Crystal Structure of Bis-(2,2′-bipyridyl)palladium(II) Nitrate Monohydrate and the Stereochemistry of Palladium(II)

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Summary Single crystal structure analysis of $Pd(bipy)_2(NO_3)_2H_2O$ shows that the configuration of $[Pd(bipy)_2]^{2+}$ is distorted towards tetrahedral co-ordination.

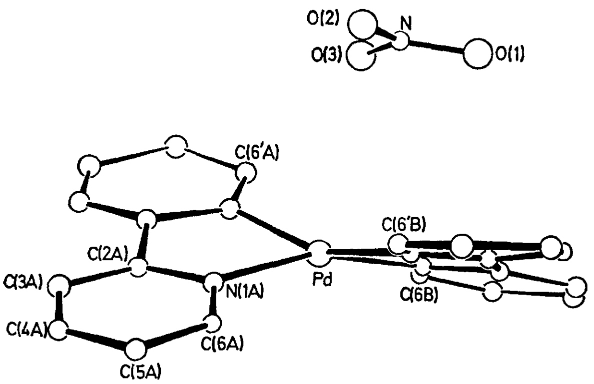
ALTHOUGH the planar co-ordination of four-co-ordinate palladium(II) is established, the existence of paramagnetic tetrahedral species of bis-(*NN*-ethylenedimorpholine)palladium(II) in acetone solution has also been reported.[1] The detailed structure of this complex is not yet known.

In bis-(2,2′-bipyridyl)palladium(II) complexes,[2] the two bipyridyl ligands are unable to assume coplanar positions because of the inter-ligand repulsion between hydrogen atoms.[3] The essentially planar conformation of the ligand molecule in the various metal chelates of bipyridyl[3,4] suggests that in $[Pd(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridyl) the two bipyridyl ligands are inclined to one another about their two-fold axes. This would lead to tetrahedrally distorted co-ordination about the Pd atom. However, if the planar co-ordination of Pd^{II} is to be preserved, each ligand must be twisted round the 2,2′-carbon bond to avoid steric repulsion. We report here a crystal structure analysis of $Pd(bipy)_2(NO_3)_2H_2O$ (**1**).

Compound (**1**) was prepared by addition of $Pd(NO_3)_2$ in aqueous solution to twice as many mols of 2,2′-bipyridyl in ethanol. Orange-red prisms were obtained on recrystallization from 1:1 ethanol-water. Elemental analyses were in agreement with the formula $Pd(bipy)_2(NO_3)_2H_2O$. The compound is diamagnetic and stable in air. *Crystal data:* monoclinic, $a = 12{\cdot}118(4)$, $b = 26{\cdot}725(8)$, $c = 6{\cdot}919(3)$ Å, $\beta = 110{\cdot}29(4)^\circ$, $Z = 4$, $D_m = 1{\cdot}76$, $D_c = 1{\cdot}77$ g cm^{-3}, space group $P\ 2_1/n$. The intensities were measured visually from integrated Weissenberg photographs by the multiple-film equi-inclination technique (Cu-K_α). After the usual corrections had been applied, the intensities were placed on a common scale by internal correlation. A total of 4095 independent structure factors were obtained. The structure was solved by the standard Patterson and Fourier technique and refined by least-squares method to an R factor of 0·12, using isotropic thermal parameters.

A part of the crystal structure is shown in the Figure. The arrangement of the nitrogen atoms around the palladium atom is not planar but is distorted towards a tetrahedral configuration. The dihedral angle between the bipyridyl planes is 33°, while that between the two N–Pd–N planes is 26°. Distances between hydrogen atoms, H[C(6A)]...H[C(6′B)] and H[C(6′A)]...H[C(6B)], are estimated to be 1·95 and 1·97 Å, respectively.† The Pd–N bond lengths range from 2·04 to 2·07(1) Å.

The two nitrate anions are at different distances from the Pd atom the one closer to it being shown in the Figure. The complex cation and the NO_3^- near it are stacked alternately along [001], thus each cation is sandwiched between two NO_3^-; the distance between O(3) and Pd is 3·17 Å, while O(2) of the other nitrate ion lies below the Pd atom at a distance of 3·16 Å. The relative orientation of the anion to the complex cation does not apparently favour the formation of a covalent Pd–O bond.



Figure

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† The calculation of co-ordinates of these hydrogen atoms was based on the assumption that C–H bond length is 1·08 Å.

[1] A. L. Lott and P. G. Rasmussen, *J. Amer. Chem. Soc.*, 1969, **91**, 6502.
[2] S. E. Livingstone, *J. Proc. Soc. New South Wales*, 1952, **86**, 32.
[3] E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.
[4] W. R. McWhinnie, and J. D. Miller, 'Advances in Inorganic Chemistry and Radiochemistry', ed. H. J. Emeléus and A. G. Sharpe, Academic Press, New York and London, 1969, vol. 12, p. 135.