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Synthesis, NMR spectral and structural studies on mixed ligand complexes of Pd(II) dithiocarbamates: First structural report on palladium(II) dithiocarbamate with SCN^-ligand

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ABSTRACT

Three new mixed ligand complexes of palladium(II) dithiocarbamates; [Pd(4-dpmpzdtc)(PPh_3)(SCN)] (**1**), [Pd(4-dpmpzdtc)(PPh_3)Cl] (**2**) and [Pd(bzbudtc)(PPh_3)Cl] (**3**), (where, 4-dpmpzdtc = 4-(diphenylmethyl) piperazinecarbodithioato anion, bzbudtc = *N*-benzyl-*N*-butyldithiocarbamato anion and PPh_3 = triphenylphosphine) have been synthesized from their respective parent dithiocarbamates by ligand exchange reactions and characterized by IR and NMR (^1H, ^{13}C and ^{31}P) spectroscopy. IR and NMR spectral data support the isobidentate coordination of the dithiocarbamate ligands in all complexes (**1**–**3**) in solid and in solution, respectively. Single crystal diffraction analysis of complexes **1**–**3** evidences that all three complexes are exhibiting distorted square planar geometry. The Pd–S distances in **1**–**3** vary in accordance with the differences in *trans* influences of PPh_3, SCN^- and Cl^- and it is in the order of PPh_3 > SCN^- > and Cl^-. Interchange of the anionic auxiliary ligand (SCN^- to Cl^-) induces asymmetry to the dithiocarbamate-metal bonds. Thioureide C–N bond distances are short in **1**–**3**, supporting a contribution of thioureide form to the structures. The observed distortions in the square planar geometry for **1**–**3**, are in the order of **1** > **2** > **3**.

1. Introduction

Palladium dithiocarbamates are used as catalysts [1], anti-cancer agents [2–7], and in materials science [8]. Recent studies on palladium dithiocarbamate complexes report their use as selective chromogenic sensors for the detection of mercury [9] as well as for the preparation of nano scale materials [8].

Among the group 10 elements a vast range of nickel dithiocarbamate complexes are reported already. However, reports on palladium dithiocarbamates are more limited and mainly concern the study of biological activity of the complexes rather than their structural chemistry. To the best of our knowledge the presented synthetic method [Scheme 1] for palladium dithiocarbamates containing PdS_3P and PdS_2PCl chromophores has not been employed in this context. Moreover, this is the first structural report on palladium dithiocarbamate complex with a SCN^- ligand. Ligand exchange reactions were performed with aiming to prepare and compare the influence of dithiocarbamate and auxiliary ligands such as Cl^- and SCN^- on the coordination geometry around the metal. Through this contribution we wish to present a structural investigation of three Pd(II) dithiocarbamates with PdS_3P and PdS_2PCl chromophores.

2. Experimental

All the reagents and solvents were commercially available analytical grade materials and were used as supplied.

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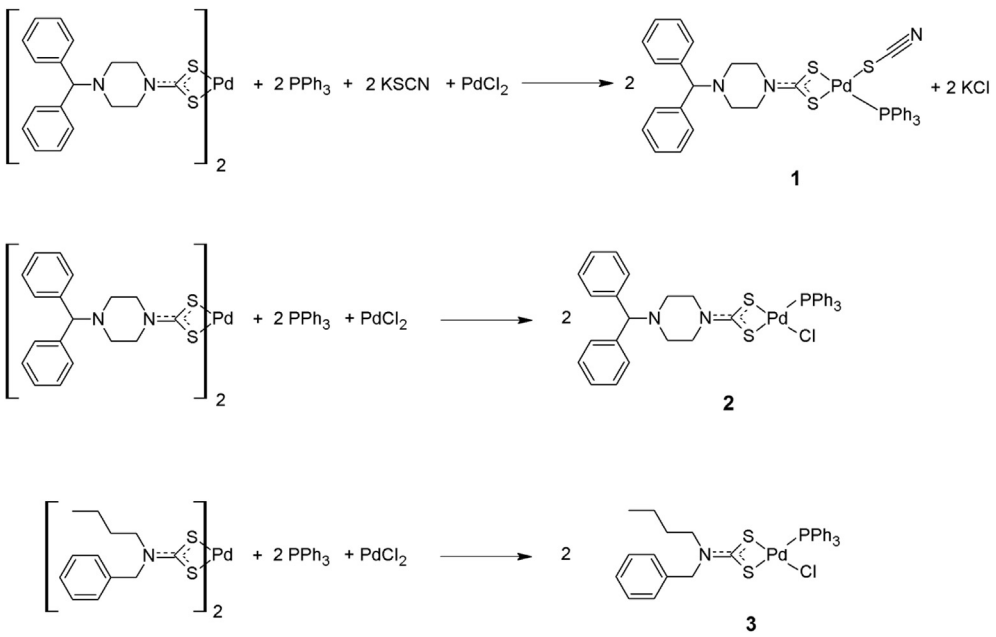

Scheme 1. Synthesis of mixed ligand complexes.

2.1. Preparation of parent complexes

2.1.1. Bis(4-(diphenylmethyl)piperazinecarbodithioato) palladium(II), [Pd(4-dpmpzdtc)$_2$]

A mixture of 1-(diphenylmethyl)piperazine (252 mg, 1 mmol) and CS_2 (76 mg, 1 mmol) in ethanol (50 mL) was kept at −5 °C for 10 min and to this pale yellow solution, $PdCl_2$ (89 mg, 0.5 mmol) in acetonitrile (25 mL) was then added slowly with vigorous stirring. The dark yellowish brown precipitate obtained was filtered, washed copiously with diethyl ether, allowed residual water to evaporate, and dried in a desiccator.

2.1.2. Bis((N-benzyl-N-butyl)dithiocarbamato) palladium(II)

[Pd(bzbudtc)$_2$] was prepared by using *N*-benzyl-*N*-butylamine instead of 1-(diphenylmethyl)piperazine according to the above described procedure.

2.2. Preparation of mixed ligand complexes

The mixed ligand complexes **1**–**3** were prepared by the ligand exchange reactions involving the parent dithiocarbamates with MS_4 chromophore as shown in Scheme 1. The complexes are stable under normal conditions and soluble in common organic solvents.

2.2.1. (4-(Diphenylmethyl) piperazinecarbodithioato)(thiocyanato)(triphenylphosphine) palladium(II), [Pd(4-dpmpzdtc)(PPh$_3$)(SCN)] (*1*)

A mixture of Pd(4-dpmpzdtc)$_2$ (381 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol), $PdCl_2$ (89 mg, 0.5 mmol) and KSCN (97 mg, 1 mmol) was refluxed for 3 h in chloroform:acetonitrile mixture (1:1, 50 mL) and was then concentrated to *ca.* 25 mL. The orange red solution obtained was filtered and allowed to evaporate. After 2 days, the solid precipitate was filtered and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2:$CHCl_3$ mixture. Yield: 75%, dec. 181–183 °C.

2.2.2. (Chloro)(4-(diphenylmethyl) piperazinecarbodithioato)(triphenylphosphine) palladium(II), [Pd(4-dpmpzdtc)(PPh$_3$)Cl] (*2*)

A mixture of Pd(4-dpmpzdtc)$_2$ (381 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol) and $PdCl_2$ (89 mg, 0.5 mmol) was refluxed for 2 h in chloroform:acetonitrile mixture (1:1, 50 mL) and then concentrated to *ca.* 25 mL. The orange red solution obtained was filtered and allowed to evaporate. After 2 days, the solid precipitate was filtered and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2:$CHCl_3$ mixture. Yield: 70%, dec. 163–165 °C.

2.2.3. (Chloro)(N-benzyl-N-butyldithiocarbamato)(triphenylphosphine) palladium(II): [Pd(bzbudtc)(PPh$_3$)Cl] (*3*)

A mixture of Pd(bzbudtc)$_2$ (291 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol) and $PdCl_2$ (89 mg, 0.5 mmol) was refluxed for 2 h in chloroform (50 mL) and then concentrated to *ca.* 25 mL. The orange solution obtained was filtered and allowed to evaporate. The solid precipitate was filtered and dried in a desiccator. Single crystals suitable for X-ray analysis were obtained by recrystallization from chloroform. Yield: 55%, dec. 150–151 °C. Attempts to prepare [Pd(bzbudtc)(PPh_3)(SCN)] were unsuccessful as the product slowly converted into **3** which was evidenced by NMR.

2.3. Analysis methods

IR spectra were recorded on Bruker VERTEX 70 spectrometer (range 4000–400 cm^{-1}). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker Avance 500 MHz spectrometer at 303 K, using $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded in proton decoupled mode. In ^{1}H and ^{13}C NMR runs the chemical shifts are referenced to the signal of the internal tetramethylsilane (TMS) and in ^{31}P NMR to the signal of the external 85% orthophosphoric acid in a 1 mm diameter capillary tube inserted coaxially inside the 5 mm NMR-tube.