# *X*-Ray Molecular Structure of Bis-(L-ornithinato)palladium(II). Conformation of the Seven-membered Chelate Ring

By Yasuji Nakayama, Keiji Matsumoto, Shun'ichiro Ooi, and Hisao Kuroya*

(*Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, Japan*)

*Summary* *X*-Ray crystal structure analysis shows that bis-(L-ornithinato)palladium(II) contains two 7-membered chelate rings in the twist-chair conformation.

Although the ornithinate ion, $H_2N{\cdot}[CH_2]_3{\cdot}CH(NH_2){\cdot}CO_2^-$, contains three donor atoms, it acts as a bidentate ligand on chelation to palladium(II).[1] The chelate ring could be formed either *via* N and O yielding a 5-membered ring or *via* co-ordination of two N atoms to Pd forming a 7-membered ring. From c.d. results Wilson and Martin have concluded that equal amounts of the 5- and 7-membered rings are formed in aqueous solution (pH 9) of the 1:2 complex of palladium(II) with L-ornithine.[1] Since an aliphatic 7-membered chelate ring is not so familiar as 5- or 6-membered ones in co-ordination chemistry, we undertook a single-crystal structure analysis of bis-(L-ornithinato)palladium(II).

Crystals were obtained by slow evaporation of the reaction mixture prepared by Martin's method.[1] Elemental analyses were in good agreement with the formula $Pd(C_5H_{11}N_2O_2)_2$. *Crystal data:* orthorhombic, $a = 10{\cdot}680(7)$, $b = 14{\cdot}207(4)$, $c = 9{\cdot}051(6)$ Å, $Z = 4$, space group $P2_12_12_1$. Intensities of 1686 independent reflections were estimated visually from multiple-film equi-inclination Weissenberg photographs taken around *a* and *b* with Cu-$K_\alpha$ radiation. The structure was solved by Patterson and Fourier techniques and refined by least-squares to *R* 0·11, isotropic temperature factors being used for all but Pd.

The molecular structure is shown in the Figure. Two 7-membered chelate rings are formed, palladium being co-ordinated by four N atoms in a square-planar arrangement. The molecule has an approximate two-fold axis passing through Pd and perpendicular to the plane defined by Pd and the four N atoms. The two H atoms occupy an axial position, being separated by 2·17 Å {Pd · · · H[C(3)], 2·79 Å; Pd · · · H[C(3′)], 2·66 Å}.† Moreover, one hydrogen bound to C(4) of the adjacent molecule occupies a *trans*-axial position {Pd · · · H[C(4)], 2·47 Å}. Thus the complex is quasi-7-co-ordinate.

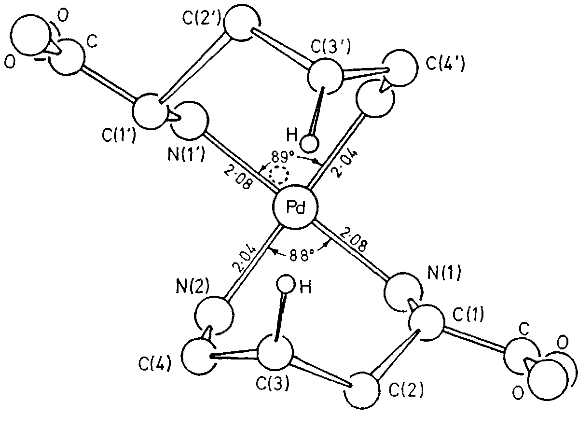

Figure. *Molecular structure of bis-*(L-*ornithinato*)*palladium*(II). *The dotted circle indicates the* H *atom linked to* C(4) *of the adjacent molecule. E.s.d.s of bond lengths and angles are* 0·02 Å *and* 0·7°, *respectively.*

Both the chelate rings assume a twist-chair conformation with the carboxylate group in a quasi-equatorial position. The average value (113°) of the Pd–N–C bond angles indicates that this angle is less strained than that (*ca.* 120°) in the 6-membered ring formed by chelation of trimethylenediamine,[2] although it is generally considered that a 6-membered chelate ring is more stable than a 7-membered one. However, there is considerable torsional strain in the present 7-membered ring. The dihedral angle between the two terminal bonds about the central C–C bond in the C(1)–C(2)–C(3)–C(4) fragment agrees well, within experi-

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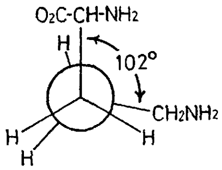
† The hydrogen co-ordinates were calculated on the assumption that the C–H bond length is 1·08 Å.



mental error with that in the C(1′)–C(2′)–C(3′)–C(4′) fragment (mean 102°).

These fragments in the chelate rings assume a nearly eclipsed conformation, and this strain would lead to Baeyer ring strain. The C–C–C and N–C–C bond angles range from 111 to 118°, but these values are not accurate enough to discuss the Baeyer strain in detail (e.s.d. of bond angles involving lighter atoms is 2°).

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[1] E. W. Wilson, jun., and R. B. Martin, *Inorg. Chem.*, 1970, **9**, 528.

[2] R. J. Geue and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 2981; J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1972, **11**, 156.