Steric Effects in a Distorted Square Planar Bis-(2,2′-bipyridyl) Metal Complex: *X*-Ray Crystal Structure of Aquobis-(2,2′-bipyridyl)palladium(II) Nitrate

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Summary The nature and magnitude of distortions induced by steric effects in a $M(bipy)_2{}^{2+}$ cation have been elucidated by a single crystal *X*-ray structural determination of $[Pd(bipy)_2](NO_3)_2H_2O$.

THERE has been considerable speculation of late concerning the nature of the distortions present in square planar $[MB_2]^{n+}$ or octahedral *trans* $[MB_2X_2]^{n+}$ (B = 2,2′-bipyridyl, 1,10-phenanthroline X = Cl, Br, I, SCN etc.) complexes.[1–5]† Indeed, the existence of an inter-ligand *ortho* proton steric interaction has been used to rationalise the apparent occurrence of only *cis* isomers of $[MB_2X_2]^{n+}$ cations.[2,3]. "Geometric analyses" of the steric effect in these systems, based on assumed structural parameters, have recently appeared.[4,5]‡

The *X*-ray analysis of aquobis-(2,2′-bipyridyl)palladium(II) nitrate reported here provides accurate data on the nature and magnitude of distortions in a planar $[MB_2]^{2+}$ moiety. The complex (orange-yellow needles) from 2,2′-bipyridyl and $Pd(NO_3)_2 2H_2O$ (2:1) in acetone had an $NO_3{}^-$ i.r. spectrum [mull; ν_3 1310—1372 vs br, ν_1 1025 m, ν_2 822 m cm^{-1}] indicative either of a low site symmetry for the $NO_3{}^-$ ion or an interaction with the metal atom or water molecule. *Crystal Data*: $(C_{10}H_8N_2)_2Pd(NO_3)_2H_2O$, M = 560·8. Monoclinic crystals, space group $P\,2_1/c$ (C^5_{2h}, No. 14) a = 6·932 (1), b = 26·721 (6), c = 11·697 (3) Å, β = 103·4 (1)°, U = 2107·7 Å^3, D_m = 1·764 g cm^{-3} (Flotation), Z = 4, D_c = 1·767 g cm^{-3}. The intensities were measured on a GE-XRD6 automatic diffractometer using Mo-K_α radiation; 2589 reflections were considered to be observed and were used in the refinement. The structure was solved by heavy-atom methods and refined by full-matrix least-squares methods assuming anisotropic thermal parameters for non-hydrogen atoms, to a final R value of 0·060. All hydrogen atoms on the bipyridyl ligands were located.

† Since submitting this note a comprehensive review of the subject has appeared. E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

‡ Attempts have also been made to predict stability based on the expected extent of distortion.[5]

The structure consists of discrete Pd(bipy)$_2^{2+}$ cations packed together with NO$_3^-$ ions and H$_2$O molecules.

The stereochemistry of the Pd(bipy)$_2^{2+}$ cation is shown in the Figure. The PdN$_4$ skeleton is distorted in two ways from a regular square plane. The "bite" of the ligand imposes a rectangular distortion such that the angles N(11)–Pd–N(21) and N(31)–Pd–N(41) are 79·9° and 80·1° respectively whereas N(11)–Pd–N(31) and N(21–Pd–N(41) are 102·1° and 102·2°. In addition a tetrahedral distortion, due to steric effects, *vide infra*, results in two diagonal nitrogen atoms being situated above and the other two below, a theoretical square plane, with diagonal N–Pd–N angles of 163·6° and 165·3°. The Pd–N distances [av, 2·034(1) Å] are closely similar to values reported for a variety of other Pd^{II} amine complexes.[6] Thus steric interactions although markedly affecting the stereochemistry and ligand conformation do not appreciably weaken the Pd–N bonds.

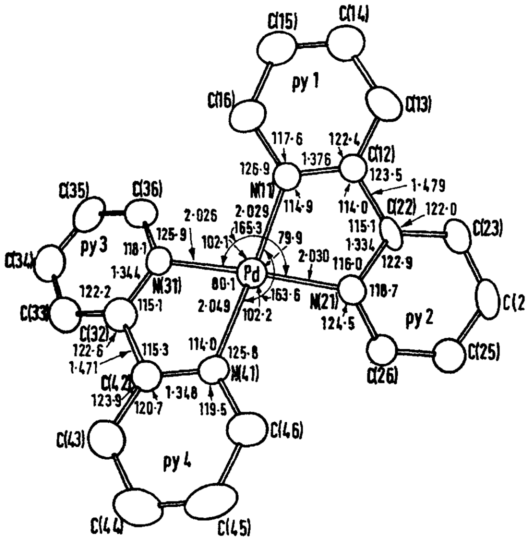

Figure. *Atomic numbering bond lengths and bond angles in the bis-(2,2′-bipyridyl)palladium*(II) *cation.*

The intra-ligand proton repulsions are partially reduced by the formation of the 5 membered PdN$_2$C$_2$ rings with N–C–C angles less than 120° (mean 114·9°);§ the distances H(13)–H(23), H(33)–H(43) are 2·0(1) Å and 2·1(1) Å respectively. The inter-ligand proton interactions [H(16)–H(36); H(26)–H(46)] are relieved by rotation of the two bipyridyl residues about axes bisecting the angles N(11)–Pd–N(21) and N(31)–Pd–N(41) such that the dihedral angle between the planes containing N(11), Pd, N(21) and N(31), Pd, N(41) is 24° 10′. This tetrahedral distortion gives inter-ligand proton distances H(16)–H(36) and H(26)–H(46) of 1·9(1) Å and 2·0(1) Å. The pyridine rings (py1 and py2) are virtually coplanar, with a dihedral angle of 1° 44′ between the planes. For py3 and py4 the analogous angle is 7° 37′. Thus the postulated "twist distortion"[5] for relief of intra-ligand proton repulsions is relatively unimportant. The H–H distances are somewhat less than twice the accepted van der Waals radius for hydrogen[7] and may represent a compromise between strong Pd–N bonding and steric repulsions.

In the light of the above *X*-ray data, it is clear that square M(bipy)$_2^{2+}$ cations can undergo severe distortion without weakening M–N bonds. Thus although the proposed destabilisation of a *trans* [M(bipy)$_2$X$_2$]$^+$ cation with respect to the *cis* isomer appears justified there is no firm basis for predicting the instability or non-existence of M(bipy)$_2^{n+}$ species, where M is a metal generally adopting square planar stereochemistry, purely from steric considerations.

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§ This "bowing" of the 2,2′-bipyridyl molecule so that the nitrogen atoms are brought closer together is in the opposite sense to that predicted for relief of inter-ligand proton repulsions.[5]

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