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X-Ray Evidence of the Metal Ion Tyrosine Aromatic Ring Interaction in Bis(L-tyrosinato)palladium(II)

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Our recent NMR studies on the interaction of Pd(II) with di- and tripeptides containing an aromatic ring in the amino acid side chain revealed that the metal ion induced a favourable conformation of that side chain [1].

In all the systems studied the aromatic ring was above the square planar complex plane in the most stable conformer. To explain the stabilization of such a rotational isomer, a direct interaction between the aromatic ring and the metal ion has been proposed [1].

X-ray studies of Cu(II) complexes with tyrosine [2–5] and tryptophane [6] containing ligands have shown that an analogous interaction is possible, but it is not the rule [4, 5].

In Pd(II) systems, however, the direct aromatic ring metal ion interaction may happen more easily as there is no apical coordination to the metal ion, which is the case in cupric complexes [2–5]. The conformation of the amino acid side chain alone, however, is not a good criterion for determining whether an interaction will occur and we have started X-ray studies on the appropriate Pd(II) systems. Some of the results for the title compound are presented in this communication.

Experimental

Crystals suitable for X-ray analysis were obtained from an aqueous solution containing $PdCl_2$ and tyrosine at 1:2 molar ratio.

All measurements were made on a Syntex $P2_1$ diffractometer using CuKα radiation.

Crystal Data

$C_{18}H_{20}N_2O_6Pd$, M = 466.76, monoclinic, space group $P2_1$, $a = 5.530(1)$, $b = 19.246(5)$, $c = 8.700(3)$ Å, $\beta = 105.40(2)°$, $V = 892.7$ Å^3, $Z = 2$, $D_c = 1.74$ g cm^{-3}, μ(CuKα) = 90.1 cm^{-1}.

The structure was solved by direct methods (MULTAN) and refined by a full-matrix least-squares procedure with anisotropic thermal parameters for all non-hydrogen atoms.

At the present stage R is 0.052 ($R_w = 0.065$) for 1133 reflections with $I > 1.96\ \sigma(I)$ measured up to $2\theta = 110°$.

Results and Discussion

The structure of the complex molecule viewed along the *b* axis is shown in Fig. 1.

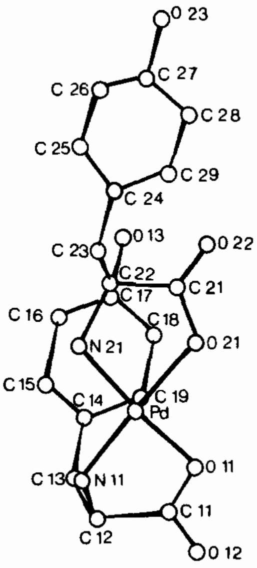

Fig. 1. The structure of the complex molecule viewed along the *b* axis. The interatomic distances and valence angles in the coordination sphere of Pd atom are: Pd–O(11), 2.01(1); Pd–O(21), 2.00(1); Pd–N(11), 2.05(1); Pd–N(21), 2.01(2) Å; O(11)–Pd–O(21), 94.3(6); N(11)–Pd–N(21), 101.6(6); O(11)–Pd–N(11), 81.2(6); O(21)–Pd–N(21), 82.9(6)°.

The coordination around the Pd atom is square planar with two tyrosine residues arranged *cis* each to other. One of the amino acid ligands exhibits a *gauche* conformation. The phenolic ring of this ligand is approximately parallel to the basal plane of the complex. The angle between both planes is 27.1° and the torsional angle N(11)–C(12)–C(13)–C(14) has a value of 50.7°.

There are two close contacts between the ring carbon atoms and Pd atom, *i.e.* Pd–C(14), 3.16(2) Å and Pd–C(15), 3.27(2) Å and these are significantly smaller than the sum of appropriate van der Waals radii. Other Pd–C contacts range from 3.68 to 4.21 Å.

The observed closest Pd–C interatomic distances strongly indicate the occurrence of the direct metal–aromatic side chain interaction found previously in

Cu(II) complexes with tyrosine [2], glycyl-L-leucyl-L-tyrosine [3] and glycyl-L-tryptophane [6].

The phenolic ring of the other coordinated tyrosine molecule is directed away from the Pd atom (Fig. 1.). It is worthwhile to note, however, that C(26)carbon atom of that phenolic ring is also quite close (3.63(2) Å) to the Pd atom from the adjacent molecule (coordinates x + 1, y, z).

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References

1 H. Kozłowski and M. Jeżowska, *Chem. Phys. Letters, 47,* 452 (1977).
H. Kozłowski, G. Formicka-Kozłowska and B. Jeżowska-Trzebiatowska, *Org. Magn. Resonance, 10,* 146 (1977).
H. Kozłowski, M. Jeżowska and H. Szyszuk, *J. Mol. Struct., 50,* 73 (1978).
H. Kozłowski, *Inorg. Chim. Acta, 31,* 135 (1978).
2 D. Van der Helm and C. E. Tatsch, *Acta Cryst., B28,* 2307 (1972).
3 W. A. Franks and D. Van der Helm, *Acta Cryst., B27,* 1299 (1971).
4 D. Van der Helm, S. E. Ealick and J. E. Burks, *Acta Cryst., B31,* 1031 (1975).
5 P. A. Mosset and J. J. Bonnet, *Acta Cryst., B33,* 2807 (1977).
6 M. B. Hursthouse, S. A. A. Jayaweera, G. H. Milburn and A. Quick, *J. Chem. Soc. D,* 207 (1971).