

THE PALLADIUM (II): DIACETYLMONOXIME - 2-BENZOTHAZOL - HYDRAZONE COMPLEX REVISITED: A SOLUTION ¹H NMR AND UV-VIS STUDY

Antonio S. Mangrich* and Anselmo L. Juliatto

Departamento de Química - Universidade Federal do Paraná - Cx.Postal 19081 - 81531-970 - Curitiba - PR

Aida Espinola

Coordenação de Programas Pós-Graduação em Engenharia - Universidade Federal do Rio de Janeiro - Cx. Postal 68505 - 21945-900 - Rio de Janeiro - RJ

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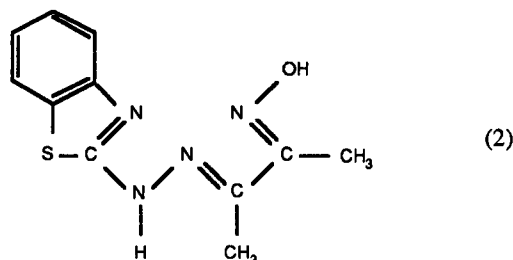
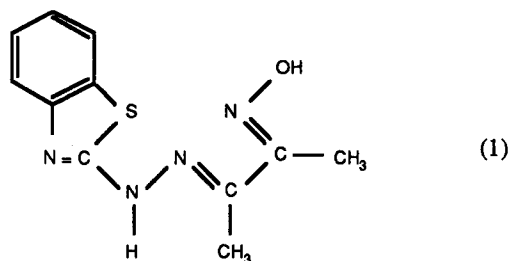
The palladium (II): DAMBETH complex (DAMBETH = diacetylmonoxime - 2 - benzothiazol - hydrazone) has been studied as a model of interactions of heavy metals and organics in polluted environments. The stoichiometry between palladium ion and DAMBETH is 1:1 and we conclusively showed it is in disagreement with the 1:2 ratio previously reported (Anal. Chim. Acta, **57**, 435 (1971)). The coordination of palladium ion in the equatorial plane occurs with a chloride ion and with the three underlined nitrogen atoms, $\text{-}\underline{\text{N}}=\text{C}-\text{C}=\underline{\text{N}}-\text{N}-\text{C}=\underline{\text{N}}\text{-}$, of the chain of the DAMBETH structure. A formation constant value of $K = 1.86 \times 10^5$ was determined. The proton NMR and UV-Vis spectra of the ligand and of the complex are discussed.

Keywords: model of heavy metal-organics interaction in environments, proton NMR and UV-Vis spectrophotometry of palladium complex.

INTRODUCTION

In recent years, one of the aims of our laboratory, first situated in Rio de Janeiro and now in Curitiba, State of Paraná, Brazil, was to study and identify sites of chelating metal ions in soil and sedimentary matter (SOM) such as Brazilian topsoils¹, peat² and coal³. SOM contains a number of types of sites capable of coordinating both hard and soft metal ions, according to Pearson's classification⁴.

Some thiosemicarbazones and hydrazones form tridentate ligands through the underlined S and N atoms of $\text{-}\underline{\text{S}}=\text{C}-\text{N}-\underline{\text{N}}=\text{C}-\text{C}-\underline{\text{N}}=\text{C}-$ and $\text{-}\underline{\text{N}}=\text{C}-\text{N}-\underline{\text{N}}=\text{C}-\text{C}-\underline{\text{N}}=\text{C}-$ chains, with a moderately high affinity for both hard and soft metal ions⁵. DAMBETH (diacetylmonoxime - 2 - benzothiazol - hydrazone) utilizes similar chains in metal ion complexation; see structures (1) and (2).



Palladium (II) is a soft ion and its faster reaction kinetics, as compared to other corresponding heavy metals⁶, makes it a convenient electrophilic analogue, for studies of heavy metal-organics interaction in polluted soil and water. Its complex with DAMBETH has been studied^{7,8}, with the purpose of developing an analytical reagent for palladium (II). By analogy with the nickel-dimethylglyoxime complex, a ratio of 1:2 for the palladium-DAMBETH complex has been proposed⁷ and confirmed⁸ by mole ratio method. According to these authors, the palladous ion in the palladium-DAMBETH complex coordinates neither with the chloride ion, nor with the thiazol ring nitrogen or sulfur atoms. The 1:2 stoichiometry for the complex appears to be wrong. The stability constant of palladium (II) mono-chloride (PdCl^+) is $\log K = 4.47$, according to Smith et al⁹. PdCl^+ is the extracted cation in the solvent extraction of palladium with oximes from palladous chloride solutions¹⁰. Furthermore, the soft sulfur atom of the DAMBETH structure is a potential coordinator for the palladous ion. Knowing this we decided to investigate the Pd:DAMBETH stoichiometry ratio and the structure of the complex. Our main purpose was to explain the reported apparently anomalous characteristics of DAMBETH upon palladous ion complexation, and to understand the chemistry of the multiple site complexation exhibited by DAMBETH, which could become a good model to mimic the action of organic pollutants in the environment.

RESULTS AND DISCUSSION
Electronic spectra

The electronic absorption spectra of the complex in chloroform and acetone are similar (Fig. 1), although a difference in the position of the absorption maxima wavelengths is observed. Both spectra have intense bands in the UV region and broad intense bands in the visible region.

The continuous variation¹¹ and molar ratio¹² methods (Figs. 2 and 3) indicate a 1:1 stoichiometry for the complex. A tenta-

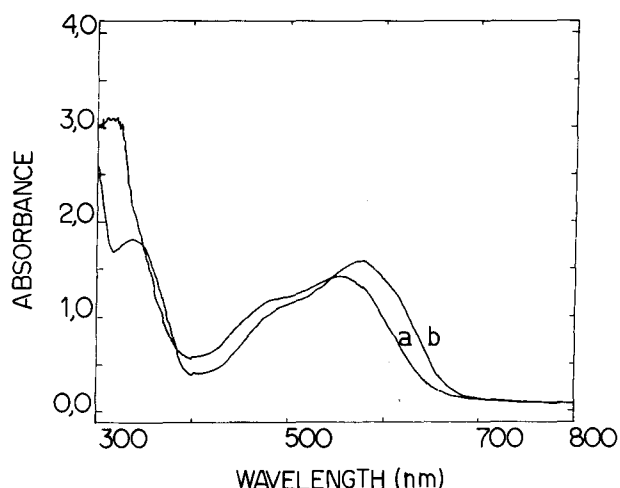


Figure 1. Electronic absorption spectra at 298 K of the Pd:DAMBETH complex: 1a. in chloroform. 1b. in acetone.

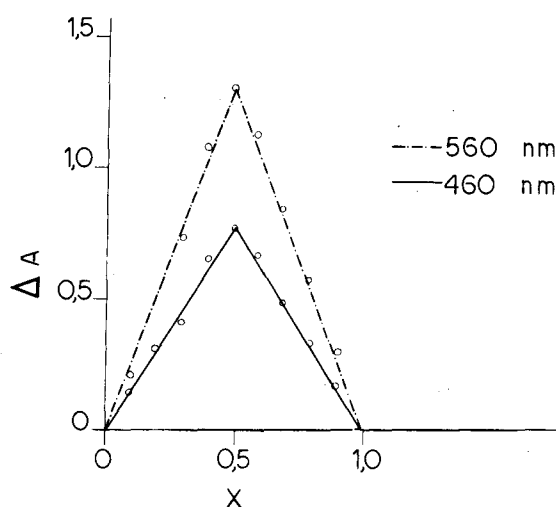


Figure 2. Absorption ΔA at 460 and 560 nm, corrected for the DAMBETH excess, due to complex formation of PdCl_2 with DAMBETH (continuous variation method). $X = ([\text{DAMBETH}]) / ([\text{PdCl}_2] + [\text{DAMBETH}])$; $[\text{DAMBETH}] = [\text{PdCl}_2] = 5.00 \times 10^{-4} \text{ M}$

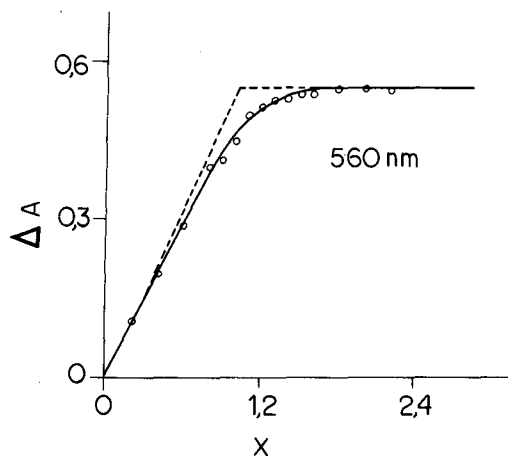


Figure 3. Absorption ΔA at 560 nm, corrected for the DAMBETH excess, due to complex formation of PdCl_2 with DAMBETH (mole ratio method). $X = [\text{DAMBETH}] / [\text{PdCl}_2]$; $[\text{PdCl}_2] = 1.000 \times 10^{-4} \text{ M}$; $[\text{DAMBETH}]$ from $0.200 \times 10^{-4} \text{ M}$ to $2.200 \times 10^{-4} \text{ M}$.

tive formation constant, $K = 1,86 \times 10^5$, was determined by the Harvey and Manning¹³ and by the continuous variation¹⁴ methods.

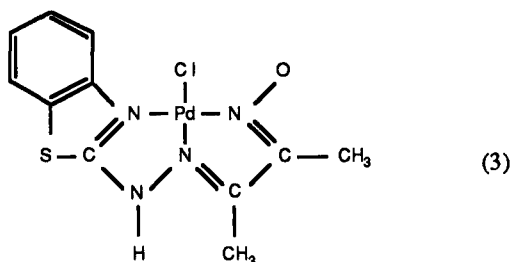
The most intense band ($\lambda_{\text{max}} = 336 \text{ nm}$) can be probably assigned to DAMBETH-centered $\pi \rightarrow \pi^*$ transitions, and the maximum and shoulders in the visible region to three Pd - DAMBETH charge-transfer (CT) transitions. According to a polarographic reduction study of the free ligand¹⁵, the hydrazone C=N group is the most susceptible to reduction, the thiazol ring C=N group the least one. This result suggests that the shoulder of longest wavelength is a consequence of the CT transition from the palladium ion to the hydrazone C=N group. The absorption in λ_{max} corresponds to the energy for the CT transition from the palladium (II) ion to the oxime C=N group and the shoulder of the shortest wavelength in the visible region is a consequence of CT transition to the thiazol ring nitrogen atom.

¹H NMR spectra

The ligand dissolved in CDCl_3 exhibited a ¹H NMR spectrum with CH_3 signals at δ 2.35 and 2.62, assigned to the $\text{NN}=\text{C}-\text{CH}_3$ (hydrazone) and $\text{ON}=\text{C}-\text{CH}_3$ (oxime) methyl protons, respectively. The signals were shifted upfield to δ 1.64 and 2.22, respectively, upon coordination of palladium ion with the nitrogen atoms of the C=N groups of the hydrazone and oxime moieties. The resonances of the benzenic protons and the H of the hydrazone HNN= group appear in the spectrum of the free ligand between δ 7.40 and 7.80. The signals of the phenyl protons move upfield to between δ 7.30 and 7.75 and that of the HNN= group moves downfield to 9.20 upon coordination of the palladium (II) with the ligand. The chemical shift changes occurring upon metal-ligand complexes formation can be interpreted as a combination of σ induction towards the metal center and π back-bonding from the metal causing changes in the electronic distribution in the ligand¹⁶. A rapid decrease in inductive polarization and an increase in the metal distance occur. The inductive effects would influence the protons nearest to palladium, such as the proton of the HNN= group. Back-bonding from the B_1 and B_2 metal orbitals, in an effective C_{2v} symmetry around the palladium ion, to the π^* C=N orbitals would affect the electron density over the entire ligand, but would be most evident at the remote H, such as the benzenic and methyl protons of the DAMBETH molecule. In these protons the opposing σ effect is very weak as explained above. The chemical shift of the near H reflects a deshielding, due to a strong withdrawal of electron density towards the metal ion, and is only partly offset by back-donation. The chemical shifts of the remote H reflect a shielding, due to an increase in electron density through back-bonding from the metal towards the three C=N groups. The same kind of effects have been noted for some metal complexes of pyrazine and N-methylpyrazinium ion¹⁷.

CONCLUSIONS

1. Diacetylmonoxime-2-benzothiazol-hydrazone forms a palladium complex with a 1:1 metal-to-ligand ratio in acidic and neutral solutions.
2. The $[\text{CIPdDAMBETH}]$ complex is insoluble in water, and slightly soluble in non-polar organic solvents, as well as in some organic solvents of poor coordinating ability such as Me_2CO .
3. We propose structure (3) for the $[\text{CIPdDAMBETH}]$ complex based on UV-visible and ¹H NMR data, C, H, N and Pd contents and on the "spot test" for chlorine.



EXPERIMENTAL

Materials and methods

All spectrophotometric analytical work, with the objective of determining Pd-DAMBETH stoichiometry and formation constant was performed at 25 °C in solutions of 0.08 M HClO₄ in acetone containing 4% of water. In all experiments, freshly prepared acetone solutions were used. Electronic spectra for structural analysis were recorded in chloroform or acetone.

Specord UV-Vis aus Jena and Hewlett Packard 84500 spectrophotometers with 10-mm silica cells were used for the UV-visible spectroscopy studies. NMR spectra were recorded using a Varian XL 100 spectrometer with deuterated chloroform (CDCl₃) as solvent, and chemical shifts were quoted with respect to tetramethylsilane (0.00 ppm). A Perkin-Elmer 240 equipment was used for C, H and N elemental analysis. Palladium was determined by a gravimetric method with dimethylglyoxime¹⁸.

DAMBETH and [ClPdDAMBETH] Complex Syntheses

DAMBETH was synthesized according to the method of Goldstein and Libergott⁷. The dry product had a melting point of 250-251 °C. Thin layer chromatography of the product, run on a silica gel 6060 Eastman Kodak plate with fluorescent indicator and chloroform as solvent, gave a single spot. ¹H NMR (CDCl₃): δ 2.35, 2.62, 7.40 to 7.80.

Treatment of an aqueous stock solution of PdCl₂ with 0.2% DAMBETH in ethanol up to quantitative precipitation afforded a red-violet product.

Analysis: Calc. for C₁₁H₁₁N₄OSCIPd.0.5 H₂O: C, 33.18%; H, 3.04%; N, 14.07%; Pd, 26.72%. Found: C, 33.82%; H, 3.00%; N, 13.51%; Pd, 27.34%. The presence of chlorine was confirmed by a "spot test"¹¹. ¹H NMR (CDCl₃): δ 1.64, 2.22,

7.30 to 7.75, 9.20. Electronic (CHCl₃): λ = nm (ε): 336 (3640), 496 (2200), 578 (3200), 611 (2520). (CH₃COCH₃): 336 (2200), 486 (1160), 553 (1480), 588 (1120).

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