Crystal and Molecular Structure of Aquobis-(2,2′-bipyridyl)palladium Dinitrate [1]

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Crystals of the title compound are monoclinic with $a = 6{\cdot}932(1)$, $b = 26{\cdot}721(6)$, $c = 11{\cdot}697(3)$ Å, $\beta = 103{\cdot}4(1)°$, space group $P2_1/c$, and $Z = 4$. The structure was determined from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares techniques to R 0·060 for 2589 observed reflections. The structure consists of discrete $Pd(bipy)_2{}^{2+}$ cations and nitrate anions. There is a weak interaction between the metal ion and one of the nitrate ions, the other nitrate ion being hydrogen bonded to a water molecule. The steric strain imposed by the interaction of interligand ortho-hydrogens is reduced by a distortion from a square planar configuration. The 'bite' of the 2,2′-bipyridyl ligand results in a rectangular distortion of the PdN_4 skeleton such that mean of the angles N–Pd–N, where both nitrogens are from the same ligand, is 80·0(3)°. The corresponding angle involving nitrogens from different ligands is 102·2(3)°. There is also a mutual twist of the two ligands to avoid interligand hydrogen contacts. The mean diagonal angle, N–Pd–N, is 164·5(5)°. The torsion angle is 24·3°

PALLADIUM- and platinum-(II) both greatly favour four-co-ordinate square-planar configurations,[2] although distorted square-planar configurations are expected for sterically hindered complexes. During the course of the present study, there was a review[3] on the steric effect in bis-(2,2′-bipyridyl)- and bis-(1,10-phenanthroline)-metal compounds, but the lack of structural data for these complexes was apparent. Molecules often deviate from the ideal geometry in a polyatomic compound to alleviate an apparently major steric effect at little cost in energy.[4] An example of severe distortion was found in a five-co-ordinate copper complex.[5] The nature of the distortions from a square-planar geometry has recently been the subject of considerable speculation.[6-10] By consideration of a mutual twist of the ligands with respect to the normal PdN_4 plane, repulsion energies from various degrees of distortion, have been calculated,[3] and the results indicated a very large torsion angle. In view of recent concern over the steric effects present in these complexes and their structural implications for related complexes we have carried out a detailed X-ray structure analysis of aquobis-(2,2′-bipyridyl)palladium nitrate.

EXPERIMENTAL

The crystals were obtained from water–acetone as orange-yellow needles elongated along a. Unit-cell data were determined from various film and diffractometer measurements, the lattice parameters being obtained by least-squares treatment based on 2θ values of 39 reflections measured on the General Electric XRD 6 with Cu-K_β ($\lambda = 1{\cdot}39217$) radiation.

Crystal Data.—$C_{20}H_{18}N_6O_7Pd$, $M = 560{\cdot}8$, Monoclinic $a = 6{\cdot}932(1)$, $b = 26{\cdot}721(6)$, $c = 11{\cdot}697(3)$ Å, $\beta = 103{\cdot}4(1)°$, $U = 2107{\cdot}7$ Å^3, $D_m = 1{\cdot}764$ (by flotation), $Z = 4$, $D_c = 1{\cdot}767$, $F(000) = 1128$. Absent reflections: $h0l$ for l odd, $0k0$ for k odd, indicate space group $P2_2/c$ (C^5_{2h}). Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 9{\cdot}3$ cm^{-1}.

The intensities of the reflections were measured on a Datex-automated General Electric XRD 6 spectrogoniometer, fitted with a scintillation counter, zirconium-filtered Mo-$K_{\bar{\alpha}}$ radiation, and a pulse-height analyser, by the θ—2θ scan method. The scan range in 2θ was $(1{\cdot}80 + 0{\cdot}6 \tan\theta)°$ and background was measured at the beginning and end of each scan. Four strong reflections were repeated after every 100 reflections to apply small corrections ($<5\%$) for the fluctuation and declining intensity over the course of the measurement. A total of 4751 reflections with maximum $2\theta < 60°$ were measured, and after averaging over equivalent reflections gave 2589 observed and 1287 unobserved reflections. No absorption correction was made. Lorentz and polarization factors were applied to the derivation of the structure amplitudes.

The palladium atom was located from the three-dimensional Patterson map and a Fourier map based on the phase of the palladium atom revealed all the non-hydrogen atom positions; however, the oxygen atom of the water molecule was not included in the least-squares refinement until a difference-Fourier map showed a distinct peak revealing its position. After two cycles of full-matrix least-squares refinement, R was 0·11; anisotropic thermal parameters were then introduced and by two further cycles R was reduced to 0·069. A difference-Fourier map was then calculated and the hydrogen atoms were located by consideration of both relative positions with respect to the ring and electron

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densities. The hydrogen atoms were then included in the refinement, but some of the parameters were alternately kept fixed. The atomic scattering factors were taken from ref. 11. for all non-hydrogen atoms, and from ref. 12 for hydrogen. Dispersion corrections were made for palladium only. The function minimized was $\Sigma(|F_o| - |F_c|)^2$ and a weighting scheme analysis based on ranges of F_o and $\sin\theta/\lambda$ (see Appendix) indicated that this (unit weight) was satisfactory. The final R is 0·060 * and the corresponding atomic parameters and thermal parameters are listed in Table 1. The numbering of the atoms are shown in Figures 1 and 2 together with their bond lengths and angles.

DISCUSSION

The bond distances and angles of the Pd(bipy)$^{2+}$ cation are given in Figure 1, together with their standard deviations. No correction was made for the anisotropic thermal motions for any bond distance. The mean Pd–N distance of 2·034(1) Å is reasonably close to the values of 2·022(9) Å found in bis-(2,2′-dipyridyliminato)-palladium(II) [13] and 2·036(7) Å for bis(ethylenediamine)-palladium(II) chloride.[14] The steric strain is therefore reduced by distortion, which will be discussed later, without weakening the Pd–N bonds.

TABLE 1

Final positional and thermal parameters with standard deviations in parentheses

Atom	x	y	z	B/Å^2
Pd	0·2285(1)	0·11948(3)	0·95722(7)	
N(11)	0·2207(14)	0·0585(3)	0·8527(7)	
C(12)	0·2368(16)	0·0133(4)	0·9104(9)	
C(13)	0·2560(19)	−0·0313(4)	0·8551(11)	
C(14)	0·2459(18)	−0·0309(5)	0·7364(11)	
C(15)	0·2380(19)	0·0140(5)	0·6788(10)	
C(16)	0·2268(17)	0·0582(4)	0·7396(9)	
N(21)	0·2502(12)	0·0642(3)	1·0786(7)	
C(22)	0·2465(13)	0·0175(3)	1·0377(9)	
C(23)	0·2571(15)	−0·0242(4)	1·1089(10)	
C(24)	0·2633(18)	−0·0173(5)	1·2272(10)	
C(25)	0·2475(18)	0·0303(5)	1·2686(9)	
C(26)	0·2378(16)	0·0714(4)	1·1918(10)	
N(31)	0·1321(13)	0·1745(3)	0·8383(7)	
C(32)	0·1643(17)	0·2213(4)	0·8804(10)	
C(33)	0·0862(17)	0·2624(4)	0·8155(11)	
C(34)	−0·0252(17)	0·2551(5)	0·7002(11)	
C(35)	−0·0630(20)	0·2075(6)	0·6602(10)	
C(36)	0·0121(16)	0·1683(4)	0·7293(10)	
N(41)	0·3208(13)	0·1810(3)	1·0601(8)	
C(42)	0·2814(14)	0·2250(4)	1·0026(10)	
C(43)	0·3543(18)	0·2687(4)	1·0555(11)	
C(44)	0·4678(16)	0·2687(4)	1·1698(11)	
C(45)	0·5128(15)	0·2224(5)	1·2254(16)	
C(46)	0·4354(17)	0·1805(4)	1·1684(10)	
O(11)	0·6121(16)	0·1378(4)	0·8662(10)	
N(10)	0·7206(16)	0·1618(3)	0·9467(10)	
O(12)	0·7275(17)	0·2074(3)	0·9436(9)	
O(13)	0·8203(17)	0·1381(3)	1·0334(9)	
O(21)	0·5760(17)	0·1301(4)	0·4168(9)	
N(20)	0·6102(18)	0·1017(4)	0·5011(9)	
O(22)	0·7827(16)	0·0845(4)	0·5379(9)	
O(23)	0·4797(16)	0·0907(5)	0·5498(10)	
O(1)	0·0902(16)	0·1225(4)	0·4252(10)	
H(13)	0·265(17)	−0·064(4)	0·910(10)	4·2(26)
H(14)	0·227(15)	−0·060(4)	0·687(9)	7·2(22)
H(15)	0·216(17)	0·009(4)	0·588(9)	2·5(25)
H(16)	0·249(16)	0·094(4)	0·708(9)	6·6(24)
H(23)	0·278(14)	−0·060(4)	1·082(8)	9·7(20)
H(24)	0·269(15)	−0·050(4)	1·282(9)	2·6(24)
H(25)	0·245(16)	0·036(4)	1·357(9)	8·1(24)
H(26)	0·227(16)	0·116(4)	1·226(9)	2·0(22)
H(33)	0·115(14)	0·294(3)	0·859(8)	1·8(21)
H(34)	−0·074(14)	0·280(3)	0·644(8)	4·2(26)
H(35)	−0·139(17)	0·198(4)	0·588(9)	3·9(20)
H(36)	0·000(14)	0·126(3)	0·710(8)	4·1(22)
H(43)	0·334(15)	0·297(3)	1·015(8)	3·4(22)
H(44)	0·524(14)	0·297(3)	1·215(8)	1·8(21)
H(45)	0·579(13)	0·219(3)	1·310(7)	6·0(19)
H(46)	0·489(15)	0·145(3)	1·213(8)	3·8(21)

TABLE 1 (*Continued*)

Anisotropic thermal parameters in the form

$\exp[-10^{-4}\{b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl\}]$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pd	175(2)	10(0)	61(1)	0(1)	19(1)	1(0)
N(11)	144(22)	8(1)	56(9)	−1(5)	9(12)	0(3)
C(12)	157(25)	4(1)	73(10)	2(5)	31(13)	−2(3)
C(13)	252(33)	7(2)	75(11)	−6(6)	45(17)	−3(4)
C(14)	170(29)	9(2)	95(11)	−10(6)	13(16)	−9(4)
C(15)	229(31)	12(2)	67(10)	5(7)	50(16)	−4(4)
C(16)	214(30)	11(2)	60(10)	5(6)	34(15)	0(3)
N(21)	101(19)	8(1)	48(7)	−1(4)	13(10)	0(2)
C(22)	76(21)	9(1)	50(8)	0(5)	3(11)	2(3)
C(23)	115(24)	11(2)	83(11)	−8(5)	14(14)	6(4)
C(24)	203(30)	17(2)	57(10)	−12(7)	−5(15)	5(4)
C(25)	219(31)	18(2)	47(10)	−13(7)	9(15)	2(4)
C(26)	166(27)	14(2)	54(10)	7(6)	26(14)	3(4)
N(31)	173(23)	10(1)	44(8)	3(5)	8(11)	1(3)
C(32)	176(27)	11(2)	60(10)	6(6)	20(14)	3(4)
C(33)	180(29)	12(2)	80(12)	7(6)	37(16)	3(4)
C(34)	163(28)	18(2)	83(13)	15(7)	30(16)	14(4)
C(35)	248(35)	22(3)	54(11)	−3(8)	−2(2)	6(4)
C(36)	131(26)	14(2)	65(10)	0(6)	19(4)	4(4)
N(41)	156(24)	8(1)	52(8)	2(4)	28(12)	−2(3)
C(42)	55(20)	14(2)	76(10)	4(5)	50(12)	2(4)
C(43)	190(29)	11(2)	81(12)	1(6)	13(16)	−3(4)
C(44)	149(27)	13(2)	93(12)	−12(6)	43(16)	−8(4)
C(45)	114(23)	17(2)	83(11)	−18(6)	39(14)	−12(4)
C(46)	177(27)	14(2)	54(10)	−6(6)	1(14)	1(4)
O(11)	348(32)	19(2)	132(12)	−15(7)	−63(17)	−6(4)
N(10)	204(25)	9(1)	81(11)	15(6)	33(13)	5(4)
O(12)	489(36)	11(1)	96(10)	2(6)	18(15)	7(3)
O(13)	455(38)	15(1)	100(10)	7(7)	−22(16)	16(3)
O(21)	414(36)	29(1)	98(11)	10(8)	32(16)	20(4)
N(20)	260(34)	14(2)	52(9)	−1(7)	5(15)	5(3)
O(22)	265(26)	26(2)	92(7)	−2(7)	13(13)	10(4)
O(23)	263(29)	46(3)	142(13)	−7(9)	104(17)	33(6)
O(1)	385(33)	17(2)	129(12)	−10(7)	29(17)	0(4)

It has been shown that palladium(II) greatly favours a square-planar configuration. Previous analyses of the cation of the present complex suggested [2,3,10] that an undistorted configuration was impossible. An analysis of the structure revealed that the steric strain is relieved mainly by rectangular and tetrahedral distortions of the PdN$_4$ skeleton. The mean of angles involving intra-ligand nitrogens [N(11)–Pd–N(21) and N(31)–Pd–N(41)] is 80·0° which is considerably smaller than that (102·2°) of the angles [N(11)–Pd–N(31) and N(21)–Pd–N(41)] involving interligand nitrogen atoms. A comparison with the corresponding values of 85·6 and 94·4 for the planar PdN$_4$ conformation found in bis-(2,2′-dipyridylinimato)palladium(II) [13] shows that the distortion is imposed by the 'bite' of the ligand as well as by the

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* Tables of observed and calculated structure factors are listed in Supplementary Publication No. SUP 20412 (3 pp., 1 microfiche). For details of Supplementary Publications see *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

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overall steric effect. A value of 83° was found for the N–Pd–N angle where both nitrogen atoms are from the bidentate ligand in dinitro-(2,9-dimethyl-1,10-phenanthroline)palladium(II);[15] an even smaller value of 76° was found for the N(nitro)–Pd–N(nitro) angle where the oxygen atoms are not in the same PdN_4 plane and the steric strain caused by the two nitro-groups is not important. The equations of the least-squares planes, maximum displacements from the plane, and the interplanar angles are listed in Table 2. The tetrahedral distortion gives rise to a torsion angle [interplanar angle between (1) and (2)] of 24·3°. In the preliminary calculation, the repulsion energy was calculated as a function of the angle of twist,[3] which is equal to half the torsion angle; however, the rectangular distortion was not considered. The observed Pd–N distance and angle of twist correspond to a repulsion energy of $2{\cdot}10 \times 10^5$ J mol^{-1} even considering the 'soft' model.[3] This shows the importance of taking into account combined rectangular and tetrahedral distortions although it is difficult to foresee the degree of distortion. By adding an additional degree of freedom, *i.e.* the rectangular distortion, the problem of calculating the repulsion energy becomes considerably more complicated. Furthermore, since we have at the present time an incomplete understanding of how the energy would vary quantitatively with conformation, the optimum distortion for such a complex cannot be predicted with any degree of accuracy.

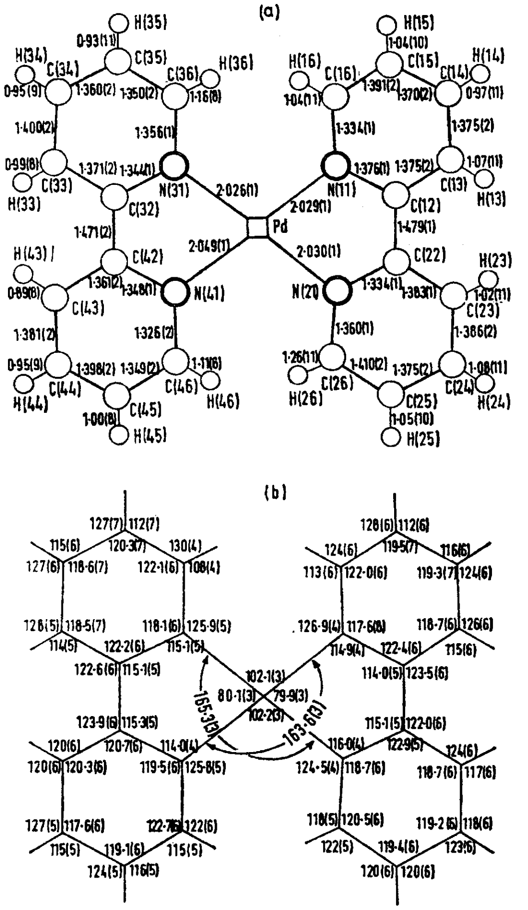

FIGURE 1 (a) Numbering of atoms and bond distances and (b) bond angles in the cation

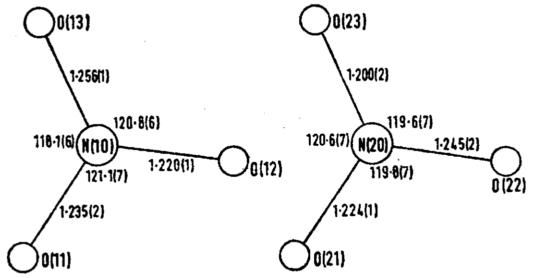

FIGURE 2 The bond distances and angles for the nitrate ions

The least-squares planes (5) and (6) (Table 2) have similar orientations (interplanar angle 1·8°) and both are bent only slightly, 4·2 and 5·2°, respectively with respect to plane (1) [Pd, N(11), N(21)]. However, the ligand containing N(31) and N(41) allows itself to twist a little more than the other ligand to give more relief for the repulsion of the α-interligand hydrogens. Such a twist has been observed in some of the known crystal

TABLE 2

Equations of mean planes in the form $lX + mY - nZ = p$ where X, Y, and Z are co-ordinates in Å, referred to orthogonal axes *a*, *b*, and *c* *

Plane	Atoms	l	m	n	p	Max. displacement (Å)
(1)	Pd, N(11), N(21)	0·9874	0·0253	0·1563	0·762	0
(2)	Pd, N(32), N(41)	0·9649	−0·0204	−0·2618	−3·914	0
(3)	Pd, N(11), N(21), C(12), C(22)	0·9862	0·0271	0·1637	0·848	0·018 [C(12)+, C(22)−]
(4)	Pd, N(31), N(41), C(32), C(42)	0·9611	−0·0190	−0·2754	−4·053	0·034 [C(32)−, C(42)+]
(5)	N(11), C(12)—(16)	0·9702	0·0756	0·2301	1·591	0·03 [C(13)+, C(14)−]
(6)	N(21), C(22)—(26)	0·9724	0·0452	0·2290	1·567	0·05 [N(21)]
(7)	N(31), C(32)—(36)	0·9317	0·0399	−0·3611	−4·559	0·024 [C(34)]
(8)	N(41), C(42)—(46)	0·9293	−0·0933	−0·3573	−5·381	0·021 [C(44)]

Interplanar angles

(1)–(2)		24·3°	
(1)–(5)	5·2°	(2)–(7)	6·9°
(1)–(6)	4·2	(2)–(8)	7·2
(5)–(6)	1·8	(7)–(8)	7·6

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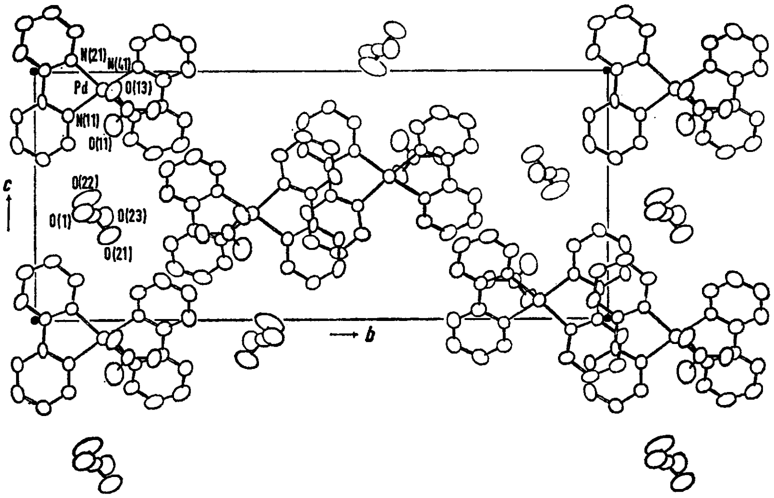

FIGURE 3 A packing diagram; palladium viewed down the *a*-axis

structures of bipyridyl complexes.[3] All these distortions have given reasonable hydrogen–hydrogen separations. The mean interligand hydrogen distance, H(16) · · · H(36) and H(26) · · · H(46), is 2·0 Å which is approximately the same as the mean intra-ligand hydrogen, H(13) · · · H(23) and H(33) · · · H(43), separation[2·1(1) Å]. These values are slightly less than twice the accepted van der Waals radius for hydrogen;[16] however, many ' overcrowded ' organic compounds have hydrogen atoms separated by even small distances.[17] It is understandable that hydrogen–hydrogen repulsions are reduced by the distortion but not eliminated entirely.

The bond distances and angles for the nitrate ions are shown in Figure 2. The differences in N–O distances should not be considered highly significant, since corrections for anisotropic thermal vibrations were not made. In the preliminary communication,[1] it was mentioned that the i.r. spectrum indicates either a low site-symmetry for the nitrate or an interaction with the metal ion or water molecules. The packing diagram (Figure 3) shows that an oxygen atom, O(13), of one nitrate ion is situation almost directly above the palladium atom, the Pd · · · O(13) distance is 3·157(1) Å, however, Pd · · · O(11) is 3·089(1) Å. A weak interaction between the metal ion and the nitrate could not therefore be completely ruled out. The oxygen atom, O(1), of the water molecule is hydrogen bonded to two oxygen atoms, O(22) and O(23), of the other nitrate ion with O(1) · · · O(22) 2·910(2) and O(1) · · · O(23) 2·851(2) Å; the angle O(22) · · · O(1) · · · O(23) is 110·5°(3).

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APPENDIX

Weighting analyses based on ranges of F_o and sin θ/λ

Range of F_o	No. of reflections	Mean $(\lvert F_o\rvert - \lvert F_c\rvert)^2$
0·0—15·0	208	1·50
15·0—17·4	240	1·39
17·4—19·9	203	0·95
19·9—22·8	222	0·70
22·8—26·0	223	0·50
26·0—29·6	218	0·47
29·6—33·6	198	0·90
33·6—38·7	224	0·73
38·7—45·6	210	0·55
45·6—56·1	213	1·12
56·1—76·9	215	0·42
76·9—up	215	0·78
		Mean 0·83
Range of sin θ/λ		
0·0—0·262	353	1·50
0·262—0·330	283	0·61
0·330—0·378	269	0·49
0·378—0·416	255	0·94
0·416—0·448	231	0·82
0·448—0·476	206	0·48
0·476—0·501	202	0·70
0·501—0·524	203	1·10
0·524—0·545	186	0·62
0·545—0·565	161	0·65
0·565—0·583	163	0·81
0·583—0·600	77	1·04
Total	2589	Mean 0·83

[2/196 *Received*, 31*st January*, 1972]

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