# Effect of palladium(II) on NMR spectra of coordinated semicarbazones

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## Introduction

Palladium(II) ($^{105}$Pd) complexes are widely used in a variety of fields, including catalysis and the pharmaceutical industry, among others [1]. Due to this, the challenge of identifying and characterizing these compounds using NMR spectroscopy, as well as understanding the effect of the $^{105}$Pd core on the nature of the spectra of these systems, remains relevant.

## The experimental basis of the study

We have synthesized several dimeric coordination complexes of palladium (II) with semicarbazone ligands $[(PdL^{1\text{-}4})_2Cl]$. The synthesis involved the reaction of a palladium precursor, $K_2PdCl_4$, with $L^1$-$L^4$ semicarbazones followed by formation of a palladacycle ($L^1$-$L^3$) or additional coordination of the phenolic hydroxyl group ($L^4$), as shown in Figure 1.

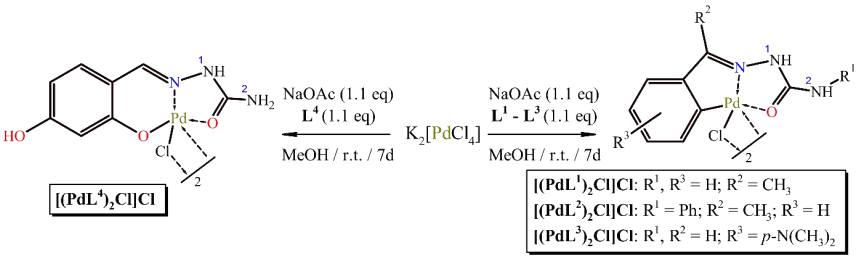


*Figure 1. General scheme of synthesis and structure of the obtained complexes*

The compounds were studied using NMR spectroscopy using Jeol ECX400A spectrometer with an operating frequency of 399.78 ($^1$H) and 100.53 ($^{13}$C) MHz ($[(PdL^1)_2Cl]Cl$, $[(PdL^2)_2Cl]Cl$) and on Bruker Avance IIITM HD 500 MHz with an operating frequency of 500.13 ($^1$H) and 125.77 ($^{13}$C) MHz ($[(PdL^3)_2Cl]Cl$, $[(PdL^4)_2Cl]Cl$) in DMSO-$d_6$ at 25°C.

## The influence of palladium(II)

### The origins of the challenging interpretation

As is well known, the primary challenges in analyzing the $^1$H and $^{13}$C NMR spectra of $^{105}$Pd compounds stem not only from the frequent presence of various paramagnetic impurities in samples, which can sometimes lead to significant line broadening of the spectra, but also from spin-spin interactions between the $^1$H and $^{13}$C nuclei in the product structure and the quadrupole moment of the palladium nuclei ($Q$ = 66 fm$^2$, $I$ = 5/2, $\gamma$ = -1.23·10$^7$ rad s$^{-1}$ T$^{-1}$) [2, 3] can also cause serious distortions in the spectral pattern.

## Interpretation of the spectra of complexes $[(PdL^1)_2Cl]Cl$ & $[(PdL^2)_2Cl]Cl$

The main pattern observed in the analysis of the spectra for the synthesized compounds is a marked broadening of signals in the $^1H$ NMR spectrum (Table 1).

*Table 1. $^1H$ NMR spectra of $L^1$, $L^2$ & $[(PdL^1)_2Cl]Cl$, $[(PdL^2)_2Cl]Cl$*

| Compound | NMR spectra, δ, ppm., DMSO-$d_6$ | | | |
|---|---|---|---|---|
| | $CH_3$ | $H^o$<br>($H^m$)<br>[$H^p$] | $H^{o'}$<br>($H^{m'}$)<br>[$H^{p'}$] | $N^1H$<br>($N^2H_2$)<br>[$N^2H$] |
| $L^1$ | 2.15 s | 7.79 d<br>(7.31 – 7.33 m)<br>[7.31 – 7.33 m] | | 9.30 s<br>(6.45 s)<br>[ - ] |
| $[(PdL^1)_2Cl]Cl$ | 2.18 s | 6.38 – 7.50 m | | 10.27 w. s<br>(6.38 – 7.50 m)<br>[ - ] |
| $L^2$ | 2.24 s | 7.87 – 7.89 m<br>(7.37 – 7.39 m)<br>[7.37 – 7.39 m] | 7.61 d<br>(7.27 – 7.29 m)<br>[7.00 t] | 9.76 s<br>( - )<br>[ 8.82 s] |
| $[(PdL^2)_2Cl]Cl$ | 2.28 s | 6.99 m<br>7.24 – 7.28 m<br>7.43 – 7.44 m<br>7.9 m | 6.99 m<br>7.24 – 7.28 m<br>7.43 – 7.44 m<br>7.9 m | 9.31 w. s<br>9.75 w. s<br>( - )<br>[ 8.95 s] |

In particular, in the compound $[(PdL^1)_2Cl]Cl$ signals of the amino group $N^2H_2$ and the benzene ring are so broadened that they "merge" into one composite multiplet at 6.38 – 7.50 ppm. This fact may also be facilitated by some weak-field shift in the signal of the protons of this amino group caused by the deshielding of the electron density of the metal center during complex formation.

However, it is worth noting that, for coordination compounds of $^{105}Pd$, spectra with normal, non-broadened signals have been observed, despite the significant quadrupole moment of $^{105}Pd$. The investigation of complex compounds $(PdL^{1\text{-}2})_2Cl$ by mass-spectrometry has revealed their dimeric nature. This suggests that the broadened signals in the spectra of the complexes we obtained are due to their binuclear structure, as well as possibly the paramagnetism of palladium compounds that may be present as impurities due to partial intramolecular reduction in DMSO. On the dimeric nature of $[(PdL^2)_2Cl]Cl$ also indicates the presence of two signals at 9.31 and 9.75 ppm in the $^1H$ NMR spectra, corresponding to protons of the $N^1H$ amino groups in different dimeric fragments. This can be explained by one of the amino groups acting as a hydrogen bond donor in a dimeric molecule, with a chloride ion coordinating to its proton [5], thus making the amino groups non-equivalent and manifesting as two signals in the spectrum.

The increase in the number of signals in the $^{13}C$ NMR spectrum is largely due to the removal of the magnetic equivalence of carbon atoms in the benzene ring of the semicarbazone during palladium coordination, as well as spin-spin interaction with the $^{105}Pd$ nucleus. In this case, a characteristic shift occurs in the region of the weak field for signals $C^1$ and $C^2$ of the carbon atoms of the benzene ring of the semicarbazone, due to the formation of a metallocycle. It is also worth noting that the formation of a metallocycle is pronounced in the $^1H$-$^{13}C$-HMQC spectrum $[(PdL^1)_2Cl]Cl$, where the fourth cross-peak appears in the region of aromatic protons and carbon atoms, due to the removal of magnetic equivalence from the atoms of the benzene ring, but the fifth cross peak does not appear due to the substitution of a proton in the second position with a $^{105}Pd$ atom.

## Interpretation of the spectra of complexes [(PdL$^3$)Cl]Cl & [(PdL$^4$)Cl]Cl

The effect of the inclusion of additional donor functional groups (4-N(CH$_3$)$_2$ (L$^3$), 2,4-OH (L$^4$)) in the ligand structure on the spectral features of $^{105}$Pd complex compounds has been investigated. Despite evidence of a similar dimeric structure (in particular, by the integral intensities of $^1$H NMR spectra and an increase in the number of signals in $^{13}$C NMR spectra), the signals remain un-broadened. At the same time, the number of signals in the proton spectra of both complexes increases significantly, probably due to the spin-spin interaction of protons with $^{105}$Pd, which can be demonstrated by the example of [(PdL$^3$)$_2$Cl]Cl (fig. 2).

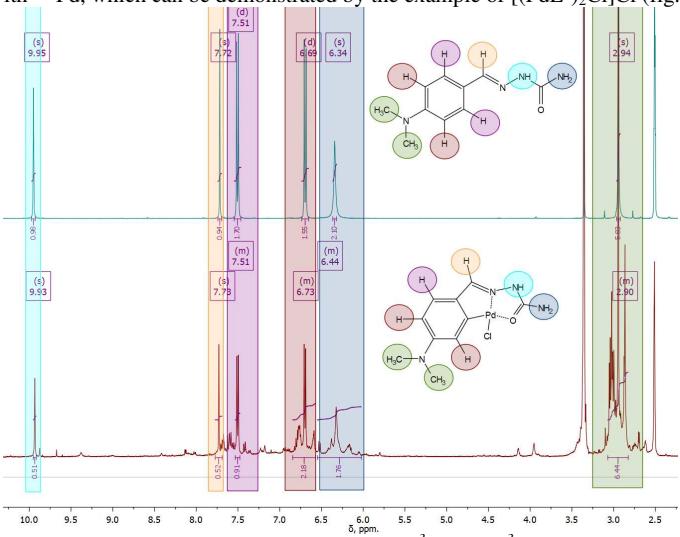


*Figure 2. Spectra of compounds L$^3$ & [(PdL$^3$)Cl]Cl*

Thus, it can be concluded that the introduction of additional donor functional groups into the structures of dimeric $^{105}$Pd complexes with semicarbazones leads to a levelling of signal broadening in the proton spectrum, however, it contributes to a greater manifestation of the spin-spin interaction of protons with $^{105}$Pd.

## References


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