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^{13}C NMR Spectra of Series of Bis(2,2′-bipyridine)cobalt(III) and Bis(1,10-phenanthroline)cobalt(III) Complexes

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Twenty-eight cobalt(III) complexes of these types: $[Co(LL)_3]^{3+}$ and $[CoXX(LL)_2]^{n+}$ (LL=2,2′-bipyridine or 1,10-phenanthroline, and XX=$2CN^-$, $2NO_2^-$, ethylenediamine, $2NH_3$, glycinate ion, $2H_2O$, $C_2O_4^{2-}$, CO_3^{2-}, $2SCN^-$, $2N_3^-$, $2CH_3COO^-$, $2Cl^-$, or $2Br^-$), were prepared, and their ^{13}C NMR spectra were recorded. Most of the resonances in the complexes were assigned mainly by the technique of selective proton decoupling. In the bpy complexes, the chemical-shift difference between corresponding carbon atoms was the greatest in the C-6 and C-6′ pair. The phen complexes also gave parallel results. The main factor responsible for the chemical-shift differences of the C-6 and C-6′ pair is explained as resulting from the difference in σ-bonding ability between the pyridyl group and the ligand, X.

Recently the ^{13}C NMR technique has been widely used as a useful tool in investigating the structures of organic[1] and organometallic compounds.[2] The application of ^{13}C NMR to the study of transition-metal complexes is also increasing, but it has not yet been systematized. The spectra of ^{13}C NMR were reported for the complexes containing a quadridentate ligand (trimethylenediamine-*N*,*N*′-diacetate, ethylenediamine-*N*,*N*′-diacetate ion) and a bidentate ligand (2,2′-bipyridine, 1,10-phenanthroline, *etc.*) by Gailey *et al.*[3] and for the platinum complexes containing 2,2′-bipyridine and various diamines by Erickson *et al.*[4] However, there exists a partial disagreement between the two sets of assignments; *i.e.*, the assignments for the C-3 and C-5 carbons of 2,2′-bipyridine differ.

The present study was undertaken in order to ascertain the assignments of the ^{13}C NMR spectra of a series of bis-type cobalt(III) complexes, $[CoXX(LL)_2]^{n+}$, where LL=2,2′-bipyridine or 1,10-phenanthroline and where XX represents unidentate ligands or a bidentate ligand, and in order to find the relationship between the chemical shift and the nature of the second ligand, X.

Experimental

Materials. *Preparation of 2,2′-Bipyridine Complexes*: Most of the 2,2′-bipyridine complexes were prepared according to the literature, with a minor modification. The dichloro complex was prepared by the method of Vlcek.[5] The carbonato complex, $[Co(CO_3)(bpy)_2]^+$, was prepared by the reaction of $K_3[Co(CO_3)_3]$ with 2,2′-bipyridine; it was then used as the starting material for the preparation of diaqua, oxalato, and diacetato complexes.[6] The dinitro, dithiocyanato, and diazido complexes were prepared by Maki's method with the modification that *cis*-$[CoCl_2(bpy)_2]Cl$ or *cis*-$[Co(H_2O)_2(bpy)_2](ClO_4)_3$ was used as the starting material instead of the compound reported as "*trans*-$[CoCl_2(bpy)_2]Cl$".[7] Each crude complex was adsorbed on a small amount of SP-Sephadex C-25. Elution with 0.1 M (1 M=1 mol dm^{-3}) NaCl, followed by the evaporation of the eluent with a rotatory vacuum evaporator, gave each pure substance. The glycinato complex was prepared by the method of Murakami *et al.*[8] and subsequently purified by using a column of SP-Sephadex C-25, with 0.3 M NaCl as the eluent.

Ethylenediaminebis(2,2′-bipyridine)cobalt(III) Chloride, $[Co(en)(bpy)_2]Cl_3\cdot 4H_2O$: The carbonato complex, $[Co(CO_3)(bpy)_2]Cl\cdot H_2O$, weighing 0.97 g (2 mmol), was dissolved in 4.2 cm^3 of 1 M HCl with heating at about 50 °C, and then 0.53 g (4 mmol) of ethylenediamine dihydrochloride, 0.15 cm^3 (2.3 mmol) of ethylenediamine, and 0.1 g of active charcoal were added. After it had stood overnight, the resulting yellow solution was filtered. The filtrate and washings were collected, and the cationic species were adsorbed at the top of a column of SP-Sephadex C-25 (120 cm long and 3 cm in diameter) and eluted with a solution of sodium pyrophosphate (pH=6.7). The first fraction was found to contain a mixture of $[Co(bpy)_3]^{3+}$ and $[Co(en)(bpy)_2]^{3+}$. They were separated on a column of SP-Sephadex C-25, using a 0.5 M NaCl solution as the eluent.

Found: C, 43.81; H, 5.17; N, 13.69; H_2O, 11.87%. Calcd for $C_{22}H_{32}N_6O_4Cl_3Co$: C, 43.33; H, 5.29; N, 13.78; H_2O, 11.82%. Absorption spectrum $\tilde{\nu}_{max}$/cm^{-1} (log ε) 21600 (2.00).

cis-*Diamminebis(2,2′-bipyridine)cobalt(III) Perchlorate,* cis-$[Co(NH_3)_2(bpy)_2](ClO_4)_3\cdot 2H_2O$: This complex was prepared and separated in a manner similar to that used in the preparation of the ethylenediamine complex.

Found: C, 32.49; H, 3.38; N, 11.34; H_2O, 4.86%. Calcd for $C_{20}H_{26}N_6O_{14}Cl_3Co$: C, 32.45; H, 3.54; N, 11.36; H_2O, 4.87%. Absorption spectrum $\tilde{\nu}_{max}$/cm^{-1} (log ε) 21700 (1.82).

cis-*Dicyanobis(2,2′-bipyridine)cobalt(III) Chloride,* cis-$[Co(CN)_2(bpy)_2]Cl\cdot 4.5H_2O$: Into a solution of 1.38 g (2 mmol) of $[Co(bpy)_3]Cl_3\cdot 3H_2O$ in 10 cm^3 of water, 0.1 g of active charcoal and 0.27 g (4.15 mmol) of KCN were stirred. Although the reaction seemed to take place within about five minutes, the solution was kept in a refrigerator overnight. It was then filtered to remove the charcoal, which was washed several times with hot water. The filtrate and washings were collected, and the cationic species in the solution were adsorbed on a small amount of SP-Sephadex C-25. The adsorbed species were eluted with 0.1 M hydrochloric acid, and the eluate was evaporated almost to dryness. The residue was washed with a small amount of cold water. It was then recrystallized from hot water and air-dried at room temperature.

Found: C, 48.77; H, 4.20; N, 15.74; H_2O, 14.91%. Calcd for $C_{22}H_{25}N_6O_{4.5}ClCo$: C, 48.95; H, 4.67; N, 15.57; H_2O, 15.02%. Absorption spectrum $\tilde{\nu}_{max}$/cm^{-1} (log ε) 26000sh. (2.2).

cis-*Dibromobis(2,2′-bipyridine)cobalt(III) Perchlorate,* cis-$[CoBr_2(bpy)_2]ClO_4$: To a solution of 1.41 g (2 mmol) of $[Co(H_2O)_2(bpy)_2](ClO_4)_3$ in 1.5 cm^3 of water, 2 cm^3 of a 2 M KBr solution and 50 cm^3 of ethanol were added. After the mixture had stood overnight in a refrigerator, it was filtered and the filtrate was evaporated to dryness with a rotatory vacuum evaporator at a bath temperature of 60 °C. The residue was redissolved in about 150 cm^3 of hot ethanol, and then, to the filtrate, an ethanol solution of $LiClO_4 \cdot 3H_2O$ was added to give the perchlorate crystals.

Found: C, 37.57; H, 2.19; N, 9.11%. Calcd for $C_{20}H_{16}N_4O_4Br_2ClCo$: C, 38.10; H, 2.56; N, 8.89%.

Preparation of 1,10-Phenanthroline Complexes: The complexes, $[Co(phen)_3]Cl_3 \cdot 4H_2O$,[9] $[Co(CN)_2(phen)_2]Cl \cdot 4H_2O$,[7] $[Co(H_2O)_2(phen)_2](NO_3)_3 \cdot 2H_2O$,[10] $[Co(SCN)_2(phen)_2]NCS$,[10] $[Co(CO_3)(phen)_2]Cl \cdot 5H_2O$,[11] and $[CoBr_2(phen)_2]Br \cdot 3H_2O$,[11] were prepared by the known methods. For the other complexes, the methods were essentially the same as those used for the preparation of the corresponding 2,2′-bipyridine complexes. The diammine complex was prepared by a method, which was different from that previously reported.[12]

cis-*Diamminebis(1,10-phenanthroline)cobalt(III) Chloride*, cis-$[Co(NH_3)_2(phen)_2]Cl_3 \cdot 3H_2O$: The complex, $[Co(NO_3)_2(phen)_2]NO_3$, was prepared by heating $[Co(H_2O)_2(phen)_2](NO_3)_3$ in an air bath at 110 °C for 4—5 h. The dinitrato complex, weighing 1.0 g, was added to 20 cm^3 of dimethyl sulfoxide, taking up sufficient ammonia gas. The resulting yellow solution was kept at room temperature for 2—3 h and then diluted with 30 cm^3 of water. The complex was adsorbed on a small amount of SP-Sephadex C-25 and eluted with 0.5 M HCl. The eluate was concentrated by evaporation, and then the chloride of the complex was precipitated by adding ethanol to the concentrated solution.

Found: C, 47.36; H, 4.26; N, 13.70; H_2O, 8.67%. Calcd for $C_{24}H_{28}N_6O_3Cl_3Co$: C, 46.96; H, 4.60; N, 13.69; H_2O, 8.80%. Absorption spectrum $\tilde{\nu}_{max}/cm^{-1}$ (log ε) 21600 (1.87).

Identification of the Complexes. The complexes prepared were identified by comparing their electronic absorption spectra with those reported in the literature. The spectra of the dicyano and dibromo complexes were different from the reported ones; *i.e.*, the latter complex showed no maxima in the d-d band region, but only some undefined shoulders. The absorption maximum of the dicyano complex is given above. The elemental analyses were performed on dicyano, dibromo, and newly prepared compounds. The water contents were also determined by measuring the weight loss under the conditions of 100 °C and 20 mmHg.

It is well established that bis-type cobalt(III) complexes of 2,2′-bipyridine or 1,10-phenanthroline take only the *cis*-configuration because of the repulsion between the ligands. The *cis* configuration of all the present complexes was confirmed by the ^{13}C NMR spectra, as will be discussed later.

Physical Measurements. The electronic absorption spectra were measured using a Shimadzu MPS-50L spectrophotometer. The ^{13}C NMR spectra were measured at 15.04 MHz on a JEOL JNM-FX60 spectrometer equipped with a Fourier transform accessory under the condition of a noise-modulated proton decoupling. A sweep width of 2500 Hz, a pulse width of 9 μs (corresponding to the tipping angle of about 90°), and a pulse interval of 3 s were employed. The free-induction signal derived after each pulse was accumulated in a JEOL JEC-980A computer (8K). From approximately 500 up to 60000 accumulations were made for each spectrum. The ambient temperature was 35 °C. The solvents used were H_2O, $CHCl_3$, CH_3NO_2, CH_3OH, and a mixture of CH_3NO_2 and DMSO, and the concentrations of the samples were 0.3 M or lower depending on the solubilities. The spectra were obtained from samples contained in 10-mm-diameter tubes; D_2O in an inner coaxial tube 5-mm in diameter was used to provide a field-frequency lock signal. The external standard used was a dioxane–tetramethylsilane (TMS) mixture contained in a capillary (approximately 1-mm). Dioxane had a δ-value of 67.37 (downfield from TMS). All the chemical shifts are given relative to TMS, with a digital resolution of 0.6 Hz.

Selectively proton-decoupled ^{13}C NMR spectra were also measured for 2,2′-bipyridine (in $CDCl_3$), $[Co(bpy)_3]Cl_3$ (in D_2O), *cis*-$[CoCl_2(bpy)_2]Cl$ (in DMSO-d_6), and *cis*-$[Co(CN)_2(bpy)_2]Cl$ (in D_2O) in 5-mm-diameter tubes. Prior to each ^{13}C NMR measurement, the ^{1}H NMR spectrum of the same sample solution was recorded at 59.80 MHz. The internal standards used were TMS for the free ligand and sodium trimethylsilylpropanesulfonate (DSS) for the complexes.

In order to avoid the dissociation of the unidentate ligand and to obtain a sufficient solubility of the complex, nitromethane and dimethylsulfoxide were used as the solvent instead of water in some cases. The solvent effects on the ^{13}C NMR spectra of 2,2′-bipyridine complexes were measured for dicyano, dinitro, carbonato, diacetato, and tris-type complexes. In general, carbon resonance positions shifted to fields higher by 0.3—0.4 ppm for nitromethane solutions than for aqueous solutions. The greatest solvent effect was observed in the chemical-shift difference between the C-6 and C-6′ signals of the diacetato complex (1.07 ppm in the aqueous solution and 2.24 ppm in the nitromethane solution); the second largest was the C-6 and C-6′ pair of the carbonato complex (1.83 ppm in the aqueous solution and 2.62 ppm in the nitromethane solution). However, these large changes are exceptional. The solvent dependence of the chemical-shift differences is small in other resonances of these complexes and in all the resonances of the other complexes.

Results and Discussion

The ^{13}C NMR spectra with noise-modulated and selective proton decoupling are given in Fig. 1 for 2,2′-bipyridine dissolved in deuterated chloroform and for $[Co(bpy)_3]Cl_3 \cdot 3H_2O$ in deuterium oxide. The three signals appearing in the lower field in the proton-decoupled bipyridine spectrum were identified as those

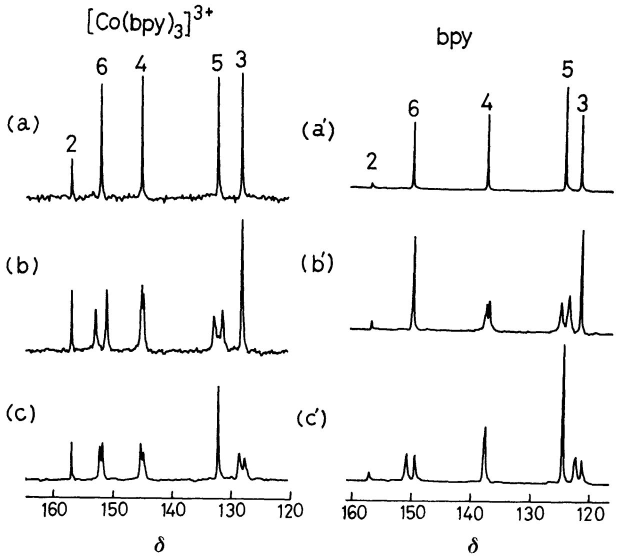


Fig. 1. Noise-modulated and selective proton-decoupled ^{13}C NMR spectra of $[Co(bpy)_3]Cl_3$ in D_2O and 2,2′-bipyridine in $CDCl_3$. (a) and (a′): Noise-modulated spectra, (b) and (b′): H-3 proton-decoupled spectra irradiated at 536 Hz from DSS and 501 Hz from TMS, respectively, (c) and (c′): H-5 proton-decoupled spectra irradiated at 475 Hz from DSS and 434 Hz from TMS, respectively.

of C-2, C-6, and C-4, in agreement with the literature.[3,4,13,14] The assignment of the C-4 signal was confirmed by comparing the spectral feature with that of 4,4′-dimethyl-2,2′-bipyridine (Fig. 2). The low intensity of the signal appearing at the lowest field is consistent with the absence of hydrogen atoms attached to C-2. The two signals appearing at the higher fields were identified as those of C-5 and C-3 in the order shown in Fig. 1 by measurement with selective proton decoupling (Figs. 1b, b′, c, and c′).

The assignments are consistent with those of Erickson *et al.*,[4] but different from those of Gailey *et al.*[3] in the C-3 and C-5 signals.

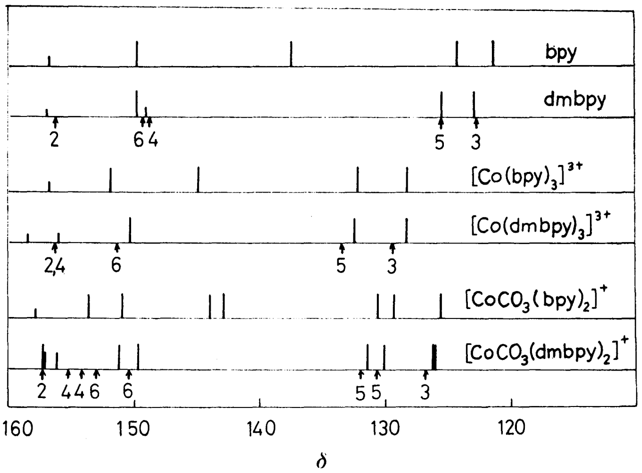


Fig. 2. Noise-modulated ^{13}C NMR spectra of 2,2′-bipyridine and 4,4′-dimethyl-2,2′-bipyridine (dmbpy) in $CHCl_3$, and their complexes in H_2O.

In Fig. 2, schematic comparisons of the ^{13}C NMR spectra are made between bipyridine and its 4,4′-dimethyl derivative, and also between their cobalt(III) complexes. The arrows under the spectra of the dimethyl derivative and its complexes show the positions of the signals predicted on the assumption that the methyl substitution at the 4 sites of bipyridine and its complexes would result in chemical-shift changes of the same magnitudes as those resulting from the corresponding substitution in pyridine.[1] The signals of the 4,4′-dimethyl derivative and its complexes appear near the predicted positions. Thus, each signal may be assigned as indicated by the nearby arrow.

The ^{13}C NMR spectra due to aromatic carbons of the $[CoXX(bpy)_2]^{n+}$-type complexes are listed in Fig. 3 in the order of the decreasing wavenumber of the first absorption band of the complex. As expected, each of the five resonance lines found in $[Co(bpy)_3]^{3+}$ splits into two in the $[CoXX(bpy)_2]^{n+}$-type complexes, except for the carbonato complex, in which the splitting was not detected in the C-2 and C-3 signals. The spectra of the 1,10-phenanthroline complexes also exhibit patterns similar to those of the bipyridine complexes. The assignment of the spectra of 1,10-phenanthroline and its complexes was made in a manner similar to the case of bipyridine, excepting that the C-5 and C-7 resonances of the complex can not be unambiguously differentiated.

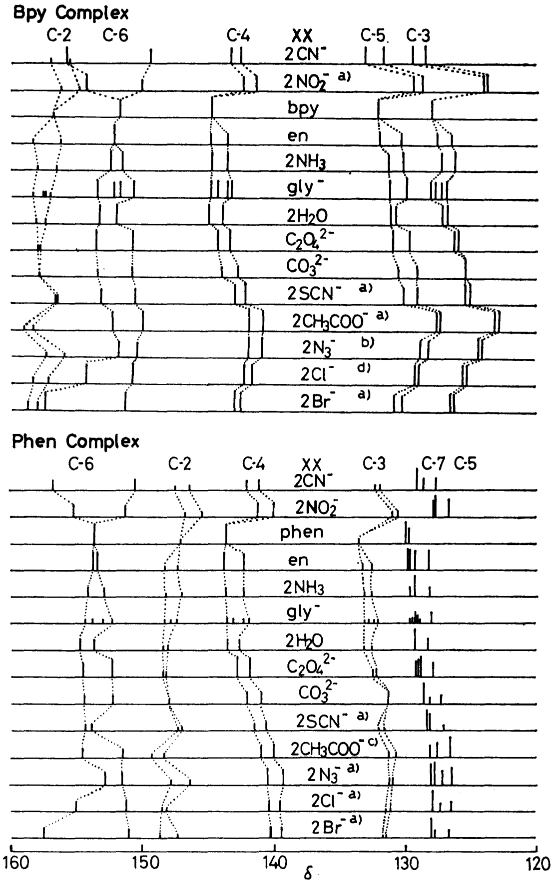
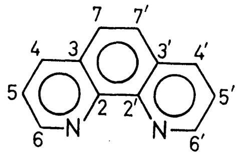


Fig. 3. Noise-modulated ^{13}C NMR spectra of cobalt(III) complexes of 2,2′-bipyridine and 1,10-phenanthroline in aqueous solutions.

a): Nitromethane solution, b): dimethyl sulfoxide solution, c): methanol solution, d): nitromethane-dimethyl sulfoxide (1 : 1) solution.

For the convenience of a ready comparison with bipyridine, the numbering system given below is here used for 1,10-phenanthroline:



In both series of complexes, the magnitude of the splitting, *i.e.*, the chemical-shift difference between corresponding carbon atoms, is the largest between C-6 and C-6′.

It is well-known that diamagnetic shielding due to the ring current of the pyridyl group causes a drastic shift of proton resonances toward a higher field.[15] Therefore, in the present complexes, $[CoXX(bpy)_2]^{n+}$ and $[CoXX(phen)_2]^{n+}$, it can be expected that the H-6 proton lying above the plane of the pyridine ring of a neighboring ligand group resonates at the highest field, and the H-6′ proton lying near the expansion of the pyridine plane, at a lower field.

Taking these facts into account, the C-6 and C-6′ signals of the spectra of $[CoCl_2(bpy)_2]Cl$ and $[Co(CN)_2$-

(bpy)$_2$]Cl were assigned by the selective proton-decoupling technique. When each complex was irradiated with the resonance frequency of the H-6 proton at the highest field, one of the ^{13}C signals at a lower field in the C-6 region split into two, while the other, at a higher field, remained unsplit; the latter is identified as a C-6 signal. This C-6 carbon nucleus is situated next to the nitrogen atom at the *trans* site of X in [CoXX(bpy)$_2$]$^{n+}$. Thus, for all complexes of the [CoXX(LL)$_2$]$^{n+}$ type (LL=bpy or phen), the resonances at the higher field may be assigned to C-6, and those at the lower field, to C-6′.

The chemical shifts of ^{13}C NMR were also measured of *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine (penp) complexes, *cis*-α-[CoXX(penp)]$^{n+}$ (XX=2CN$^-$, en, 2NH$_3$, 2H$_2$O, 2N$_3^-$, 2Cl$^-$, and 2Br$^-$), in which two pyridyl groups are located in positions *trans* to each other. The signal of the pyridyl C-6 of each complex of this series appeared near the C-6′ signal of the corresponding bis(bipyridine) complex.[16] This is consistent with the assignment given above for the C-6′ signal.

The difference between the C-6 and C-6′ chemical shifts in [CoXX(LL)$_2$]$^{n+}$ might be due to diamagnetic shielding, analogously to the cases of H-6 and H-6′. However, the observed shift differences are too large to be attributed to this effect only.

Recently, Nakashima *et al.*[17] gave a theoretical equation for use in calculating the chemical shift of a ligand proton under the influence of the paramagnetic anisotropy of the central cobalt(III) ion of a complex. The chemical-shift differences estimated for the present phenanthroline complexes after Nakashima *et al.*[17] are much smaller than the observed splittings; thus, the paramagnetic anisotropy of the cobalt(III) ion cannot be the main cause of the chemical-shift differences observed between the corresponding atoms of each ligand.

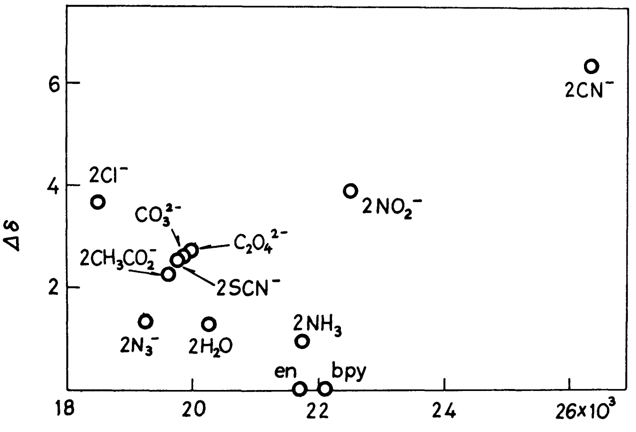


Fig. 4. A plot of the chemical-shift difference of C-6 and C-6′ carbons *vs.* the $\tilde{\nu}_{\max}$ value of the first absorption band of the complex, [CoXX(bpy)$_2$]$^{n+}$.

When the difference between the C-6 and C-6′ chemical shifts is plotted against the wavenumber of the first absorption band for each complex of the [CoXX(LL)$_2$]$^{n+}$ type (LL=bpy or phen), a roughly linear relationship can be observed (Fig. 4). The dinitro and dicyano complexes, however, greatly deviated from the linear relationship. This may be due to the strong π-interaction of NO$_2^-$ and CN$^-$. Thus, the difference between the C-6 and C-6′ chemical shifts seems to be related to the σ-donating ability of the ligand, XX. For other carbon atoms, however, no simple relationship was observed between the chemical-shift difference and the ligand-field strength.

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