The Structure of Two Yellow Tris(2,2'-bipyridine)iridium(III) Complexes: Bis(2,2'-bipyridine-N,N')(NH^+-2,2'-bipyridinium-3-yl-N'')iridium(III) Trisperchlorate–Water (1/1), [Ir($C_{10}H_8N_2$)$_3$](ClO$_4$)$_3$.H$_2$O, and Tris(2,2'-bipyridine-N,N')iridium(III) Trisperchlorate–Water (1/2⅓), [Ir($C_{10}H_8N_2$)$_3$](ClO$_4$)$_3$.2⅓H$_2$O

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Abstract. [Ir(bpy-C^3,N')(bpy)$_2$](ClO$_4$)$_3$.H$_2$O (bpy-C^3,N' = NH^+-2,2'-bipyridinium-3-yl-N', bpy = 2,2'-bipyridine-N,N'): M_r = 977.2, monoclinic, $P2_1/c$, a = 16.700 (5), b = 16.279 (5), c = 13.600 (6) Å, β = 108.86 (4)°, V = 3499 (2) Å^3, Z = 4, D_x = 1.855 (1) Mg m^{-3}, Mo $K\alpha$, λ = 0.71069 Å, μ = 4.104 (3) mm^{-1}, F(000) = 1920, room temperature, R = 0.031 for 2531 reflexions [$I > 3\sigma(I)$] and 514 variables. Iridium is bonded to two bipyridine groups *via* the nitrogen atoms, the bipyridiniumyl group is bonded *via* one nitrogen and one carbon atom. The non-coordinating nitrogen atom is hydrogen bonded to a water molecule which is in the plane of the ligand. The carbon-bonded bipyridiniumyl ligand is disordered. The mean Ir–N distance is 2.082 (5) Å for N *trans* to C, and 2.042 (4) Å for the others; the value for the long bonds is the average of a normal Ir–N bond and of one *trans* to C. [Ir(bpy)$_3$](ClO$_4$)$_3$.2⅓H$_2$O: M_r = 1001.1, trigonal, $R3c$, a = 30.370 (11), c = 20.922 (8) Å (hexagonal setting), V = 16705 (12) Å^3, Z = 18, D_x = 1.791 (1) Mg m^{-3}, Mo $K\alpha$, λ = 0.71069 Å, μ = 3.87 (3) mm^{-1}, F(000) = 8880, room temperature, R = 0.040 for 2870 reflexions [$I > 3\sigma(I)$] and 490 variables. The iridium atom is coordinated *via* the nitrogen atoms to all three bipyridine groups, with mean Ir–N distance 2.021 (6) Å.

Introduction. Polypyridyl complexes of the platinum-group metals are currently of interest because of their potential use as solar-energy converters. Tris(bipyridine)iridium(III) perchlorate was first described by Martin & Waind (1958) as an orange compound. Later, Flynn & Demas (1974) isolated a pale yellow complex, *Y*, which was formulated as [Ir(bpy)$_3$](ClO$_4$)$_3$.3H$_2$O; the ^{1}H NMR spectrum resembled that of the Os and Fe tris(bipyridine) complexes, and the ^{13}C NMR spectrum showed five lines corresponding to the five distinct carbon atoms of a D_3-symmetry tris complex (Fig. 1*a*). Watts, Harrington & Van Houton (1977) prepared another pale yellow complex which analysed as a tris(bipyridine) complex but which differed in many respects from *Y*. The complex is a monobasic acid with

pK = 3.0. The ^{1}H NMR spectra (Kahl, Hanck & DeArmond, 1979) of both the acid form, *WA*, and the base form, *WB*, differ from that of *Y*. Both *Y* and *WA* are highly luminescent, and photosensitize the conversion of norbornadiene to quadricyclene (Kutal, 1978), *WA* doing so with high efficiency (quantum yield 0.7 at 366 nm). Watts, Harrington & Van Houton (1977) proposed structures with a monodentate bipyridine ligand, and H$_2$O or OH$^-$ bound directly to iridium (Fig. 1*b*) and suggested that the analogous ruthenium compound was an intermediate in the photolysis of [Ru(bpy)$_3$]$^{2+}$. Gillard, Lancashire & Williams (1979), however, claimed *WA* to be a covalent hydrate (Fig. 1*c*). ^{13}C NMR spectroscopy (Spellane & Watts, 1981) showed no evidence for the tetrahedral carbon atoms which the covalent hydrate would require.
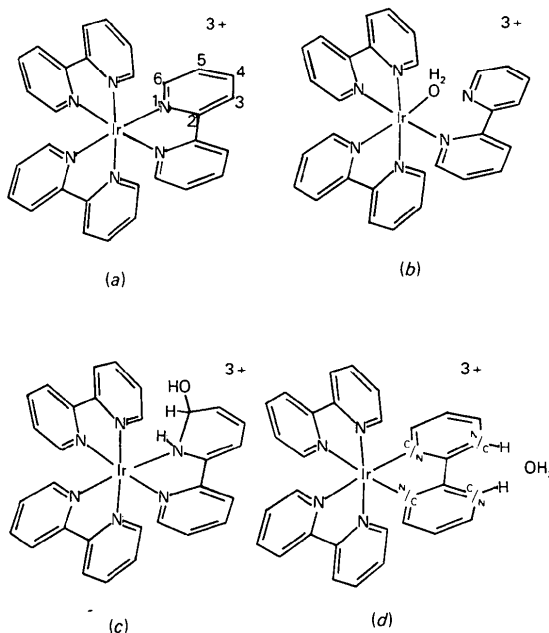

Fig. 1. (*a*) *Y*, (*b*) Watts, Harrington & van Houton's (1977) model for *WA*, (*c*) Gillard, Lancashire & Williams's (1979) model for *WA*, (*d*) disordered model for *WA*, this work.

A crystal structure determination (Hazell, 1981) showed *WA* to have neither of these structures but to contain apparently normal tris(bipyridine)iridium(III) cations. The most obvious unusual feature was a water molecule in the plane of one bipyridine ligand, 3 Å from C(3) and C(3′). Wickramasinghe, Bird & Serpone (1981), henceforth referred to as WBS, published an independent study of *WA* obtaining similar results. According to them one bipyridine was rotated about the central bond so that it was bonded to iridium *via* one nitrogen and one carbon. The close proximity of the water molecule could then be explained by N—H···O hydrogen bonding and the acid–base behaviour by the removal or addition of a proton to the nitrogen which was not bonded to iridium. No crystallographic evidence was presented by WBS for there being a carbon atom attached to iridium.

A crystallographic and spectroscopic investigation (Nord, Hazell, Hazell & Farver, 1983) of a red iridium(bipyridine) complex showed it to contain [Ir(bpy⁻-C^3,N')(bpy)₂]²⁺,* *i.e.* the base form, *WB*, of Watts's compound. The structure contains three independent complex ions, each iridium being bonded to five nitrogens and one carbon. The evidence for Ir—C bonding is: (1) Refinement assuming all pyridine rings to be bonded *via* nitrogen gave abnormal thermal parameters for N(1) and C(3) of one ring per complex (Fig. 2a). Refinement with one carbon bonded to iridium gave normal thermal parameters. (2) The Ir—C bonds, 1·980 (6) Å, were shorter than the normal Ir—N bonds, 2·053 (5) Å. Furthermore, the bonds *trans* to Ir—C were longer, 2·131 (5) Å, in accordance with the expected *trans* effect of the C-bonded pyridine. (3) The geometry of the pyridine rings also fitted with one ring being bonded *via* carbon. Since we have no reason for believing that our data for *WA* were any worse than those of the red complex, we have re-examined our data applying the above criteria and have also considered the possibility of disorder.

The sample of the red complex contained a few crystals of a yellow impurity. The crystal structure of this has also been determined showing it to be the normal tris complex [Ir(bpy)₃](ClO₄)₃ with 2⅓ waters of crystallization, probably identical to *Y* as prepared by Flynn & Demas (1974).

Experimental. *WA*: unit-cell dimensions determined from setting angles of 20 reflexions, $18 \leq \theta \leq 32°$, Cu *K*α radiation ($\lambda = 1·5418$ Å); 3286 reflexions, $0 \leq h \leq 16$, $0 \leq k \leq 15$, $-12 \leq l \leq 12$, $\sin\theta/\lambda_{max} = 0·48$ Å⁻¹, Picker FACS-1 diffractometer, Zr-filtered Mo *K*α radiation, 2531 $I > 3\sigma(I)$; 2 reflexions, 400 and 041, monitored every 60 reflexions, overall decay in intensity 2·2%; ω–2θ step scan, the extent of the peaks being determined by the $\sigma(I)/I$ criterion

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* bpy⁻-C^3,N' = 2,2′-bipyridin-3-yl-*N'*.

(Lehmann & Larsen, 1974); crystal described by the following faces and their distances in mm from an arbitrary origin: {110}, ±0·117; {1Ī0}, ±0·175; {001}, ±0·205; intensities processed and corrected for absorption using modified versions of *PROFILE*, *DATAP* and *DSORT* (State University of New York, Buffalo); transmission factors 0·27 to 0·44. *Y*: unit-cell dimensions determined from setting angles of 15 reflexions, $12 \leq \theta \leq 23°$, Cu *K*α radiation; 4879 reflexions, $-24 \leq h_m \leq 20$, $0 \leq k_m \leq 29$, $0 \leq l_m \leq 12$ (indices refer to the monoclinic cell), $\sin\theta/\lambda_{max} = 0·54$ Å⁻¹, Picker FACS-1 diffractometer, Zr-filtered Mo *K*α radiation, 2870 $I > 3\sigma(I)$; 2 reflexions, 840 and 036, monitored every 60 reflexions, overall decay in intensity 6·5%; crystal used was an irregular lump with max. dimensions $0·35 \times 0·35 \times 0·41$ mm, no absorption correction. Structure of *WA* determined by Patterson and Fourier methods, refined by least squares (on *F*) using a modified version of *ORFLS* (Busing, Martin & Levy, 1962), hydrogen atoms located from difference map but constrained to calculated positions, 1 perchlorate [Cl(3)] disordered and refined with 8 half oxygens; refinements were carried out for the following possibilities: all bipyridines bonded to iridium *via* N, ring 1 bonded *via* C, ring 2 bonded *via* C, both 1 and 2 bonded *via* C, atoms 1 and 3 of rings 1 and 2 having scattering factors which were the mean of those for C and N; fractional atomic coordinates and isotropic thermal parameters for the disordered structure are given in Table 1;* $R(F) = 0·031$, $wR(F) = 0·038$ for 514 variables and 2531 reflexions, $S = 1·28$, $(\Delta/\sigma)_{max} = 0·07$, $\Delta\rho$ from $-0·76$ (9) to $1·00$ (9) e Å⁻³, $w = 1/\sigma(F)$, $\sigma(F) = [\sigma(F_c^2) + 1·03F^2]^{1/2} - |F|$, $\sigma(F_c^2)$ being the standard deviation of F^2 determined from counter statistics; corrections made for the anomalous dispersion of iridium.

Intensity statistics showed *Y* to be non-centrosymmetric; atomic positions determined by direct methods (*MULTAN*; Germain, Main & Woolfson, 1971) and from Fourier syntheses, structure refined by least squares (on *F*) assuming anisotropic thermal parameters for all non-hydrogen atoms, H atoms of bipyridine groups at calculated positions with $U_{iso} = 0·1$ Å²; perchlorate ions, which were highly disordered, were described by superposition of 4 half oxygen atoms on a freely rotating ClO₂ group;* $R(F) = 0·040$, $wR(F) = 0·059$ for 490 variables and 2870 reflexions, $S = 1·31$, $(\Delta/\sigma)_{max}$ 0·32, $\Delta\rho$ from $-0·7$ (2) to $1·1$ (2) e Å⁻³, *w* as for *WA*; imaginary part

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, coordinates for hydrogen atoms and close intermolecular distances, and the geometry of the perchlorate groups have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39204 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. $[Ir(bpy-C^3,N')(bpy)_2](ClO_4)_3.H_2O$ (WA); fractional atomic coordinates ($\times 10^5$ for Ir, $\times 10^4$ for other atoms) and U_{eq} ($\text{Å}^2 \times 10^3$)

The numbers of the atoms are $10r + c$, where r is the ring number and c the chemical number.

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ir	75704 (2)	55297 (2)	28440 (3)	43 (0·3)
Cl(1)	2641 (2)	5834 (2)	3325 (2)	72 (2)
Cl(2)	9820 (2)	3411 (2)	953 (2)	77 (2)
Cl(3)	4654 (3)	3152 (3)	1273 (3)	113 (3)
N(11)	7771 (6)	4326 (5)	3281 (6)	44 (6)
C(12)	7145 (7)	3972 (6)	3530 (7)	54 (8)
C(13)	7168 (7)	3171 (7)	3808 (9)	85 (9)
C(14)	7873 (10)	2693 (7)	3819 (11)	102 (12)
C(15)	8511 (9)	3042 (8)	3564 (11)	96 (12)
C(16)	8461 (7)	3875 (7)	3272 (9)	72 (9)
N(21)	6491 (5)	5277 (5)	3187 (7)	45 (6)
C(22)	6430 (6)	4513 (6)	3511 (7)	51 (7)
C(23)	5747 (7)	4263 (7)	3789 (9)	83 (8)
C(24)	5109 (8)	4785 (9)	3736 (10)	85 (11)
C(25)	5156 (7)	5568 (9)	3417 (10)	83 (10)
C(26)	5856 (7)	5820 (7)	3133 (9)	72 (9)
N(31)	7179 (5)	5121 (5)	1351 (6)	48 (6)
C(32)	7766 (7)	5139 (6)	846 (8)	52 (8)
C(33)	7583 (8)	4870 (7)	−157 (8)	66 (9)
C(34)	6790 (9)	4569 (7)	−670 (9)	82 (10)
C(35)	6203 (7)	4537 (7)	−171 (9)	70 (9)
C(36)	6415 (7)	4823 (6)	832 (8)	59 (8)
N(41)	8664 (5)	5681 (4)	2455 (7)	49 (6)
C(42)	8590 (6)	5475 (6)	1452 (8)	49 (7)
C(43)	9270 (7)	5563 (7)	1103 (9)	67 (9)
C(44)	10025 (7)	5886 (7)	1769 (11)	79 (10)
C(45)	10080 (7)	6103 (7)	2748 (10)	79 (10)
C(46)	9384 (6)	5994 (7)	3073 (9)	64 (8)
N(51)	8071 (5)	6016 (5)	4300 (7)	56 (7)
C(52)	8075 (6)	6834 (7)	4323 (8)	59 (9)
C(53)	8461 (8)	7274 (7)	5230 (10)	75 (9)
C(54)	8828 (8)	6840 (9)	6128 (10)	93 (12)
C(55)	8779 (8)	5984 (8)	6096 (9)	83 (10)
C(56)	8409 (7)	5590 (7)	5182 (8)	67 (8)
N(61)	7325 (5)	6775 (4)	2493 (7)	51 (6)
C(62)	7675 (6)	7274 (6)	3357 (9)	60 (9)
C(63)	7586 (8)	8116 (7)	3172 (11)	87 (12)
C(64)	7161 (8)	8443 (8)	2226 (11)	89 (11)
C(65)	6812 (7)	7910 (7)	1452 (10)	78 (10)
C(66)	6911 (7)	7085 (6)	1562 (9)	65 (9)
O(1)	3168 (6)	5219 (6)	3950 (8)	126 (8)
O(2)	2172 (6)	6192 (7)	3907 (8)	128 (9)
O(3)	3167 (7)	6422 (7)	3086 (9)	150 (11)
O(4)	2111 (6)	5463 (6)	2413 (7)	124 (8)
O(5)	9178 (6)	3720 (5)	76 (7)	110 (7)
O(6)	10084 (7)	2659 (6)	731 (10)	155 (11)
O(7)	10535 (6)	3967 (6)	1190 (8)	125 (8)
O(8)	9535 (7)	3398 (10)	1779 (8)	180 (12)
O(9)	3741 (28)	3434 (29)	785 (34)	305 (67)
O(10)	4779 (14)	3309 (18)	235 (16)	153 (25)
O(11)	4758 (25)	2464 (15)	615 (20)	243 (38)
O(12)	3898 (14)	2814 (15)	998 (17)	127 (25)
O(13)	4639 (19)	4014 (13)	1625 (20)	192 (27)
O(14)	5364 (17)	2820 (18)	1870 (20)	192 (30)
O(15)	4717 (19)	2780 (14)	2296 (17)	164 (27)
O(16)	5088 (30)	3645 (19)	1141 (33)	311 (66)
H$_2$O(1)	6099 (18)	2517 (11)	4903 (18)	391 (30)

of the anomalous dispersion for iridium included as $\eta f''$ and η refined as a least-squares variable; η was expected to be $+1$ or -1 depending on whether the polarity had been chosen correctly (Rogers, 1981), value obtained -0.94 (3); no extinction correction deemed necessary; structure solved and refined assuming monoclinic space group Cc with $a = 22.397$ (8), $b = 30.387$ (11), $c = 18.853$ (7) Å, $\beta = 119.77$ (2)° and $Z = 12$; transformation matrix from monoclinic to

trigonal cell is $(0.0, -1.0, 0.0 / -0.5, 0.5, 1.0 / -1.0, 0.0, -1.0)$; final refinement carried out in trigonal space group; fractional atomic coordinates and isotropic thermal parameters are given in Table 2.

Calculations carried out on a VAX-780 computer; atomic scattering factors from *International Tables for X-ray Crystallography* (1974) for Ir, Cromer & Mann (1968) for Cl, O, N and C, and Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion correction for Ir from Cromer & Liberman (1970).

Discussion. In *WA* the iridium atom is coordinated in a distorted octahedron. There is no evidence for either a covalently bonded water molecule or for a monodentate bipyridine. There remains the question as to whether one of the pyridine rings is bonded to iridium *via* a carbon atom as was suggested by WBS. It should be possible to distinguish C from N from the anomalous thermal parameters obtained on refining with the incorrect scattering factors. For *WB* the ratio of $B(1)/B(3)$ was 0·68 when the atoms were correctly assigned and 1·8 to 2·7 (Fig. 2a) when C and N were interchanged; for *Y* (Fig. 2b) a mean value of 0·70 was obtained. For *WA* (Fig. 2c) refinement assuming C bonding for rings 1 and 2 gave a ratio of only 0·31, whilst N bonding gave 0·86 which is much smaller than the value from *WB*. The 'N' atoms of these rings have very similar thermal parameters which implies that they are of a similar type, *i.e.* both N or both C, or that there is disorder so that one sees the mean of C and N. Refinement with mean values for both 'N' and 'C'(3) gave a ratio of 0·53; the ratios for the other atoms range from 0·59 to 0·76 with a mean value of 0·70. Thus the model with both rings C bonded can be discarded, but that with both rings N bonded or the disordered model cannot be distinguished from the thermal parameters alone. All the refinements gave the same R values. In *WB* the Ir—N bonds *trans* to C were long. For *WA* the two longest Ir—N bonds are the two *trans* to rings 1 and 2, with values 2·072 (7) and 2·092 (7) Å, which compare with 2·092 (4) Å, the mean of an ordinary and a long Ir—N bond in *WB*, *i.e.* the value which would be expected if there were disorder. The other Ir—N bonds range from 2·035 (7) to 2·045 (8) Å. Short bonds are not observed between Ir and rings 1 and 2, since when C and N are almost superimposed the refinement will tend to locate the atom close to the position of the heavier atom. WBS also find the two Ir—N bonds *trans* to the carbon-bonded bipyridine to be the longest. Thus, the evidence from both suggests that in *WA* there is one, and only one, iridium to carbon bond, though disordered between two sites (Fig. 1d). This is in agreement with the fact that *WA* is a monobasic acid and that the corresponding base *WB* has one iridium to carbon bond. Bond distances and angles are listed in Table 3. The water molecule is 2·87 (2) Å from 'C'(3) of ring 1 and

Table 2. [Ir(bpy)$_3$](ClO$_4$)$_3$.2$\frac{1}{3}$H$_2$O (Y); fractional atomic coordinates ($\times 10^5$ for Ir, $\times 10^4$ for other atoms) and U_{eq} (Å$^2 \times 10^3$)

The numbers of the atoms are $10r + c$, where r is the ring number and c the chemical number.

U_{eq} defined in Table 1.

	x	y	z	U_{eq}
Ir(1)	14471 (3)	−10943 (3)	228	64 (0·4)
N(11)	1805 (6)	−1246 (6)	729 (8)	75 (12)
C(12)	1758 (7)	−1113 (7)	1312 (9)	70 (13)
C(13)	1961 (9)	−1209 (7)	1833 (11)	95 (16)
C(14)	2239 (9)	−1437 (9)	1738 (11)	105 (18)
C(15)	2313 (7)	−1575 (8)	1138 (11)	90 (14)
C(16)	2087 (7)	−1455 (8)	648 (9)	84 (15)
N(21)	1259 (6)	−814 (6)	793 (8)	74 (13)
C(22)	1448 (7)	−867 (7)	1376 (9)	72 (13)
C(23)	1340 (9)	−682 (10)	1924 (9)	101 (18)
C(24)	1061 (13)	−449 (10)	1865 (14)	130 (27)
C(25)	843 (10)	−422 (9)	1296 (13)	116 (21)
C(26)	978 (9)	−612 (9)	788 (10)	93 (17)
N(31)	900 (6)	−1821 (5)	111 (7)	70 (10)
C(32)	937 (11)	−2174 (9)	−307 (12)	96 (19)
C(33)	587 (11)	−2672 (10)	−242 (14)	108 (22)
C(34)	204 (10)	−2829 (8)	206 (13)	110 (18)
C(35)	178 (7)	−2499 (10)	617 (10)	97 (16)
C(36)	528 (9)	−1977 (8)	526 (11)	86 (16)
N(41)	1636 (7)	−1431 (7)	−682 (7)	65 (11)
C(42)	1364 (9)	−1942 (11)	−723 (10)	73 (17)
C(43)	1461 (10)	−2225 (9)	−1126 (14)	109 (19)
C(44)	1874 (14)	−1939 (15)	−1497 (12)	108 (24)
C(45)	2157 (10)	−1449 (12)	−1481 (12)	108 (20)
C(46)	2033 (10)	−1197 (8)	−1065 (10)	94 (16)
N(51)	2010 (7)	−374 (6)	−156 (8)	78 (12)
C(52)	1900 (9)	−99 (8)	−532 (10)	82 (16)
C(53)	2248 (10)	397 (9)	−690 (10)	96 (17)
C(54)	2713 (12)	612 (9)	−421 (15)	120 (22)
C(55)	2842 (9)	338 (10)	−17 (13)	109 (19)
C(56)	2468 (9)	−169 (8)	124 (10)	87 (16)
N(61)	1109 (7)	−863 (7)	−619 (6)	71 (12)
C(62)	1391 (11)	−371 (9)	−797 (10)	89 (18)
C(63)	1167 (12)	−161 (10)	−1178 (13)	114 (22)
C(64)	706 (15)	−439 (13)	−1389 (12)	129 (24)
C(65)	400 (9)	−926 (13)	−1236 (11)	113 (20)
C(66)	644 (10)	−1140 (8)	−852 (11)	91 (16)
Cl(1)	88 (3)	−2539 (3)	−1906 (3)	108 (5)
O(1)	−176 (16)	−2903 (21)	−1377 (25)	253 (49)
O(2)	57 (50)	−2153 (21)	−1778 (27)	753 (114)
O(3)	580 (11)	−2212 (25)	−1840 (13)	315 (45)
O(4)	−13 (16)	−2574 (14)	−2567 (26)	233 (44)
Cl(2)	−914 (3)	582 (3)	428 (4)	123 (6)
O(5)	−714 (12)	335 (12)	784 (17)	144 (30)
O(6)	−764 (14)	1083 (12)	666 (17)	141 (32)
O(7)	−715 (31)	687 (18)	−137 (21)	307 (68)
O(8)	−1421 (12)	306 (13)	361 (31)	280 (54)
Cl(3)	1988 (3)	−469 (2)	−2495 (3)	109 (5)
O(9)	1911 (22)	−126 (16)	−2912 (22)	247 (54)
O(10)	1960 (7)	−856 (9)	−2951 (10)	79 (16)
O(11)	2440 (11)	−339 (10)	−2130 (14)	162 (23)
O(12)	1532 (9)	−787 (11)	−2106 (9)	97 (18)
H$_2$O(1)	−848 (8)	−1969 (8)	−1815 (9)	170 (18)
H$_2$O(2)	−441 (8)	−1446 (8)	2213 (10)	181 (19)
H$_2$O(3)	−3333	−6667	636 (31)	302 (35)

Table 3. [Ir(bpy-C^3,N')(bpy)$_2$](ClO$_4$)$_3$.H$_2$O (WA): bond lengths (Å) and angles (°)

The disorder in rings 1 and 2 is such that N(1) and C(3) are occupied by C or N.

E.s.d.'s are 0·007 Å for Ir–N, 0·01 Å for C–C or C–N, and 0·02 Å for C–H$_2$O.

Ring	1	2	3	4	5	6
Ir–N(1)	2·043	2·044	2·036	2·072	2·045	2·092
N(1)–C(2)	1·33	1·33	1·36	1·37	1·33	1·39
N(1)–C(6)	1·37	1·36	1·34	1·33	1·34	1·33
C(2)–C(3)	1·36	1·37	1·37	1·37	1·39	1·39
C(3)–C(4)	1·41	1·35	1·38	1·40	1·37	1·36
C(4)–C(5)	1·35	1·36	1·36	1·35	1·40	1·34
C(5)–C(6)	1·41	1·40	1·38	1·38	1·36	1·36
C(2)–C(2')	1·48		1·47		1·46	

H$_2$O(1)–C(13)	2·87 (2)		H$_2$O(1)–C(23)	3·19 (2)

Ir–N–C, C–N–C, N–C–C and C–C–C angles (e.s.d.'s 1°)

Ring	1	2	3	4	5	6
Ir–N(1)–C(6)	125	126	126	125	126	126
Ir–N(1)–C(2)	115	115	116	115	114	112
C(6)–N(1)–C(2)	120	119	117	120	120	122
N(1)–C(6)–C(5)	119	120	123	122	121	119
C(6)–C(5)–C(4)	120	120	119	119	120	123
C(5)–C(4)–C(3)	119	119	119	120	119	117
C(4)–C(3)–C(2)	119	121	119	119	118	123
C(3)–C(2)–N(1)	122	122	122	120	122	115
C(3)–C(2)–C(2')	122	124	123	125	120	130
N(1)–C(2)–C(2')	116	115	115	115	118	115

N–Ir–N angles (e.s.d.'s 0·3°)

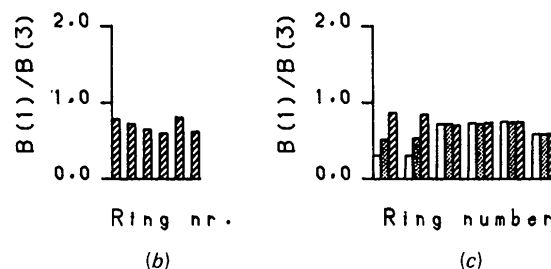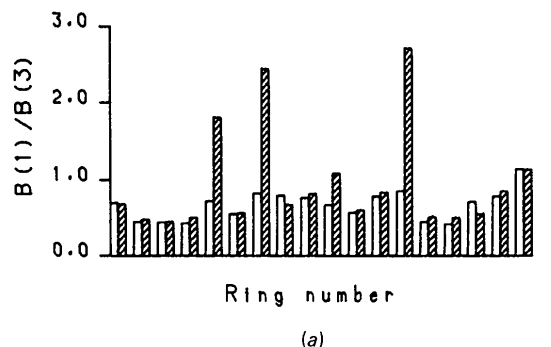|	N(21)	N(31)	N(41)	N(51)	N(61)
N(11)	79·4	87·0	96·4	96·4	175·5
N(21)		97·9	175·0	88·5	97·2
N(31)			79·1	173·2	96·4
N(41)				94·7	87·2
N(51)					80·5

Fig. 2. Histograms showing $B(1)/B(3)$ for (a) WB: cross hatched, all rings bonded via N; blank, rings 5, 7 and 13 bonded via C (there are three cations in the asymmetric unit); (b) Y: all rings bonded via N; (c) WA: cross hatched, all rings bonded via N; blank, rings 1 and 2 bonded via C; dotted, disordered model.

3·19 (2) Å from 'C'(3) of ring 2, both distances being short enough for hydrogen bonding; WBS* find distances of 2·86 and 3·03 Å. In bpy.2HSO$_3$F (Belin, Roziere & Potier, 1981), the N–H···O distance is 2·745 (5) Å, the O is 3·335 (5) Å from C(3) of the other ring. The infrared spectrum of bpy.2HSO$_3$F contains a maximum at ca 2550 cm^{-1} (Belin, Pichvay & Potier, 1980) which is attributed to hydrogen

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* The published value of 2·75 Å by WBS is a misprint, 2·86 Å is the value obtained from the coordinates deposited with the Cambridge Crystallographic Data Centre.

bonding; in comparison *WA* shows a band at 2650 cm^{-1} (Watts, Harrington & Van Houton, 1977) which is absent in the base form. Watts *et al.* also describe a dibasic complex which they formulate as $[Ir(bpy)_2(H_2O)_2]^{3+}$ which absorbs at 2680 cm^{-1}, whereas the basic form does not; this presumably has two Ir—C bonds.

The intraligand N—Ir—N and N—Ir—'N' angles range from 79·1 to 80·5°, the interligand angles from 87·0 to 88·5° and from 94·7 to 97·9° (e.s.d.'s 0·3°), the larger angles being between bonds related by the pseudo-threefold axis. The perchlorates are tightly bound to the cation; there are 15 perchlorate-oxygen to carbon distances less than 3·2 Å. Short water—O

distances, 2·71 (4) and 2·74 (3) Å, indicate hydrogen bonding.

The structure is very similar to that described by WBS except that we find one of the perchlorate ions to be disordered. A half-normal probability plot (Abrahams & Keve, 1971) for atomic coordinates, other than those of the disordered oxygen atoms, gave a straight line with a gradient of 1·76 (2). E.s.d.'s were assumed to be the same for the two sets of coordinates since the data base does not contain standard deviations.

Y contains $[Ir(bpy)_3]^{3+}$ ions in which the iridium atom is coordinated in a distorted octahedron to six nitrogen atoms of the bipyridines. The Ir—N distances range from 2·00 (2) to 2·02 (2) Å. The intraligand N—Ir—N angles range from 78·5 to 79·1°, the interligand angles from 85·7 to 90·7° and from 94·8 to 99·2° (e.s.d.'s 0·6–0·8°). Bond distances and angles are given in Table 4. As in *WA* the perchlorate ions are tightly bound to the cation; there are 13 perchlorate-oxygen to carbon distances less than 3·2 Å. Unlike *WA* there are no short contacts (<3·6 Å) between water and C(3) or C(3').

Ir—N and Ir—C bond distances for several iridium(III) complexes are compared in Table 5. The normal distance between iridium and the nitrogen of a pyridine group is about 2·04 Å; this is as expected slightly shorter than the distance to the tetrahedral nitrogen of ethylenediamine. Carbon exhibits a large *trans* effect which leads to a lengthening of Ir—N bonds by about 0·1 Å.

We are indebted to Dr G. Nord of the University of Copenhagen for the crystals of $[Ir(bpy)_3](ClO_4)_3.2\frac{1}{3}H_2O$, to Dr R. J. Watts of the University of California, Santa Barbara, for the crystals of $[Ir(bpy-C^3,N')(bpy)_2](ClO_4)_3.H_2O$, and to Professor G. S. Sheldrick of the University of Göttingen for showing that $[Ir(bpy)_3](ClO_4)_3.2\frac{1}{3}H_2O$ could be indexed using a trigonal unit cell.

Table 4. $[Ir(bpy)_3](ClO_4)_3.2\frac{1}{3}H_2O$ (*Y*): *bond lengths* (Å) *and angles* (°)

E.s.d.'s are 0·015–0·019 Å for Ir—N, 0·02–0·03 Å for C—C or C—N.

Ring	1	2	3	4	5	6
Ir—N(1)	2·019	2·032	2·000	2·032	2·026	2·019
N(1)—C(2)	1·32	1·39	1·43	1·35	1·31	1·35
N(1)—C(6)	1·31	1·28	1·31	1·32	1·34	1·32
C(2)—C(3)	1·35	1·39	1·35	1·34	1·38	1·39
C(3)—C(4)	1·35	1·35	1·38	1·36	1·35	1·30
C(4)—C(5)	1·38	1·38	1·35	1·29	1·37	1·33
C(5)—C(6)	1·38	1·37	1·41	1·33	1·41	1·45
C(2)—C(2')	1·47			1·42		1·45

Ir—N—C, C—N—C, N—C—C and C—C—C angles (e.s.d.'s 2°)

Ring	1	2	3	4	5	6
Ir—N(1)—C(6)	125	126	123	126	123	126
Ir—N(1)—C(2)	117	115	116	117	117	115
C(6)—N(1)—C(2)	118	118	121	117	120	119
N(1)—C(6)—C(5)	124	128	122	122	120	123
C(6)—C(5)—C(4)	115	113	117	117	118	114
C(5)—C(4)—C(3)	122	123	122	126	121	125
C(4)—C(3)—C(2)	117	118	121	112	118	121
C(3)—C(2)—N(1)	124	119	118	125	123	119
C(3)—C(2)—C(2')	121	129	129	120	123	126
N(1)—C(2)—C(2')	116	113	113	114	114	115

N—Ir—N angles (e.s.d.'s 0·6–0·8°)

	N(21)	N(31)	N(41)	N(51)	N(61)
N(11)	79·1	85·7	95·6	97·0	172·7
N(21)		97·8	173·8	87·5	94·8
N(31)			78·5	174·4	99·2
N(41)				96·3	90·7
N(51)					78·6

Table 5. Ir^{III}—*X distances* (Å), *X* = N, N_t (N *trans to* C) *or* C; *distances to carbonyl groups are not included*

		N	N_t	C	References
$[Ir(bpy-C^3,N')(bpy)_2](ClO_4)_3.H_2O$	*WA*	2·042 (4)	2·082 (5)*		(a)
$[Ir(bpy-C^3,N')(bpy)_2](ClO_4)_3.H_2O$	*WA*	2·03	2·08*		(b)
$[Ir(bpy^-C^3,N')(bpy)_2](ClO_4)_3.\frac{1}{3}H_2O$	*WB*	2·053 (5)	2·131 (5)	1·980 (6)	(c)
$[Ir(bpy)_3](ClO_4)_3.2\frac{1}{3}H_2O$	*Y*	2·021 (6)			(a)
Chlorobis[2-(diphenoxyphosphinooxy) phenyl](triphenyl phosphite)Ir				2·105 (7)†	(d)
Chlorobis(γ-picoline)[tris(*o*-tolyl) phosphite-*P,C,C*]Ir			2·170 (7)	2·045 (7)	(e)
(bpy)carbonyldiiodo(methyl formato)Ir			2·14 (2)	2·05 (2)	(f)
$[Ir(en)(enH)Cl_3]Cl.H_2O$‡		2·076 (4)			(g)
$[(en)_2(OH)Ir(OH)Ir(H_2O)(en)_2]^{4+}$‡		2·071 (3)			(g)

References: (a) This work; (b) Wickramasinghe, Bird & Serpone (1981); (c) Nord, Hazell, Hazell & Farver (1983); (d) Guss & Mason (1972); (e) Nolte, Singleton & van der Stok (1977); (f) Albano, Bellon & Sansoni (1969); (g) Rasmussen (1983).

* Disordered, overlap of N and N_t.
† *trans* to P.
‡ en = ethylenediamine.

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Structure of Hexaaquairon(II) Bis{tris[1,3-dimethyl-2,4,5,6(1H,3H)-pyrimidinetetrone 5-oximato]ferrate(II)} Dodecahydrate, $[Fe(H_2O)_6]^{2+}.2[Fe(C_6H_6N_3O_4)_3]^-.12H_2O$

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Abstract. $M_r = 1596.6$, hexagonal, $R\bar{3}$, $a = 16.329$ (3), $c = 21.275$ (9) Å, $V = 4913$ (2) Å^3, $Z = 3$, $D_x = 1.62$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 0.766 mm^{-1}, $T = 298$ K, $F(000) = 2484$, $R = 0.049$ for 2078 observed reflexions. The two Fe atoms are located in special positions along the threefold axis, and exhibit octahedral coordination. An array of cations, each lying between two anions, is repeated along the threefold axis. Coordinated and uncoordinated water molecules contribute to structural packing through hydrogen bonds.

Introduction. Relatively little work has been carried out on complexes of organic nitroso ligands with transition-metal ions, and this has been almost entirely concerned with ligands of the *o*-nitrosophenolate or isonitroso ketone type.

The available structural data are about salts of the type $M^+[FeV_3]^-.xH_2O$ where M^+ is an alkali-metal cation and V the violurate anion (Raston & White, 1976).

We now report the crystal structure of the title compound, prepared by J. D. López González and co-workers, Department of Inorganic Chemistry, University of Granada (Spain).

Experimental. Black metallic crystal, $0.7 \times 0.4 \times 0.3$ mm. Enraf–Nonius CAD-4 F automatic diffractometer. Cell dimensions by least-squares fitting of the θ values of 25 reflexions. $\omega/2\theta$ scans. No appreciable drop in intensity of three standard reflections, checked every hour. 6050 reflexions within $1° < \theta < 30°$ and *hkl* range 0,0,−29 to 22,22,29 collected; 3417 unique reflexions; $R_{int} = 0.039$; 2078 considered observed $[I > 2\sigma(I)]$. Lorentz–polarization correction; no absorption correction, $\mu R = 0.54$. Scattering factors for neutral atoms and anomalous-dispersion corrections for