REACTIONS OF Pd(II) AND Pt(II) COMPLEXES WITH TETRAETHYLTHIOURAM DISULFIDE

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Abstract

The reactions of tetraethylthiouram disulfide (DTS), an inhibitor of the nephrotoxicity of Pt(II) drugs, an efficient agent in the treatment of chronic alcoholism, in the treatment of HIV infections, AIDS and heavy metal toxicity, and a fungicide and herbicide, with K₂[PtCl₄], in ratio 1:1 and 1:2, gave the compounds [PtCl₂DTS] and [Pt(S₂CNEt₂)₂] respectively. The reaction of the complexes K₂[PdCl₄], Pd(AcO)₂ and [PdCl₂(PhCN)₂], where PhCN = Benzonitirle, with tetraethylthiouram disulfide in ratio 1:1 or 1:2, yielded orange crystals identified as [Pd(S₂CNEt₂)₂]. The crystals were suitable for study by X-ray diffraction. The -S-S- bridge in the tetraethylthiouiram disulfide molecule was broken and the two molecules of the thiocarbamatederivative were bound to the Pd(II) by the equivalents sulfur atoms. All the compounds were characterized by IR, ¹H and ¹³C NMR spectroscopies.

Introduction

Cisplatin and other Pt(II) complexes are nephrotoxic. A number of nucleophilic agents, mainly sulfur compounds, inhibit these toxic effects¹⁻³. The interaction of cisplatin with several of these compounds such as methionine, penicillamine and glutathione, has been studied in recent years⁴⁻¹³. To elucidate the mechanisms involved in the inhibition of toxicity, we have studied the behavior of Pt(II) complexes containing ligands with -S-S- bonds such as tetraethylthiouram disulfide [DTS,bis(diethylthiocarbamoyl) disulfide, 1,1'-dithiobis(N,N'-diethylthioformamide), dithiosulfiram, Antabuse®, Noxal®, Abstensil®, BAN] (1). This compound is used in the treatment of the chronic alcoholism, as a fungicide and herbicide, and also to inhibit the secondary effects of the cisplatin, in the treatment of HIV infections, AIDS and heavy metal toxicity¹⁴⁻¹⁵. The study was also extended to the interaction of the tetraethylthiouiram disulfide molecule with Pd(II) complexes.

On the other hand, the diethyldithiocarbamate molecule (DEDTC, Imuthiol®) (2), related with tetraethylthiouiram disulfide is present in rubbers and plastics¹⁶ and it has also been used as inhibitor of cisplatin toxicity without inhibition of the antitumor activity¹⁷,¹⁸. This may be due to its high affinity for Pt, which causes the breaking of Pt-protein adducts¹⁹ without capture of the Pt bound to DNA²⁰. Pt(II)-diethyldithiocarbamate complexes have been found in plasma of patients treated with this inhibitor²¹.

Both substances, tetraethylthiouiram disulfide (DTS) and its derivative diethyldithiocarbamate (DEDTC) have similar applications as fungicides, pesticides, antioxidants, lubricants, flotation agents, and vulcanization accelerators²² and they are active against some typus of leukemia, probably due to their immunomodulation properties²³. The mutual interconversion is easily produced, especially in the biological medium²⁰ and inside lubricants DTS is also converted into DEDTC¹⁶.

The crystal structure of tetraethylthiouiram disulfide was studied previously²⁴. The most important feature of this molecule is that, although there is no C₂ symmetry, the two halves are
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chemically equivalent. Wang et al. had shown interest in deformation density studies due to the short distances and forced angles found at room temperature. However, these studies showed a low electronic density in the zone between the two bound S atoms. This feature facilitates the breaking of the molecule at this point, and two dithiocarbamate ions are produced. Studies on the thermal dissociation of DTS showed that the radical free process is reversible and that the solvent has no influence on it. At 120°C DTS dissociates to DEDTC. The process can be reversed by the action of cytochrome c or hydrogen peroxide, among others.

Due to the proclivity of DTS to dissociate to DEDTC, only a few compounds of DTS have been described. Brinkhoff et al. synthesized derivatives of Hg, Cuadrado et al. compounds of Ti and V and Contreras et al. complexes of Cr(III). Pd(II) and Pt(II) derivatives of tetramethylthiuram disulfide were obtained but not spectroscopically characterized. Only one study on crystal structure has been reported for a methyl derivative of DTS, [HgI₂(Me₄DTS)]²⁻. In this compound, the Me₄DTS is coordinated to the metal in bidentate mode by the two sulfur atoms from the C=S groups.

We have studied the reactions of tetraethylthiouram disulfide with K₂[PdCl₄], Pd(II), and [PdCl₂(PhCN)₂], where PhCN = Benzonitrile, and K₂[PtCl₄]. In some cases, we have observed the breaking of the S-S bond of the tetraethylthiouram disulfide to give two molecules of the corresponding dithiocarbamate, which binds to the metal ion giving a very stable complex as a product, with similar structural characteristics to the Ni(II) diethylidithiocarbamates studied by Bonamico et al., Pd(II) by Gessner et al. the Pt(II) by Amanov et al. and the Mo(V) diethylidithiocarbamate compound characterized by Kocaba et al. No [M(DEDTC)₂] (M = Pd, Pt) compound has yet been described from reaction with DTS.

Experimental

Materials and Methods

The complexes were prepared using K₂[PdCl₄], Pd(II), and K₂[PtCl₄] products from Johnson Matthey and tetraethylthiouram disulfide from Sigma. The [PdCl₂(PhCN)₂] complex was prepared by reaction of PdCl₂ (Johnson Matthey) with benzonitrile (Fluka) at reflux during five hours. The product was recrystallized from chloroform or THF.

Elemental analyses were carried out on a Carlo Erba 1500 microanalyzer at the Serveis Científico-Técnicos at the University of Barcelona. The infrared spectra were recorded in solid state (KBr pellets) on a FT-IR Nicolet 6700 spectrometer in the 4000-400 cm⁻¹ range and on a FT-IR Bomem DA-3 spectrometer in the 400-1500 cm⁻¹ range. ¹H{¹³C} and ¹³C{¹H} NMR spectra were obtained on a Varian Gemini 300 spectrometer using CDCCl₃ as solvent. Chemical shifts were measured relative to TMS.

Suitable crystals for X-ray diffraction experiments were mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from 25 reflections and refined by the least-squares method. Intensity data were collected using graphite monochromated MoKα radiation. Lorentz and polarization corrections were applied but not corrections for absorption due to the small volume of the crystal selected. The structure was solved locating the Pd atom by direct methods using the MULTAN 11/84 program. The positions of the remaining non-hydrogen atoms were determined by weighted Fourier synthesis. Refinement was carried out using the SHELX-76 program. Hydrogen atoms were located by difference Fourier synthesis and introduced in the refinement with a global isotropic temperature factor after the convergence of the anisotropic thermal parameters for non-H atoms. Methyl groups were allowed to rotate axially in the last stages of refinement.

Syntheses of the Complexes

(a) [Pd(S₂CNEt₂)₂] (3). 1 mmol of K₂[PdCl₄] and 2 mmol of tetraethylthiouram disulfide (DTS) were dissolved in 20 mL of 50% mixture ethanol/water. The solution was stirred for 1 h at 40 °C and then a yellow precipitated appeared. The solid was filtered, washed in ethanol and dried overnight under silica gel. Found: C, 29.53; N, 7.06; S, 32.51. PdCl₂H₂O₂N₂S₄ requires: C, 29.81; N, 6.95; S, 31.83. When the compound (3) was recrystallized in THF or in chloroform, bright orange crystals were formed. These crystals were suitable for study by X-ray. Found: C, 29.80; N, 6.78; S, 32.13. PdCl₁H₂O₂N₂S₄ requires: C, 29.81; N, 6.95; S, 31.83. The reactions of the complexes Pd(II) and [PdCl₂(PhCN)₂] with DTS in 1:2 ratio in chloroform or THF, also yielded similar bright orange crystals identified as [Pd(S₂CNEt₂)₂]. The reaction in the 1:1 ratio gave a brown solid, possibly a Pd(II) DTS derivate, which in THF or chloroform yielded the bright orange crystals of [Pd(S₂CNEt₂)₂] and a dark residue. Other attempts to obtain a Pd(II)-DTS, by changing the solvent, or in absence of oxygen failed and [Pd(S₂CNEt₂)₂] was always identified as final product.

(b) [PtCl₂(DTS)₂] (4). 1 mmol of K₂[PtCl₄] and 1 mmol of tetraethylthiouram disulfide were dissolved in 20 mL of 50% mixture ethanol/water. The solution was stirred for 1 h at 40 °C and a dark brown precipitated was formed. The solid was filtered, washed in ethanol and dried overnight under silica gel. Found: C, 18.44; N, 4.16; S, 20.63; Cl, 10.05. PtCl₂H₂O₂N₂S₄Cl₂ requires: C, 18.46; N, 4.31; S, 19.71; Cl, 10.90. All efforts to obtain crystals suitable for study by X-ray were unsuccessful. Only macleed needles could be isolated.
(c) \(\{\text{Pt}(\text{S}_2\text{CNEt}_2)\}_2\) (5) 1 mmol of \(\text{K}_2[\text{PdCl}_4]\) and 2 mmol of finely powdered tetraethylthiouram disulfide were mixed and 20 mL of ethanol was added. The solution was stirred for 1 h at 40 °C and a pale pink precipitate formed, which evolved to dark brown. After 36 h stirring at room temperature the solid was filtered but it could not be identified. Brown needles suitable for X-ray diffraction were obtained from the solution. Found: C, 24.87; H, 4.12; N, 5.95; S, 25.94. \(\text{PtCl}_6\text{H}_2\text{N}_2\text{S}_4\) requires: C, 24.43; H, 4.07; N, 5.70; S, 26.02.

\[
\begin{align*}
\text{K}_2\text{PdCl}_4 + \text{DTS} & \quad \overset{1:2 \text{ or } 1:1}{\text{H}_2\text{O/EtOH}} \quad \overset{1 \text{ h } 40^\circ\text{C}}{\longrightarrow} \quad [\text{Pd}(\text{S}_2\text{CNEt}_2)\text{]}_2 \\
\text{Pd}(\text{AcO})_2 + \text{DTS} & \quad \overset{1:2}{\text{HCCl}_3 \text{ or THF}} \quad \overset{1 \text{ h } 40^\circ\text{C}}{\longrightarrow} \quad [\text{PdCl}_2(\text{PhCN})\text{]}_2 + \text{DTS} \\
[\text{PdCl}_2(\text{PhCN})\text{]}_2 + \text{DTS} & \quad \overset{1:2}{\text{HCCl}_3 \text{ or THF}} \quad \overset{1 \text{ h } 40^\circ\text{C}}{\longrightarrow} \\
\text{K}_2\text{PtCl}_4 + \text{DTS} & \quad \overset{1:1}{\text{H}_2\text{O/EtOH}} \quad \overset{1 \text{ h } 40^\circ\text{C}}{\longrightarrow} \quad [\text{PtCl}_2(\text{DTS})\text{]}_2 \\
\text{K}_2\text{PtCl}_4 + \text{DTS} & \quad \overset{1:2}{\text{EtOH}} \quad \overset{36 \text{ h room t}}{\longrightarrow} \quad [\text{Pt}(\text{S}_2\text{CNEt}_2)\text{]}_2
\end{align*}
\]

Scheme 2. Reactions of tetraethylthiouram disulfide with Pt(II) and Pd(II) complexes

Results and discussion

**FTIR study**

The main IR frequencies of the tetraethylthiouram disulfide, the diethyldithiocarbamate and their Pd(II) and Pt(II) complexes obtained are reported in Table I. The spectra of tetraethylthiouram disulfide and diethyldithiocarbamate molecules are very similar. The main difference is the presence of a band at 434 cm\(^{-1}\) in the spectrum of the DTS. This band is assigned to the stretching mode \(\nu(\text{S-S})\)\(^{39,40}\). In the spectrum of (4) this band appears but it is absent in the spectra of (3) and (5), confirming the breaking of the S-S bond. The band assigned to \(\nu(\text{CN})\) and \(\nu_3(\text{CNC})\) coupled with the inner modes from alkyl groups\(^{41}\), also called thioureid band\(^{42,43}\) appears at 1497 cm\(^{-1}\) in DTS and at lower frequency in free DEDTC. This band moves to higher frequencies (30-40 cm\(^{-1}\) for DTS and 40-50 cm\(^{-1}\) for DEDTC) in the new complexes. This is due to the ability of the amines to transfer density of charge towards the S atoms through the \(\pi\) system, thus reforcing the C-N bond\(^{44}\). In the case of dithiocarbamates, the resonant form IV (Scheme 3) explains the shift of the band towards higher frequencies\(^{42}\).

\[
\begin{align*}
\text{R}_2\text{N-C} & \quad \overset{\text{S}^-}{\text{S}^-} \quad \overset{\text{S}^-}{\text{S}^-} \quad \overset{\text{S}^-}{\text{S}^-} \\
\text{(I)} & \quad \text{(II)} & \quad \text{(III)} \quad \overset{\text{R}_2\text{N}= \quad \text{S}^-}{\text{(IV)}}
\end{align*}
\]

Scheme 3. Resonant forms for dialkyldithiocarbamate anions
Table 1. IR frequencies (cm⁻¹) for Pd(II) and Pt(II) derivatives of DTS and DTDTC

| Assignment       | DTS          | Na-DEDTC     | Pd-DEDTC     | Pt-DTS       | Pt-DEDTC     |
|------------------|--------------|--------------|--------------|--------------|--------------|
| ν(C-N) and ν(C-N-C) | 1497 vs      | 1476 s       | 1520 vs      | 1533 vs, br  | 1526 vs      |
| ν(C-N)           | 1296 m       | 1297 m       | 1299 m       | -            | 1300 w       |
| ν(C-S) asym      | 1001 m       | 984 s        | 988 m        | 987 m, br    | 987 m        |
| ν(C-S) sym       | 555 m        | 566 m        | 570 m        | 574 w        | 568 m        |
| ν(S-S)           | 434 w        | -            | -            | 438 w        | -            |
| ν(M-S)           | -            | -            | 356 m        | 330 m, b     | 340 m        |
| ν(M-Cl)          | -            | -            | -            | 324 m        | -            |
| ν(C-S) sym       | -            | -            | 554 w        | -            | 554 w        |
| ν(C-S) asym      | -            | -            | 554 w        | -            | 554 w        |

The resonant forms which contribute to the electronic structure for the DTS complexes are shown in Scheme 4. The lesser contribution is that of the form IV because the band ν(CN) is absent in the complexes of DTS.

The band at 1296 cm⁻¹ assigned to ν(CN) appears in the spectra of (3) and (5) but not in the spectrum of (4), confirming the formation of DEDTC complexes in the former and of DTS complex in the latter. The stretching frequency ν(C-S) asym appears at 1000 cm⁻¹ for DTS and at 987 cm⁻¹ for DEDTC. In the Pd(II) and Pt(II) complexes of DEDTC only one band appears in this zone, as corresponds to bidentate dithiocarbamates. In the spectrum of (4) only one band is observed which also indicates bidentate coordination for DTS. This band shifts to lower frequencies as a consequence of the lengthening of the end C-S bond when it is coordinated to the metal ion. The vibration ν(C-S) sym appears as a single band at 555 cm⁻¹ in the DTS spectrum and at 566 cm⁻¹ in the DEDTC spectrum. The band appears split in the spectrum of (4), but not in the spectrum of (3) or (5). In all cases this band is shifted towards higher frequencies in the complexes. The new bands that appear at low frequencies are assigned to ν(M-S) and ν(M-Cl), (Table 1).

Scheme 4. Resonants forms for dialkyldithiouram disulfide complex

**X-Ray Study**

Crystal parameters and a summary of the data collection and refinement process corresponding to compound (3) are given in Table 2. Although the cell parameters suggest a
tetragonal cell, the analysis of the equivalence between symmetry related reflections shows that the cell is monoclinic. A perspective view of the molecule, including the atom labeling, is shown in Figure 1. Fractional atomic coordinates with the equivalent temperature factors are listed in Table 3. Table 4 contains the corresponding bond distances and angles with their esd. Anisotropic thermal parameters and the listing of observed and calculated structural factors may be obtained on request from the authors. Crystal packing is depicted in Figure 2. The Pd atoms are situated in the crystallographic center of the cell.

The palladium atom is in planar coordination, the Pd-S distances being equivalent. The angles do not correspond exactly to a square distribution but a rhombus. For example, for the Pd atom one, the angles S12-Pd1-S11 and S12-Pd1-S11 are equal to 75.6° and the S12-Pd1-S12 and S11-Pd1-S11 are equal to 104.4°. There are two crystallographically non-equivalent molecules (Figure 1, a and b) which have the ethyl groups in different orientation but the distances and angles of both molecules have the same values. The C21-N22 and C11-N12 distances are shorter than expected indicating bond order greater than one. This fact is consistent with the IR data commented above. The diethiocarbamate C-S distances are also equivalent in all cases, indicating the delocalization of the anion charge produced when the initial molecule of dithiosulfiram breaks in the presence of the Pd(II) ion. The bond order is smaller in this case than in the whole ligand.

The crystal data of this Pd(II) complex was compared with that from the crystal structure of the tetraethylthiouram disulfide24,25 and with Ni(II), Cu(II), Zn(II), and Mo(V) diethylthiocarbamates complexes reported in the literature32-34,36. The C-S distances found for the Pd(II) compound range from 1.735 Å to 1.715 Å, which is very similar to the values for the Ni(II), Cu(II) and Zn(II) diethylthiocarbamate complexes, which are between 1.700 Å and 1.725 Å. However, the C-N distance in the Pd(II) complex, 1.294 Å, is shorter than corresponding to the Ni(II), Cu(II) and Zn(II) derivatives, which are between 1.35 Å and 1.33 Å, and shorter than the C-N distances in each perpendicularly half of the tetraethylthiouram disulfide molecule, 1.33Å and 1.36 Å. Thus, the bond order for C-N is higher in the Pd(II) compound than in tetraethylthiouram disulfide and the other complexes. The other lengths are similar and as expected in this type of compound.

The data corresponding to [Pd(SCNEt2)2] (3), can be also compared with [Pt(SCNEt2)2]. Table 2. Crystal data and Summary of Data collection and refinement for [Pd(SCNEt2)2]

| Crystal system | Monoclinic |
|----------------|------------|
| Space group    | P2/n       |
| a(Å)           | 16.430 (2) |
| b(Å)           | 6.237 (1)  |
| c(Å)           | 16.430 (2) |
| β(°)           | 90.00 (1)  |
| V(Å³)          | 1683.5     |
| Z              | 4          |
| Dm (gcm⁻³)     | 1.59       |
| Crystal size (mm) | 0.45 x 0.37 x 0.25 |
| F(000)         | 884        |
| µ(cm⁻¹)        | 15.3       |
| Radiation      | MoKα(λ=0.71073Å) |
| Scan method    | w-29       |
| Data collection range(2θ) | 2-60.8° |
| Range of hkl   | -22<h<22, 0<k<8, 0<l<23 |
| N. of measured refl. | 5160     |
| N. of unique refl. | 4804   |
| N. of obs.refl.(I>2σ(I)) | 4108 |
| N. of variables | 170       |
| R              | 0.031      |
| Rw             | 0.048      |
| Weighting scheme k, w=1/(σ²(Fo)+ kF²) | 0.018084 |

The C-N length in [Pt(SCNEt2)2] is 1.32 Å, while the C-N length in [Pd(SCNEt2)2] is 1.29 Å; therefore, the bond order is lower than that of the Pd compound, but slightly higher than that corresponding to the DTS molecule.

The study of the electronic densities at low temperature in tetramethyl and tetraethylthiouram disulfides carried out by Wang et al.25, explains the breaking of the S-S bond to give two negative halves. The shorter C-N bond gives greater density accumulation (0.5 e Å⁻³) at the midpoint of the bond than is observed for the longer bonds (0.3 e Å⁻³). The C=S double bond gives 0.4 e Å⁻³ whereas the C-S single bond is 0.2 e Å⁻³. There is little density accumulation along the S-S bond.
Lone-pair electron density is apparent around all the S atoms. The degree of the density accumulation at the midpoint of bonded atoms follows the order: shorter C-N > C-C > longer C-N, C=S > C-S > S-S. The soft metal ion Pd(II) can easily coordinates to the S atoms to produce the stable neutral dithiocarbamate complex.

The non equivalence of the protons of -CH2- and -CH3 can be observed in the spectrum of DTS. In the case of CH2, instead of the expected quadruplet, a multiple appears. Likewise, two triplets can be observed for the CH3 groups. This means that the two ethyl groups from SC(S)N(Et)2 are not equivalent as a consequence of the hinderance of free rotation due to the high order of the (S2C)-(NEt2) bond25,47, as observed for DMF27. On the other hand, in the spectrum of DEDTC only one signal is observed for both CH2 and CH3, indicating the equivalence of the protons. When DTS is broken, the two fragments are equivalent (DEDTC anion) and the resonant form III, which allows the free rotation of (S2C)-(NEt2) bond, predominates. Therefore, in the spectra of [Pd(S2CNEt2)2] (3) and [Pt(S2CNEt2)2] (5) the quadruplets and triplets observed were assigned to CH2 and to CH3 respectively. Both groups are equivalent, as confirmed by the X-ray results. The upfield shifts observed for all the protons in comparison with those corresponding to DEDTC are also present in other DEDTC complexes27. In contrast, in the spectrum of [PdCl2(DTS)]2 (4), the non-equivalence of the protons in CH2 and CH3 is evident, which confirms the presence of DTS in the complex. The resonances appear as upfield-shifted, broad multiple signals in comparison to those of DTS. The double bond character for C-N in the complex is greater than the corresponding to DTS27 and as a consequence the hinderance to rotation increases. This observation is consistent with the IR results.

Table 3. Fractional atomic coordinates (x104) with the equivalent tempertaure factors.

|        | X/A  | Y/B  | Z/C  | Beq |
|--------|------|------|------|-----|
| Pd1,* | 10000 | 0    | 5000 | 3.44 |
| Pd2   | 0    | 5000 | 10000| 3.46 |
| S11   | 8714(1) | 1171(1) | 4641(1) | 4.62 |
| S12   | 9149(1) | -2625(1) | 5348(1) | 4.32 |
| S13   | -347(1) | 2178(1) | 9148(1) | 4.30 |
| S14   | 358(1) | 6171(1) | 8714(1) | 4.65 |
| C1    | 8360(1) | -1274(4) | 5004(2) | 3.89 |
| N1    | 7594(1) | -1836(4) | 4988(1) | 4.38 |
| C13   | 7334(2) | -3914(6) | 5337(2) | 5.99 |
| C14   | 6961(2) | -447(6) | 4635(2) | 5.70 |
| C15   | 6890(2) | 791(8) | 3710(2) | 6.84 |
| C16   | 7097(3) | -3635(9) | 6237(3) | 8.48 |
| C21   | 7(2) | 3759(4) | 8355(1) | 3.86 |
| N2    | 4(2) | 3167(4) | 7600(1) | 4.52 |
| C23   | 363(2) | 4578(6) | 6966(2) | 5.58 |
| C24   | -335(2) | 1112(6) | 7333(2) | 5.93 |
| C25   | 1280(3) | 4214(8) | 6881(2) | 6.95 |
| C26   | -1224(3) | 1322(9) | 7096(3) | 8.31 |
| H31   | 6812(2) | -449(6) | 5005(2) | 8.46 |
| H32   | 7826(2) | -505(6) | 5285(2) | 8.46 |
| H33   | 6383(2) | -814(6) | 4915(2) | 8.46 |
| H34   | 7115(2) | 1209(6) | 4750(2) | 8.46 |
| H35   | 6348(2) | 38(8) | 3512(2) | 8.46 |
| H36   | 6820(2) | -2490(8) | 3605(2) | 8.46 |
| H37   | 7408(2) | -206(8) | 3372(2) | 8.46 |
| H38   | 6806(3) | -5102(9) | 6429(3) | 8.46 |
| H39   | 6662(3) | -2338(9) | 6255(3) | 8.46 |
| H40   | 7598(3) | -3278(9) | 6641(3) | 8.46 |
| H41   | 76(2) | 4218(6) | 6390(2) | 8.46 |
| H42   | 255(2) | 6236(6) | 7121(2) | 8.46 |
| H43   | 7(2) | 527(6) | 6817(2) | 8.46 |
| H44   | -292(2) | -26(6) | 7827(2) | 8.46 |
| H45   | 1457(3) | 4975(8) | 6317(2) | 8.46 |
| H46   | 1374(3) | 2505(8) | 6833(2) | 8.46 |
| H47   | 1645(3) | 4842(8) | 7373(2) | 8.46 |
| H48   | 1050(3) | -176(9) | 6931(3) | 8.46 |
| H49   | -1245(3) | 2409(9) | 6585(3) | 8.46 |
| H50   | -1544(3) | 2021(9) | 7605(3) | 8.46 |

* atoms fixed at special positions
The most spectacular difference in the $^{13}$C NMR spectra can be found in the chemical shift corresponding to C=S. In tetraethylthiouram disulfide this signal appears at 192.67 ppm and the coordination to the platinum (4) produces a shift to upper fields. In the DEDTC the signal appears at 207.29 ppm but in the complexes (3) and (5) it shifts down-field. In the spectrum of $\{\text{PtCl}_2(\text{DTS})\}_2$ (4), all the signals are split due to the non-equivalence of the two halves of the DTS molecule or to the presence of two structurally non-equivalent molecules of DTS. Both CH$_2$ and CH$_3$ carbon atoms in (3) and (5) are equivalent as expected for DEDTC complexes. In the platinum complex the shifts are slightly higher than in the palladium complex which is consistent with the higher acceptance ability of the platinum.

![Figure 1](image1)

**Figure 1.** Two crystallographically non-equivalent molecules in the structure off $[\text{Pd}(S_2\text{CNEt}_2)_2]$. Figures a) and b) show the different orientation of the ethyl groups.

![Scheme 5](image2)

**Scheme 5.** Structure proposed for the dimer Pt(II)-tetraethylthiouram disulfide complex
$^1$H, $^{13}$C NMR and $^{195}$Pt Spectra

The $^1$H and $^{13}$C NMR spectra of tetraethylthiouram disulfide, the sodium diethylidithiocarbamate and the Pd(II) and Pt(II) complexes (3), (4) and (5) are given in Table 5.

The $^{195}$Pt NMR spectrum of $[\text{PtCl}_2(\text{DTS})]_2$ gave only one signal at -1763 ppm (K$_2\text{PtCl}_4$ as reference). This resonance appears slightly shifted as expected for a PtCl$_2$S$_2$ environment, which could be attributed to the anomalous charge density arrangement on the sulfur atom in DTS before described. The appearance of only one signal indicates that the arrangement of the two platinum atoms in the dimer is equivalent and that only one specie is present in solution$^{48}$.

Table 4. Bond Lengths (Å) and Bond Angles (°) with their e.s.d.'s for $[\text{Pd(S}_2\text{CNEt}_2)_2]$.

| Bond                | Length (Å) | Angle (°) |
|---------------------|------------|-----------|
| $S_{11}$-$Pd_1$     | 2.312 (1)  |           |
| $S_{12}$-$Pd_1$     | 2.320 (1)  |           |
| $C_{11}$-$S_{11}$   | 1.738 (3)  |           |
| $C_{11}$-$S_{12}$   | 1.713 (2)  |           |
| $C_{12}$-$S_{21}$   | 1.735 (2)  |           |
| $C_{21}$-$C_{22}$   | 1.715 (2)  |           |
| $N_{12}$-$C_{11}$   | 1.307 (3)  |           |
| $C_{13}$-$N_{12}$   | 1.479 (4)  |           |
| $C_{14}$-$N_{12}$   | 1.472 (4)  |           |
| $C_{16}$-$C_{13}$   | 1.540 (6)  |           |
| $C_{15}$-$C_{14}$   | 1.539 (5)  |           |
| $N_{22}$-$C_{21}$   | 1.294 (3)  |           |
| $C_{23}$-$N_{22}$   | 1.486 (4)  |           |
| $C_{24}$-$N_{22}$   | 1.465 (4)  |           |
| $C_{25}$-$C_{23}$   | 1.530 (6)  |           |
| $C_{26}$-$C_{24}$   | 1.517 (6)  |           |

Table 5. $^1$H and $^{13}$C NMR shifts (ppm) of Pd(II) and Pt(II) DEDTC and DTS complexes$^*$. $^1$H NMR

| Compound          | CH$_2$ | CH$_3$ |
|-------------------|--------|--------|
| DTS               | 4.03 m | 1.50 t |
| Na-DEDTC          | 4.02 q | 1.23 t |
| $[\text{Pt(S}_2\text{CNEt}_2)_2]$ | 3.73 q | 1.29 t |
| $[\text{Pt(S}_2\text{CNEt}_2)_2]$ | 3.57 q | 1.29 t |

$^{13}$C NMR

| Compound          | C=S    | CH$_2$ | CH$_3$ |
|-------------------|--------|--------|--------|
| DTS               | 192.67 | 52.02  | 13.26  |
| Na-DEDTC          | 186.03 | 45.24  | 12.45  |
| $[\text{PtCl}_2(\text{DTS})]_2$ | 186.71 | 44.64  | 12.39  |
| $[\text{PtCl}_2(\text{DTS})]_2$ | 207.29 | 48.00  | 12.71  |

Acknowledgements

We are grateful to DGICYT Ref. PB94-0922-C02-01, to European Community HCM, ref. ERBCHRXCT 920016 and to Johnson Matthey for K$_2$PdCl$_4$ and K$_2$PtCl$_4$ supplied.
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Received: August 11, 1997 - Accepted: August 19, 1997 - Received in revised camera-ready format: October 30, 1997