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Spectroscopic Studies of Perpendicular Nitrile-Metal Interactions

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Metal complexes of the ligand 8-cyanoquinoline of the forms $[M(8\text{-cyanoquinoline})_2X_2]$ ($M = \text{Pd(II), Pt(II), Cu(II)}$; $X^- = \text{Cl}^-, \text{Br}^-$) and $[M(8\text{-cyanoquinoline})_2X]$ ($M = \text{Ag(I)}$, $X^- = \text{NO}_3^-$) have been prepared. Upon coordination, the 8-cyanoquinoline shows small shifts to lower energy in the nitrile stretching frequency which are attributed to perpendicular nitrile-metal interactions. The effects on the metal orbitals of the perpendicular interactions are studied using uv-visible and ESR spectroscopy. Red shifts in the electronic absorption spectra and increases in the g_{\parallel} values are found in the 8-cyanoquinoline complexes in comparison with the corresponding quinoline complexes. A molecular orbital description of the perpendicular nitrile-metal interactions is developed.

Introduction

Nitriles generally utilize the lone pair of electrons on the nitrogen to form linear $M-N\equiv C-R$ bonds in transition metal coordination complexes. However, a small number of perpendicular nitrile-metal interactions have recently been reported²⁻⁸ (and in part questioned).^{9,10} Perpendicular nitrile-metal interactions shift the nitrile stretching frequency to lower energy in contrast to linear interactions which generally result in a shift to higher energy.¹¹ The reported compounds include *o*-cyanodiphenylphosphine-manganese(I) and -rhenium(I) complexes,⁸ cyanamide-nickel(0) complexes,² dinitrile-manganese(I) complexes,^{3,4} and aminoacetonitrile complexes of group 4 elements⁶ showing shifts to lower energy in the nitrile stretching frequency of about 200, 200, 190, and 70 cm^{-1} , respectively. A platinum(II) complex believed to involve perpendicularly coordinated acetonitrile was reported¹² but was later shown to have an amidine linkage to the metal.¹³ In most cases, spectroscopic studies of the perpendicular interaction have been restricted to ir or Raman measurements of the nitrile stretching frequency shifts.

In this study, we report the syntheses and spectroscopic studies of perpendicular nitrile-metal interactions in "classical" coordination complexes of Pd(II), Pt(II), Cu(II), and Ag(I) with 8-cyanoquinoline (Figure 1). The geometrical properties of the rigid ligand 8-cyanoquinoline are used to position the nitrile group perpendicular to a metal coordinated to the ring nitrogen (Figure 1). This ligand allows the perpendicular nitrile-metal interaction to be studied in complexes where a nitrile is ordinarily linearly coordinated.

Experimental Section

Materials. 8-Cyanoquinoline. The ligand was prepared using a previously reported sealed-tube reaction¹⁴ with the following modifications. After the reaction mixture from the sealed tube was extracted with benzene-ether-aqueous ammonium hydroxide, all volatile liquids in the organic layer were removed on a rotoevaporator. The pyridine was removed at room temperature under vacuum using a cold trap to collect the vaporized solvent. The remaining liquid was stirred with hexane resulting in formation of a solid which was collected and redissolved in ether. The crude product was precipitated from the ether solution with the addition of hexane, and the final product was recrystallized from ether-hexane: mp 81.5-82.5 °C;¹⁵ ir peaks (in cm^{-1}) 1609 (m), 1592 (s), 1569 (m), 1491 (s), 1466 (w), 1416 (w), 1383 (s);¹⁶ ¹³C NMR shifts τ -151.97, -136.02, -135.02, -132.42, -125.44, -122.35.¹⁷ Anal. Calcd for $\text{C}_{10}\text{H}_6\text{N}_2$: C, 77.90; H, 3.89. Found: C, 77.79; H, 4.08.

8-Cyanoquinoline Hydrochloride. The protonated ligand salt was

prepared by dissolving a 1:1 molar ratio of 8-cyanoquinoline and hydrochloric acid in absolute methanol with stirring. The product was slowly precipitated as a white powder by adding a large excess of ether. The compound was collected, washed, and dried in vacuo.

The ligands quinoline and 3-cyanopyridine were obtained from Matheson Coleman and Bell Chemical Co. and Aldrich Chemical Co., respectively. They were used without further purification.

Dichlorobis(8-cyanoquinoline)palladium(II). Dichlorobis(benzonitrile)palladium(II)¹⁸ was dissolved in benzene and the ligand was added in excess as a benzene solution. Upon addition of the ligand, the red solution of the starting material immediately turned yellow and produced a yellow precipitate. After refluxing for 1 h, the solvent was decanted and the remaining yellow precipitate was suspended in a chloroform solution of the ligand. The mixture was again refluxed for 1 h before the final product was collected, washed, and dried in vacuo. Anal. Calcd for $\text{Pd}(\text{C}_{10}\text{H}_6\text{N}_2)_2\text{Cl}_2$: C, 49.45; H, 2.47. Found: C, 49.36; H, 2.62.

Dichlorobis(quinoline)palladium(II). This complex was prepared in a manner analogous to that of the 8-cyanoquinoline complex.

Dichlorobis(3-cyanopyridine)palladium(II). Dichlorobis(benzonitrile)palladium(II)¹⁸ was dissolved in benzene and the ligand was added dropwise in excess as a benzene solution. Upon addition of the ligand, the red solution of the starting material turned yellow and produced a yellow precipitate. The precipitate was collected, washed with benzene, and dried in vacuo. Anal. Calcd for $\text{Pd}(\text{C}_6\text{H}_8\text{N}_4)_2\text{Cl}_2$: C, 37.37; H, 2.10. Found: C, 37.57; H, 2.67.

Dichlorobis(8-cyanoquinoline)platinum(II). A solution of the ligand was prepared by dissolving 0.2 g of 8-cyanoquinoline in 2 ml of ethanol and diluting with water. A 2:1 molar excess of the ligand in solution was added to a hot solution of potassium tetrachloroplatinate in water. With stirring, a yellow precipitate slowly formed which was collected, washed, and dried in vacuo. Anal. Calcd for $\text{Pt}(\text{C}_{10}\text{H}_6\text{N}_2)_2\text{Cl}_2$: C, 41.82; H, 2.11. Found: C, 42.01; H, 2.49.

Dichlorobis(quinoline)platinum(II). This complex was prepared by heating dichlorodiammineplatinum(II)¹⁹ in quinoline. The dichlorodiammine complex gradually dissolved forming a red-orange solution from which a light yellow precipitate was formed. The product was collected, washed, and dried in vacuo.

Dichlorobis(8-cyanoquinoline)copper(II). Hydrated copper(II) chloride was dissolved in triethyl orthoformate to remove the water of hydration. The metal solution was added to a 2:1 excess of the ligand dissolved in triethyl orthoformate. Upon heating, a gray-green precipitate gradually formed which was collected, washed, and dried in vacuo. Anal. Calcd for $\text{Cu}(\text{C}_{10}\text{H}_6\text{N}_2)_2\text{Cl}_2$: C, 54.24; H, 2.73. Found: C, 54.26; H, 2.93.

Dichlorobis(quinoline)copper(II). This complex was prepared in a manner analogous to that of the 8-cyanoquinoline complex.

Bis(8-cyanoquinoline)silver Nitrate. A solution of the ligand was prepared by dissolving 0.2 g of 8-cyanoquinoline in 2 ml of ethanol and diluting with water. An aqueous solution of silver nitrate was

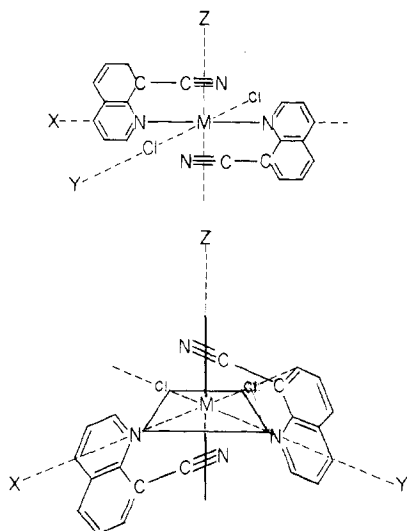


Figure 1. Proposed structures of *cis*- and *trans*-bis(8-cyanoquinoline)metal complexes.

Table I. Nitrile Stretching Frequencies and Shifts

Compd	$\nu_{\text{C}\equiv\text{N}}$, cm^{-1}	Shift rel to free ligand, cm^{-1}
8-Cyanoquinoline	2227 \pm 0.5	
8-Cyanoquinoline·HCl	2233 \pm 0.5	+6 \pm 1
Ag(8-cyanoquinoline) ₂ NO ₃	2219 \pm 0.5	-8 \pm 1
Pd(8-cyanoquinoline) ₂ Cl ₂	2221 \pm 0.5	-6 \pm 1
Cu(8-cyanoquinoline) ₂ Cl ₂	2224 \pm 0.5	-3 \pm 1
Pt(8-cyanoquinoline) ₂ Cl ₂	2228 \pm 0.5	+1 \pm 1
3-Cyanopyridine	2232 \pm 0.5	
Pd(3-cyanopyridine) ₂ Cl ₂	2240 \pm 0.5	+8 \pm 1

added to the ligand and the mixture was stirred. A white precipitate gradually formed which was collected, washed, and dried in vacuo. Anal. Calcd for Ag(C₁₀H₆N₂)₂NO₃: C, 50.22; H, 2.53. Found: C, 50.31; H, 2.50.

Bis(quinoline)silver Nitrate. This complex was prepared in a manner analogous to that of the 8-cyanoquinoline complex.

Spectral Measurements. **IR.** The infrared spectra in the 4000–700- cm^{-1} region were obtained on a Perkin-Elmer 421 recording spectrophotometer using Nujol mulls or chloroform solution. The cyanide stretching frequencies were measured using Nujol mulls on a Beckman IR-4 recording spectrophotometer calibrated with cyclohexane. The peaks were reproducible to within 1 cm^{-1} .

UV-Visible. The near-ultraviolet and visible spectra were taken on a Cary Model 14 recording spectrophotometer at both room temperature and liquid nitrogen temperature. All spectra were taken in mulls. In addition, the spectra of the copper complexes were taken in ethanol solutions.

ESR. The ESR spectra were taken on a Varian E12 spectrometer calibrated with DPPH.

Results

Nitrile Stretching Frequency Shifts. The C \equiv N stretching frequencies of 8-cyanoquinoline and its metal complexes are shown in Table I. The differences between the nitrile stretching frequencies of the free and coordinated ligands, also reported in Table I, are accurate to $\pm 1.0 \text{ cm}^{-1}$. For comparison, the nitrile stretching frequency shift in the opposite direction caused by protonation of the ring nitrogen is also shown.

In order to assess the effect of coordination to the ring nitrogen on a remote nitrile which is spatially removed from the metal, the nitrile stretching frequencies of free and coordinated 3-cyanopyridine were measured. These results are reported in Table I.

Electronic Absorption Spectra. The electronic absorption bands for the 8-cyanoquinoline and quinoline complex pairs,

Table II. Electronic Absorption Spectra^a

Compd	Ligand	
	8-Cyanoquinoline	Quinoline
[AgL ₂]NO ₃ ^b	31500 30400	32000 31000
[PdL ₂ Cl ₂] ^b	41700 32000 sh 30500	42000 36500 sh 31700 sh
[CuL ₂ Cl ₂] ^c	29800 sh 35700 33000 31700 11000	30300 36100 33300 32000 11900 sh
[PtL ₂ Cl ₂] ^b	10200 sh 35100 31300 24700	11300 37600 29400 27800
L ^c (free ligand)	45900 35600 32900 31300	44600 36400 33400 32200

^a The absorption band energies are in cm^{-1} . ^b Spectra were taken in mulls at room temperature and 77 K. ^c Spectra were taken in ethanol solution.

Table III. Effect of Axial Interactions on *g* Values of Copper Complexes

Compd	g_{\perp}	g_{\parallel}	Medium	Ref
Cu(8-cyanoquinoline) ₂ Cl ₂	2.055	2.235	Powder	This work
Cu(quinoline) ₂ Cl ₂	2.057	2.117	Powder	This work
CuII(acac) ₂	2.056	2.256	Toluene	
	2.060	2.304	10% pyridine- 90% toluene	24
CuIICl ₂ ·2py	2.079	2.241	40% pyridine- 60% chloroform	<i>a</i>
CuIICl ₂ ·1,10-phen	2.08	2.22	40% toluene- 60% chloroform	<i>a</i>

^a H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, 16, 3221 (1962).

representing similar complexes with and without the perpendicular nitrile-metal interaction, are tabulated in Table II. For comparison, the near-uv bands of the free ligands are also given. The spectra were taken in mulls at both room temperature and liquid nitrogen temperature.

Electron Spin Resonance Spectra. The *g* values of the pair of paramagnetic copper complexes with and without the perpendicular nitrile-metal interaction are shown in Table III. The changes of the *g* values caused by the presence and absence of coordinating ligands in the axial positions of other square-planar copper complexes are also shown.

Discussion

8-Cyanoquinoline (Figure 1) was chosen as the ligand to study perpendicular nitrile interactions because of its geometrical and bonding properties. In addition to its strongly coordinating ring nitrogen binding site, 8-cyanoquinoline has a nitrile which is forced into close proximity to a metal by the rigid ring structure. Coordination of the quinoline nitrogen to a metal at a distance of 2.17 Å requires that the nitrile triple bond be centered perpendicular to the metal at a distance of 2.35 Å (Figure 1). The effects of the perpendicular nitrile-metal interaction on the C \equiv N stretching frequency and on the metal d orbitals are discussed, along with a simple molecular orbital description of the interaction.

1. Effect of the Perpendicular Nitrile-Metal Interaction on the Nitrile. The observed shifts in the nitrile stretching frequencies shown in Table I could be a result of either direct nitrile-metal interactions or inductive effects resulting from

coordination of the quinoline nitrogen. Alterations in the electron distribution on the ring nitrogen resulting from coordination to the metal would be expected to transfer throughout the ring. To determine the direction and magnitude of the inductive effects on the C≡N stretching frequencies, dichlorobis(3-cyanopyridine)palladium(II) was prepared. A shift of the nitrile stretching frequency of 8 cm⁻¹ to *higher* energy relative to the free ligand was found. The meta position of the nitrile excludes direct nitrile-metal interaction indicating that the observed shift results from inductive effects. The similarity between resonance structures of 3-cyanopyridine and 8-cyanoquinoline makes the complex of the former a good model for complexes of the latter without the possibility of direct nitrile-metal interaction. A second experimental determination of the inductive shift involved protonated 8-cyanoquinoline. Protonation decreases the electron density of the quinoline nitrogen simulating coordination. A shift of 6 cm⁻¹, again to *higher* energy was found. These two experiments indicate that a resonance shift to higher frequency of about 7 cm⁻¹ is expected when the quinoline nitrogen of 8-cyanoquinoline coordinates to a metal. The net observed shifts to *lower* frequencies in the 8-cyanoquinoline complexes indicate direct nitrile-metal interaction.

Linear coordination of nitriles (utilizing the lone pair of electrons on the nitrogen) generally causes an increase of the C≡N stretching frequency. Acetonitrile complexes of the metals used in this study show increases of about 50 cm⁻¹ in the nitrile stretching frequency.^{20,21} The only reported exceptions to the increased frequency observed in linear nitrile systems are in ruthenium(II) and cobalt(I) complexes.²² The exceptions are believed to be a result of the unusual back-bonding properties of these metals.

The observed decrease in C≡N stretching frequency on coordinated 8-cyanoquinoline could be caused by metal-nitrile steric repulsion resulting in a bent nitrile carbon-ring carbon bond. This bending would decrease the overlap between the nitrile π orbitals and the ring π orbitals thus reducing delocalization. However, comparing a series of alkyl- and aryl nitriles,^{22,23} loss of delocalization results in an increase in the nitrile stretching frequency. On the basis of all the above observations, the best explanation for the observed decrease in C≡N stretching frequency accompanying coordination is perpendicular nitrile-metal covalent interactions.

Although the magnitudes of our observed shifts are small compared to those of other studies,²⁻⁸ the results are consistent with the properties of the metal complexes we studied. Our complexes are intermediate between the low-valent, strongly back-bonding metals such as Ni(0) and the high-valent, highly electronegative metals such as Sn(IV). None of the systems we studied exhibits a strong affinity for good π-acceptor ligands such as carbon monoxide. In addition, coordination of two quinoline nitrogens and two chlorides satisfies the square plane of the metal, leaving only the weakly interacting z axis open to accept the nitriles. Finally, in all cases, the metal σ orbital along the axis of metal-nitrile interaction (d_{z²}) is filled. Despite these unfavorable conditions, a definite interaction with the nitrile causing a decrease in the C≡N stretching frequency is observed.

2. Effect of Perpendicular Nitrile Coordination on the Metal.

A. Electronic Absorption Spectra. The electronic absorption bands of the complexes studied and the free ligands are shown in Table II. The two lowest energy bands, which are also observed in most of the metal complexes, show a red shift in the 8-cyano derivative compared to the unsubstituted quinoline.

The ligand localized bands are most clearly identifiable in the silver and copper complexes where they occur slightly red shifted from those of the free ligand. In the remaining complexes, the ligand-localized bands are also observed, but

Table IV. Ligand Interactions with Metal d_π Orbitals^a

	Trans		Cis			
	L (±x axis)	Cl (±y axis)	L (x axis)	L (y axis)	Cl (x axis)	Cl (y axis)
d _{xy}	π* _{py}	π	π* _{py}	π* _{py}	π	π
d _{xz}	π* _{CN}		π* _{CN}	π* _{CN}	π	
d _{yz}	π* _{CN}	π	π* _{CN}	π* _{CN}		π

^a The ligand orbitals are π antibonding orbitals on the ring nitrogen, π*_{py}, π bonding and antibonding orbitals on the nitrile, π*_{CN} and π*_{CN}, respectively, and p_π orbitals on the chloride, π.

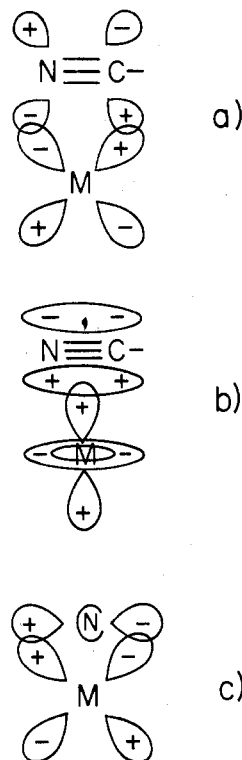


Figure 2. Molecular orbital overlaps for perpendicular nitrile-metal interactions: (a) nitrile π*, metal d_{xz} orbitals; (b) nitrile π^b, metal d_{z²}; (c) nitrile π^b, metal d_{yz} viewed along the C≡N axis.

they are superimposed on charge-transfer bands of the complexes. In all cases, the ligand-localized bands are lower in energy than those of the free ligand, but definitive assignments are more difficult because of the interference of the charge-transfer bands.

Well-separated bands which can be associated with metal d-d transitions are present only in the spectra of the copper complexes. These bands (occurring lower than 13000 cm⁻¹) exhibit a red shift in the 8-cyanoquinoline complexes compared to the quinoline complexes. The red shift can be interpreted using the changes in the one-electron d-orbital energies deduced from simple ligand field theory shown in Table IV, employing the axis system of Figure 1. The d_{xz} and d_{yz} orbitals are of proper symmetry to mix with the π bonding and/or antibonding orbitals localized primarily on the nitrile as shown in Figure 2. Because the filled π bonding orbitals on the nitrile are closer in energy to the metal orbitals than the π antibonding nitrile orbitals, the largest expected effect of mixing the d orbitals with the nitrile π bonding orbitals will be to raise the energy of the d orbitals which interact with the nitrile π bonding orbitals. A smaller effect would be the stabilization of the d orbitals which mix with the empty acceptor orbitals on the nitrile. It is thus expected that, upon interaction with the nitrile, the d_π orbitals will rise in energy producing a red shift

in the absorption spectra of the 8-cyanoquinoline complexes compared to the quinoline complexes. The relative energy of the d_{z^2} orbital is not known. However, interaction with the π bonding orbitals of the nitrile would be expected to raise its energy. Thus, it could become the highest filled orbital in the 8-cyanoquinoline complexes. In this case, the observed red shift would occur because of a change in the nature of the transition from $d_{\pi} \rightarrow d_{x^2-y^2}$ to $d_{z^2} \rightarrow d_{x^2-y^2}$. No choice can be made between these two alternative assignments on the basis of the available data.

In the case of the platinum complexes, the lowest energy transition is much lower in energy than the ligand-localized transitions but has an intensity comparable to them. We tentatively assign this transition to a metal to quinoline charge-transfer transition. The large red shift is consistent with the changes in the d-orbital energies discussed above.

The above interpretation of the electronic absorption bands, although consistent with the observed shifts, does not provide a definitive assignment. Qualitatively, it is clear that the metal-nitrile interaction produces a readily discernible change in the axial ligand field. A more quantitative discussion of the orbital mixings, based on molecular orbital considerations, will be presented later.

B. Electron Spin Resonance Spectra. A second method of measuring the effect of perpendicular nitrile-metal interactions on the copper d orbitals is electron spin resonance spectroscopy. ESR has been used as a sensitive probe of axial interactions between square-planar copper complexes and donor molecules.²⁴⁻²⁷ Complex formation with donor molecules results in an increase in the isotropic g value primarily because of increases in the value of g_{\parallel} .

Representative changes in the g_{\parallel} and g_{\perp} values for copper chelates interacting with donor molecules are shown in Table III. The changes in the g values for the quinoline and 8-cyanoquinoline complexes are also shown. The magnitude of g_{\parallel} for the 8-cyanoquinoline complex is close to that of the bis(pyridine)dichlorocopper(II) and 1,10-phenanthroline-dichlorocopper(II) complexes and is typical of the value found for an axial interaction with a coordinating solvent. The g_{\parallel} value of the quinoline complex is smaller than usual and probably represents a combination of inhibition of axial interactions caused by the steric properties of the quinoline and absence of solvent interaction in powder spectra. The increase in g_{\parallel} from the quinoline complex to the 8-cyanoquinoline complex and the magnitude of g_{\parallel} in the latter complex are indicative of an appreciable interaction between the metal and the perpendicular nitrile.

3. Molecular Orbital Description of Perpendicular Nitrile-Metal Interactions. On the basis of this work and the previous reports of perpendicular nitrile complexes, the following general pattern is apparent. For low-valent metals with good π -acceptor ligands, a large decrease in the $C\equiv N$ stretching frequency is observed; for the "classical" coordination complexes of the type studied here, a small decrease in the $C\equiv N$ stretching frequency is found; for highly ionic metals, a large decrease is again observed.

These trends can be readily explained using the bonding model in Figure 2. For the low-valent metals, the filled metal d_{π} orbitals are high enough in energy to mix efficiently with the empty π antibonding nitrile orbitals. This mixing reduces the bond order of the carbon-nitrogen bond and causes a large decrease in the stretching frequency. In addition, the metal d_{z^2} orbital, if empty, could mix with a $C\equiv N$ π bonding orbital, further reducing the bond order. This situation is analogous to the bonding in transition metal-acetylene complexes, where the back-bonding, if strong enough, has been considered to reduce the acetylene bond order to 2.²⁸

In the case of the highly ionic transition metals, the d

orbitals are tightly bound to the metal. In such cases, the empty metal d_{z^2} orbital could have a low enough energy to mix strongly with the nitrile π bonding orbital. The nitrile would act as a pseudo σ donor to the metal. The net effect of such donation would be to decrease the nitrile bond order and increase the stretching frequency.

In the case of the complexes studied in this paper, the metal orbitals are not of the proper energy to mix strongly with either the π bonding or π antibonding orbitals of the nitrile. The major nitrile bond weakening is caused by a weak interaction between the d_{π} metal orbitals and the empty π antibonding nitrile orbitals. Such back-donation is not expected to be efficient and thus does not cause a large decrease in the nitrile bond order.

Our simple MO analysis is based on the overlap picture of Figure 2. Two effects can alter the picture. First, if the metal is not roughly centered between the carbon and the nitrogen, the π interactions will be diminished and the interaction between d_{z^2} and one of the antibonding lobes will be increased. Thus, we expect that the interactions involving d_{z^2} will in general be nonzero. Second, the nitrile is not symmetrical; the coefficients of the carbon and nitrogen contributions to the antibonding orbitals are not equal. This inequality will also have the effect of increasing the interactions with the metal d_{z^2} orbital. If the trends in bond orders are dominated by the changes in the oxidation states and the concomitant changes in orbital mixings, the asymmetries discussed above will probably not have severe effects. However, within members of a similar series with similar oxidation states, such asymmetries could dominate the trends in the observed stretching frequencies.

Registry No. Ag(8-cyanoquinoline)₂NO₃, 57738-98-4; Pd(8-cyanoquinoline)₂Cl₂, 57739-03-4; Cu(8-cyanoquinoline)₂Cl₂, 57739-02-3; Pt(8-cyanoquinoline)₂Cl₂, 57739-01-2; Pd(3-cyanoquinoline)₂Cl₂, 57793-78-9; Pd(quinoline)₂Cl₂, 57738-99-5; Pt(quinoline)₂Cl₂, 57793-79-0; Cu(quinoline)₂Cl₂, 13422-47-4; Ag(quinoline)₂NO₃, 12176-75-9; Pd(benzonitrile)₂Cl₂, 14220-64-5; potassium tetrachloroplatinate, 10025-99-7; Pt(NH₃)₂Cl₂, 26035-31-4.

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