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^{15}N, ^{31}P and ^{195}Pt NMR Studies of Thiocyanate Complexes

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^{15}N-NMR studies of thiocyanate metal complexes show that chemical shifts are diagnostic for determining whether this ligand is N- or S-bonded. ^{195}Pt- and, to a lesser extent, ^{31}P-NMR parameters of complexes containing these nuclei are also diagnostic for the mode of coordination of the thiocyanate ion. Several linkage isomers of the $[Pt(^{15}NCS)_n(SC^{15}N)_{4-n}]^{2-}$ ion are shown to exist in methylene chloride solution.

Introduction

The ambidentate thiocyanate ligand, SCN^-, is well known to coordinate to transition metals either through nitrogen or sulfur [1]. The factors affecting the mode of coordination are: 1) the nature of the metal, 2) the nature of the remaining ligands within the coordination sphere, 3) the steric size of the other ligands and 4) the solvent. The interplay of these factors is such that complexes which contain both N and S bound thiocyanate ligands are possible. The chemistry of SCN^- complexes has been recently reviewed [2].

A variety of spectroscopic methods have been employed in an attempt to distinguish between the two modes of coordination. These include infra-red [3], X-ray [4] and NQR [5] methods as well as nitrogen-14 [6] and phosphorus-31 [7] NMR spectroscopy.

Our previous NMR measurements [8, 9] on enriched nitrogen-15 (I = ½, natural abundance = 0.36%) complexes have led us to believe that an NMR study of this nucleus can provide a useful complement to ^{14}N NMR. Specifically, the ^{15}N method is superior to ^{14}N NMR when the latter affords extremely broad signals and/or when a broadened resonance obscures the signal of a less intense resonance of similar chemical shift. The utility of ^{15}N NMR in thiocyanate chemistry is based on the expectation [6, 8] that coordination of the nitrogen lone-pair will affect a relatively large increase in the ΔE term of the paramagnetic screening constant*, σ_p, equation 1,

$$\sigma_p(^{15}N) \propto -(1/\Delta E) \qquad (1)$$

resulting in an upfield (lower frequency) shift

$$\nu(^{15}N) \propto (1 - \sigma_p) \qquad (2)$$

(see equation 2), whereas for sulfur coordination, the electron density of nitrogen will be changed to a lesser extent. In order to test this hypothesis, and facilitate the measurements, we have synthesized a series of thiocyanate complexes enriched with >95 atom% ^{15}N and measured their ^{15}N NMR spectra. Those thiocyanate complexes which contain other readily measured I = ½ nuclei, *e.g.* ^{31}P and ^{195}Pt are expected to couple to the ^{15}N, and provide an additional structural probe. For the specific case of platinum–thiocyanate complexes, the metal resonance (^{195}Pt, I = ½; natural abundance = 33.7%) should provide yet another tool for determining the mode of coordination since it is well known that substitution of sulfur for nitrogen results in an upfield shift of the ^{195}Pt resonance by several hundred ppm [10]. We report here our ^{15}N, ^{195}Pt and ^{31}P NMR results for our enriched ^{15}N thiocyanate complexes.

Experimental

^{15}N, ^{31}P and ^{195}Pt NMR spectra were measured on samples contained in 10 mm tubes using a Bruker HX-90 E spectrometer. The basic frequency of 19.3 MHz for the ^{195}Pt measurements was derived from a Bruker frequency synthesizer, whereas for the ^{15}N

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*ΔE is the mean triplet excitation energy approximation. We presume that nitrogen coordination increases the excitation energy of one or more transitions associated with the nitrogen lone pair. *E.g.* a low lying n → π^* is removed.

TABLE I. NMR Parameters[a] for the Thiocyanate Complexes.

^{15}N Data		
Complex	$\delta\,^{15}N$	$\Delta\delta$
S-Bound		
$(Bu_4N)_2[Pd(SC^{15}N)_4]$	225.3	36.3
$(Bu_4N)_2[Pt(SC^{15}N)_4]$	224.1	35.1
$(Bu_4N)_2[Hg(SC^{15}N)_4]$	214.5	25.5
N-Bound		
$(Bu_4N)_2[Zn(^{15}NCS)_4]$	131.1	57.3
$(Bu_4N)_2[Cd(^{15}NCS)_4]$	148.7	40.3
trans-$[Pt(^{15}NCS)_2(PBu^n_3)_2]$	43.2	145.8
trans-$[Pt(^{15}NCS)(SC^{15}N)(PBu^n_3)_2]$	71.9	117.1

^{195}Pt Data			
Complex	^{195}Pt	$^1J(^{195}Pt, ^{15}N)$	$^3J(^{195}Pt, ^{15}N)$
$(Bu_4N)_2[Pt(SC^{15}N)_4]$	−3961		12
$(Bu_4N)_2[Pt(^{15}NCS)(SC^{15}N)_3]$	−3431	525	12
trans-$[Pt(^{15}NCS)_2(SC^{15}N)_2]$[b]	−2805	617	10
trans-$[Pt(^{15}NCS)_2(PBu^n_3)_2]$[c]	−3881	589	
trans-$[Pt(^{15}NCS)(SC^{15}N)(PBu^n_3)_2]$[d]	−4244	491	20
trans-$[Pt(SC^{15}N)_2(PBu^n_3)_2]$[e]	−4526		20

[a] ^{15}N and ^{195}Pt chemical shifts are given in ppm relative to $^{15}NH_4Cl(aq)$ (±0.3) and Na_2PtCl_6 (±0.5), respectively. A negative sign indicates a shift to higher field (lower frequency). Coupling constants are in Hz (±3). [b] *Trans*-isomer assigned based on $^1J(^{195}Pt, ^{15}N)$ value. [c] $^1J(^{195}Pt, ^{31}P) = 2207$ Hz; $^2J(^{31}P, ^{15}N) = 4.5$ Hz. [d] $^1J(^{195}Pt, ^{31}P) = 2244$ Hz; $^2J(^{31}P, ^{15}N) = 4.4$ Hz. [e] $^1J(^{195}Pt, ^{31}P) = 2271$ Hz.

and ^{31}P measurements the built-in units functioning at 9.12 and 36.43 MHz sufficed.

Preparation of the Complexes

The unlabelled thiocyanate complexes were prepared first, using an excess, and subsequently, using a stoichiometric amount of thiocyanate ligand. The complexes obtained showed I.R. spectra and melting points in agreement with the literature. The preparations were then repeated using stoichiometric amounts of $NaSC^{15}N$ as shown below.

$(Bu_4N)_2[Zn(^{15}NCS)_4]$

An aqueous solution of $NaSC^{15}N$ (0.131 g; 1.60 mmol) was added to $ZnSO_4 \cdot 7H_2O$ (0.115 g; 0.40 mmol) dissolved in a minimum amount of water and the resulting colorless solution stirred at room temperature for 2 h. Addition of 2 ml of a 0.4 *M* aqueous solution of $(Bu_4N)NO_3$ afforded a white precipitate which was extracted into CH_2Cl_2. Drying over $MgSO_4$ followed by filtration and concentration gave 0.297 g of a yellow oil which eventually solidified (94.5% yield).

$(Bu_4N)_2[Cd(SC^{15}N)_4]$

Solid $NaSC^{15}N$ (0.389 g; 4.00 mmol) was added to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.308 g; 1.00 mmol) in 5 ml of water and the solution stirred for several minutes. Addition of an aqueous solution of $(Bu_4N)NO_3$ (prepared by filtering the suspension from Bu_4NCl (0.556 g; 2.00 mmol), $AgNO_3$ (0.340 g; 2.00 mmol) and 5 ml of H_2O) was followed by extraction of the resulting solid with CH_2Cl_2. Drying of the CH_2Cl_2 layer followed by filtration and concentration gave 0.648 g of product (78.2% yield).

$(Bu_4N)_2[Hg(SC^{15}N)_4]$

To a concentrated solution of $NaSC^{15}N$ (0.164 g; 2.00 mmol) in water was added a concentrated aqueous solution of $HgCl_2$ (0.136 g; 0.50 mmol) and the resulting suspension stirred at room temperature for 24 h. The remaining precipitate was dissolved by the addition of further water followed by addition of an aqueous solution containing two equivalents of $(Bu_4N)NO_3$ (prepared by filtering the suspension which results from Bu_4NCl (0.278 g; 1.00 mmol), $AgNO_3$ (0.170 g; 1.00 mmol) and a minimum volume of water).

Extraction of the resulting precipitate with CH_2Cl_2, followed by drying ($MgSO_4$), filtration and concentration afforded 0.437 g of a yellow oil which slowly crystallized (94.8% yield).

$(Bu_4N)_2[Pd(SC^{15}N)_4]$

Solid $Pd(NO_3)_2 \cdot 2H_2O$ (0.107 g; 0.40 mmol) was added to a solution of $NaSC^{15}N$ (0.131 g; 1.60 mmol) in 1 ml of H_2O. The red suspension which resulted was diluted with 15 ml H_2O and stirred for 2 h at room temperature. Addition of 2 ml of a 0.4 *M* aqueous solution of $(Bu_4N)(NO_3)$ was followed by extraction with CH_2Cl_2. Drying of $MgSO_4$ followed by filtration and concentration afforded 0.321 g of product as a dark red solid (97.0% yield)).

$(Bu_4N)_2[Pt(SC^{15}N)_4]$

A solution prepared from K_2PtCl_4 (0.208 g; 0.50 mmol) and $NaSC^{15}N$ (0.164 g; 2.00 mmol) in 2 ml of H_2O was stirred at room temperature for 2 h. To this was added a solution of Bu_4NCl (0.278 g; 1.00 mmol) in 4 ml of CH_2Cl_2 followed by vigorous stirring for several hours. Extraction with additional CH_2Cl_2 followed by drying ($MgSO_4$), filtration and concentration gave 0.434 g of product (94.8% yield).

trans-*$[Pt(^{15}NCS)_n(SC^{15}N)_{2-n}(PBu^n_3)_2]$*

Mixing solutions of *trans*-$[PtCl_2(PBu^n_3)_2]$ (0.983 g; 1.467 mmol) in 10 ml ethanol and $NaSC^{15}N$ (0.241 g; 2.93 mmol) in 4 ml ethanol precipitates NaCl and product almost instantaneously. The reaction mixture was taken to dryness and then extracted with CH_2Cl_2. Filtration to remove NaCl followed by concentration and drying i.V. gave 1.032 g of product (98.1% yield).

Results and Discussion

^{15}N NMR

In Table I we show the ^{15}N chemical shifts for a series of complexes containing ^{15}N-thiocyanate ligands. For the complex anions $Pd(SC^{15}N_4^{2-}$, $Pt(SC^{15}N)_4^{2-}$ and $Hg(SC^{15}N)_4^{2-}$, in which the thiocyanate is believed to be coordinated through sulfur, we observe ^{15}N resonances between 214.5 and 225.3 ppm. These represent coordination chemical shifts, $\Delta\delta$, [= δ(complex) – δ(free ligand)] ranging from +25.5 to +36.3 ppm. This downfield shift brings the signals into the area of nitrile resonances (*e.g.* $Ph{-}C{\equiv}^{15}N$, δ = 231.0 ppm [11]), in keeping with the formulation $L_nM{-}S{-}C{\equiv}^{15}N$. For the anions $Zn(^{15}NCS)_4^{2-}$ and $Cd(^{15}NCS)_4^{2-}$ in which the thiocyanate is reported [2] to be coordinated to nitrogen, the ^{15}N signals shift to *higher* field at 131.1 and 148.7 ppm, respectively. These represent coordination chemical shifts of –57.3 and –40.3 ppm. The phosphine complex *trans*-$[Pt(^{15}NCS)_n(SC^{15}N)_{2-n}(PBu^n_3)_2$ shows nitrogen resonances at 43.2 ppm and 71.9 ppm, which represent $\delta\Delta$ values of –145.8 ppm and –117.1 ppm, $^1J(^{195}Pt, ^{15}N)$ = 589 Hz and 491 Hz, respectively clearly indicating nitrogen coordination of thiocyanate ligands.

We assign the signal at 43.2 ppm to *trans*-$[Pt(^{15}NCS)_2(PBu^n_3)_2]$ and that at 71.9 ppm to *trans*-$[Pt(^{15}NCS)(SC^{15}N)(PBu^n_3)_2]$*. This assignment is supported by the ^{195}Pt data which we discuss later. In a solution containing primarily *trans*-$[Pt(NCS)_2(PEt_3)_2]$ a second isomer formulated as *trans*-$[Pt(NCS)(SCN)(PEt_3)_2]$ has been observed [12].

As noted above, a freshly prepared solution of $(Bu_4N)_2[Pt(SC^{15}N)_4]$ in methylene chloride affords a single ^{15}N resonance at 224.1 ppm, flanked by ^{195}Pt satellites. The platinum–nitrogen coupling of 12 Hz is consistent with the presence of only S-bonded thiocyanate ligands. Remeasurement of this sample after several months revealed new ^{15}N signals at 83.8, 50.3 and 40.8 ppm, suggestive of N-bound thiocyanate, as well as additional signals in the region around 224 ppm. Although we were not able to locate the corresponding ^{195}Pt satellites for the new resonances, clearly, the possibility of linkage isomerism is indicated. This problem is also discussed further in the next section.

We conclude from our ^{15}N data that, for thiocyanate complexes, ^{15}N NMR provides a general method for assessing the mode of coordination of this ligand. The large upfield coordination chemical shift of the N-bound isomer contrasts markedly with the moderate downfield shift on S-coordination, allowing a clear distinction between the two possibilities. Further, ^{15}N NMR can provide evidence for the existence of small quantities of linkage isomers which might go unnoticed using other spectroscopic forms. Large high field ^{15}N coordination chemical shifts have been found for imine [13] and azo [8] complexes of platinum, suggesting that this may be a general phenomenon for sp^2 nitrogen bound to metals.

^{195}Pt NMR

Our inability to satisfactorily characterize all the components of the solutions of $(Bu_4N)_2[Pt(^{15}NCS)_n(SC^{15}N)_{4-n}]$ and *trans*-$[Pt(^{15}NCS)_n(SC^{15}N)_{2-n}(PBu^n_3)_2]$ prompted us to measure the ^{195}Pt NMR spectra of these solutions. For the former complex we find at least** four sets of signals, three of which are shown in Fig. 1.

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*The failure to observe the non-coordinated ^{15}N resonance of the S-bonded thiocyanate in this complex suggests a much longer T_1 for this nitrogen relative to the coordinated nitrogen.

**There are other smaller sets of resonances which we cannot readily identify.

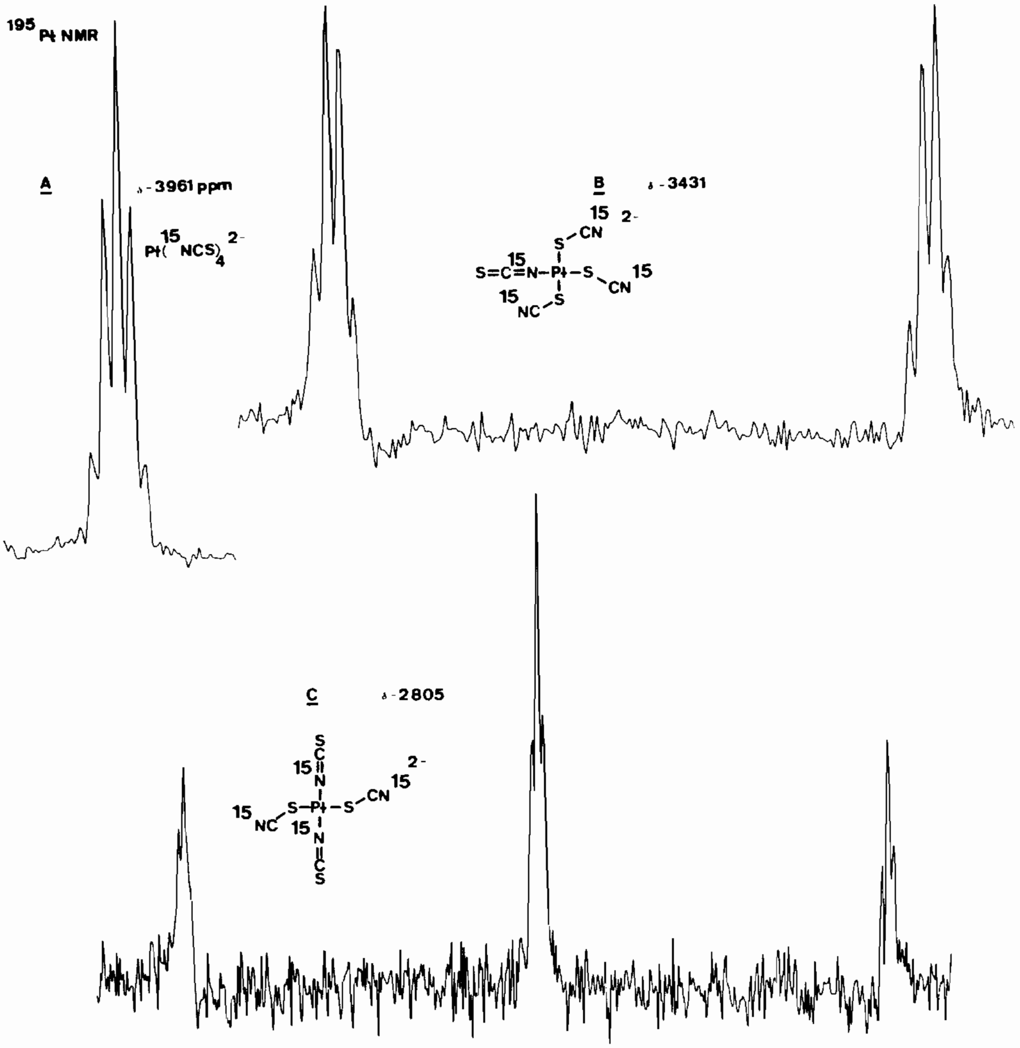

Fig. 1. The ^{195}Pt resonance from the A) $[Pt(^{15}NCS)_4]^{2-}$, B) $[Pt(^{15}NCS)(SC^{15}N)_3]^{2-}$, and C) *trans*-$[Pt(^{15}NCS)_2(SC^{15}N)_2]^{2-}$ anions. The data were obtained from an aged CH_2Cl_2 solution of the complex $(Bu_4N)_2[Pt(^{15}NCS)_n(SC^{15}N)_{4-n}]$.

The pentet at –3961 ppm represents the $[Pt(SC^{15}N)_4]^{2-}$ ion and stems from the coupling of four equivalent ^{15}N atoms. The appearance of a doublet of quartets at –3431 ppm stemming from one large $^1J(^{195}Pt, ^{15}N)$ coupling and three small $^3J(^{195}Pt, ^{15}N)$ couplings is consistent* with an isomer of the type $[Pt(^{15}NCS)(SC^{15}N)_3]^{2-}$. Another group of signals contains a triplet of triplets centered at –2805 ppm, derived from two large $^1J(^{195}Pt, ^{15}N)$ couplings and two much smaller $^3J(^{195}Pt, ^{15}N)$ interactions to which we assign the structure *trans*-$[Pt(^{15}NCS)_2(SC^{15}N)_2]$. The deshielding of these platinum resonances by 530 and 1156 ppm as a thiocyanate is stepwise inverted from S- to -N coordination is in keeping with the data concerning ^{195}Pt NMR [10, 14]. There is another set of resonances at –3547 ppm, similar in multiplicity to that at –3431 ppm, which may be due to the presence of bridging thiocyanates, but this assignment is uncertain. Thus it would seem that the initial formation of a single product containing four sulfur bonded thiocyanates may be kinetically controlled and that, at least in CH_2Cl_2 solution, several isomers are sufficiently stable, thermodynamically, to be observed at room temperature using NMR methods.

The ^{195}Pt spectrum of *trans*-$[Pt(^{15}NCS)_n(SC^{15}N)_{2-n}(PBu^n_3)_2]$ (Fig. 2) reveals all three of the linkage isomers, I–III, with chemical shifts of –3881, –4244 and –4526 ppm, respectively. Isomer I is readily identified as a triplet of triplets stemming from one-bond $^1J(^{195}Pt, ^{31}P)$, and $^1J(^{195}Pt, ^{15}N)$ interactions. Complex II shows a triplet due to

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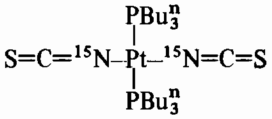
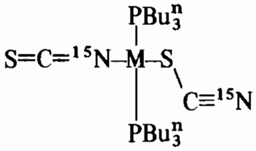
*The digital resolution is insufficient to resolve the different types of $^3J(^{195}Pt\text{–}S\text{–}C\equiv{}^{15}N)$ couplings.

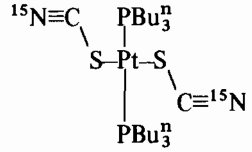


$$S{=}C{=}{}^{15}N{-}\overset{\overset{\displaystyle PBu^n_3}{|}}{\underset{\underset{\displaystyle PBu^n_3}{|}}{Pt}}{-}{}^{15}N{=}C{=}S$$

(I)



(II)



(III)

$^1J(^{195}Pt, ^{31}P)$, further split into a large doublet from $^1J(^{195}Pt, ^{15}N)$ and a small doublet from $^3J(^{195}Pt, ^{15}N)$. The S, S isomer, III, which we and others [12] had thus far been unable to observe, appears as a triplet of triplets, in which the fine structure stems from two equivalent small three-bond couplings. The $^1J(^{195}Pt, ^{15}N)$ values for I and II (589 and 491 Hz respectively) are consistent with those found in the $Pt(C^{15}NS)_4^{2-}$ isomers, with N *trans* to N showing a slightly larger value than N *trans* to S.

Once again the differences in ^{195}Pt chemical shifts provide supportive evidence for the bonding in these isomers, with sulfur coordination affording a high field shift relative to nitrogen coordination. This type of chemical shift empiricism should prove useful in cases where there is no other convenient nuclear spin in the molecule. It seems that direct observation of the ^{195}Pt NMR spectrum is superior to either ^{195}Pt INDOR or direct ^{15}N measurements for this type of mixture of isomers.

^{31}P *NMR*

For the complexes *trans*-$[Pt(^{15}NCS)_n(SC^{15}N)_{2-n}(PBu^n_3)_2]$, the identification of all three species is made simpler by the presence of the phosphine ligands. The ^{31}P NMR spectrum of the mixture shows a triplet (for I), a doublet (for II) and a singlet (for III), all with the appropriate ^{195}Pt satellites. That these are all *trans* isomers may be deduced from both the magnitudes of $^1J(Pt, P)$ [10] and $^2J(^{31}P, ^{15}N)$ [9]. We note that the values $^1J(^{195}Pt, ^{31}P)$ increase slightly (2207, 2244 and 2271 Hz, respectively) and that the ^{31}P chemical shift decreases slightly (10.4, 8.3 and 6.0 ppm, respectively) on proceeding from I to III.

These observations should prove helpful in identifying linkage isomers of thiocyanate in other phosphine complexes. Of the three NMR methods, discussed so far, the phosphorus probe is the most

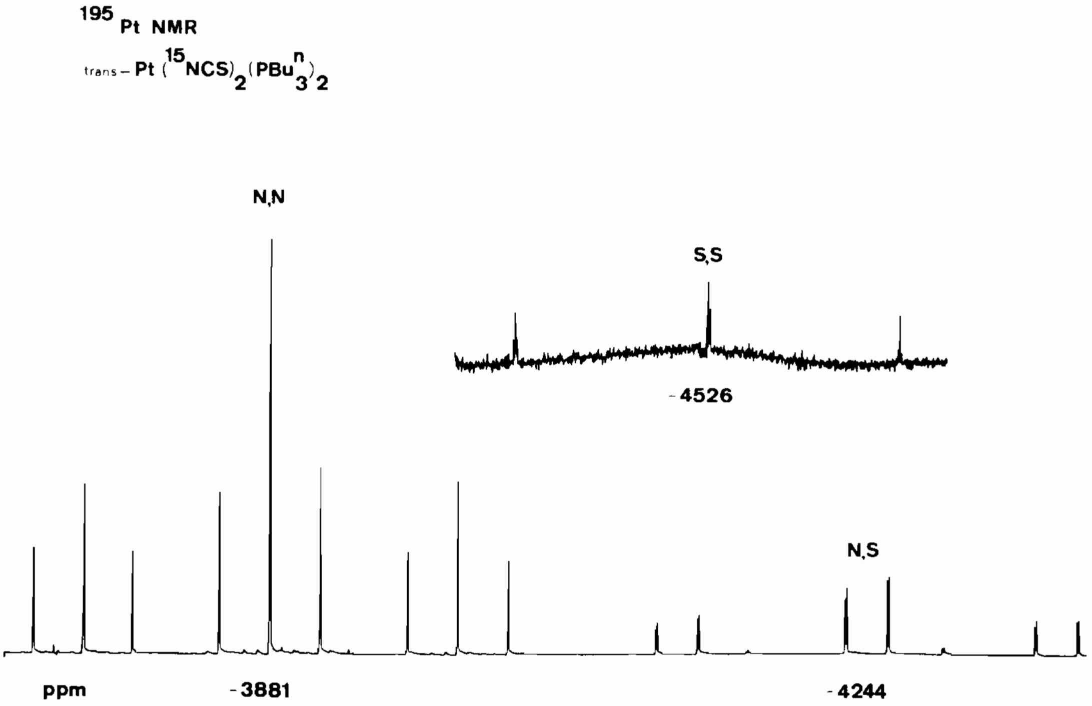


Fig. 2. The ^{195}Pt NMR spectrum of *trans*-$[Pt(^{15}NCS)_n(SC^{15}N)_{2-n}(PBu^n_3)_2]$.

easily applied (10^{-2} *M* solutions present no serious problem), though necessarily restricted to complexes containing phosphorus ligands.

In conclusion we have shown that ^{15}N NMR is a useful general NMR probe for determining the nature of the thiocyanate bonding in a variety of metal complexes. Where other centers are magnetically active, a combination of NMR methods is superior. This is especially true in platinum chemistry where the favorable NMR characteristics of this metal make it the NMR probe of choice.

Acknowledgments

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