

Cationic and Neutral Bis(4-*p*-tolylthiosemicarbazido)platinum(II) Complexes: a Preparative as well as ^1H and ^{195}Pt NMR Study of the Question of *cis/trans* Isomerism

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Abstract

Complexes of the type $[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2$ and $[\text{Pt}(\text{LH}_3)_2]$ have been prepared and studied by ^1H , ^{13}C and ^{195}Pt NMR. It has been found that both *cis* and *trans* isomers of the above complexes are formed, although the *trans* isomer presumably predominates as product. The cationic complexes are readily deprotonated with ammonia in dimethylsulphoxide solution to yield the corresponding neutral species, which may be further deprotonated and oxidized.

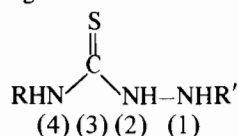
Introduction

Transition metal complexes of thiosemicarbazides (hydrazinecarbothioamides) and their derivatives have been the subject of considerable interest in the last decade, probably in view of their significant pharmacological activity coupled with a suggestion that metal ions appear to enhance the biological activity of thiosemicarbazides in some cases [1, 2]. Additionally, the analytical potential of related thiosemicarbazones as selective reagents for the spectrophotometric determination of several transition metals has been extensively investigated [3–5].

Although there have been several previous reports of the synthesis and characterization of platinum(II) and palladium(II) complexes of unsubstituted thiosemicarbazides [6–8], structural details of these deceptively simple compounds are lacking; moreover their behaviour in solution has not been extensively examined. Most previously reported studies of complexes of the type $[\text{ML}_2]\text{X}_2$ and $[\text{ML}_2]$ (where $\text{M} = \text{Pt}(\text{II}), \text{Pd}(\text{II}), \text{Ni}(\text{II})$, $\text{L} = \text{NH}_2\text{CSNHNH}_2$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{SO}_4^{2-}, \text{NO}_3^-$) were based entirely on elemental analysis and infrared spectroscopic studies of these substances [6–8]. On the other hand Holm *et al.* have shown that the bis(1,4-diphenylthiosemicarbazido)platinum(II) complex undergoes facile oxidation and reduction reactions concomitant with a loss of

protons, to yield a complete five-membered electron transfer series [9]. The latter aspect clearly has important implications in the synthesis and characterization of thiosemicarbazide transition metal complexes, but appears to have been overlooked by some workers [7, 8].

From the basic structure of the thiosemicarbazide ligand



(R, R' = H, alkyl or aryl groups)

the mode of coordination may be anticipated. In the majority of cases, the thiosemicarbazide moiety behaves as a bidentate ligand involving the sulphur and hydrazinic nitrogen atom N(1) [1]. The possibility of *cis* and *trans* coordination in the case of square planar metal complexes is exemplified by the two isomers of Ni(II), the crystal and molecular structure of *trans*-bis(thiosemicarbazido)nickel(II) having been determined by X-ray diffraction methods [10]. Several other examples of *cis/trans* transition metal complexes involving these ligands are known [1]. Haines and Sun [6] reported that in the preparation of cationic bis(thiosemicarbazido)platinum(II) the geometric isomerism is strongly dependent on the anion present; for the chloride anion only the *trans* isomer could be isolated. On the other hand, Murthy and co-workers reported to have prepared pure *cis* and *trans*- $[\text{PtL}_2]\text{Cl}_2$ ($\text{L} = \text{NH}_2\text{CSNHNH}_2$) complexes in which platinum is taken to be divalent although these compounds were stated to be prepared from $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ [7]. The *cis* complex was reported to be obtained from 'hot' ethanol solutions of metal and ligand, while the *trans* complex was obtained by mixing reagents in the 'cold' condition. The proposed *cis/trans* isomerism of these isolated substances was based on infrared spectroscopic arguments. However, since it is not possible to distinguish between the Pt(IV) and Pt(II) complexes on the basis of elemental analysis alone, the proposed nature of the substances isolated by Murthy *et al.* must remain tentative.

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In this paper we report a critical study of the synthesis and constitution in solution of cationic and neutral bis(4-*p*-tolylthiosemicarbazido)platinum(II) complexes. The traditional numbering system of thiosemicarbazides (N(4)–C(3)S–N(2)–N(1)) will be adhered to throughout [1]; for convenience the neutral ligand will be denoted LH₄, while consecutively deprotonated forms will be denoted LH₃[–] and LH₂.

Experimental

Preparation of 4-*p*-Tolylthiosemicarbazide

4 g of *p*-tolylisothiocyanate (26.9 mmol) in 50 cm³ methanol were added dropwise to a cold solution of 2.8 cm³ hydrazine hydrate solution (1 cm³ = 9.9 mmol NH₂NH₂) in 20 cm³ methanol. After stirring for 30 min at room temperature the white plates were collected and recrystallized from pure methanol (dry yield 70–80%). Calc. for C₈N₃H₁₁S: C, 53.05; N, 23.18; H, 6.12. Found: C, 53.2; N, 23.5; H, 5.75%.

Preparation of *cis/trans* [Pt(LH₄)₂]Cl₂ Complexes

A variety of different procedures were examined at room temperature and at near boiling point of the solutions (95 °C). Metal solutions were added to ligand solution or vice versa. In general all experiments were performed under dinitrogen. A typical procedure giving good yields is as follows: to a 30 cm³ solution, consisting of 1 mmol K₂PtCl₄ (0.416 g) in 2 M HCl/CH₃OH (80:20), 40 cm³ of the ligand in the same solvent is added dropwise. On completion of the ligand addition, the solution is allowed to stir for 20–30 min at the desired temperature. The precipitated, pale cream to grey coloured complex, is collected by filtration, washed several times with cold 2 M HCl followed by methanol and dried under vacuum at 70 °C. The complex may be purified by dissolution in a minimum of DMSO or DMF followed by rapid reprecipitation with 2 M HCl. Typical yields 85–95%. Calc. for PtC₁₆N₆H₂₂S₂Cl₂: C, 30.58; N, 13.37; H, 3.53. Found: C, 30.3; N, 13.1; H, 3.7%.

Preparation of *cis/trans* [Pt(LH₃)₂] Complexes

The most satisfactory procedure of preparation of these unchanged complexes is via the corresponding cationic precursor. A typical method is as follows. To a solution of 1 mmol of [Pt(LH₄)₂]Cl₂ in a minimum of DMF (or DMSO) is added an excess of aqueous ammonia solution (5 cm³ 10% NH₃). The precipitated bright green to blue–green complex is reasonably pure and was used without further purification. Calc. for PtC₁₆N₆H₂₀S₂: C, 34.59; N, 15.12; H, 3.63. Found: C, 34.4; N, 14.8; H, 3.8%.

¹H NMR and ¹⁹⁵Pt NMR spectra were obtained using a Bruker WM-250 FT spectrometer operating at 250 MHz for ¹H and 53.7 MHz for ¹⁹⁵Pt. All solutions were freshly prepared in anhydrous DMSO-d₆ and spectra recorded at a temperature of 301 K. ¹⁹⁵Pt chemical shifts are given relative to an external aqueous solution of Na₂PtCl₆ and are estimated accurate to ±3 ppm.

Infrared spectra were obtained from samples in KBr disks.

Results and Discussion

Cationic complexes of the type [Pt(LH₄)₂]Cl₂ are obtained in good yields (85–95%) by the dropwise addition of a degassed solution of PtCl₄^{2–} (80 + 20 volume parts 2 M HCl + methanol) to a well stirred solution of 4-*p*-tolylthiosemicarbazide at room temperature. In order to prevent possible oxidation reactions involving dioxygen, all syntheses were carried out under a dinitrogen atmosphere. The crude, off-white complex [Pt(LH₄)₂]Cl₂, may occasionally appear very pale green in colour, probably due to traces of presumably the neutral [Pt(LH₃)₂] complex(es) (see below). The cationic compounds [Pt(LH₄)₂]Cl₂ may be purified by dissolving the crude product in a minimum of *N,N'*-dimethylformamide (DMF) or dimethylsulphoxide (DMSO), followed by the rapid reprecipitation with excess 2 M HCl. In this context it should be noted that DMSO solutions of [Pt(LH₄)₂]Cl₂ appear pale green shortly after dissolution, while addition of a small amount of aqueous ammonia solution results in the immediate formation of intensely coloured turquoise to olive green solutions (λ_{max} 683 and 368 nm). These colour changes may be associated with the deprotonation of the [Pt(LH₄)₂]²⁺ cation to yield a neutral complex [Pt(LH₃)₂]. These neutral complexes can readily be isolated as blue–green solids by precipitation, when concentrated DMSO or DMF solutions of the [Pt(LH₄)₂]Cl₂ complex are treated with excess dilute aqueous ammonia solution. A significant advantage of the latter method of preparing the neutral [Pt(LH₃)₂] complexes is that the isomeric composition (relative quantities of *cis* and *trans* isomers) of these compounds appears to be determined by that of their protonated precursors; *i.e.* [Pt(LH₄)₂]Cl₂. In contrast, previously reported methods of preparation of related neutral bis(thiosemicarbazido)platinum(II) complexes involved the addition of excess aqueous ammonia directly to the mixture of metal and ligand [6, 7]. In our hands, this procedure always resulted in a mixture of *cis* and *trans* isomers of [Pt(LH₃)₂], as is clearly evident from the ¹H NMR spectra (see below). Another disadvantage of this one-step synthesis of [Pt(LH₃)₂] lies in the danger of further deprotonation of [Pt-

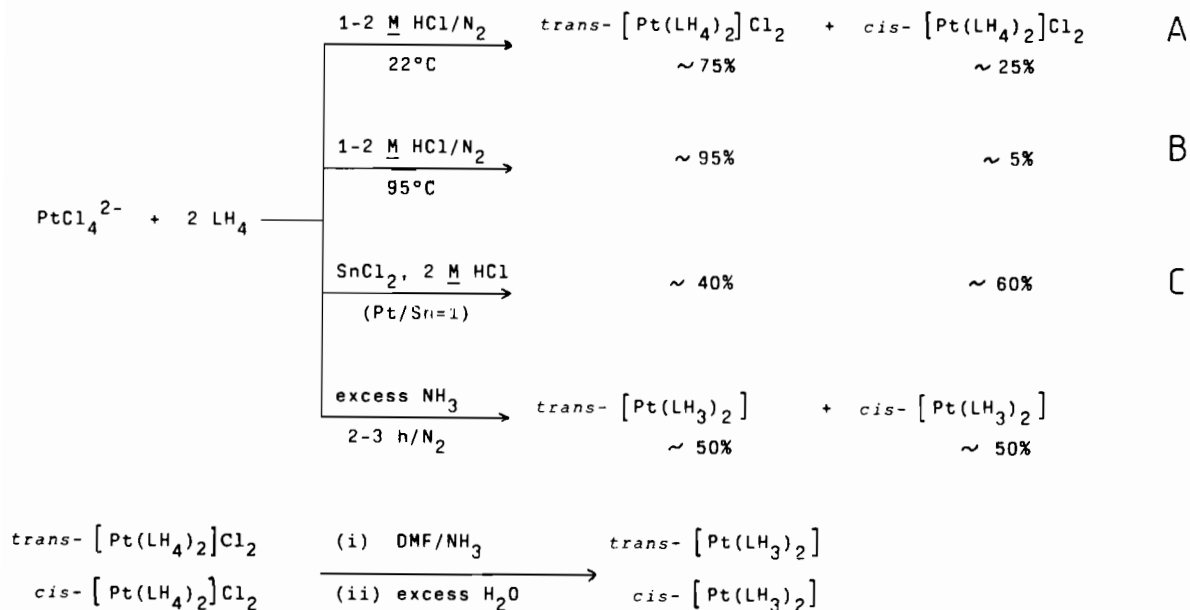


Fig. 1. Synthesis and product distribution of cationic and neutral bis(4-*p*-tolylthiosemicarbazido)platinum(II) complexes.

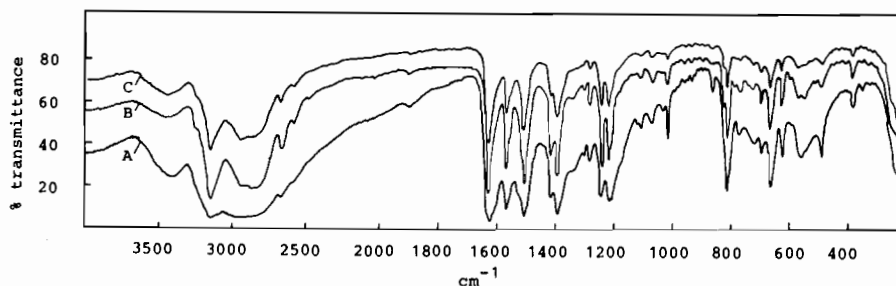


Fig. 2. Infrared data for three separate samples of $[\text{Pt}(\text{LH}_4)_2] \text{Cl}_2$ A, B and C corresponding to products as in Fig. 1.

$(\text{LH}_3)_2$ to anionic species followed by oxidation to uncharged complexes. Holm *et al.* have shown that such a double deprotonation/oxidation reaction leads to the preparation of bis(phenylazo-*N*-phenylthioformamido)platinum(II) from 1,4-diphenylthiosemicarbazide and PtCl_4^{2-} [9]. In the present study we find that using 4-*p*-tolylthiosemicarbazide as ligand, under similar conditions as reported by Holm *et al.*, leads mainly to the formation of $[\text{Pt}(\text{LH}_3)_2]$ in the first instance. Nevertheless on prolonged stirring of the reaction mixture at room temperature (24 h open to air, excess concentrated ammonia) a dark grey product is obtained which appears to be a mixture of several neutral complexes (indicated by TLC), presumably the $[\text{Pt}(\text{LH}_3)_2]$ and oxidized $[\text{Pt}(\text{LH}_2)_2]$ species.

cis/trans Isomerism

Several attempts to prepare isomerically pure (either *cis* or *trans*) cationic $[\text{Pt}(\text{LH}_4)_2]^{2+}$ and neutral $[\text{Pt}(\text{LH}_3)_2]$ complexes were made by varying the reaction conditions. Figure 1 summarizes the overall

observations made. In all cases mixtures of *cis* and *trans* complexes were obtained, although certain conditions lead to the formation of one major isomer, presumably the *trans* complex. Thus if an acid (2 M HCl) solution of PtCl_4^{2-} is added dropwise to a solution of LH_4 at room temperature ($22 \pm 2^\circ\text{C}$), a mixture of ca. 25% *cis* and 75% *trans* $[\text{Pt}(\text{LH}_4)_2] \text{Cl}_2$ is obtained, while at near boiling point of the solutions ($95 \pm 5^\circ\text{C}$) mainly the *trans* isomer is obtained (90%). On the other hand at room temperature, in the presence of one equivalent of SnCl_2 (added to the PtCl_4^{2-} solution prior to reaction with LH_4), a mixture containing predominantly the *cis* isomer ($\sim 60\%$) results. These observations stand in contrast to the reported reaction of thiosemicarbazide with nickel(II), palladium(II) and platinum(II/IV) in which boiling metal–ligand solutions were claimed to yield the essentially *cis* isomer, while ‘cold’ solutions yielded the *trans* cationic complexes [6–8]. Since previous assignments were based exclusively on infrared studies the possibility that the authors unwittingly worked with mixtures of isomers cannot

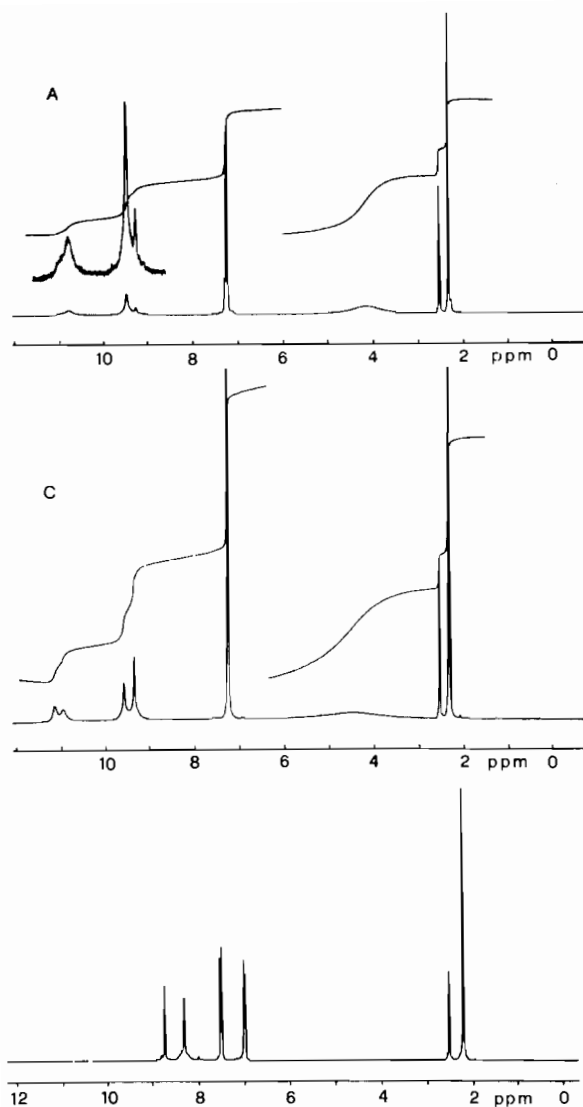


Fig. 3. Typical ^1H NMR spectra in anhydrous DMSO-d_6 of products A and C corresponding to mixtures of *cis/trans* isomers of $[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2$. Shown also is a spectrum of nearly pure *trans*- $[\text{Pt}(\text{LH}_3)_2]$.

TABLE I. ^1H and ^{195}Pt NMR Data of Complexes in DMSO-d_6 Solution (Given in parenthesis is the relative resonance integral corresponding to the appropriate number of ^1H atoms)

Compound	$\delta(^1\text{H})$ (ppm) ^a						$\delta(^{195}\text{Pt})$ (ppm) ^b
	N(1)H	N(2)H	N(4)H	H(2,6)	H(3,5)	CH_3	
LH_4	4.8(2)	9.6(1)	9.1(1)	7.48(2) ^e	7.09(2) ^e	2.37(3)	
<i>trans</i> $[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2$	4.4 ^d	10.9	9.5 ^d			2.30(3)	-3351
<i>cis</i> $[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2$		11.1	9.3 ^d		7.22(4) ^e		-3565
<i>trans</i> $[\text{Pt}(\text{LH}_3)_2]$	8.30 ^f		8.72		6.97(2)	2.19(3)	-3379
<i>cis</i> $[\text{Pt}(\text{LH}_3)_2]$	7.99		8.79	7.47(2)	7.00(2)		-3602

^aShift relative DMSO-d_6 multiplet at 2.50 ppm at ambient temperature. ^bShift relative Na_2PtCl_6 in D_2O at 301 K. ^c $^3J(\text{H}2, 6-\text{H}3,5) = 8.0$ Hz. ^dBroad resonances, integral sum of 4.4 and 9.52/9.28 resonances $\approx 3\text{H}$ atoms. ^eAX spin system as in free ligand degenerated into A_2 limiting case. ^fAt 2.1 Tesla $|^2J(^{195}\text{Pt}-^1\text{H})| = 50 \pm 2$ Hz.

be excluded. In the present study it is evident from the infrared spectra obtained for three separate samples of $[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2$ (with differing relative amounts of *cis* and *trans* isomers), that it is not possible to clearly distinguish between mixtures of or the pure *cis/trans* isomers of the dichlorobis-(4-*p*-tolylthiosemicarbazido)platinum(II) complexes (Fig. 2).

Irrefutable evidence for the presence of both *cis* and *trans* isomers is, however, obtained from the ^1H and ^{195}Pt NMR spectra of either $[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2$ or $[\text{Pt}(\text{LH}_3)_2]$ in DMSO-d_6 solution. It should be noted that although absolute confirmation of the *cis* or *trans* configuration in these complexes must await X-ray diffraction analyses of suitable crystals of either $[\text{Pt}(\text{LH}_4)_2]\text{X}_2$ or $[\text{Pt}(\text{LH}_3)_2]$, we have based our assignment on the observation that, in general, the chemical shift of the ^{195}Pt resonance of a *cis* isomer occurs at higher field relative to the corresponding *trans* isomer [12]. This assignment is consistent with the findings of Haines and Sun [6] who reported isolation only of a *trans* isomer of the cationic complexes if Cl^- is the corresponding anion. Figure 3 shows some typical ^1H spectra obtained for products A and C (prepared as in Fig. 1). By integration of the resonances ascribed to the N(1)H and N(2)H atoms in the complexes, or by integration of the corresponding ^{195}Pt resonances, it is possible to estimate the relative amounts of the two isomers present. Table I lists the relevant assignments and NMR parameters for these complexes.

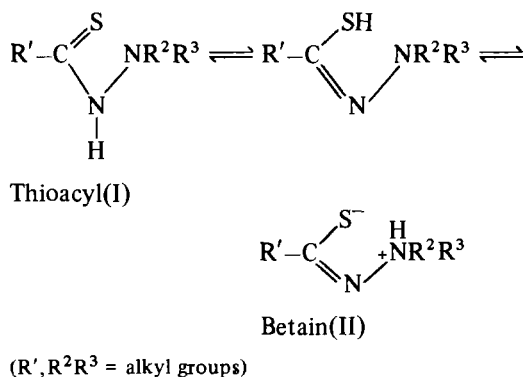
Unambiguous assignment of the N(2)H and N(4)H resonances in the free ligand LH_4 is complicated by exchange phenomena displayed by these H atoms. Thus the resonances ascribed to the N(1)H₂ and N(2)H moieties are extremely broad in anhydrous DMSO-d_6 solution, while the resonance at 9.1 ppm assigned to the N(4)H group is relatively sharp at ambient temperatures. These observations are consistent with the finding of Roberts and Yavari [11], that in the case of thiosemicarbazide and 4-methylthiosemicarbazide, the hydrazino protons N(2)H

exchange 6–200 times faster than the amide protons (N(4)H) in the presence of either aqueous acid or base in DMSO solutions. On this basis we have assigned the resonance at 9.1 ppm to the N(4)H and at 9.6 ppm to N(2)H moieties, respectively. In the case of the $[\text{Pt}(\text{LH}_4)_2]^{2+}$ cation only the resonances at 10.89/11.09 ppm give rise to a relative resonance integral clearly equivalent to 1H atom per ligand moiety. The sum of the resonance integrals at 4.4 ppm and 9.52/9.28 ppm relatively account for 3H atoms, confirming the formulation of the complex cation as $[\text{Pt}(\text{LH}_4)_2]^{2+}$. Furthermore, no ^{195}Pt – ^1H scalar coupling satellites are observable in these spectra, rendering unambiguous assignments difficult. A further interesting feature of the ^1H spectra of these complex cations, is that the AX spin system (H2,6–H3,5) of the *p*-tolyl moiety degenerates into an A_2 limiting case (Fig. 3). This suggests that the chemical shift difference between the H2,6 and the H3,5 protons is significantly reduced. This effect may be as a result of either substantial perturbations to the electronic integrity of the *p*-tolyl group of LH_4 as a result of complex formation, or as a result of the time averaged orientation of the *p*-tolyl moiety with respect to the square plane of the $[\text{Pt}(\text{LH}_4)_2]^{2+}$ complex cation. Square planar Pt(II) complexes are thought to display significant chemical shift anisotropy [13], a phenomenon also implicated in the disappearance of ^{195}Pt – ^1H coupling constants, especially at high magnetic fields (see below). In any event, models show that it certainly is not unreasonable to expect the *p*-tolyl moiety to assume orientations at approximately right angles to the square plane of the coordination sphere of Pt(II), with a possible effect on the shielding of the H2,6 protons. In contrast, in the neutral $[\text{Pt}(\text{LH}_3)_2]$ species, the H2,6–H3,5 spin system of the *p*-tolyl group, is again seen to be an AX system, as observed for the uncomplexed ligand, LH_4 .

Considering the ^1H spectrum of the neutral $[\text{Pt}(\text{LH}_3)_2]$ complexes (Fig. 3) two further points are noteworthy. In the first place it is possible to observe the ^{195}Pt – ^1H coupling satellites corresponding to the *ca.* 33% ^{195}Pt containing isotopomer of the neutral complex. Significantly the ^{195}Pt – ^1H scalar coupling satellites are only just evident at a field of 5.87 Tesla (250 MHz, ^1H), while at 2.1 Tesla (90 MHz, ^1H) these couplings are readily measurable, for the 8.3 ppm resonance ($|^2J(^{195}\text{Pt}-^1\text{H})| = 50 \pm 1$ Hz). Consequently the latter resonance has been assigned to the N(1)H₂ moiety as indicated in Table I. The broadness of the resonances of the ^{195}Pt containing isotopomers at high magnetic fields, is thought to be due to significant chemical shift anisotropy relaxation of the ^{195}Pt nucleus [13]. Furthermore it is evident that both the N–H resonances are relatively sharp, suggesting that the N–H exchange processes are relatively slower than in the corresponding cationic complexes.

Nature of Complexes

In the absence of reliable X-ray diffraction data, the correct detailed formulation of both the cationic and neutral bis(4-*p*-tolylthiosemicarbazido)platinum(II) complexes must remain tentative. In particular, given the known tendency of uncomplexed 1,1,4,4-tetrasubstituted thiosemicarbazides to display thioacyl–betain tautomerism in solution [14], then the correct formulation of the $[\text{Pt}(\text{LH}_4)_2]^{2+}$ and $[\text{Pt}(\text{LH}_3)_2]$ complexes is not necessarily straightforward. The 1,1,4,4-tetrasubstituted thiosemicarbazides have been found to exist as an equilibrium mixture of the thioacyl(I) and betain(II) tautomer in solution as shown below.



Our data suggests that the cationic complexes may best be thought of as complexes predominantly involving the thioacyl tautomer(I) of the 4-*p*-tolylthiosemicarbazide, while the neutral complexes may best be considered to involve the thiosemicarbazido in the betain(II) form. The extreme ease with which the cationic complexes $[\text{Pt}(\text{LH}_2)_4]^{2+}$ are deprotonated to yield neutral $[\text{Pt}(\text{LH}_3)_2]$ species, as well as the ^1H NMR assignments in Table I, is consistent with this view. Further evidence in support of the above contention is provided by the ^{13}C chemical shifts of the thiocarbonyl carbon atom in the ^{13}C spectra of these substances. Table II lists the relevant chemical shifts of the carbon atom in question. Evidently the thiocarbonyl carbon atom becomes more shielded in passing from the uncomplexed ligand through the cationic to the neutral complex. This trend is consistent with a decrease in the C=S bond order, which may be associated with an increased C–N(2) bond order in the neutral $[\text{Pt}(\text{LH}_3)_2]$ complex. Similar shifts to higher field in ^{13}C spectra of some Pt(II) thioamido complexes, have also been interpreted in terms of a decrease in the C=S bond order on metal complex formation [15]. Furthermore an X-ray diffraction study of the *trans*-bis-(thiosemicarbazido)nickel(II) complex shows that the bond distances C–N(2) (1.25 Å) and C–S (1.7 Å) are consistent with an essentially localized C–N(2) double and a C–S single bond respectively [10].

TABLE II. ^{13}C Chemical Shift of Thiocarbonyl group

Thiocarbonyl group	LH_4	$[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2^{\text{a}}$	$[\text{Pt}(\text{LH}_3)_2]^{\text{a}}$
$\delta(^{13}\text{C})$ ppm ^b	179.6	175.5	171.4

^aOnly the shift for *trans* isomer given. ^bRelative to DMSO-d_6 at 39.5 ppm at ambient temperature.

In conclusion our results indicate that

(i) In the synthesis of simple cationic and neutral substituted thiosemicarbazido complexes of platinum(II), it does not appear possible to prepare isomerically pure complexes in one step the predominant product being assigned the *trans* isomer.

(ii) Cationic complexes $[\text{Pt}(\text{LH}_4)_2]\text{Cl}_2$ are extremely readily deprotonated to yield neutral species $[\text{Pt}(\text{LH}_3)_2]$ which may undergo further deprotonation and oxidation to other uncharged species. Compounds in this work appear to form the initial members of a series of complexes postulated but not isolated by Holm *et al.* in their study of a complete electron-transfer series of bis(phenylazo-*N*-phenylthioformamido)platinum(II) complexes [9].

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