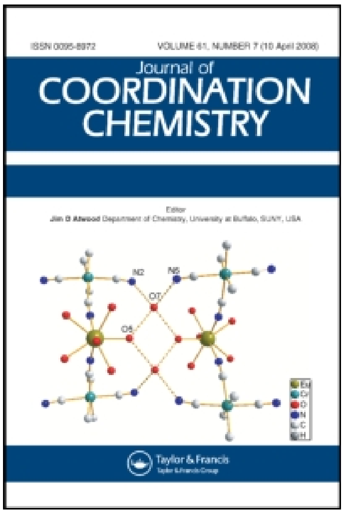

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# A Multinuclear NMR Study of Platinum(II) Complexes of *N*-Phenyl and *N*-(3-Allyl) Substituted 2-(2-Pyridinemethylene) Hydrazine Carbothioamides

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**To cite this Article** Koch, Klaus R.(1990) 'A Multinuclear NMR Study of Platinum(II) Complexes of *N*-Phenyl and *N*-(3-Allyl) Substituted 2-(2-Pyridinemethylene) Hydrazine Carbothioamides', Journal of Coordination Chemistry, 22: 4, 289 — 298

**To link to this Article: DOI:** 10.1080/00958979009408227

**URL:** http://dx.doi.org/10.1080/00958979009408227

. Coord. Chem. 1991, Vol. 22. pp. 289–298
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# A MULTINUCLEAR NMR STUDY OF PLATINUM(II) COMPLEXES OF *N*-PHENYL AND *N*-(3-ALLYL) SUBSTITUTED 2-(2-PYRIDINEMETHYLENE) HYDRAZINE CARBOTHIOAMIDES

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*(Received August 5, 1990)*

Neutral platinum(II) complexes of type [Pt(LH)Cl], where $LH^-$ denotes the *N*-phenyl and *N*-allyl-2-(2-pyridinemethylene)hydrazine carbothioamide anion, have been prepared and characterized. These complexes, as well as the hydrochloride salts of these ligands, have been examined in DMSO-$d_6$ solution by H, $^{13}C$ and $^{195}Pt$ NMR spectroscopy. From the observed chemical shift, the $^{195}Pt$–$^{1}H$ and $^{195}Pt$–$^{13}C$ oupling constant trends, the mode of coordination of Pt(II) to these ligands has been deduced to be *via* he thiocarbonyl atom, the pyridyl N(3) and hydrazinic N(2) nitrogen atoms respectively. In these omplexes the resolved $^{195}Pt$–$^{13}C$ coupling constants to the carbon atoms of the pyridyl group of the gand follow the order $^2J > {^3J} > {^4J}$, in contrast to trends observed for other simple Pt(II) complexes nvolving a coordinated pyridine molecule. Indications are that in DMSO solution, the complexes Pt(LH)Cl] undergo some solvolysis to yield $[Pt(LH)DMSO]^+Cl^-$.

**Keywords:** 2-pyridinecarbaldehyde thiosemicarbazone, platinum(II) complexes, $^{195}Pt$, $^{13}C$, $^{1}H$ NMR

## NTRODUCTION

The coordination chemistry of hydrazine-carbothioamides (commonly known as hiosemicarbazides and thiosemicarbazones) has attracted considerable attention in ecent years, notably as a result of the significant pharmacological activity of these ubstances and some of their transition metal complexes.[1–3] The structures of opper(II) complexes of 2-(2-pyridinemethylene)hydrazine carbothioamide, which ossess significant anti-tumour activity, have recently been published,[4–5] showing he formation of dimeric, anion bridged complexes in the solid state. Essentially erdentate N,N,S–bonding of both the non-deprotonated and deprotonated (2-yridinemethylene)hydrazine carbothioamide ligand has been found.[5] Apart from he potential pharmacological activity of transition metal complexes of thiosemiarbazones derived from 2-pyridinecarbaldehyde, these ligands have also been extenvely investigated as selective reagents for the spectrophotometric determination of a ariety of metal ions.[6–9] Nevertheless there appears to be relatively little information bout the structure and properties in solution of transition metal complexes of ·pyridinecarbaldehyde thiosemicarbazones.

We here report a multinuclear NMR examination of the structure in solution diamagnetic *N*-phenyl and *N*-allyl-2-(2-pyridinemethylene)hydrazine carbothionide platinum(II) complexes. For convenience the neutral ligands are denoted $H_2(A)$ and $LH_2(B)$, while the deprotonated forms will be denoted $LH_1(A)^-$ and

$LH_1(B)^-$, representing the *N*-phenyl and *N*-allyl substituted molecules, respectively. Figure 1 shows the structure of (A) and (B) respectively, and also gives the numbering scheme used throughout.

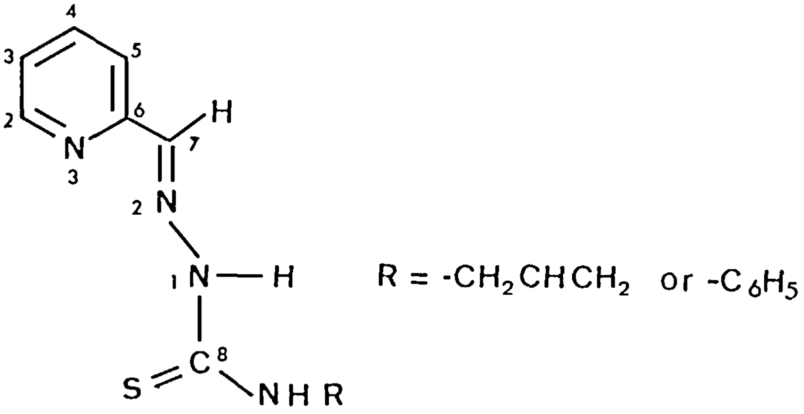

FIGURE 1. Structure and numbering scheme for ligands (A) and (B).

## EXPERIMENTAL

### *Preparative work*

*N*-phenyl-(A) and *N*-allyl-2-(2-pyridinemethylene)hydrazine carbothioamide (B) were prepared from the corresponding phenyl- and allylisothiocyanates, hydrazine and 2-pyridinecarbaldehyde by published methods.[10] Recrystallization from ethanol/dilute hydrochloric acid mixtures followed by drying at 60°C under vacuum afforded the yellow hydrochloride salts; (A).HCl: 53.53%C, 4.50%H, 19.12%N; (B).HCl: 46.80%C, 5.15%H, and 21.85%N. ($C_{13}H_{12}N_4S.HCl$ requires 53.23%C, 4.48%H and 19.13%N while $C_{10}H_{12}N_4S.HCl$ requires 46.78%C, 5.46%H and 21.95%N).

The yellow salts may readily be converted to the 'free bases' by treating solutions of the salts in ethanol with excess dilute aqueous ammonia, from which the off-white precipitates (A) (m/e = 256) and (B) (m/e = 220) were collected by means of centrifugation.

Platinum(II) complexes of compounds (A) and (B) may readily be prepared by the following general procedure. A solution containing 1 mmol of ligand dissolved in 40 $cm^3$ methanol + 10 $cm^3$ 1*M* HCl, was added dropwise to 40 $cm^3$ of a hot (70°C) well-stirred solution consisting of 1 mmol $K_2PtCl_4$ (416 mg) dissolved in equal volumes of methanol and 1*M* HCl. After all the ligand solution had been added the mixture was allowed to stir for a further 15 min. The red-orange precipitate was collected by centrifugation, washed twice with 0.1 *M* HCl, followed by water and dried at 60°C under vacuum (typical yields 70–95%). Both complexes are readily soluble in polar solvents such as dimethylsulphoxide (DMSO) and *N,N*-dimethylformamide (DMF). Elemental analysis of the complexes gave for $[PtLH_1(A)Cl]$ 32.5%C, 2.45%H and 11.6%N, m/e = 486 (C), and for $[PtLH_1(B)Cl]$ 24.2%C, 2.35%H and 11.3%N, m/e = 449 (D). ($PtC_{13}H_{11}N_4SCl$ and $PtC_{10}H_{11}N_4SCl$ require 32.14%C, 2.26%H, 11.53%N and 26.7%C, 2.45%H, 12.5%N, respectively).

### *NMR Spectroscopy*

$^1H$, $^{13}C$ and $^{195}Pt$ NMR spectra were recorded at 200.06, 50.30 and 42.94 MHz, respectively, using a Varian VXR-200 spectrometer. All samples were dried under vacuum prior to dissolution in DMSO-$d_6$. $^1H$ and $^{13}C\{^1H\}$ spectra were recorded in 5 mm tubes at 30°C (unless otherwise stated). Chemical shifts were measured relative to the DMSO-$d_6$ signal, and related to TMS with the relationships, $\delta\ ^1H(TMS) = \delta\,(DMSO\text{-}d_6) + (2.49 \pm 0.01)$ ppm and $\delta\ ^{13}C(TMS) = \delta\,(DMSO\text{-}d_6) \pm (39.5 \pm 0.1)$ ppm, respectively. In addition to standard 1 D techniques, 2 D homonuclear (COSY) and heteronuclear (HETCOR) correlation spectroscopy,[11] using standard Varian version 6.1(d) software, was used for unambiguous assignments.

$^{195}Pt$ spectra were recorded at 30°C in DMSO-$d_6$ solutions, typically using a 60° pulse (90° pulse ~ 14 μsec) with a 1.5–2.0 s pulse delay. Shifts are quoted relative to the widely used external reference compound, $H_2PtCl_6$ in $^2H_2O$ ($\delta\ ^{195}Pt = 0$), at the same temperature.[12]

## RESULTS AND DISCUSSIONS

Substances (**A**) and (**B**) are readily protonated to yield stable hydrochloride salts ($LH_2.HCl$) and deep red, uncharged complexes of type, [Pt(LH)Cl], are easily prepared. The latter complexes are quite soluble in DMSO-$d_6$ and give well resolved $^1H$ and $^{13}C$ NMR spectra. Table I summarises the $^1H$ NMR data for the ligands (**A**), (**B**), the corresponding salts and the platinum(II) complexes (**C**) and (**D**). The respective $^1H$ assignments were confirmed by 2-D COSY spectroscopy. Inspection of the chemical shift trends observed on protonation of both (**A**) and (**B**) suggests that this takes place predominantly at the pyridine nitrogen (N(3)) atom. On the other hand, on complex formation (which occurs with deprotonation of the ligand) the very similar $^1H$ chemical shift trends suggest very similar coordination by both ligands. These trends are much more clearly evident from the $^{13}C$ spectra as discussed below.

The anticipated $^nJ(^{195}Pt–^1H)$ coupling satellites around certain resonances in the $^1H$ spectra of the complexes (**C**) and (**D**) are, however, not obvious for spectra recorded in DMSO-$d_6$ at 30°C. Raising the temperature to 50°C results in the satellites becoming clearly evident about the resonances assigned to H(2′) and H(7) in both complexes (Figure 2). For comparison, a part of the $^1H$ spectrum of (**C**) in acetone-$d_6$ is also shown, in which the respective $^3J(^{195}Pt–^1H)$ satellites are clearly visible throughout the temperature range 25–50°C. These observations are consistent with the demonstrated dominance of the chemical shift anisotropy (CSA) relaxation mechanism associated with the $^{195}Pt$ nucleus, which manifests itself by often very broad $^{195}Pt$ satellites, particularly at higher magnetic field (the satellites, of course, correspond to the $^{195}Pt$ containing isotopomer). The characteristic feature of the CSA relaxation times $T_1$ and $T_2$, is their inverse proportionality to the square of the static magnetic field, $B_0$ as well as the rotational correlation time, $\tau_c$ of the complex.[13,14] Thus at constant field, a higher temperature results in a less viscous DMSO solution, corresponding to a shorter $\tau_c$ and thus sharper $^{195}Pt$ satellites.

Apart from these relaxation effects, we find that the difference in chemical shift between H(2′) and H(7), defined as Δ Hz, depends on the solvent and temperature. In the case of (**C**) for example, Δ increases from 20 Hz at 25°C to 28 Hz at 50°C in DMSO-$d_6$, while in acetone-$d_6$, Δ varies from 76–82 Hz for this temperature range.

TABLE I

$^1$H NMR data in DMSO-$d_6$ at 25°C unless otherwise stated.[a] Shifts relative to neutral ligands given.

| | pyridyl moiety | | | | | | | phenyl/allyl moiety | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | H(2′) | H(3′) | H(4′) | H(5′) | H(7) | H(10) | H(11) | H(12) | H(13) | H(14) | N(1)H | N(4)H |
| $LH_2$ (A) | 8.58 | ~7.4 | 7.84 | 8.44 | 8.20 | 7.55 | 7.38 | 7.22 | 7.38 | 7.55 | 12.02 | 10.42 |
| $LH_2$.HCl | 8.70 | 8.39 | 7.78 | 8.28 | 8.17 | 7.55 | 7.27 | 7.11 | 7.27 | 7.55 | 12.48 | 10.91 |
| | (−0.12) | (−0.99) | (0.06) | (0.16) | (0.03) | | (0.11) | (0.11) | (0.11) | | (−0.46) | (−0.49) |
| $LH_2$ (B) | 8.55 | 7.34 | 7.80 | 8.24 | 8.12 | 4.24 | 5.92 | 5.16<br>5.09 | | | 11.89 | 8.77 |
| $LH_2$.HCl | 8.76 | 7.85 | 8.49 | 8.33 | 8.16 | 4.22 | 5.93 | 5.15<br>5.09 | | | 12.29 | 9.76 |
| | (−0.21) | (−0.51) | (−0.69) | (−0.09) | (−0.04) | (0.02) | (−0.01) | (−0.01) | | | (−0.40) | (0.99) |
| Pt(LH)Cl (C) (T = 50°C), | 8.74 | 7.77 | 8.15 | 7.70 | 8.60 | 7.58 | 7.32 | 7.05 | 7.32 | 7.58 | | 10.31 |
| | (−0.16) | (−0.37) | (−0.31) | (0.74) | (−0.40) | (−0.03) | (0.05) | (0.17) | (0.05) | (−0.03) | | (0.11) |
| Pt(LH)Cl (D) | 8.71 | ~7.7 | 8.12 | ~7.7 | 8.34 | 4.00 | 5.85 | 5.18<br>5.12 | | | | ~9.1 |
| | (−0.16) | (−0.31) | (−0.31) | (0.55) | (−0.22) | (−0.24) | (0.07) | (−0.02)<br>(−0.03) | | | | (0.33) |
| Pt(LH)Cl (C) | | | | | | | | | | | | |
| (Acetone-$d_6$, T = 25°C) | 8.91 | 7.85 | 8.21 | 7.76 | 8.51 | 7.69 | 7.35 | 7.08 | 7.35 | 7.69 | | 10.2 |
| (nitromethane-$d_3$, T = 50°C) | 8.85 | ~7.7 | 8.12 | ~7.7 | 8.28 | 7.58 | 7.40 | 7.16 | 7.40 | 7.58 | | 10.4 |

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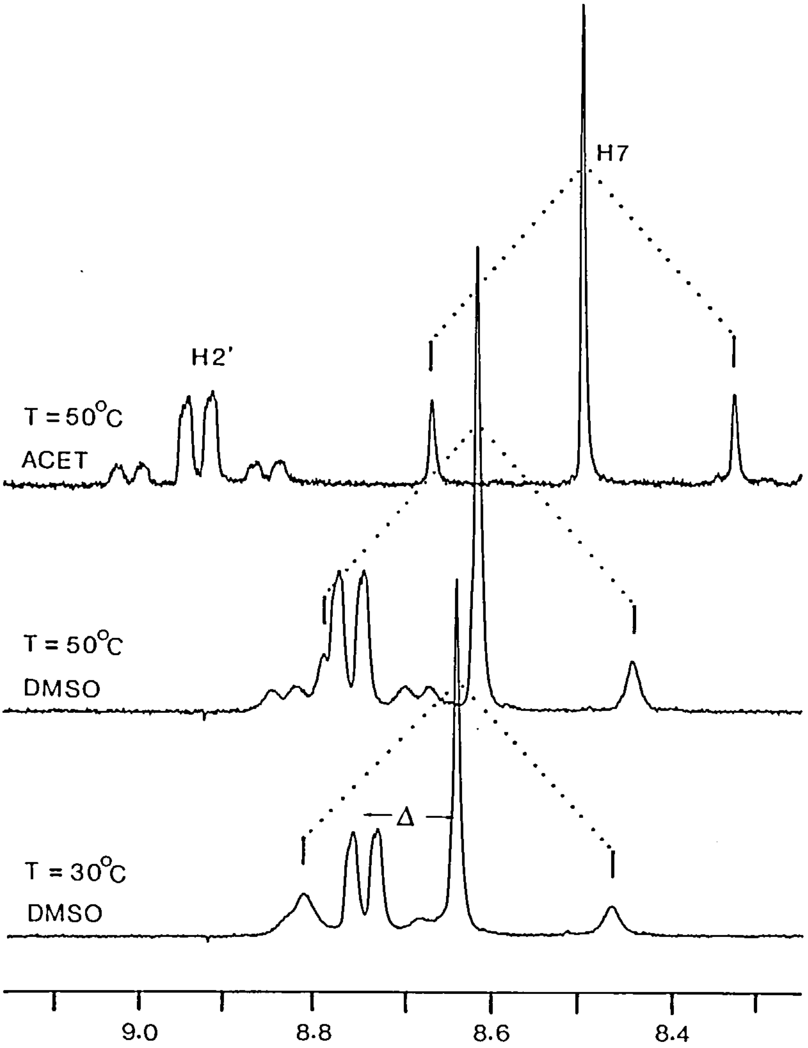
[a] For clarity only the centre of the multiplet is reported in ppm relative to DMSO-$d_6$ at $\delta = 2.49$ ppm (downfield shifts are negative).



IGURE 2. Expanded part of $^1H$ NMR spectrum of the complex (C) showing the H(2′) and H(7) sonances and $^{195}Pt$ coupling satellites in DMSO-$d_6$ (a) at 30°C, (b) at 50°C and (c) in acetone-$d_6$ at 50°C.

n nitromethane-$d_3$, in which (C) is only poorly soluble, $\Delta = 113$ Hz at 50°C. lthough we have not examined this phenomenon in greater detail, it seems likely hat the variation of Δ reflects a degree of solvolysis in which the $Cl^-$ ion is displaced rom the coordination sphere of the platinum atom, particularly in the case of )MSO-$d_6$ and to a lesser extent in acetone-$d_6$:

$$[Pt(LH)Cl] + \text{solvent} \rightleftharpoons [Pt(LH)\text{solvent}]^+ + Cl^-$$

f the mode of coordination of (A) and (B) to Pt(II) *via* N(3), N(2) and the sulfur tom is anticipated for the moment, then it is reasonable to expect that displacement f the $Cl^-$ ion *trans* to the formimide group (–N(2)=CH–) by a solvent molecule should lead to changes in the chemical shifts of H(7) and to a lesser extent H(2′). Such postulated solvolysis might be expected to follow the order of Gutmann donicity (DMSO > acetone > nitromethane) of the solvents.[15] In the absence of a conductivity study, however, the extent to which solvolysis occurs must remain speculative. A similar phenomenon has recently been observed for the dimeric copper acetate complex with 2-formylpyridine thiosemicarbazone [{CuL($CH_3COO$)}$_2$], which was reported to disproportionate yielding [CuL(solvent)]$^+$ species in solution.[5]

TABLE II

$^{195}$Pt–$^{13}$C and $^{195}$Pt–$^{1}$H spin coupling constants observed (absolute values in Hz).

| | $^2$J(C2′) | $^3$J(C3′) | $^4$J(C4′) | $^3$J(C5′) | J(C6′) | $^2$J(C7) | $^3$J(H2′) | $^3$J(H7) |
|---|---|---|---|---|---|---|---|---|
| Pt($LH_2$)Cl (C) | 46 | 23 | ~10 | 20 | 28 | 77 | 29 | 66 |
| Pt($LH_2$)Cl (D) | 48 | 25 | [a] | 18 | 28 | ~80 | 29 | 71 |

[a] Not resolved.

The magnitude of the $^3$J($^{195}$Pt–$^1$H) coupling for H(7) is significantly larger (66 and 71 Hz) than for H(2′) (29 ± 1 Hz) in both (C) and (D) respectively (Table II). Although formally the spin coupling is transmitted *via* a similar molecular fragment (Pt–N=C–H), these differences may be ascribed to differing relative configurations of the $^{195}$Pt nucleus with respect to H(7) (*trans*) and H(2′) (*cis*). These data are consistent with Pt(II) coordinating to (A) and (B) *via* the pyridyl nitrogen N(3), the formimine nitrogen atom N(2), as well as the thiocarbonyl atom as already inferred above. Very similar coordination has been confirmed by an X-ray diffraction study of the related copper complexes described by Bell[4] as well as Müller and Brodie.[5]

The $^{13}$C NMR spectra of the HCl salts of (A) and (B), as well as the complexes (C) and (D) are particularly informative. Table III lists the various $^{13}$C NMR assignments, which were confirmed with 2-D heteronuclear shift correlation spectroscopy (HECTOR). Inspection of these data shows that the changes in the $^{13}$C shifts induced in (A) and (B) on protonation and complex formation are remarkably similar, as may be ascertained by plotting the shifts induced for the respective carbon atoms. In the hydrochloride salts of (A) and (B) the observed upfield shifts of C(2′) and C(6′), together with the downfield shifts of C(3′), C(4′) and C(5′) of the pyridine group are qualitatively similar to the characteristic pattern observed for the pyridinium ion.[15] The actual shifts for C(5′) (−0.77, −2.06 ppm), and C(6′) (+4.17, +3.79 ppm) observed for the HCl salts of (A) and (B), respectively, are the result of a combination of protonation and substituent effects. It is likely that the magnetic anisotropy of the –C=N– moiety attached at C(6′) may be significant, although this would depend on the average orientation of this formimide group relative to the pyridyl ring in both the neutral and unprotonated forms of (A) and (B).

The comparatively large downfield shifts for C(2′), C(3′), and C(4′) in the platinum complexes (C), and (D) are noteworthy. Although in general paramagnetic shifts are invariably induced when a pyridine molecule coordinates to Pt(II), the relative magnitudes of the shifts for the α, β, and γ carbon atoms are variable.[16–18] As is evident from data in Table IV, the unusually large downfield shifts of (C2′) and (C3′) for (C) and (D) are striking. Vrieze *et al.*[18] have examined in detail the $^{13}$C shift trends for complexes of type *trans*-[$PtCl_2X$(pyridine)] where X = CO or $C_2H_4$, concluding that the most important contribution to the $^{13}$C shieldings of the pyridyl groups in these complexes is the local paramagnetic term, $\sigma_p$, together with a

TABLE III

$^{13}C$ chemical shifts[a] of ligands (A) and (B), as well as the corresponding hydrochloric salts and Pt(II) complexes in DMSO-$d_6$ (shift differences in parentheses, negative downfield).

| | pyridyl group | | | | | | | phenyl/allyl group | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | C(2′) | C(3′) | C(4′) | C(5′) | C(6′) | C (7)[b] | C(8)[c] | C(9) | C(10) | C(11) | C(12) | C(13) | C(14) |
| $LH_2$ (A) | 153.06 | 120.49 | 136.30 | 125.35 | 149.12 | 143.00 | 176.38 | 138.85 | 125.78 | 127.96 | 124.07 | 127.96 | 125.78 |
| $LH_2$.HCl | 146.55 | 125.56 | 133.43 | 126.12 | 145.02 | 143.23 | 176.50 | 138.55 | 125.90 | 127.99 | 126.00 | 127.99 | 125.90 |
| | (+6.51) | (−5.07) | (+2.87) | (−0.77) | (+4.17) | (−0.23) | (−0.12) | (+0.30) | (−0.12) | (−0.03) | (−1.93) | (−0.03) | (−0.12) |
| Pt(LH)Cl (C) | 158.92 | 126.73 | 139.89 | 126.12 | 146.74 | 150.68 | 180.17 | 140.77 | 120.69 | 128.45 | 123.70 | 128.45 | 120.69 |
| | (−5.86) | (−6.24) | (−3.59) | (−0.77) | (+2.38) | (−7.68) | (−3.79) | (−1.92) | (+5.09) | (−0.49) | (+0.37) | (−0.49) | (+5.09) |
| $LH_2$ (B) | 153.20 | 120.09 | 136.24 | 123.87 | 149.16 | 142.26 | 177.50 | 45.75 | 134.73 | 115.51 | | | |
| $LH_2$.HCl | 147.50 | 126.53[d] | 134.43 | 125.93[d] | 145.37 | 143.98 | 178.17 | 46.43 | 133.87 | 116.81 | | | |
| | (+5.70) | (−6.44) | (+1.81) | (−2.06) | (+3.79) | (−1.72) | (−0.67) | (−0.68) | (+0.86) | (−1.30) | | | |
| Pt(LH)Cl (D) | 159.44 | 125.83 | 140.49 | 125.16 | 146.50 | 147.47 | 181.98 | 48.22 | 134.20 | 116.05 | | | |
| | (−6.24) | (−5.74) | (−4.25) | (−1.29) | (+2.66) | (−5.21) | (−4.48) | (−2.47) | (+0.53) | (−0.54) | | | |

[a] Recorded relative to DMSO-$d_6$ at $\delta = 39.5$ ppm at 40°C. [b] Formimide carbon. [c] Thiocarbonyl carbon. [d] Assignment ambiguous.

diamagnetic term, $\sigma_d$ ascribable to the platinum ion. In terms of Ramsey's theoretical treatment of magnetic shieldings,[19] the $\sigma_p$ term depends, *inter alia*, inversely on the average electronic excitation energy, ΔE. Hence the considerable paramagnetic shifts observed for C(2') and C(3') in complexes (C) and (D) may qualitatively be understood in terms of a significant decrease in ΔE, resulting in a large paramagnetic shift contribution. This follows from the considerable red shift of the absorption maxima which occurs when (A) ($\lambda_{max} = 328$ nm, $\varepsilon \sim 32800$ M$^{-1}$ cm$^{-1}$) forms the platinum complex (C) ($\lambda_{max} = 415$ nm, $\varepsilon \sim 18833$ M$^{-1}$ cm$^{-1}$). The latter absorption band may be assigned to a M → L charge-transfer band similar to those observed in related Cu(II) complexes.[5] In this context it is reasonable to expect that the ligands (A) and (B) assume a coplanar configuration with the square plane preferred by the Pt(II) ion on complexation. In addition to probably enabling extensive π-electron conjugation in the ligand system, such enforced planarity of the pyridyl ring may well result in favourable $d \rightarrow \pi^*$ interactions (to the extent that these exist), accounting for the large paramagnetic shifts for C(2') and C(3') in these complexes. According to Vrieze,[18] the charge transfer absorptions in *trans*-[PtCl$_2$X(pyridine)] complexes are rotationally allowed, as the pyridine ring is assumed to rotate with respect to the square plane of the platinum ion. On the other hand, for the complex *trans*-[PtCl$_2$(C$_2$H$_4$)(2,4,6-trimethylpyridine)] the small paramagnetic shifts for the C(2')/C(6') atoms (0.8 ppm) of the pyridine ring, have been interpreted in terms of rotationally forbidden $d \rightarrow \pi^*$ transitions, as the trimethylpyridine ring is thought to be perpendicular to the square plane on steric grounds.[18]

TABLE IV

$^{13}$C shifts[a] induced (ppm) in the pyridine group on coordination to Pt(II).

| Compound | C2' | C3' | C4' | C5' | C6' | Ref. |
|---|---|---|---|---|---|---|
| Pt(pyr)$_4$$^{2+}$ | −2.1 | −4.0 | −5.6 | −4.0 | −2.1 | 14 |
| Pt(NH$_3$)$_2$(pyr)$_2$$^{2+}$ | −2.5 | −4.0 | −5.3 | −4.0 | −2.5 | 15 |
| PtCl$_2$X(pyr) | | | | | | 16 |
| X = CO | −1.40 | −2.60 | −5.60 | −2.60 | −1.40 | |
| X = C$_2$H$_5$ | −1.80 | −2.40 | −5.10 | −2.40 | −1.80 | |
| (C) | −5.86 | −6.24 | −3.59 | −0.77 | +2.38 | this work |
| (D) | −6.24 | −5.74 | −4.25 | −1.29 | +2.66 | this work |

[a] Shifts are given relative to the free ligand, (−) downfield, (+) upfield.

The $^nJ(^{195}Pt{-}^{13}C)$ spin coupling satellites in the $^{13}$C spectra of (C) and (D) provide (Table II) conclusive evidence from which the mode of Pt(II) coordination to (A)/(B) may be deduced to be through the N(3), N(2) and the S atoms. The interesting possibility exists of the allyl moiety of ligand (B) coordinating to the Pt(II) atom in complex (D); we find no evidence that such an interaction takes place.

It should be noted that $^2J(^{195}Pt{-}C2')$, denoted $^2J(C2')$ for short, is significantly larger than $^2J(C6')$ (46–48 Hz and 28 Hz, respectively). Furthermore, the magnitude of these spin couplings follows the general order $^2J > {}^3J > {}^4J$ for the pyridine carbon atoms of both (C) and (D). This order is in contrast to the observed trends for complexes such as [Pt(pyridine)$_4$]$^{2+}$ and *trans*-[PtCl$_2$(pyridine)CO] in which the magnitude of $^{195}Pt{-}^{13}C$ spin couplings follow the order $^3J > {}^2J > {}^4J$,[16,18] while for *cis*-[Pt(NH$_3$)$_2$(pyridine)$_2$](ClO$_4$)$_2$ the order is $^3J > {}^4J > {}^2J$.[17] The reason for the differences in these trends is not clear at present, although the order $^2J > {}^3J > {}^4J$

erved for (C) and (D) in this work might be related to the enforced co-planarity of pyridine group with the square plane of the Pt(II) ion, in contrast to the other nplexes above. In any event, it is clear that it is not possible to predict the gnitudes of these spin coupling constants over two or more bonds with any tainty as far as the coordination of a pyridyl fragment to Pt(II) is concerned. The ge coupling $^{2}J(C7)$ of 77–80 Hz is in sharp contrast to the unresolved ($<3$ Hz)$^{2}$ J pling to the thiocarbonyl atom C(8). Indeed any measurable coupling to the ocarbonyl atom is conspicuous by its absence. It is not clear at present why such plings are not observed, although similar observations have been reported for ne Pt(II) thioamido complexes.[20]

inally it should be noted that complexes (C) and (D) give rise to single, relatively rp $^{195}$Pt resonances at $\delta = -3157$ and $-3102$ ppm respectively, (DMSO-$d_6$ at C). No $^{14}$N spin coupling was resolved in these systems, presumably as a result of nificant scalar relaxation of the second kind, ascribable to the quadrupolar $^{14}$N leus.[21]

he detailed multinuclear NMR study of these neutral substituted hydrazine bothioamide-complexes of Pt(II) has demonstrated the wealth of information ilable from NMR spectra, from which the mode of coordination in these nplexes may be clearly deduced. In the absence of an X-ray diffraction study, the nplexes (C) and (D) may best be represented as in Figure 3.

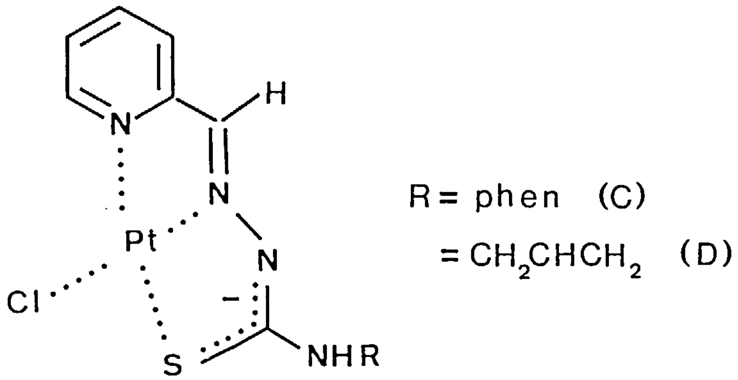


FIGURE. 3. Mode of coordination in the complexes (C) and (D).

exchangeability of the Cl$^-$ ion for other anionic and neutral donors in solution is rly of interest when considering the potential bioactivity of these and related plexes. These and other questions concerning the NMR spectroscopic properties hese systems are being further studied.

## NOWLEDGEMENTS

ancial assistance from the FRD and the University of Cape Town is gratefully nowledged. Special thanks are due to Prof. Dr A. Kettrup and Dr M. Grote of ewandte Chemie, University of Paderborn, Paderborn, West Germany for their port, both material and intellectual. I am indebted to the Heinrich Herz ndation for a fellowship.

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