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The Crystal Structure of Bis(2,2′-bipyridyl)palladium(II) Picrate [Pd(bpy)$_2$](pic)$_2$. A Novel "Bow" Distortion

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Synopsis. The title complex crystallized in the triclinic space group $P\bar{1}$ with a=8.228(2), b=13.493(2), c=7.753(1) Å; α=96.96(1), β=106.16(1), γ=99.99(1)°; Z=1. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method to R=0.0366. It is found that picrate ions above and below the [pd(bpy)$_2$]$^{2+}$ cation stack with the bpy molecules and that this stacking leads to a novel bow distortion of the cation.

It is known that the bis(2,2′-bipyridyl)palladium(II) ion ([Pd(bpy)$_2$]$^{2+}$) is essentially planar, but is slightly distorted from a rigorous plane because of interligand steric repulsion.[1] Two types of distortions, i.e., bow and twist (Fig. 1), have been found for the cation. It seems that the type of distortion depends upon the counter ion, and bow distortion has been found for the salt with the tetracyano-*p*-quinonedimethane anion (TCNQ$^-$).[3,4] It is presumed that the stacking between bpy and TCNQ$^-$ is associated with the unique bow distortion. In this study, the crystal structure of [Pd(bpy)$_2$](pic)$_2$ with the 2,4,6-trinitrophenolate ion (picrate ion, pic$^-$) has been determined and discussed in terms of the noncovalent interaction between the bpy molecule of the [Pd(bpy)$_2$]$^{2+}$ cation and the pic anion.

Experimental

Preparation. [Pd(bpy)$_2$](pic)$_2$ was obtained as yellow crystals by the reaction of bis(2,2′-bipyridyl)palladium(II) perchlorate (1.25 g) and 2,4,6-trinitrophenol (1 g) in water. Anal. Found: C, 44.05; H, 2.39; N, 15.96%. Calcd for $C_{32}H_{20}N_{10}O_{14}Pd$: C, 43.83; H, 2.53; N, 15.97%. Single crystals were obtained by slow crystallization from a dilute methanolic solution.

X-Ray Analysis. A crystal with dimensions of 0.2×0.2×0.3 mm was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 Automated Four-circle Diffractometer with graphite monochromated Mo$K\alpha$ radiation (λ=0.71609 Å) at 291 K. The intensity data were collected by the 2θ—ω scan technique with a scan rate of 6° min^{-1}; they were corrected for the Lorentz and polarization effects, but not for absorption (μ=7.0 cm^{-1}). A total of 3821 reflections within the $2<\theta<55°$ range were collected, of which independent 3377 reflections ($|F_o|\geq 3\sigma(F_o)$) were employed in the solution and refinement.

Crystal Data: [Pd($C_{10}H_8N_2$)$_2$]($C_6H_2N_3O_7$)$_2$, F.W.=874.99, triclinic $P\bar{1}$, a=8.227(2), b=13.493(2), c=7.753(1) Å; α=96.96(1), β=106.51(1), γ=99.99(1)°; D_m=1.81, D_c=1.81 g cm^{-3}, Z=1.

The structure was solved by the heavy-atom method, assuming the position of the palladium atom at (0,0,0), and was refined by the block-diagonal least-squares method to the final R value of 0.0366. The final atomic coordinates, the anisotopic temperature factors of the non-hydrogen atoms, a full list of bond distances (Å) and angles (°), and the complete F_o—F_c data are deposited as Document No. 8630 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. All the calculations were carried out on a M-200 computer

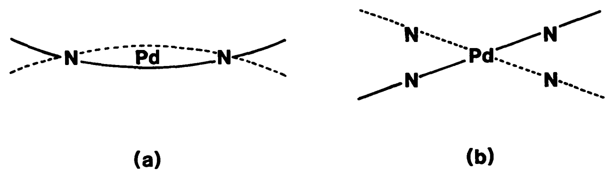

Fig. 1. Schematical representation of (a) bow and (b) twist distortions.

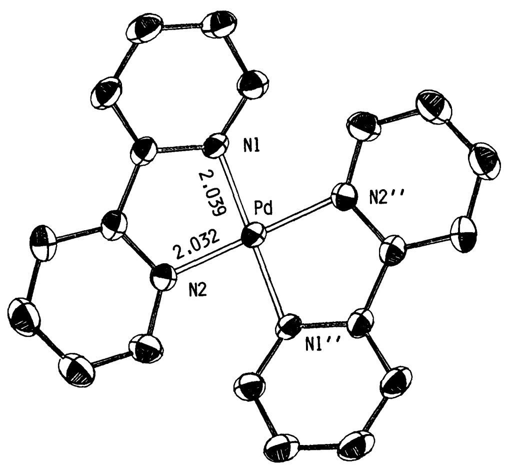

Fig. 2. Molecular structure of [Pd(bpy)$_2$]$^{2+}$ with bond distances.

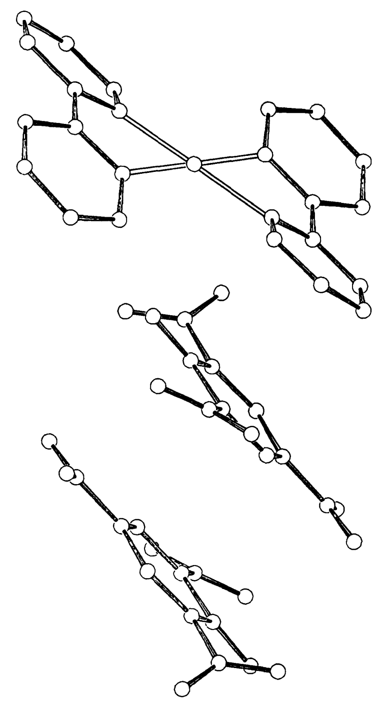

Fig. 3. Perspective view of the crystal packing.

at the Computer Center of Kyushu University using the local version[5] of the UNICS system.[6] The atomic-scattering factors were taken from the International Tables for X-Ray Crystallography.[7]

Results and Discussion

A perspective drawing of the $[Pd(bpy)_2]^{2+}$ cation is shown in Fig. 2, together with the bond lengths. The palladium atom lies at the center of the complex molecule; the mean Pd–N distance is 2.04 Å which is close to the previously reported Pd–N distances of the NO_3^- [8,9] and $TCNQ^-$ [3,4] salts. The angles of N1–Pd–N2 and N1–Pd–N2″ are 78.9° and 101.1° respectively.

The $[Pd(bpy)_2]^{2+}$ cations are separated by pair of picrate ions, which are stacked with each other in a head-to-tail manner with an interplane distance of 3.41 Å, as is shown in Fig. 3. The picrate anions above and below the cation also stack with the bpy molecule with an interplane distance of ca. 3.57 Å. The picrate oxygens are located at the apical sites of the metal; however, the considerably long Pd–O distances (3.20 Å) suggest that there is no appreciable bonding.

In spite of the planar configuration of the PdN_4 part, the whole of the cation is not planar, and the two pyridine rings within one ligand are tilted by 21.3° to cause the bow distortion. Probably this distortion is attributable to the bpy/pic stacking interaction in the crystal. That is, when the pic stacks with the bpy, the nitro groups at the 2- and 6-positions exert a steric effect so as to bend the bpy molecule. So far as we know, this complex is only the second example of a bow distortion in the $[Pd(bpy)_2]^{2+}$ cation.

References

1) E. D. Mckenzie, *Coord. Chem. Rev.*, **6**, 187 (1971).

2) A. Hazell and A. Mukhopadhyay, *Acta Crystallogr., Sect. B.*, **36**, 1647 (1980).

3) V. Dung, H. Endres, H. J. Keller, W. Moroni, and D. Nothe, *Acta Crystallogr., Sect. B.*, **33**, 2428 (1977).

4) H. Endres, H. J. Keller, W. Moroni, D. Nothe, and V. Dung, *Acta Crystallogr., Sect. B.*, **34**, 1823 (1978).

5) S. Kawano, *Rep. Comp. Cent. Kyushu Univ.*, **13**, 39 (1980).

6) "Universal Crystallographic Computer Program System (UNICS)," ed by T. Sakurai, The Crystallographic Society of Japan, Tokyo (1964).

7) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham (1962).

8) P. C. Chieh, *J. Chem. Soc., Dalton Trans*, **1972**, 1643.

9) M. Hinamoto, S. Ooi,and H. Kuroya, *J. Chem. Soc., Chem. Commun.*, **1972**, 356.