

Synthesis and structural characterization of Pd(II) and Pt(II) complexes with L-citrulline

Bruno Z. Mascaliovas (IC), Fernando R. G. Bergamini (PG), Pedro P. Corbi (PQ), Alexandre Cuin (PQ)

Abstract

Synthesis and structural characterization of Pd(II) and Pt(II) complexes with the amino acid L-citrulline (cit, $C_6H_{13}N_3O_3$) are presented in this work. Elemental and thermal analyses indicate the molecular compositions $PdC_{12}H_{24}N_6O_6$ and $PtC_{12}H_{24}N_6O_6$, respectively, and the crystal structures were solved by powder X-ray diffraction.

Key words: L-citrulline, palladium, platinum.

Introduction

Platinum and palladium complexes have been extensively studied as potential antitumoral and antibacterial agents since the serendipitous discovery of the antitumor activities of cisplatin, or *cis*-diamminedichloridoplatinum(II) in the 1960's. In this context, our research group has prepared and characterized new metal complexes of Pt(II) and Pd(II) with amino acids and derivatives. Amino acids have been considered as versatile ligands in coordination chemistry, and they show low toxicity and high affinity for specific sites in the human body. L-Citrulline ($C_6H_{13}N_3O_3$, cit) is an endogenous mammal's amino acid intermediate in the urea cycle. It is also found in foods such as watermelons, cucumbers, pumpkins and muskmelons, and it is known to act on body process of ammonia detoxification through its conversion to urea. This amino acid may also act as a potent hydroxyl scavenger. The present study describes the synthesis and structural characterization of Pt(II) and Pd(II) complexes with L-citrulline.

Results and Discussion

The synthesis of the complexes were based on the reaction of aqueous solutions of K_2MCl_4 (M = Pt or Pd) with freshly prepared aqueous solutions of potassium L-citrullinate at constant stirring for 2 and 24 hours, respectively. The yellow (Pd complex) and brown (Pt complex) solids were vacuum filtered, washed with water and ethyl ether and dried in a desiccator with P_4O_{10} . Both complexes were insoluble in water and in most of organic solvents. Elemental analysis confirm the composition 1:2 metal/ligand, as shown in Chart 1. Infrared and ^{13}C NMR spectroscopic analyses suggest coordination of cit to metal centers by the oxygen of the carboxylate group and by the nitrogen atom of the amino group. The structures of the complexes were solved by powder X-ray diffraction. The structural formula of the Pd(II) complex is shown in Image 1.

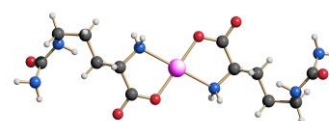


Image 1. Molecular structure of $[Pd(cit)_2]$ complex. Nitrogen, oxygen and Pd are in blue, red and pink.

Chart 1. Elemental analysis for the complexes. Values in the parenthesis are the theoretical ones.

Compound	C (%)	H (%)	N (%)
$PdC_{12}H_{24}N_6O_6$	29.9 (31.7)	4.87 (5.32)	17.4 (18.5)
$PtC_{12}H_{24}N_6O_6$	24.6 (26.5)	4.25 (4.45)	14.1 (15.5)

Conclusions

Metal complexes of Pd(II) and Pt(II) with L-citrulline were obtained in a 1:2 M/L molar composition. The structures of the complexes were solved by powder X-ray diffraction, and coordination of the ligand to the metal centers was shown to occur by the nitrogen atom of the amino group and by the oxygen atom of the carboxylate group. The obtained results about the synthesis and structural characterization of the Pd(II) complex have just been accepted for publication in the form of a scientific paper¹. In addition, this project provided to the undergraduate student the opportunity of learning about the routine of a research lab in Bioinorganic and Medicinal Chemistry, which will be important to the sequence of his career.

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