

CRYSTAL AND MOLECULAR STRUCTURE OF BIS (4-HYDROXY-L-PROLINATO) PALLADIUM (II) TRIHYDRATE

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ABSTRACT

The crystal and molecular structure of the title compound has been determined from single crystal x-ray data; the results show a square-planar coordination for the palladium ion with the imino-nitrogen and carboxyl oxygen atoms coordinating in the *cis*-configuration. It appears that hydrogen bonding involving water molecules is the predominant packing force in the crystal structure.

INTRODUCTION

IN keeping with our current interest on the preparation and structural aspects of palladium compounds¹, we have prepared and undertaken the crystal and molecular structure of the title compound with a view to deducing the coordination around the metal ion and also to compare its structure with known structures of related compounds.

EXPERIMENTAL

Yellow needle-shaped crystals of the title compound were obtained from the reaction of Pd (II) chloride and 4-hydroxy-L-proline in 1 : 2 molar ratio in water. Elemental analysis showed the presence of three water molecules. The crystals, when dried over P₂O₅, crumbled to powder. Microthermogravimetric analysis of the crystals confirmed the presence of three water molecules and also showed them to be uncoordinated.

The 3D x-ray intensity data with Zr filtered Mo-K α radiation for 2057 reflections were collected on an indigenously fabricated four-circle diffractometer (controlled by Electronics Corporation of India Ltd., Computer TDC-312 system). The structure was analysed by Patterson and Fourier synthesis. At the present stage of refinement R-factor (without hydrogen atoms) based on F is 6.2%.

Crystal data

Pd C₁₀H₁₆O₆N₂·3H₂O

Monoclinic

a = 9.751 (2)

b = 7.691 (3)

c = 10.989 (4) Å

β = 114.29 (2)°

Z = 2, space group, *P*2₁

*D*_m = 1.83 g.cm⁻³ (floatation), *D*_c = 1.86 g.cm⁻³

μ = 12.27 cm⁻¹.

RESULTS AND DISCUSSION

Of the three spin allowed *d-d* transitions in square planar complexes of the type ML₂X₂ (X=Cl, L=ligand), absorption bands due to the higher energy transitions are generally obscured by intense ligand to metal charge transfer bands as well as by ligand bands². In the present complex a band at 31,250 cm⁻¹ (λ_{max} , 320 nm; ϵ = 249) has been observed which is assigned to a transition 'A₁ → A₂'. The other two *d-d* transitions have been obscured by bands originating from the ligand.

The infrared (examined as mull in nujol and hexachlorobutadiene) and the powder laser Raman spectra of the complex in the region 4000–200 cm⁻¹ show bands respectively at 1610 and 1387 cm⁻¹ which are assigned to ν as COO⁻ and ν_s COO⁻. The absence of any band in the region 1750–1700 cm⁻¹ and also the reduction in N–H stretching frequency of 20 cm⁻¹ clearly show that the carboxyl oxygen (one from each carboxyl group) and the imino-nitrogen atoms are coordinated to the palladium ion resulting in a five membered chelate ring. The broad band around 3500 cm⁻¹ shows the presence of water molecules. Pd–N is assigned to a band at 557 cm⁻¹ which is most intense in the Raman spectrum. Unambiguous assignment for ν_{Pd-O} could not be made in view of ligand modes absorbing in the corresponding region. However, the band at 405 cm⁻¹ is tentatively assigned to ν_{Pd-O} ⁴. As optically active proline and related amino acids are known to coordinate to palladium (II) and platinum (II) ions in the *cis*-configuration it is presumed that the coordination of the prolinato ions to palladium (II) ion in the present complex is *cis*-square planar.

Our preliminary x-ray results show that the coordination around the palladium ion is nearly square planar with the carboxyl oxygen and the imino-nitrogen atoms coordinating in the *cis*-configuration. A projection of the structure of the molecule as viewed down the *b* axis is shown in figure

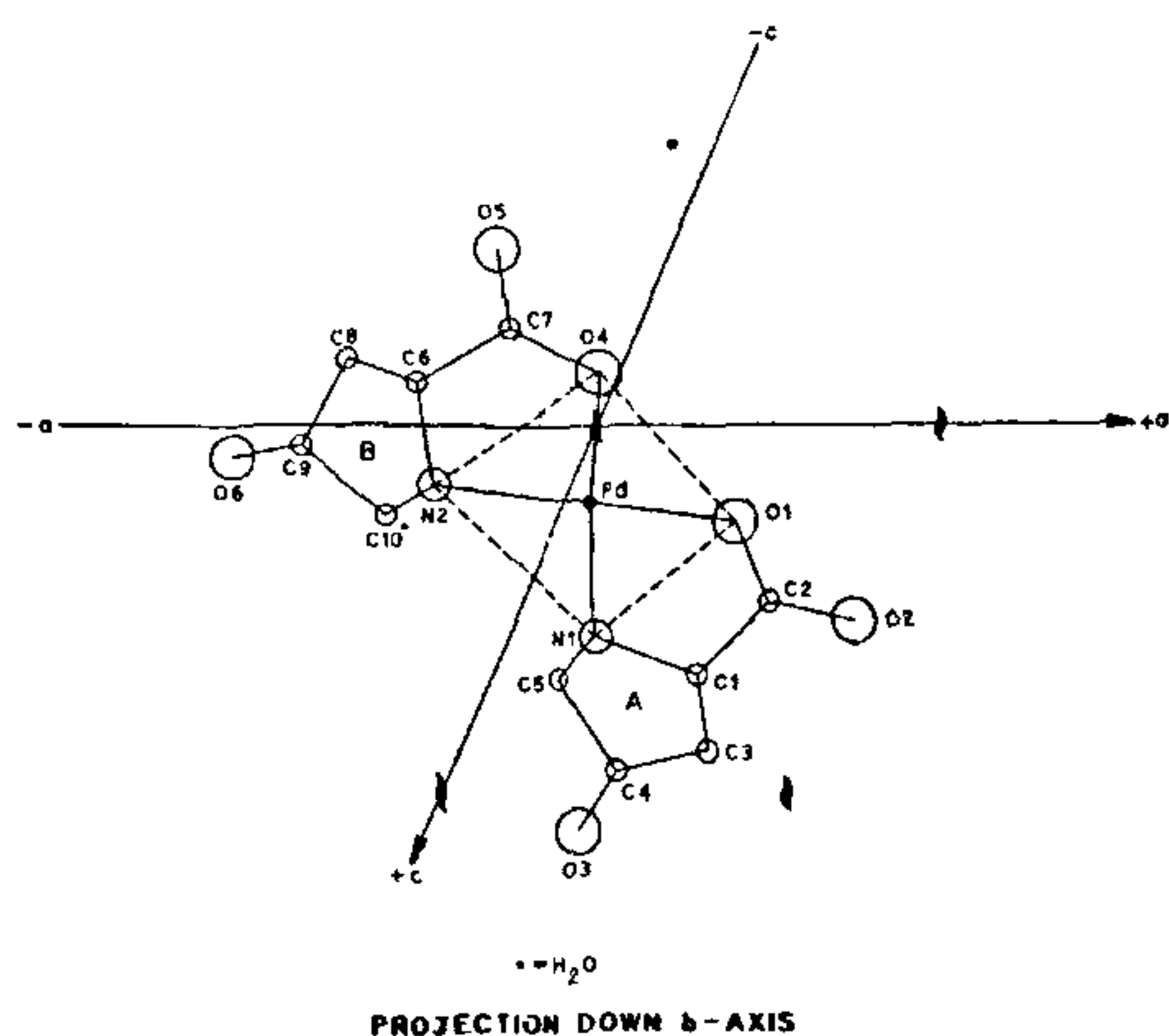


Figure 1. General view of the molecule along the b-axis.

1. The angles around the palladium ion are close to the expected 90° and 180° but there are some distortions due to slight strain caused by chelation. The N_1 -Pd- O_1 and N_2 -Pd- O_4 angles (83.4° and 85.4°) are smaller than the N_1 -Pd- N_2 and O_1 -Pd- O_4 angles (98.6° and 92.4°). The O_1 -Pd- N_2 and O_4 -Pd- N_1 angles (173.9° and 175.3°) are smaller than expected. The Pd- N_1 and Pd- N_2 lengths are 2.01 \AA and 2.01 \AA and the Pd- O_1 and Pd- O_4 lengths are 1.98 \AA and 1.99 \AA respectively. These are normal and agree with published data.⁵ The water molecules are not coordinated to the metal ion but are involved in hydrogen bonding with the

carboxylic oxygen and imino-nitrogen atoms. It appears that the hydrogen bonding involving water molecules is the predominant packing force in the crystal structure. In the pyrrolidine ring A, the atoms C_1 and C_5 are found to be on the opposite side of the coordination plane; C_1 and C_5 being below and above the plane respectively. The carboxyl group $O_1C_2O_2$ and the C_4 atom are in the trans position with respect to the plane of the ring. In the pyrrolidine ring B, deviations from the expected geometry and large thermal parameters for atoms C_8 and C_{10} have been found. Such deviations have been reported earlier for C_9 atom, in the complex *bis* (DL-proline) manganese (II)-dibromide dihydrate⁶. Since in the present structure C_9 is attached to a bulky hydroxyl group, it is felt that the distortion is manifest in C_8 and C_{10} atoms. Further refinement by assuming disordered state for the two atoms is in progress. Full structure details will be published in due course.

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NEUTRON DIFFUSION THROUGH A BARE PRISMATIC SOLID

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ABSTRACT

The problem of diffusion of neutrons through a bare prismatic solid with a cross-section of isosceles right triangle has been solved by the use of integral transform.

INTRODUCTION

THE neutron distribution in a fissionable solid is governed by the diffusion and multiplication of neutrons and is determined by the geometrical form of the solid. Hence the critical size depends on the geometry. The values of critical size for

geometries such as parallelo-piped cylinder, sphere and prism with equilateral triangular cross-section are known¹. We consider the diffusion of neutrons through a bare prismatic solid with cross-section as an isosceles right triangle. The solution of this problem is obtained by the use of integral transform and critical size is determined.