0.469, respectively.[27] It seems possible that η may be near 1 for this nitrogen, and that ν_+ occurs around 4200 kHz. This would lead to e^2Qq of around 4200 kHz, in reasonable agreement with results on related compounds. However, a thorough search has failed to reveal a signal in the region of 4200 kHz.

The ^{14}N field gradient parameters characteristic of the $C{\equiv}N^-$ ligand in the biscyano complex are typical of a C-coordinated terminal cyanide grouping.[28] Similarly, the ^{14}N field gradient parameters characteristic of the FMN ligand are not unexpected for an organic type cyanide. The rather large departure of η from zero may be associated with distortion of the ligand from planarity upon interaction with palladium.

The values reported here are the first of which we are aware for a coordinated nitro group. We have recently measured the ^{14}N parameters for nitro groups in a series of nitrobenzenes.[29] The values for e^2Qq/h and η are in ranges from 1250 to 1500 kHz and 0.29–0.40, respectively. In the NO_2^- ion, e^2Qq and η are about 5600 kHz and 0.36, respectively.[30] The ^{14}N EFG parameters for NO_2^- bound to Pd(II) are intermediate. The major source of the variation probably arises in the increased occupancy of the nitrogen orbital involved in bonding to the metal as compared with carbon.

Summary

The present work shows that a simple semiempirical model based on the Townes–Dailey model can be adapted to account for changes in the field gradient at ^{14}N in phenanthroline complexes of Pd(II). There is little reason to doubt that the model should be applicable to phenanthroline complexes with other metals as well. The ^{14}N NQR data provide a measure of the effective nuclear charge of the metal, and thus provide information regarding interaction of the metal with the other ligands to which it is coordinated. The ^{14}N NQR signals due to other ligands in the complexes reveal a broad range of resonance frequencies. In many cases the ^{14}N signals are strongly indicative of structural environment, as in the distinction between S- and N-bonded thiocyanate, or the presence of a coordinated nitro group.

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References and Notes

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Carbon-13 Chemical Shifts as a Measure of π-Back-Bonding in Pentacyanoferrate(II) and -cobaltate(III) Complexes of Substituted Pyridines

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Abstract: The degree of π-back-bonding in the isoelectronic pentacyanoferrate(II) and -cobaltate(III) complexes of unsaturated nitrogen heterocyclic ligands has been investigated using ^{13}C nuclear magnetic resonance. The chemical shift changes (with respect to free ligand) indicate that the π-back-bonding observed in the Fe(II) analogues is not prominent in the Co(III) complexes. The degree of π-back-bonding into remote rings in the Fe(II) complexes of the heterocyclic ligands is dependent on the ligand conformation. When the remote ring is coplanar with the bound ring (isoquinoline), π-back-bonding into the remote ring is observed. No π-back-bonding is observed into the remote ring when coplanarity is not a constraint of the ligand (4,4′-bipyridine). The best measures of the magnitude of π-back-bonding in the pentacyanoferrate(II) complexes appear to be the change in γ-carbon shift in the heterocycle upon coordination and the relative differences in the cis and trans ^{13}CN resonances as the heterocycle is varied. In general, additivity of carbon-13 shifts through the binding of similar ligands to $(CN)_5Fe^{II}$ and CH_3^+ is observed.

Introduction

The importance of substituent effects on the energy of the charge transfer to ligand (CTTL) bands for a series of pentaammineruthenium(II) species was first demonstrated by Ford et al.[1] A variety of physical methods, including ^1H NMR,[2,3] Mössbauer spectroscopy,[4] and ^{13}C NMR,[5] have been used to study the extent of π-back-bonding from the Ru(II) metal center into unsaturated ligands. Toma and Malin[6] have shown that pentacyanoferrate(II) complexes with unsaturated, nitrogen-coordinating, heterocyclic bases follow the same trend in charge transfer band maxima vs. the nature of the sixth ligand as do the analogous pentaammineruthenium(II) complexes. The presence and magnitude of the π-back-bonding interaction in the pentacyanoferrate(II) system has been studied by infrared,[7] electronic,[6,7] Mössbauer,[7] and NMR[6,8] spectroscopy.

The ^{13}C and ^1H NMR data of Malin and co-workers[8] suggest a definite correlation between the chemical shifts of the carbon and proton resonances of a few nitrogen-bound

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