

Ligand Isomerism and Stacking in Square Planar Platinum(II) Complexes. 2. Evidence for Mixed-Isomerism in Pt[dmbp(CSN)₂]

M. J. Coyer,[†] R. H. Herber,^{*†} J. Chen,[‡] M. Croft,[‡] and S. P. Szu[†]

Departments of Chemistry and Physics, Rutgers University, New Brunswick, New Jersey 08903

Received July 21, 1993[⊙]

Three linkage isomers of Pt[dmbp(CSN)₂], where dmbp = 4,4'-dimethylbipyridine, have been prepared and examined by FT-IR, ¹³C solution and ¹⁵N MAS NMR, and Pt-L₃ EXAFS spectroscopies, in order to elucidate the bonding properties of these square planar complexes. The spectral data show that these complexes can exist as the kinetically favored -(SCN)₂ form I, the -(SCN)(NCS) form II, obtained by heating I as the neat solid, and the thermodynamically favored -(NCS)₂ form III, obtained by recrystallization of I from aprotic solvents. Evidence for a Pt–Pt interaction in solid III is inferred from the Pt-L₃ EXAFS results.

Introduction

The bonding mode of the thiocyanate ligand in its metal complexes—whether S-bonded, N-bonded, bridging, or ionic—has been the subject of detailed studies, and a number of spectroscopic techniques have been brought to bear on this problem.¹ While the “hard/soft” rule implies a preference for S-bonding in going from Ni to Pt, a variety of ligand isomers of the latter can be isolated, and it can be inferred that several effects are simultaneously involved in determining the structure of the complexes which are formed. For Pt(II), in particular, the tendency to achieve an 18-electron configuration in the solid by the stacking of monomers so as to permit Pt–Pt bonding interactions has been shown to play a significant role.²

Of particular interest in this context is the class of square planar *cis*-Pt(II) thiocyanate complexes of the form Pt(L)-(CSN)₂, where L is a bidentate amine and the CSN notation denotes the possibility of either -(SCN)₂ or -(NCS)₂ bonding, which have been shown to exist in both S- and N-bonded forms.³ Several of the N-bonded species have been shown to exhibit interesting polychromic and solubility properties,⁴ and the variation of properties in these complexes has been ascribed to variations of the metal–metal interaction (i.e. shorter Pt–Pt distances^{3,5}), arising from an overlap between Pt(II) 5d_{z²} and 6p_z orbitals of adjacent molecular units, forming stacked complexes.⁶

Employing a variety of spectroscopic techniques, the characterization of two forms (i.e. yellow and red) of Pt[2,2'-bipyridine)-(CSN)₂] has recently been reported.³ The yellow to red conversion can occur either by heating the neat solid or by recrystallization from aprotic solvents and, for the solid, has been found to be irreversible. It was shown in this study that the yellow material corresponds to the kinetically favored di-S-bonded “monomeric” form and that the red material is the thermodynamically more favorable di-N-bonded “polymeric” or “stacked” material. The intense color and lower solubility of the red bpy complex, compared

with the yellow complex, is due to shorter intermolecular Pt–Pt contacts (i.e. 3.2–3.4 Å).^{5,6}

The study of the bipyridine complexes has been extended to several methyl-substituted bpy derivatives. In the present study the FTIR, ¹³C and ¹⁵N NMR, and EXAFS spectroscopic data are reported for three forms of the Pt[dmbp(CSN)₂] (dmbp = 4,4'-dimethylbipyridine) complex, namely, the -(SCN)₂ (I), -(SCN)(NCS) (II), and -(NCS)₂ (III) forms. The correlations of the thiocyanate bonding modes and the stacking properties of the dmbp complexes compared with the unsubstituted homologues are discussed.

Experimental Section

I. Synthesis of Pt[dmbp(CSN)₂] Complexes. (1) Pt[dmbp(SCN)₂] (I). Commercial K₂PtCl₄ (Aldrich) was used without further purification and converted to Pt[dmbp(Cl)₂] by literature methods.⁷ A known quantity of the dichloride complex was dissolved in a minimum amount of DMSO with heating. To this solution was added twice the stoichiometric amount of AgClO₄ in a small amount of H₂O, yielding immediately a gray precipitate of AgCl. The reaction mixture, protected from light, was stirred at 100 °C for 1 h and filtered through an F-grade sintered glass frit to remove solid AgCl, yielding a clear yellow solution which was then cooled to 0 °C, and an excess of aqueous KSCN was added dropwise to immediately afford a bright yellow solid. This solid was separated by filtration, washed with cold H₂O, EtOH, and Et₂O, and dried under vacuum at room temperature. Spectroscopic analyses verified this material to be the di-S-bonded complex. ¹³C and ¹⁵N isotopically labeled samples were prepared by substituting the appropriate NaS^{*}C^{*}N species (MSD Corp.) in the final step.

(2) Pt[dmbp(SCN)(NCS)] (II). Complex I can be converted to II by heating the neat solid in air or vacuum at ~160 °C for about 1 h. The rate of this transformation is temperature dependent and can be observed in a pressed KBr pellet. The transformation is essentially complete in ~2 h at 85 °C. Infrared data (*vide infra*) confirm the product of this transformation to be Pt[dmbp(NCS)(CSN)], rather than a mixture of the di-S-bonded and di-N-bonded isomers.

(3) Pt[dmbp(NCS)₂] (III). Complex I can be converted to III by dissolving the former in DMSO with heating to ~150 °C and allowing the solution to cool slowly to room temperature. The resulting solid was filtered out, washed with EtOH and Et₂O, and dried in vacuum at room temperature. Infrared data (*vide infra*) confirmed this material to be the di-N-bonded complex.

II. Infrared Studies. Midrange FTIR spectra were acquired on microcrystalline powder samples, using standard pelleting techniques, employing a Matteson Instruments Cygnus-100 spectrometer (DTGS or MCT detector) operated at 2-cm⁻¹ resolution. Typically, 64 scans were co-added and ratioed to a KBr background.

* To whom correspondence should be addressed.

[†] Department of Chemistry.

[‡] Department of Physics.

[⊙] Abstract published in *Advance ACS Abstracts*, January 15, 1994.

- (1) (a) Burmeister, J. L. *Coord. Chem. Rev.* **1968**, *3*, 225. (b) Basolo, F. *Coord. Chem. Rev.* **1990**, *100*, 47. (c) Burmeister, J. L. *Coord. Chem. Rev.* **1990**, *105*, 77.
- (2) Krogman, K. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*(1), 35.
- (3) (a) Bertini, I.; Sabatini, A. *Inorg. Chem.* **1966**, *5*, 1025. (b) Coyer, M. J.; Croft, M.; Chen, J.; Herber, R. H. *Inorg. Chem.* **1992**, *31*, 1752.
- (4) Kukushkin, Yu. N.; Vrublevskaia, L. V.; Vlasova, R. A.; Isachkina, T. S.; Sheleshkova, N. K. *Zh. Neorg. Khim.* **1985**, *30*, 401; *Russ. J. Inorg. Chem. (Engl. Transl.)* **1985**, *30*, 224.
- (5) Bielli, E.; Gidney, R. D.; Gillard, R. D.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1974**, 2133.
- (6) Thomas, T. W.; Underhill, A. E. *Chem. Soc. Rev.* **1972**, *1*, 99.

(7) Rosenblatt, F.; Schleede, A. *Ann. Chim. (Paris)* **1933**, *501*, 51. Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1934**, 965.

Table 1. Infrared Data for the Forms of Pt[dmbp(CSN)₂] Discussed in the Text with All Data for KBr pellets at 295 K Ratioed to a KBr Background

form	$\nu_{\text{CN}}, \text{cm}^{-1}$ ^a	$\Gamma_{\text{CN}}, \text{cm}^{-1}$	$\nu_{\text{CS}}, \text{cm}^{-1}$	amine modes, cm^{-1}
-(SCN) ₂	2122 s, sp	16		842 s, 828 s
-(SCN)(NCS)	2125 sh, 2113 s	48	859 sh ^b	
-(NCS) ₂	2129 sh, 2117 s, br		857 ^c	832 s

^a Overlapping bands have been resolved using a curve-resolution program (GRAMS1, Spectracalc). ^b ν_{CS} appears as a weak shoulder. ^c ν_{CS} appears as a medium-intense, well-resolved shoulder, reflecting Pt-(NCS)₂ bonding.

III. NMR Studies. (1) **Solution ¹³C Spectra.** The ¹³C NMR data were obtained on natural-abundance samples using a 200-MHz Varian Model XL spectrometer. Solutions of the sample compound (ca. 1 mL) were prepared from saturated solutions in *N*-methylpyrrolidone and filtered to remove solids. Spectra were acquired at room temperature, utilizing a 2-s delay time between pulses to allow adequate time for the characteristically slow relaxation mechanism of the thiocyanate C atom.

(2) **Solid-State ¹⁵N MAS Spectra.** The ¹⁵N MAS NMR measurements were carried out on a 200-MHz Varian Model-XL spectrometer using a 7-mm DOTY probe. The ¹⁵N chemical shifts were measured at a transmitter frequency of 15.00 MHz referenced to 99% enriched (¹⁵NH₄)₂SO₄ at 0.00 ppm, with a spinning rate of ca. 3000 Hz. Exploratory experiments afforded appropriate delay times (*D*₁) of 30 s for the Pt-(SC¹⁵N)₂ compounds and 60 s for the Pt-(NCS)₂ and Pt-(SCN)(NCS) complexes. The acquisition time (AT) was 0.320 s on the basis of a fit of the free induction decay (fid) signal. The time required to obtain acceptable signal-to-noise ratio spectra was about 8 h.

IV. Pt-L₃ EXAFS Studies. The Pt-EXAFS measurements were carried out in the absorption mode on beam lines X-19A and X18B at the Brookhaven National Laboratory Light Source. Multiple absorption coefficient scans over a range of 1000 eV above the Pt-L₃ edge were needed to obtain spectra of sufficient quality to extract significant high-*k* information about the Pt-Pt interaction (*vide infra*). A Displex refrigerator (Air Products Co.) was used to effect cooling (15 K) for the low-temperature measurements. Data analysis was performed using a modified version of the University of Washington program.⁸

Results and Discussion

I. Infrared Spectra. The midrange infrared data, summarized in Table 1, were examined in detail in the CN (~2100 cm⁻¹) and CS (700–900 cm⁻¹) stretching regions. The positions of these bands in the IR spectrum have been shown to be indicative of the type of pseudohalide bonding that exists in metal-thiocyanate complexes.^{3,9} Generally, the metal-thiocyanate CN stretching absorbances for S-bonded complexes appear as relatively narrow bands above 2100 cm⁻¹, while the N-bonded forms exhibit IR absorbances well above 2150 cm⁻¹.³ Similarly, the CS stretching modes are observed between 720 and 680 cm⁻¹ for M-SCN complexes, while features between 860 and 790 cm⁻¹ are associated with Pt-NCS bonding. Difficulties sometimes arise in the metal-thiocyanate bonding assignment using the ν_{CS} modes which may be too weak or are obstructed by the coincidental presence of other ligand modes in the same energy range.

In the infrared spectrum of I, a single, strong ν_{CN} stretch is observed at 2122 cm⁻¹, indicative of an S-bonded metal complex on the basis of the above systematics (Figure 1).^{3,9} Since the bidentate amine ligand in these complexes occupies two adjacent coordination sites, these compounds possess exclusively C_{2v} symmetry. The C_{2v} symmetry point group dictates two IR-active C-N stretching modes (i.e. symmetric and asymmetric). As previously reported,^{3b} these modes are well resolved in the yellow S-bonded bipyridine analogue but unresolved in the red N-bonded form. Examination of the ν_{CN} stretch of the latter shows an

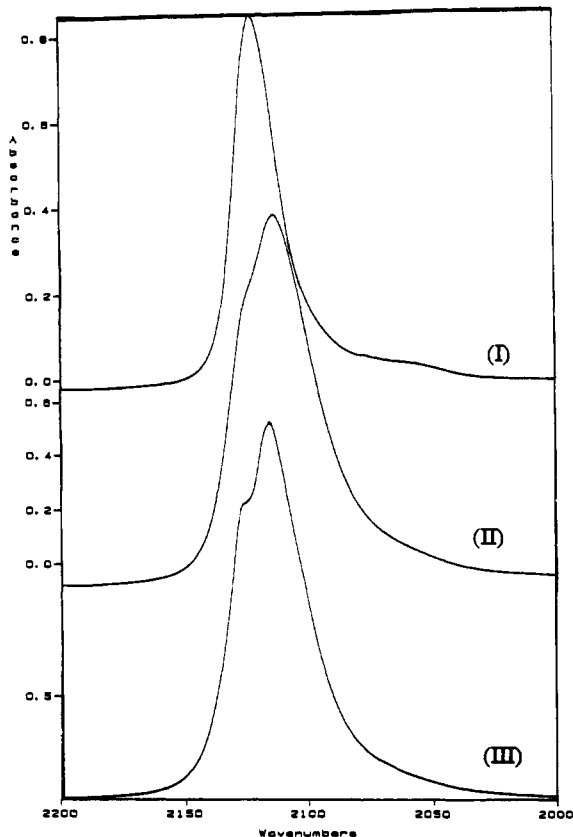


Figure 1. IR spectra in the CN stretching region of the three Pt[dmbp(CSN)₂] complexes discussed in the text: (top) complex I, the di-S-bonded complex, showing a single band ($\Gamma_{1/2} = 21 \text{ cm}^{-1}$) centered at 2122 cm⁻¹; (middle) complex II, the S,N-bonded homologue, which shows a broad band ($\Gamma_{1/2} = 48 \text{ cm}^{-1}$) centered at 2113 cm⁻¹ with a shoulder at 2125 cm⁻¹; (bottom) complex III, the di-N-bonded species, showing a single, asymmetric band ($\Gamma_{1/2} = 35 \text{ cm}^{-1}$) at 2117 cm⁻¹ and a partially resolved shoulder at 2127 cm⁻¹.

obvious shoulder on the high-energy side of the absorbance indicating the presence of another band. The lack of resolution of these bands has been attributed^{3a} to an accidental degeneracy of the two IR-allowed modes. The spectra in Figure 1 show that the anomalies associated with the bpy analogue are not observed in the case of the dmbp analogue, for which only an unresolved CN absorbance is observed for the S-bonded form. The slight asymmetry of the CN band indicates the possibility that this band originates from more than one absorbance. The width of this band ($\Gamma_{1/2} = 19 \text{ cm}^{-1}$) agrees well with the stretching mode in the corresponding yellow S-bonded bipyridine analogue ($\Gamma_{1/2} = 21 \text{ cm}^{-1}$).^{3b}

The infrared spectrum of II, obtained by heating the neat solid I, exhibits a very broad unresolved C-N stretch ($\Gamma_{1/2} = 40 \text{ cm}^{-1}$) centered at 2113 cm⁻¹, with a shoulder at 2125 cm⁻¹. The larger line width in II (about twice that of the corresponding red N-bonded bipyridine analogue (i.e. ~26 cm⁻¹)) is due to the simultaneous presence of both S- and N-bonded thiocyanate ligands. The evidence for this is detailed in the following discussion of the ¹⁵N MAS NMR results; *vide infra*.

Finally, the ν_{CN} stretching frequency of complex III, obtained by recrystallization of I from DMSO, appears as an unresolved absorbance multiplet, centered at 2117 cm⁻¹, with an obvious shoulder at 2127 cm⁻¹. It is clear, from the presence of the characteristic shoulder, that this band includes the IR-allowed symmetric and asymmetric stretching modes dictated by the C_{2v} symmetry of the molecule. These bands, as in the N-bonded bpy analogue, are not resolvable, presumably due to an accidental degeneracy of the symmetric and asymmetric IR-allowed modes.^{3b} In the context of the above summarized characteristic ranges, the small red shift (i.e. ~5 cm⁻¹) of the CN band, accompanying

(8) University of Washington Program for EXAFS Data Analysis. See also: Kincaid, B. M.; Shulman, R. In *Advances in Inorganic Biochemistry*; Parnall, D. W.; Wilkins, R. G., Eds.; Elsevier Pub. Co.: New York, 1980; Vol. 2, pp 303–309 and references therein.

(9) Mitchell, P. C. H.; Williams, R. J. P. *J. Chem. Soc.* 1960, 1912.

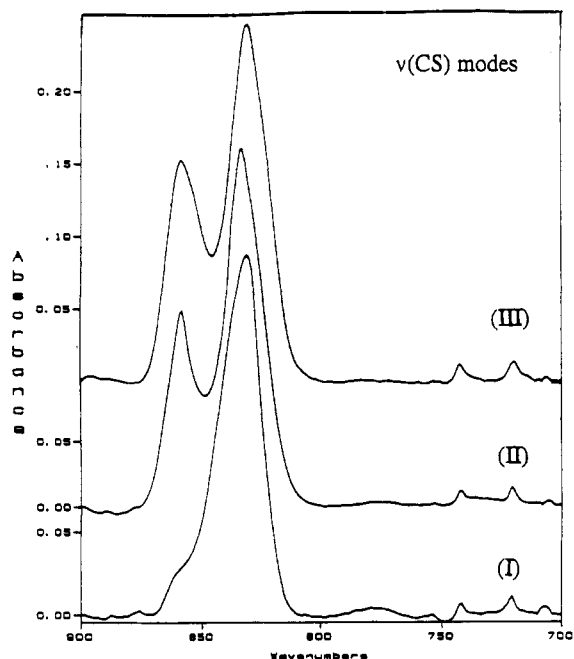


Figure 2. IR spectra of the three forms of Pt[dmbp(CSN)₂] in the ν_{CS} stretching region. The bottom trace is of the di-S bonded complex I and shows only a very weak absorbance due to the dmbp ligand at 859 cm^{-1} . The middle trace is of complex II obtained from the thermal conversion of the neat solid I and shows the ν_{CS} band superimposed on the dmbp ligand band at 859 cm^{-1} , arising from a single N-bonded thiocyanate per molecule. The top trace is of complex III, the di-N-bonded compound recovered from DMSO. The ν_{CS} band is centered at $\sim 857 \text{ cm}^{-1}$ and has approximately twice the integrated intensity (1.98:1.00) of the same band in the middle trace, indicative of di-N bonding in III.

the conversion of the S- to the N-bonded form, does not afford conclusive evidence as to the type of thiocyanate bonding that occurs in complexes II and III, and additional spectroscopic evidence is needed to elucidate the type of bonding present in these compounds.

Absorbances in the region between 900 and 700 cm^{-1} arise from the C-S stretching mode. Examination of this region for complex I showed no observable ν_{CS} stretching modes in either the S- or N-bonded range. The ν_{CS} band for complex I is either too weak to be observed or is masked by the absorbance of other more intense dmbp ligand modes.¹⁰ Inspection of the same range of the IR spectrum for complex II, indicated the presence of a Pt-NCS bonded species, as suggested by the appearance of a ν_{CS} band at 859.2 cm^{-1} as a shoulder of a dmbp ligand band (see Figure 2). Similarly, for complex III, a more intense band corresponding to the ν_{CS} stretching mode of an N-bonded thiocyanate species appears also as a shoulder at 858.2 cm^{-1} . Calculations of the relative ratios of integrated intensities for the ν_{CS} absorbances for compounds II and III (referenced to the dmbp ligand band at 828 cm^{-1}) reveal a 1.00:1.98 ratio. This ratio is in agreement with the hypothesis that there is presumably only a single ligand isomerization in complex II (i.e. ¹³C and ¹⁵N, separately) of the SCN ligand. The characteristic shifts of these bands as a result of isotopic substitution were observed but gave smaller than expected values on the basis of the reduced mass calculations.¹¹ The observed and calculated values, summarized in Tables 2 and 3, imply that ν_{CS} of the N-bonded species is effected by the N-atom of the thiocyanate ligand. The observed ν_{CS} frequencies of the ¹³C and ¹⁵N isotopically labeled samples,

Table 2. Infrared Data for the ¹³C-Labeled Forms of Pt[dmbp(CSN)₂] Discussed in the Text with All Data for KBr Pellets at 295 K Ratioed to a KBr Background

form	$\nu_{^{13}\text{CN}}$, cm^{-1}		$\nu_{^{13}\text{CS}}$, cm^{-1}		$\nu_{\text{N}^{13}\text{C-S}}$, cm^{-1}
	obsd	calcd	obsd	calcd	
-(SCN) ₂	2074	2077			
-(SCN)(NCS)	2068	2071 ^a	846.8 ^b	834.8	848.0
-(NCS) ₂	2070	2071	843.8	834.8	848.2

^a Both ν_{CN} stretches calculated from the corresponding ¹²C values.

^b The ν_{CS} stretch for the ¹³C-labeled species appears as a shoulder on a mode of the dmbp ligand.

Table 3. Infrared Data for the ¹⁵N-Labeled Forms of Pt[dmbp(CSN)₂] Discussed in the Text with All Data for KBr Pellets at 295 K Ratioed to a KBr Background

form	$\nu_{^{15}\text{N}}$, cm^{-1}		ν_{CS} , cm^{-1}		$\nu_{^{15}\text{NC-S}}$, cm^{-1}
	obsd	calcd	obsd	calcd	
-(SCN) ₂	2085	2089			
-(SCN)(NCS)	2087, v br	2091	848.0 ^a	794.3	850.2
-(NCS) ₂	2096, sh	2097	845.7	792.4	848.2
	2088	2086			

^a The ν_{CN} stretch appears as a shoulder on a dmbp ligand band.

compared with the natural-abundance species, can be accounted for, assuming that the CN moiety acts as a single entity of mass 26 units. This assumption is reasonable in view of the higher CN bond order (i.e. approximately third order) than would be expected for a metal-N-bonded thiocyanate complex.¹²

II. NMR Spectra. NMR studies of metal-thiocyanate complexes are most appropriately studied using ¹³C and ¹⁵N probes. With respect to ¹³C spectra, the resonance arising from the carbon atom of the thiocyanate ligand generally appears below ~ 120 ppm for the S-bonded species and above ~ 120 ppm for the N-bonded form;¹³ however, the assignment of the type of thiocyanate bonding based solely on ¹³C data can at times be misleading, due to overlap of the chemical shift ranges.¹⁴ More definitive are the ranges associated with the ¹⁵N thiocyanate resonances; the S-bonded complex appears as a singlet much further downfield (i.e. >200 ppm) than the "triplet" N-bonded isomer,¹⁵ i.e. in the ¹⁵N NMR of the Pt-N-bonded forms arising from $s = 1/2$ for both the ¹⁹⁵Pt and ¹⁵N nuclei. This coupling is not seen in the ¹⁵N NMR of the Pt-SCN-bonded complexes because of $s = 3/2$ for the ³²S atom. The ¹⁵N data thus afford more conclusive evidence as to the type of thiocyanate bonding.

¹³C Solution Data. The ¹³C solution experiments were performed only on the S-bonded species for two reasons: (1) the insolubility of the "polymeric" N-bonded forms and (2) the re-isomerization of the N-bonded complexes to the S-bonded species which occurs upon dissolution in NMP.¹⁶ All three dmbp complexes in NMP solution were yellow in color and exhibited S¹³CN resonances at ~ 114 ppm, corresponding to S-bonded species.¹⁶ No significant chemical shift differences were observed for the dmbp ligand carbon atoms of the thiocyanate complex compared with the Pt[dmbp(Cl)₂] analogue.

¹⁵N MAS Data. The ¹⁵N MAS NMR data provided the most convincing spectroscopic evidence for the type of thiocyanate bonding that occurs in these Pt(II) amine complexes. The ¹⁵N MAS NMR spectrum of sample I showed a single resonance at

(10) See Figure 2. The out-of-plane hydrogen bonding mode of the dmbp ligand appears at approximately 830 cm^{-1} .

(11) See, for example: Ebsworth, E. A. V.; Rankin, D. W. H.; Cradock, S. *Structural Methods in Inorganic Chemistry*; Blackwell Scientific Public.: Oxford, U.K., 1987; p 217 ff. Vemulapalli, G. K. *Physical Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1993; p 408 ff, p 434 ff.

(12) Reference 1c. See also: Brock, C. P.; Huckaby, J. L.; Attig, T. G. *Acta Crystallogr.* **1984**, *B40*, 595. MacDougall, J. F.; Nelson, J. H.; Fultz, W. C.; Burmeister, J. L.; Holt, E. M.; Alcock, N. W. *Inorg. Chim. Acta* **1982**, *63*, 75 and references therein.

(13) Kargol, J. A.; Crecey, R. W.; Burmeister, J. L. *Inorg. Chem.* **1979**, *18*, 2532.

(14) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heydon: London, 1978.

(15) (a) Yavari, I.; Staral, J. S.; Roberts, J. D. *Org. Magn. Reson.* **1979**, *12*, 340. (b) Gifford, M.; Cousseau, J.; Martin, G. J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 157.

(16) Coyer, M. J. Ph.D. Thesis, Rutgers University, 1991.

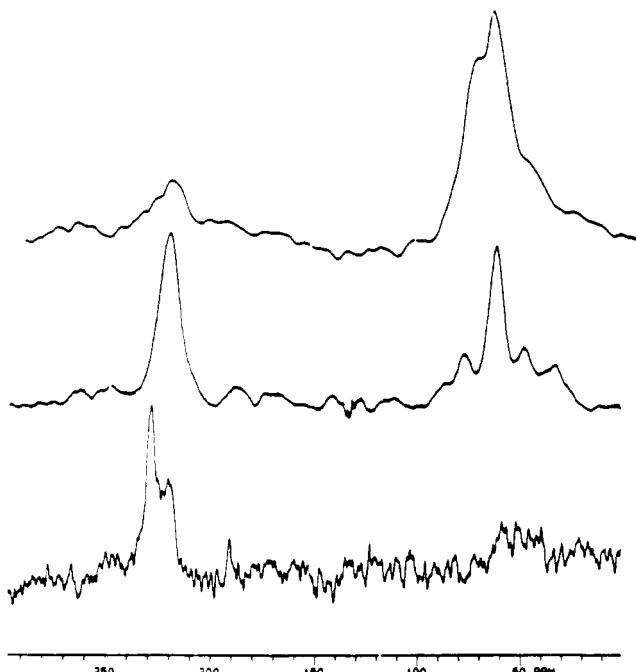


Figure 3. ^{15}N MAS NMR spectra of $\text{Pt}[\text{dmdbp}(\text{CSN})_2]$. The bottom spectrum represents the di-S bonded species I with a single resonance at 228.0 ppm. The middle spectrum is of II, obtained by thermal conversion, and shows the presence of both S- and N-bonded thiocyanates as resonances at 227.0 and 63.1 ppm, respectively. The top spectrum of III is diagnostic of di-N bonding by the appearance of a single resonance at 64.5 ppm. The small peak at ~ 228 ppm corresponds to a small amount of the S-bonded species, present as an equilibrium product. The $^1J\{^{195}\text{Pt}-^{15}\text{N}\}$ coupling constants for complexes II and III are summarized in Table 4.

Table 4. ^{15}N MAS Chemical Shifts for the Thiocyanato Ligand of the $\text{Pt}[\text{dmdbp}(\text{CSN})_2]$ Complexes Discussed in the Text with All Shifts Relative to $[\text{NH}_3]_2\text{SO}_4$

conversion method	form	^{15}N shift, ppm	$^1J\{^{195}\text{Pt}-^{15}\text{N}\}$, Hz
none	$-(\text{SCN})_2$	228.05	na
thermal ^a	$-(\text{SCN})(\text{NCS})$	227.0, 63.1	220.5, 237.8
DMSO ^b	$-(\text{NCS})_2$	64.50	190.0, 90.0 ^c

^a Neat solid heated twice at $T \geq 160$ °C for ca. 1 h. ^b The S-bonded equilibrium product appears above 220 ppm. ^c Resolution of the $^1J\{^{195}\text{Pt}-^{15}\text{N}\}$ coupling constants is poor.

228.1 ppm, Figure 3, which, according to the reported systematics,¹⁷ is indicative of S-bonding. The splitting observed for this peak may be attributable to solid-state sampling effects.¹³ There are no observable resonances in any other region of the spectrum of I, indicating that only S-bonding exists in this complex. The ^{15}N MAS NMR spectrum of II, obtained by thermal conversion of neat solid I, exhibited a pair of resonances at 227.0 and 63.1 ppm, in an approximate 1:1 integrated ratio, which seems to indicate that incomplete (i.e. single ligand) isomerization to the $\text{Pt}-(\text{SCN})(\text{NCS})$ form had occurred. This result is consistent with the IR data obtained in the investigation of the CS stretching region of complex II. The resonance at 63.1 ppm, due to $\text{Pt}-\text{NCS}$ bonding, was accompanied by "satellite peaks" due to the 1J coupling of the ^{195}Pt and ^{15}N nuclei (i.e. $s = 1/2$ for both nuclei). The $^1J\{^{195}\text{Pt}-^{15}\text{N}\}$ values of ~ 225 Hz agree well with reported values.¹⁸ To be assured that the solid-state conversion of I to II was complete, sample II was reheated for an additional 1 h at ~ 170 °C and the ^{15}N MAS NMR experiment was repeated.

(17) Pregosin, P. S.; Streit, H.; Venanzi, L. M. *Inorg. Chim. Acta* **1980**, *38*, 237.

(18) (a) Kerrison, J. S.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1977**, 861. (b) Pregosin, P. S.; Omura, H.; Venanzi, L. M. *J. Am. Chem. Soc.* **1973**, *95*, 2047. (c) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1985**, *24*, 2685.

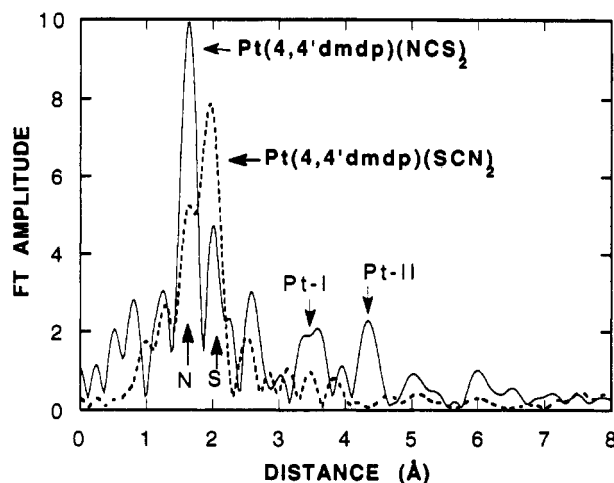


Figure 4. The $k^3\chi(k)$ Fourier Transform (FT) spectra for $\text{Pt}[4,4'-(\text{CH}_3)_2-2,2'\text{-bpy}(\text{NCS})_2]$ (solid curve) and $\text{Pt}[4,4'-(\text{CH}_3)_2-2,2'\text{-bpy}(\text{SCN})_2]$ (dashed curve). The N-, S-, and Pt-related features are labeled (see text).

The intensity ratio of the two resonances remained unchanged within experimental error. This suggests that the thermal conversion of I to II was complete after the initial heating and did not progress further under these conditions. Finally, complex III, obtained by recrystallization of I from DMSO, exhibited a single resonance at 64.5 ppm with the corresponding $^1J\{^{195}\text{Pt}-^{15}\text{N}\}$ coupling constants, indicating full thiocyanate isomerization to the di-N-bonded species. A weak resonance at ~ 228 ppm is presumably due to the presence of a small amount of the S-bonded species which occur as a result of the recrystallization process.

Thus, the ^{15}N MAS NMR results give clear evidence for the three types of thiocyanate linkage which can exist for $\text{Pt}[\text{dmdbp}(\text{CSN})_2]$ complexes. The NMR results also agree with the infrared spectral interpretations regarding the ν_{CS} stretching frequencies of the three forms of the title complexes. Similar results for mixed thiocyanate ligand isomerization have been reported for the dmdbp-palladium analogue.^{3a}

III. Pt-L₃ EXAFS. Although it is evident from the IR and ^{15}N MAS NMR results that linkage isomerization occurs in $\text{Pt}[\text{dmdbp}(\text{CSN})_2]$ complexes, no information regarding the stacking properties of these compounds can be extracted from these data. The technique of Pt-L₃ EXAFS has been applied earlier to the analogous bipyridine complexes to identify Pt stacking.^{3b} Results from similar experiments for the dmdbp complexes are reported herein.

EXAFS analysis is based on the normalized wavenumber (k) dependent oscillation of the X-ray absorption coefficient about the average $\chi(k)$.^{19,20} The Fourier transform of the weighted function $k^n\chi(k)$ to real space (denoted hereafter as FT) exhibits peaks at positions corresponding to backscattering maxima from atomic near-neighbor shells. Thus, FT curves convey information similar to a radial distribution function (RDF) but with two differences: the FT peak intensities involve both the atomic backscattering cross section and the k -weighting factor,^{19,20} the FT peak positions involve an atomic backscattering phase shift and, hence, the FT peaks occur at distances shifted from the true interatomic separation.²¹ The $k^3\chi(k)$ FT curves for the title complexes are shown in Figure 4. The interpretations of the origins of the central features in these spectra have been labeled in Figure 4. In the discussion to follow, the spectral features will be examined in order of increasing interatomic distances.

(19) Lee, P. A.; Citrin, P.; Eisenberger, P.; Kincaid, B. *Rev. Mod. Phys.* **1981**, *53*, 769 and references therein.

(20) Teo, B.-K.; Kijima, K.; Bau, R. S. *J. Am. Chem. Soc.* **1978**, *100*, 621.

(21) Hitchcock, A. P.; Lock, C. J.; Lippert, B. *Inorg. Chim. Acta* **1986**, *124*, 101.

(22) Stern, E. A.; Sayers, D. E.; Lytle, F. *Phys. Rev. B* **1975**, *11*, 4836.

Linkage Isomerization of the thiocyanate ligand is evident from a comparison of the FT spectra in the 1.3–2.4-Å range. The N-bonded compound (solid line) exhibits a strong N-related peak near 1.7 Å due to the N backscattering both from the N-bonded thiocyanate and the two nitrogens from the bidentate amine ligand. In contrast, the spectrum of the di-S-bonded complex (dashed curve) manifests an intense S-peak near 1.9 Å, with an unresolved N-peak near 1.7 Å. The roughly 50% reduction in the intensity of the N-feature between the di-N- and di-S-bonded materials is completely consistent with the assumption of the flipping of the thiocyanate ligands. The residual S-feature in the spectrum of the di-N-bonded complex is consistent with the presence of a small amount of a Pt–SCN impurity which remains as an equilibrium product resulting from the conversion in DMSO, in agreement with the ^{15}N MAS-NMR results discussed in the previous section.

The N and S features are essentially the same as observed previously (as noted above) in the study of the yellow and red forms of $\text{Pt}[\text{bpy}(\text{SCN})_2]$ (bpy = 2,2'-bipyridine). In that study, a two-shell fitting procedure yielded a Pt–N distance of 1.99 ± 0.02 Å and a Pt–S distance of 2.24 ± 0.02 Å. Within the limitations of the fitting method, the compounds examined in the present study manifest identical bond lengths.

Turning to the FT features in Figure 4 lying beyond 2 Å, it should be observed that although the Debye–Waller factor reduction¹⁹ dampens such features, three spectral characteristics are worth noting. The FT spectral intensity in the 2.2–2.8-Å range is related to the four carbon atoms of the bpy ligand which lie between 2.90 and 2.96 Å from the central absorbing Pt atom. Also notable in Figure 4 is the appearance of two features above 3 Å in the N-bonded form, where the S-bonded form spectrum is devoid of structure. In the earlier study^{3b} similar Pt–Pt scattering features were observed as a result of the conversion from N- to S-bonding of the thiocyanate ligand. In analogy, in the present instance, these features have been labeled Pt_I and Pt_{II} in Figure 4.

Turning first to the Pt_I feature, confirmation that this originates from a Pt–Pt interaction is based on a filtered back-transformation which is illustrated in Figure 5. The maximum of the amplitude envelope of the Pt_I back-FT is at ~ 13 Å⁻¹, indicative of a high- k -dependent (i.e. high Z) Pt atom.²¹ The structure below 8 Å⁻¹ is probably due to contributions from the amplitude function of overlapping peaks partially included in the back-FT window. It should be noted that both the outer C atoms of the bpy moiety and the N atoms of the neighboring stacked Pt atoms could conceivably make contributions in this range.

Determination of the interatomic distance related to this Pt_I feature has been carried out by a single-shell fitting method.²³ The standard for this fit was derived from a single-atom scattering calculation with a central Pt atom which is 2-fold coordinated to two Pt atoms. This fit for the Pt_I feature yielded a Pt–Pt distance of 3.63 ± 0.02 Å. The coordination number appropriate in this fit is rather uncertain and tied closely to the Debye–Waller factor; a coordination number of 1 cannot be ruled out.

The 3.63-Å distance for the Pt–Pt coordination determined from the Pt_I feature corresponds to the typical distance associated with stacking of adjacent square-planar Pt moieties. It should be noted, however, that this Pt–Pt stacking distance (Pt_I) is 0.39 Å longer than that in the $\text{Pt}[\text{bpy}(\text{SCN})_2]$ analog reported earlier.^{3b} This result is consistent with the hypothesis that the Pt–Pt stacking distance in the methyl-substituted analogue would be larger than in the unsubstituted complex because of the steric influence of the methyl groups. A similar observation was seen in the Pt–Pt stacking distances found in the comparison of the single-crystal X-ray diffraction analysis data for the $\text{Pt}(\text{L})-$

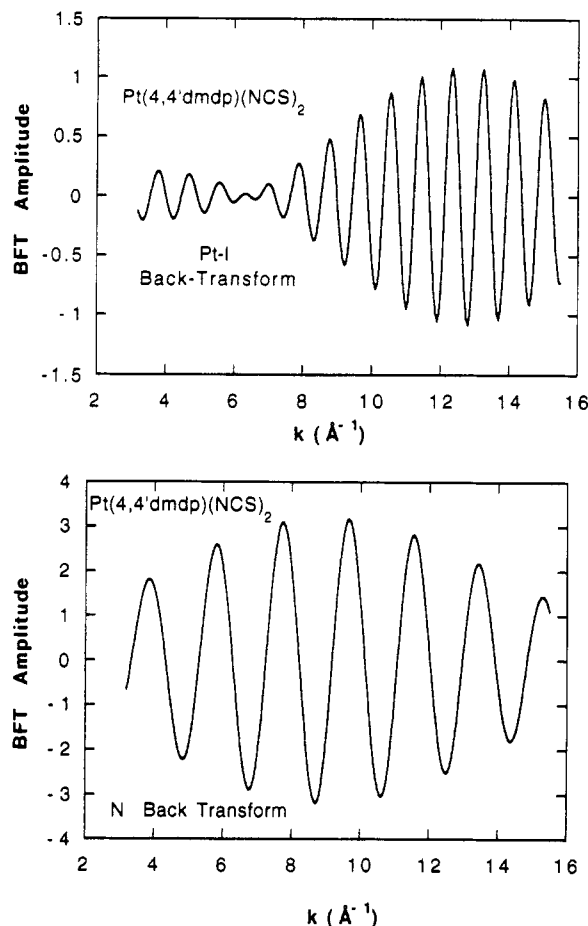


Figure 5. (a) Top: Filtered back-Fourier transform of the Pt_I feature of the FT spectrum of $\text{Pt}[4,4'-(\text{CH}_3)_2-2,2'\text{-bpy}(\text{NCS})_2]$ (Figure 4). The window for the back-transform was $2.90 \leq R \leq 3.64$ Å. The envelope of the oscillations peaking at high k (i.e. near 13 Å⁻¹) is a signature of high Z (in this case, Pt) backscattering. (b) Bottom Filtered back-Fourier transform of the N feature of the FT spectrum of $\text{Pt}[4,4'-(\text{CH}_3)_2-2,2'\text{-bpy}(\text{NCS})_2]$ (Figure 4). The back-transform window was $1.38 \leq R \leq 1.94$ Å.

(NCO)₂] complexes, where L = bpy²⁴ and dmbp.²⁵ The Pt–Pt distance in the methyl-substituted isocyanate complex is ~ 0.03 Å longer compared to the unsubstituted complex. These isocyanate complexes stack in a configuration with only a single Pt–Pt distance, presumably corresponding to the Pt_I features in the thiocyanate homologues. *It is therefore concluded that the longer Pt–Pt distance in the dmbp–(NCS)₂ complex compared to the bpy–(NCS)₂ complex is due to the steric hindrance induced by the methyl groups.*

Finally, addressing the Pt_{II} feature, it is noted that the back-FT of this feature does not peak at as high as k as the Pt_I back-transform, so that its identification as due to a Pt–Pt scattering process is less definitive. This smaller k_{max} may be attributable to a larger thermal and structural Debye–Waller factor dampening at high k , which shifts the back-transform envelope to lower k values. Fitting the Pt_{II} feature to a single shell, as above, yielded a Pt–Pt distance of 4.48 ± 0.05 Å. This distance is essentially the same as the corresponding Pt–Pt distance calculated for the red form of $\text{Pt}[\text{bpy}(\text{NCS})_2]$.^{3b} Thus, it appears likely that the second or “longer” Pt–Pt distances in these complexes are too large to be affected by methyl substitution at the 4- and 4'-positions.

In addition to the information obtained from the Pt-EXAFS data about the Pt–Pt bonding properties of these complexes, these

(23) Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135. Mustre de Leon, J.; Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev.* **1991**, *B44*, 4146.

(24) Coyer, M. J.; Herber, R. H.; Cohen, S. *Inorg. Chim. Acta* **1990**, *175*, 47.

(25) Coyer, M. J.; Herber, R. H.; Cohen, S. *Acta Crystallogr.* **1991**, *C47*, 1376.

results also provided persuasive evidence for the origin of the color changes observed in these complexes. Since analysis of the title complexes showed that solvation does not occur in these materials, the possibility of hydration⁵ being the source of the polychromic properties of these complexes can be eliminated. Furthermore, although complete linkage isomerization occurs in the conversion of complex I to III, no visible color change was observed in this step. *These observations make Pt-Pt interaction the most probable origin of the polychromic properties of these Pt[(L)(CSN)₂] complexes.* From the results of the study of the dmbp derivatives, it may be concluded that the methyl group steric hindrance inhibits the approach of adjacent molecules (i.e.

Pt-Pt molecular orbital interaction) sufficiently so that the electronic spectra are essentially unaffected by the isomerization.

In summary, the Pt-L₃ EXAFS results elucidate two properties of the title complexes: (1) A significant Pt-Pt bond exists in the di-N-bonded thiocyanate complexes in the neat solids. The shorter distance (Pt_I) is affected by substitution of the bidentate amine ring systems, whereas the longer distance (Pt_{II}) seems unaffected, in comparison to the bpy analogue. (2) The color of these Pt[(L)(CSN)₂] complexes can be associated with the strength of the Pt-Pt (i.e. Pt_I) interaction as reflected by the Pt-Pt distances.