93.8–97.8°. This result implies that the different ring puckerings are compensated for mainly by the P–C–P angle, which varies from 90.0° for compound **1** and 90.8° for compound **12** to 99.4° for compound **4**.

In all of these dppm complexes, the C(phenyl)–P–C(phenyl) angles and the C(phenyl)–P–C(sp^3) angles are less than tetrahedral, with ranges of 103–108 and of 104–109° and respective mean values of 105.1 and of 106.8°. The M–P–C(phenyl) angles are always larger than tetrahedral, however, and show a much greater range of values, from 111 to 127°. The mean value is 120.3°. These M–P–C(phenyl) angles are usually, but not always, larger for the phenyl rings A and C, the average value being 122.3° for these phenyl rings, with a smaller value of 118.4° found for the downward-pointing rings B and D. The P–C(phenyl) distances lie in the range 1.78–1.83 Å, with a mean value of 1.812 Å. The P–C(sp^3) distances are on average longer, with a mean value of 1.850 Å, and they show a wider range, from 1.824 to 1.89 Å. We were not able to find any correlation between the length of the P–C(sp^3) bond and the chelate ring geometry.

In nearly all of the dppm complexes listed, the two M–P distances within the chelate ring are not the same, with significant differences of 0.01–0.11 Å. For the iridium dioxygen complexes (**6** and **8**), the rhodium carbonyl complex (**7**), and the molybdenum carbonyl chloride (**1**), these differences are readily understood, as the diphosphine ligand bridges two nonequivalent sites in the metal coordination sphere. Various trans-influence effects have been invoked for several of the other complexes. It may be that the precise metal–phosphorus bond length is sensitive to nonsymmetrical environments for the bulky diphosphine ligand in the crystal, and variations of 0.01–0.02 Å could be due to nonbonded repulsions.

In conclusion, the widely differing shapes found for the chelating dppm ligand in these metal complexes arise mainly from variations in the amount of buckling of the four-membered chelate ring. This ring buckling is not correlated with the stereochemistry at the metal atom but may represent response to different packing requirements.

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Registry No. **3**, 74096-45-0.

Supplementary Material Available: Listings of final observed and calculated structure factors (Table S1), final anisotropic thermal parameters (Table S2), final hydrogen atom positional and thermal parameters (Table S3), and parameters for the constrained atoms (Table S4) (25 pages). Ordering information is given on any current masthead page.

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A Carbon-Bonded Tris(2,2′-bipyridine)iridium(III) Complex: (2,2′-Bipyridinyl-C^3,*N*′)bis(2,2′-bipyridine-*N*,*N*′)iridium(III) Perchlorate–Water (3/1)

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The title compound has been prepared as large red diamagnetic crystals. X-ray analysis showed that there are three iridium(III) cations coordinated in distorted octahedra in an asymmetric unit containing six perchlorate ions and one water molecule. In each case the iridium is coordinated to five nitrogens and one carbon of the bipyridine ligands. The bond distances in the coordination sphere are 1.980 (6) Å for Ir–C, 2.131 (5) Å for the Ir–N trans to the Ir–C bond, and 2.053 (5) Å for the remaining four Ir–N bonds. New features in the ultraviolet and NMR spectra of solutions of the complex accord with the above structure. These spectra can be used as diagnostic for a C-bonded bipyridine complex. The possible mechanistic significance of C coordination for reactions of metal–bipyridine complexes is discussed.

Two yellow[2,3] and one orange[4] tris(2,2′-bipyridine)iridium(III) complexes have been reported. All contain a triply charged cation and are diamagnetic. The two former were separated from excess ligand and other Ir(III) products by elution from an exchange column and then isolated from aqueous acid. The latter, which was reported much earlier,[4] was a single product precipitated from aqueous sodium perchlorate. The main features of the different synthetic procedures are included in Scheme I. The spectra (UV, ^{1}H NMR, and ^{13}C NMR) of solutions of one of the yellow compounds[2,6] clearly show it to be the "normal" tris(2,2′-bipyridine-*N*,*N*′)iridium(III) complex written below as Ir(bpy-*N*,*N*′)$_3^{3+}$. The analogous spectra of the second yellow complex show equally clearly that at least one of the ligands is modified; this complex is referred to below as Watts' complex.

Two recent papers are significant for discussion of the structure of Watts' complex. Serpone and co-workers[7] reported a preliminary crystal structure that showed, first, that Ir was bound to the six ligand rings and, second, that although a water molecule was in a position that could be hydrogen bonded to the H at what would be the 3-position in one ring, there were no OH groups bound to any of the ring atoms. Watts' compound therefore contains neither a monodentate ligand[3] nor the deprotonated form of a "covalent hydrate"[5] as previously suggested. In addition, Serpone et al. proposed that one of the bipyridine rings had rotated and that C3 of this ring was both deprotonated and ligated. The proton was suggested to be transferred to the N now occupying the

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(1) (a) H. C. Ørsted Institute, University of Copenhagen. (b) Aarhus University. Crystallographic questions should be addressed to these authors. (c) Royal Danish School of Pharmacy.

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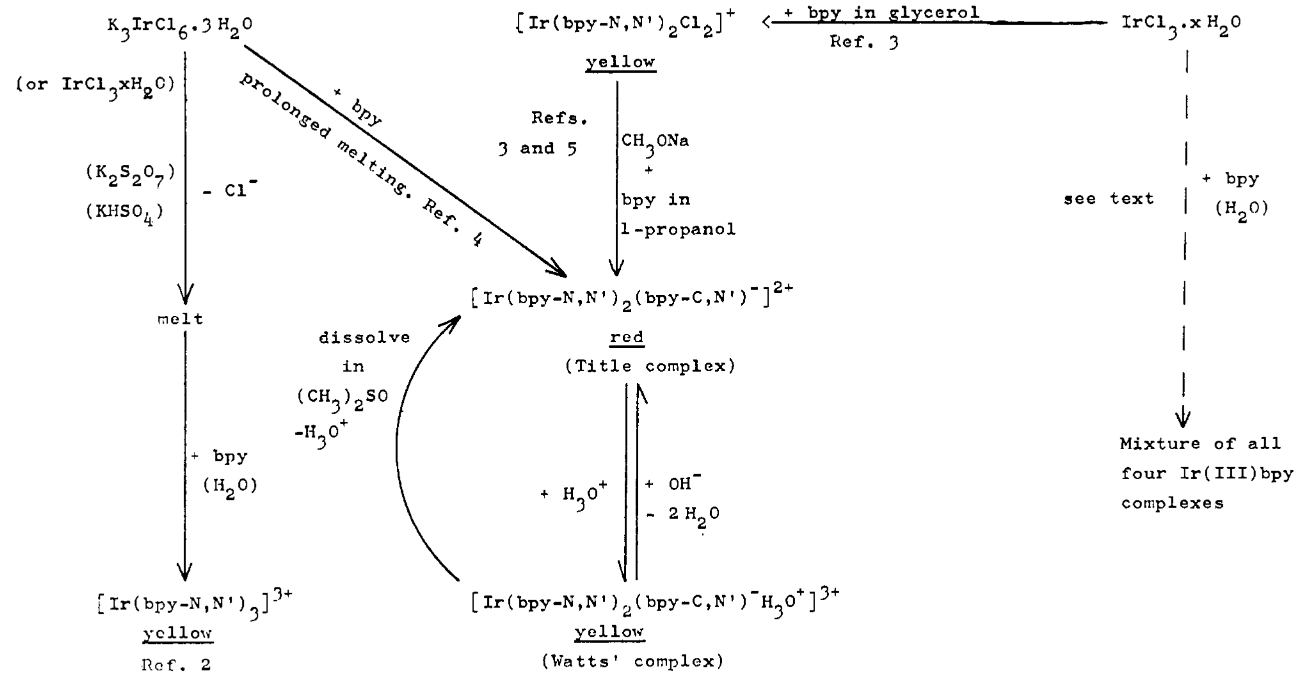
Scheme I



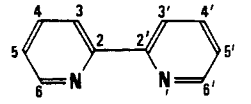


Figure 1. System of numbering.

"normal" C3 position. The numbering is given in Figure 1. Although neither this study[7] nor another independent one[8] gave any further structural evidence for Ir–C bonding, a paper by Constable and Seddon[9] did give further credence to Serpone's suggestion. These authors[9] found that addition of deuterated sodium methoxide and methanol to a solution of Ru(bpy-*N,N'*)$_3^{2+}$ in dimethyl sulfoxide resulted in slow deuterium–hydrogen exchange at the 3,3'-positions of the coordinated ligands. The conditions of the experiment were analogous to those used by Watts et al.[3] for the preparation of an orange solution that on acidification became yellow and yielded his complex. There is also evidence[10] for weak acidic character of the H3's in Os(bpy-*N,N'*)$_3^{2+}$ and possibly in a Pt^{II}bpy complex (see Discussion). Watts' complex is a fairly strong acid (pK_A ~ 3),[3] and because of this, together with the similar formula and UV absorbance of Watts' complex and the orange compound,[4] it seemed likely to us that the latter was in fact Watts' complex with a trace of a red complex coprecipitated in the medium of higher pH. We have now isolated this red complex and determined both its crystal structure and its solution spectra. We conclude that it is the title complex [Ir(bpy-*N,N'*)$_2$(bpy-*C,N'*)$^-$]$^{2+}$ that is converted by aqueous acid to Watts' complex [Ir(bpy-*N,N'*)$_2$(bpy-*C,N'*)$^-$H$_3$O$^+$]$^{3+}$. We report here details of the experimental evidence on which these conclusions are based.

Experimental Section

Synthesis. A 3-mL portion of H_2O and 3 g of 2,2'-bipyridine were warmed in a test tube until the bipyridine melted. A 2-g portion of $IrCl_3\cdot H_2O$ (49% Ir) was added to the melt in small portions and the mixture allowed to stand overnight in a water bath with magnetic stirring. The tube was then sealed and kept in a autoclave at 170 °C for 14 days when a large amount of a yellow precipitate, [Ir(bpy-*N,N'*)$_2$Cl$_2$]Cl·2H$_2$O, suspended in a dark red liquid was obtained. After filtration, the filtrate was evaporated to dryness ,at ~40 °C, in a vacuum rotator. The residue was dissolved in 100 mL of absolute alcohol and allowed to stand, at 0 °C, overnight when an additional amount of the above bis complex was formed and removed by filtration. The filtrate was again evaporated to dryness and the residue then dissolved in 25 mL of boiling absolute ethanol. After cooling and removal of more bis complex, the filtrate was absorbed on an L.H. Sephadex column. Elution with ethanol resulted in three fractions. First excess ligand was eluted, next a yellow band (presumed to be still more of the bis complex), and finally a well-separated region containing overlapping red-orange bands. This last fraction was evaporated to dryness and then dissolved in 25 mL of 1 M aqueous sodium perchlorate. This solution was slowly evaporated (in a haybox) until crystals were formed. These were washed with cold water and dried in air and were of two kinds, which were separated by hand under a microscope. Small yellow crystals of Ir(bpy-*N,N'*)$_3$(ClO$_4$)$_3$·2H$_2$O used for the X-ray structure given in ref 11 were separated from large red crystals of the title complex that were used for the work reported here. Anal. Calcd for $[Ir(C_{10}H_8N_2)_2(C_{10}H_7N_2)(ClO_4)_2\cdot{}^1/_3H_2O]$: C, 41.43; H, 2.64; N, 9.87; Cl, 8.17. Found: C, 41.41; H, 2.71; N, 9.65; Cl, 8.15.

Crystallographic Measurements. Unit cell dimensions were determined from the setting angles of 20 reflections measured with Cu Kα radiation (λ = 1.5418 Å). Intensities were measured by a step-scanning technique, the extent of the peaks being determined by the $\sigma(I)/I$ criterion.[12] Intensities were processed and corrected for absorption by using modified versions of the SUNY—Buffalo programs PROFILE, DATAP, and DSORT.

Structure Analysis. A Patterson synthesis yielded the following coordinates for the iridium atoms: $^1/_2$, $^1/_8$, 0.25; $-^1/_6$, $^1/_8$, 0.23; $^1/_6$, $^1/_8$, 0.28. Thus, the iridium atoms fit the centrosymmetric space group *C*2/*c*; furthermore, there is a pseudo repeat distance of *a*/3. Conventional Fourier refinement did not reveal the rest of the structure, nor was the structure soluble by means of conventional direct methods; the latter did however show the space group to be *Cc* and not *C*2/*c*. The program system DIRDIF,[13] a direct-methods program specially written for structures in which the heavy atoms have a higher symmetry than the rest of the structure, was tried starting with the positions

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Table I. Data for the X-ray Diffraction Study of $[Ir(C_{10}H_8N_2)_2(C_{10}H_7N_2)](ClO_4)_2 \cdot {}^1/_3H_2O$

A. Crystal Data

cryst syst: monoclinic	$V = 9375$ Å^3
space group: *Cc*	$Z = 12$
$a = 28.583$ (4) Å	mol wt = 865
$b = 25.122$ (3) Å	ρ(calcd) = 1.826 g/cm^3
$c = 13.056$ (1) Å	μ(Mo Kα) = 44.9 cm^{-1}
$\beta = 89.48$ (1)°	

B. Measurement of Intensity Data

diffractometer	Picker FACS-1
cryst faces	{010}, {101}, $\{30\bar{1}\}$
cryst dimens	0.26 × 0.38 × 0.46 mm^3
transmssn factors	18–34%
radiation	Mo Kα (λ = 0.710 69 Å)
filter	Zr
scan type	θ–2θ
step length	0.04°
scan width	(3.0 + 0.692 tan θ)°
sec/step	1
data collcn range	$0 < 2\theta < 35°$; $+h, +k, \pm l$
no. of unique data	6094
no. of data with $I > 3\sigma(I)$	4901
no. of variables	308
R_F	0.056
R_{wF}	0.071

of two of the iridium atoms. This gave the positions of the third iridium atom, the bipyridyl ligands, two perchlorate ions per iridium, and one water molecule. Least-squares refinement assuming the bipyridyls to be bonded to iridium via the nitrogen atoms gave an *R* value of 0.061. At this stage it was observed that the thermal parameters for atoms N(5), N(7), and N(13) were abnormally large while those of the carbon atoms C3, i.e. C(53), C(73), and C(133), were too low. The ratios *B*(N)/*B*(C3) were 1.81, 2.44, and 2.71 whereas the mean value for the other nitrogen–carbon pairs was 0.68, the same value as observed[11] for $[Ir(bpy)_3][(ClO_4)_3] \cdot 2H_2O$. Furthermore, the Ir–N distances for the bonds trans to N(5), N(7), and N(13) were all exceptionally long (ca. 2.15 Å). The abnormal thermal parameters could be explained if rings 5, 7, and 13 were rotated about C2–C2′ so that they were bonded via carbon and not via nitrogen. The presence of only two and not three perchlorates agrees with the C-bonded ring having lost a proton.

Refinement assuming three carbon-bonded bipyridyls gave physically reasonable thermal parameters (ratios of *B*(C3)/*B*(N) of 0.63, 0.84, and 0.77, i.e., the atom bonded to iridium having the smallest thermal vibration) and a slightly lower *R* value of 0.059. It was not possible to locate the hydrogen atoms, but in the final cycles, hydrogen atoms were included at the calculated positions for atoms of the type C4, C5, and C6. The final *R* value was 0.056 for 4901 reflections and 308 parameters. In view of the large number of atoms, a constrained least-squares procedure[14] was used. The following constraints wer imposed: all perchlorate ions to be regular tetrahedra with identical Cl–O distances; all 15 N-bonded pyridine fragments to be identical and planar; the C3-bonded pyridines to be identical and planar but not necessarily identical with the N-bonded pyridines. No constraints were imposed on the thermal parameters except that the hydrogen atoms were kept fixed at $B = 8.0$ Å^2. The iridium atoms were refined anisotropically, and the remaining atoms isotropically. No extinction correction was deemed necessary. The imaginary part of the anomalous dispersion for iridium was 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;[15] the value obtained was −1.03 (6).

Fractional atomic coordinates and isotropic thermal parameters are given in Table II; the constraint parameters, i.e., coordinates relative to molecular axes, and the origins and the Euler angles for the different axial systems referred to orthogonal Å axes with $A \| a$, $B \| b$, and $C \| c^*$ given in Tables III and IV.

Calculations were carried out on a VAX 780 computer. Atomic scattering factors were taken from ref 16 for Ir, ref 17 for Cl, O, N, and C, and ref 18 for H. Anomalous dispersion corrections for Ir were taken from ref 19.

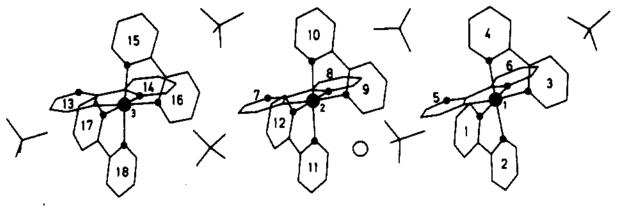

Figure 2. An asymmetric unit viewed down *c* showing the numbering of the rings. The *a* axis is across the page. Nitrogen atoms are represented by small filled circles, iridium atoms by large filled circles, and the water molecule by a large open circle.

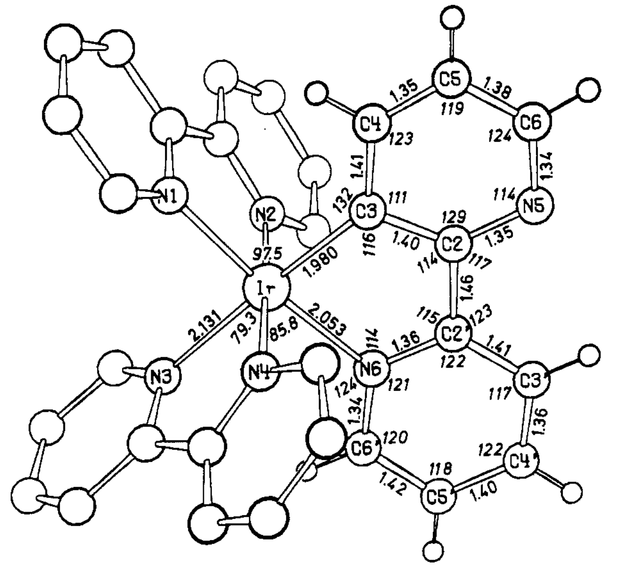

Figure 3. Perspective view of a cation showing mean bond lengths and angles. Hydrogen atoms aree included on rings 5 and 6 to show the interaction of H4 with the pyridine ring 1. Esd's are 0.01 Å and 1° for bonds and angles within the N-bonded pyridines and 0.03 Å and 2° for those within the C-bonded pyridine. C2–C2′ ranges from 1.45 (2) to 1.48 (3) Å. Sample standard deviations are 0.005 Å for Ir–N, 0.006 Å for Ir–C, and 0.5° for angles not in the rings.

Spectroscopic Measurements. These were all made at room temperature (22 ± 1 °C). The NMR measurements were made as described in ref 20.

Results

The red crystals were diamagnetic.

X-ray Structure. There are three tris $[Ir(bpy)_3]^{2+}$ ions in the asymmetric unit (Figure 2). Each iridium atom is coordinated in a distorted octahedron to five nitrogen atoms and one carbon atom of the bipyridyl ligands. The mean bond distances in the coordination sphere are 1.980 (6) Å for Ir–C, 2.131 (5) Å for Ir–N trans to the Ir–C bond, and 2.053 (5) Å for the remaining Ir–N bonds. Selected bond lengths and angles are given in Table V or in Figure 3. The geometry of the bipyridyl groups has not been determined with any great accuracy; however, in both the N-bonded rings and the C-

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(21) While the standard deviations for bond lengths and angles within pyridine rings and within perchlorate ions can be readily calculated directly from those of the constraint parameters, those involving bonds between rings or between iridium and other atoms require an estimate of the standard deviations of the atoms in a crystal system. These have been estimated as $\sigma^2 = \sigma_O^2 + \sigma_M^2$, where σ_O is the standard deviation of the origin and σ_M the standard deviation in the molecular system of axes.

Table II. Fractional Atomic Coordinates and Isotropic Thermal Parameters[a]

	x	*y*	*z*	*B*, Å^2		*x*	*y*	*z*	*B*, Å^2
Ir(1)	0.49999	0.12695 (4)	0.25003	2.8[b]	C(123)	0.5979	0.4759	−0.0090	5.1 (7)
Ir(2)	0.66720 (5)	0.37824 (5)	−0.22926 (12)	2.9[b]	C(124)	0.5816	0.4411	0.0630	4.7 (7)
Ir(3)	0.82310 (5)	0.11031 (4)	−0.69005 (11)	2.8[b]	C(125)	0.5899	0.3864	0.0561	5.7 (8)
N(1)	0.4718	0.0934	0.3796	3.2 (5)	C(126)	0.6160	0.3671	−0.0287	4.5 (7)
C(12)	0.4684	0.0397	0.3721	4.8 (7)	N(13)	0.7437	0.1355	−0.9549	3.4 (4)
C(13)	0.4438	0.0093	0.4461	4.6 (7)	C(132)	0.7750	0.1287	−0.8796	3.1 (6)
C(14)	0.4236	0.0364	0.5254	5.7 (8)	C(133)	0.7683	0.1085	−0.7810	2.9 (5)
C(15)	0.4269	0.0918	0.5340	5.1 (7)	C(134)	0.7213	0.0943	−0.7641	3.6 (6)
C(16)	0.4520	0.1200	0.4575	4.4 (6)	C(135)	0.6878	0.0998	−0.8354	2.7 (5)
N(2)	0.5150	0.0488	0.2205	3.4 (5)	C(136)	0.7000	0.1205	−0.9297	5.6 (8)
C(22)	0.4928	0.0152	0.2862	4.5 (6)	N(14)	0.8545	0.1285	−0.8271	1.7 (4)
C(23)	0.4944	−0.0406	0.2728	7.5 (9)	C(142)	0.8244	0.1414	−0.9029	2.9 (5)
C(24)	0.5192	−0.0592	0.1907	7.0 (9)	C(143)	0.8405	0.1617	−0.9979	3.8 (5)
C(25)	0.5422	−0.0251	0.1223	5.5 (7)	C(144)	0.8876	0.1677	−1.0100	5.9 (8)
C(26)	0.5393	0.0304	0.1398	3.7 (6)	C(145)	0.9190	0.1546	−0.9324	5.1 (7)
N(3)	0.5593	0.1463	0.3394	2.4 (4)	C(146)	0.9008	0.1345	−0.8389	3.6 (6)
C(32)	0.5615	0.1981	0.3677	4.3 (6)	N(15)	0.8292	0.1908	−0.6715	2.1 (4)
C(33)	0.5978	0.2174	0.4304	5.4 (7)	C(152)	0.8702	0.2073	−0.6308	6.2 (8)
C(34)	0.6306	0.1815	0.4612	6.7 (8)	C(153)	0.8840	0.2613	−0.6342	5.0 (7)
C(35)	0.6287	0.1279	0.4326	5.7 (8)	C(154)	0.8543	0.2961	−0.6803	6.6 (8)
C(36)	0.5914	0.1110	0.3697	4.6 (6)	C(155)	0.8119	0.2796	−0.7227	4.1 (6)
N(4)	0.4882	0.2069	0.2842	2.8 (4)	C(156)	0.8000	0.2250	−0.7169	4.1 (6)
C(42)	0.5248	0.2324	0.3279	3.5 (6)	N(16)	0.8835	0.1155	−0.5958	3.4 (5)
C(43)	0.5259	0.2884	0.3373	6.5 (8)	C(162)	0.8975	0.1663	−0.5799	4.7 (6)
C(44)	0.4885	0.3158	0.3005	4.2 (7)	C(163)	0.9367	0.1783	−0.5187	4.8 (7)
C(45)	0.4505	0.2901	0.2553	4.5 (7)	C(164)	0.9598	0.1363	−0.4764	7.3 (10)
C(46)	0.4514	0.2339	0.2480	4.2 (6)	C(165)	0.9457	0.0837	−0.4922	7.7 (10)
N(5)	0.4143	0.1258	−0.0109	4.3 (5)	C(166)	0.9062	0.0743	−0.5543	5.1 (7)
C(52)	0.4462	0.1303	0.0637	2.7 (5)	N(17)	0.7858	0.0893	−0.5626	2.9 (4)
C(53)	0.4424	0.1171	0.1673	3.1 (6)	C(172)	0.7757	0.0367	−0.5550	2.8 (5)
C(54)	0.3979	0.0963	0.1906	4.3 (6)	C(173)	0.7469	0.0166	−0.4755	3.7 (6)
C(55)	0.3639	0.0905	0.1204	4.7 (7)	C(174)	0.7296	0.0525	−0.4066	5.2 (7)
C(56)	0.3731	0.1055	0.0207	5.3 (7)	C(175)	0.7397	0.1068	−0.4135	5.5 (7)
N(6)	0.5235	0.1563	0.1107	2.9 (4)	C(176)	0.7688	0.1246	−0.4949	4.0 (6)
C(62)	0.4917	0.1534	0.0344	2.4 (5)	N(18)	0.8244	0.0290	−0.7029	4.0 (5)
C(63)	0.5021	0.1720	−0.0654	5.3 (7)	C(182)	0.7977	0.0030	−0.6329	2.8 (5)
C(64)	0.5455	0.1929	−0.0818	5.4 (7)	C(183)	0.7925	−0.0530	−0.6352	3.5 (5)
C(65)	0.5787	0.1961	−0.0039	5.0 (7)	C(184)	0.8156	−0.0796	−0.7112	6.4 (8)
C(66)	0.5662	0.1768	0.0946	4.0 (6)	C(185)	0.8433	−0.0533	−0.7840	4.5 (6)
N(7)	0.5858	0.3734	−0.4962	2.8 (4)	C(186)	0.8472	0.0028	−0.7776	4.3 (6)
C(72)	0.6172	0.3719	−0.4201	2.4 (5)	Cl(1)	0.6705	0.2724	−0.8237	4.8 (2)
C(73)	0.6115	0.3850	−0.3169	2.3 (5)	O(1)	0.6313	0.2967	−0.7840	9.1 (7)
C(74)	0.5655	0.4018	−0.2958	4.2 (6)	O(2)	0.7066	0.3085	−0.8292	11.2 (9)
C(75)	0.5319	0.4045	−0.3676	3.3 (6)	O(3)	0.6831	0.2307	−0.7616	11.1 (8)
C(76)	0.5431	0.3901	−0.4667	4.1 (6)	O(4)	0.6611	0.2535	−0.9202	10.4 (8)
N(8)	0.6964	0.3581	−0.3704	3.0 (4)	Cl(2)	0.3244	0.0454	0.7538	5.4 (2)
C(82)	0.6652	0.3556	−0.4478	2.9 (5)	O(5)	0.3072	0.0385	0.6568	14.2 (11)
C(83)	0.6789	0.3407	−0.5480	3.8 (6)	O(6)	0.3233	−0.0024	0.8051	19.6 (17)
C(84)	0.7249	0.3288	−0.5635	4.7 (6)	O(7)	0.3697	0.0635	0.7478	16.7 (13)
C(85)	0.7575	0.3312	−0.4844	5.1 (7)	O(8)	0.2974	0.0819	0.8056	10.9 (9)
C(86)	0.7417	0.3464	−0.3856	3.1 (5)	Cl(3)	0.9785	0.0253	0.7980	5.3 (2)
N(9)	0.7278	0.3646	−0.1378	4.2 (5)	O(9)	0.9539	−0.0136	0.7479	9.8 (8)
C(92)	0.7338	0.3134	−0.1081	4.0 (6)	O(10)	1.0059	0.0526	0.7287	19.2 (16)
C(93)	0.7712	0.2981	−0.0444	5.5 (7)	O(11)	0.9478	0.0600	0.8445	13.7 (11)
C(94)	0.8011	0.3372	−0.0142	6.4 (8)	O(12)	1.0064	0.0024	0.8708	18.2 (15)
C(95)	0.7954	0.3902	−0.0443	6.5 (9)	Cl(4)	0.8234	0.2292	−0.3167	5.3 (2)
C(96)	0.7572	0.4030	−0.1081	5.2 (7)	O(13)	0.7767	0.2310	−0.3404	7.6 (6)
N(10)	0.6654	0.2974	−0.2062	3.8 (5)	O(14)	0.8445	0.1884	−0.3699	13.3 (10)
C(102)	0.7011	0.2755	−0.1529	5.3 (7)	O(15)	0.8442	0.2767	−0.3432	14.1 (11)
C(103)	0.7067	0.2198	−0.1450	5.7 (7)	O(16)	0.8283	0.2208	−0.2134	12.4 (10)
C(104)	0.6745	0.1889	−0.1934	3.7 (6)	Cl(5)	0.1362	0.4633	0.3627	6.2 (2)
C(105)	0.6375	0.2108	−0.2486	5.8 (8)	O(17)	0.1819	0.4473	0.3491	12.6 (9)
C(106)	0.6338	0.2670	−0.2538	4.3 (6)	O(18)	0.1244	0.4983	0.2865	9.1 (7)
N(11)	0.6718	0.4587	−0.2408	3.7 (5)	O(19)	0.1073	0.4197	0.3591	14.9 (11)
C(112)	0.6454	0.4865	−0.1726	4.6 (7)	O(20)	0.1315	0.4878	0.4563	22.4 (18)
C(113)	0.6418	0.5426	−0.1775	6.5 (9)	Cl(6)	0.4968	0.2260	−0.3530	6.5 (2)
C(114)	0.6660	0.5675	−0.2539	7.0 (9)	O(21)	0.4860	0.2400	−0.4518	11.1 (9)
C(115)	0.6934	0.5394	−0.3248	5.0 (7)	O(22)	0.5393	0.2004	−0.3520	16.8 (14)
C(116)	0.6957	0.4832	−0.3159	4.3 (7)	O(23)	0.4990	0.2710	−0.2934	18.9 (16)
N(12)	0.6320	0.4012	−0.0995	4.0 (5)	O(24)	0.4628	0.1926	−0.3148	22.8 (18)
C(122)	0.6238	0.4543	−0.0919	4.7 (7)	H20	0.2557 (14)	0.0255 (18)	−0.0096 (31)	19.0 (15)

[a] Standard deviations of atoms other than iridium and water estimated from those of the constraint parameters: N-bonded rings $\sigma(x) = 0.0006$, $\sigma(y) = 0.0007$, $\sigma(z) = 0.0013$; C-bonded rings $\sigma(x) = 0.0008$, $\sigma(y) = 0.0010$, $\sigma(z) = 0.0018$; Cl atoms $\sigma(x) = 0.0003$, $\sigma(y) = 0.0003$, $\sigma(z) = 0.0006$; O atoms of ClO_4 $\sigma(x) = 0.0004$, $\sigma(y) = 0.0004$, $\sigma(z) = 0.0008$. The carbon atoms have numbers $10r + c$ where r is the number of the ring (that of the nitrogen atom) and c the chemical number. [b] Values derived from anisotropic thermal parameters.

Table III. Coordinates (Å) Referred to the Orthogonal Axial Systems in Which Chemically Equivalent Groups Were Constrained[14] To Be Identical

	x	*y*	*z*
	N-Bonded Pyridine		
N(1)	1.279 (7)	−1.051 (7)	0.000
C(2)	0.736 (7)	0.191	0.000
C(3)	1.542 (10)	1.352 (10)	0.000
C(4)	2.892 (10)	1.168 (10)	0 000
C(5)	3.467 (9)	−0.107	0.000
C(6)	2.607 (9)	−1.232 (9)	0.000
H(4)	3.462	1.928	0.000
H(5)	4.407	−0.216	0.000
H(6)	2.971	−2.110	0.000
	C-Bonded Pyridine		
N(1)	1.467 (17)	−1.289 (17)	0.000
C(2)	0.759 (17)	−0.145 (18)	0.000
C(3)	1.210 (21)	1.175 (20)	0.000
C(4)	2.616 (20)	1.320 (20)	0.000
C(5)	3.400 (18)	0.132	0.000
C(6)	2.799 (23)	−1.108 (22)	0.000
H(4)	3.032	2.079	0.000
H(5)	4.355	0.214	0.000
H(6)	3.354	−1.887	0.000
	Perchlorate		
Cl	0.000	0.000	0.000
O	−1.374 (6)	0.000	0.000

Table IV. Euler Angles (rad) and Origins Relative to an Orthogonal Å System with *A*‖*a*, *B*‖*b*, and *C*‖*c**

	ϕ	θ	ψ
ring 1	1.899 (11)	1.014 (8)	−4.595 (11)
ring 2	1.114 (11)	4.119 (9)	−4.659 (11)
ring 3	2.472 (17)	0.619 (9)	−1.927 (17)
ring 4	0.768 (20)	3.607 (9)	−1.723 (20)
ring 5	−0.184 (8)	4.917 (10)	−3.485 (9)
ring 6	2.844 (9)	4.965 (10)	−3.502 (9)
ring 7	−0.162 (8)	4.509 (9)	−2.872 (8)
ring 8	2.854 (8)	4.489 (10)	−2.953 (8)
ring 9	2.492 (17)	2.512 (10)	−4.423 (17)
ring 10	0.833 (17)	5.686 (9)	−4.717 (18)
ring 11	4.162 (11)	0.928 (9)	1.463 (12)
ring 12	−1.072 (11)	4.170 (8)	1.441 (11)
ring 13	−0.128 (8)	5.055 (10)	−3.346 (8)
ring 14	2.882 (9)	5.080 (10)	−3.209 (9)
ring 15	4.171 (19)	2.640 (9)	−4.372 (20)
ring 16	−0.894 (17)	5.653 (10)	−4.622 (17)
ring 17	2.073 (10)	0.962 (8)	−0.550 (11)
ring 18	0.991 (10)	4.079 (9)	−4.591 (11)
ClO_4 1	−4.508 (3)	3.538 (1)	−3.990 (3)
ClO_4 2	−1.775 (1)	5.056 (1)	−4.491 (1)
ClO_4 3	2.639 (1)	1.417 (1)	−4.001 (1)
ClO_4 4	2.791 (2)	0.715 (1)	−2.838 (2)
ClO_4 5	−0.158 (2)	5.313 (1)	−2.753 (2)
ClO_4 6	1.901 (1)	1.696 (1)	−2.657 (1)
	X_0	Y_0	Z_0
rings 1, 2	13.824 (17)	0.895 (18)	4.215 (13)
rings 3, 4	15.470 (13)	5.235 (15)	4.448 (16)
rings 5, 6	13.489 (12)	3.534 (15)	0.835 (17)
rings 7, 8	18.338 (11)	9.142 (15)	−5.464 (17)
rings 9, 10	20.363 (15)	7.559 (16)	−1.762 (16)
rings 11, 12	18.172 (16)	11.644 (17)	−1.831 (14)
rings 13, 14	22.808 (10)	3.374 (16)	−11.439 (17)
rings 15, 16	25.058 (15)	4.541 (15)	−7.979 (16)
rings 17, 18	22.494 (15)	0.670 (14)	−7.850 (13)
ClO_4 1	19.070 (8)	6.843 (7)	−10.754 (7)
ClO_4 2	9.360 (8)	1.140 (8)	9.842 (8)
ClO_4 3	28.061 (8)	0.637 (8)	10.418 (8)
ClO_4 4	23.500 (8)	5.759 (8)	−4.135 (7)
ClO_4 5	3.936 (9)	11.639 (8)	4.735 (8)
ClO_4 6	14.158 (9)	5.678 (9)	−4.609 (9)

bonded rings the C2–N and C6–N distances are short, between 1.34 and 1.36 Å, giving further confirmation that rings 5, 7, and 13 are bonded to iridium via carbon.

Table V. Ir–X Distances[a]

	Ir(1)		Ir(2)		Ir(3)	
X	ring	*d*, Å	ring	*d*, Å	ring	*d*, Å
N	1	2.05	12	2.05	17	2.04
N	2	2.05	11	2.03	18	2.05
N	3	2.12	9	2.14	16	2.13
N	4	2.09	10	2.05	15	2.04
C	5	1.99	7	1.98	13	1.97
N	6	2.07	8	2.08	14	2.05

[a] Arranged so that similarly placed rings in the three ions are next to one another. Esd(Ir–N) = 0.02 Å; esd(Ir–C) = 0.03 Å.

Table VI. Ultraviolet Absorption Spectra of Solutions of Some Ir^{III}bpy Complexes

complex	λ_{max}, nm ($10^{-4}\epsilon_{max}$)
$[Ir(bpy\text{-}N,N')_3]^{3+}$ [a]	320 (4.7), 310 (4.4), 250 (5.3)
$[Ir(bpy\text{-}N,N')_2(bpy\text{-}C',N)^-H_3O^+]^{3+}$ (Watts' complex)[b]	315 (3.1), 305 (2.9), 250 (4.0)
$[Ir(bpy\text{-}N,N')_2(bpy\text{-}C,N')^-]^{2+}$ (title complex)[c]	315 (2.70), 303 (2.70), 249 (4.30)
$[Ir(bpy\text{-}N,N')_2Cl_2]^+$	316 (2.19), 305 (2.08), 253 (2.53)

[a] From Figure 2 of ref 2. [b] From Figure 1 of ref 3; 0.1 M HCl. [c] From 3.36 × 10^{-5} M title complex in water and also Watts' complex in 0.1 M NaOH (Figure 4 of ref 3).

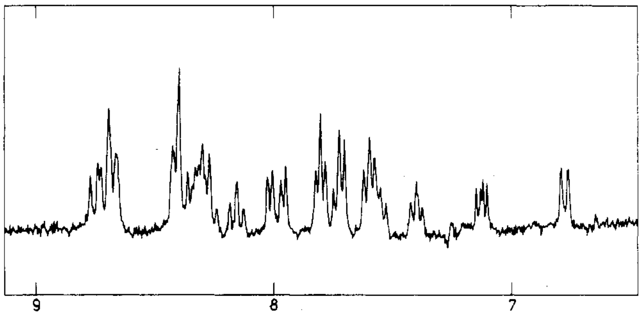

Figure 4. 270-MHz ^1H NMR spectrum of the title complex in 50% D_2O and 50% $(D_3C)_2SO$ at 300 K. The spectrum was obtained on a Bruker HX-270 instrument in the Fourier transform mode (200 scans) using a pulse width of 8 μs. The chemical shifts were measured relative to Me_2SO and are given as ppm relative to Me_4Si.

The cations form rows parallel to the *a* axis with a separation of *a*/3, all cations in one row having almost identical orientations. The water molecules occupy channels parallel to the *a* axis, and it is possible that water molecules may be readily added or removed, giving crystals of variable composition.

Spectral Properties of Solutions. NMR Spectra. The ^1H NMR spectrum of the title compound in $(CD_3)_2SO/D_2O$ is given in Figure 4. This was found to be a better resolved version of the literature spectrum for Watts' complex in Me_2SO. Especially noteworthy are the δ 6.8 doublet and neighboring δ 7.12 multiplet. We find that this latter becomes a pure doublet on selectively decoupling the δ 6.8 doublet (see Discussion). The spectrum is unaltered in NaOD, but in DCl it changes as reported in ref 22. The ^{13}C spectrum was also found to be that previously reported.

UV Spectra. These are summarized in Table VI, together with those of the "normal" tris and bis 2′,2-bpy-*N*,*N*′ Ir(III) complexes.

Discussion

The crystallographic evidence for Ir–C bonding is (1) the abnormal thermal parameters for N if Ir–N bonding to all six

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(22) Spellane, P. J.; Watts, R. J. *Inorg. Chem.* **1981**, *20*, 3561.

atoms is assumed, (2) the geometry of the pyridine rings, and (3) the fact that in the distorted-octahedral complex the presumed Ir–C bond (1.980 (6) Å) is shorter than Ir–N and the Ir–N trans to the Ir–C is longer (2.135 (5) Å) than the other four Ir–N bonds (2.053 (5) Å). The lengthening of the bond trans to Ir–C is similar to that in *cis*-bis(2,2′-bipyridine-*N*,*N*′)carbonylchlororuthenium(II) perchlorate[23] where Ru–N is 2.177 (16) Å for the bond trans to Ru–Cl and 2.097 (12) Å and 2.104 (15) Å for the Ru–N bonds trans to each other. In trimethyl(acetylacetonyl)(2,2′-bipyridine-*N*,*N*′)platinum(IV) the Pt–N bonds trans to Pt–CH_3 have also been found[24] to be exceptionally long (2.16 (1) and 2.14 (1) Å). The Ir–N bond distances in Figure 3 may be compared with the Ir–N distance of 2.04 (1) Å in Ir(bpy-*N*,*N*′)$_3$(ClO_4)$_3$·$2H_2O$[11] and 2.05 (4)[7] or 2.056 (3) Å[8] for Watts' compound. In the present structure the geometry of the ligand rings has not been determined with any great accuracy; however, in both the N-bonded rings and the C-bonded rings there are short bonds to the atom assumed to be N, giving further confirmation that the rings labeled 5, 7, and 13 in Figure 2 are bonded to Ir via C.

The ^1H NMR spectrum (Figure 4) includes a doublet δ 6.8 that integrates for 1 proton in a total of 23 ± 1, and this can now be assigned to the H4 proton of the C-bonded ring. This follows from the structure (Figure 3) in which this H4 proton is situated immediately above the pyridine ring of an adjacent ligand and therefore will experience a high ring–current shielding. The shift is 2 ppm upfield from the position of the H4 protons in the (bpy-*N*,*N*′)$_3$ complex[6] in which all the H6 protons are shifted by ring-current shielding. A similar upfield shift of ~2 ppm was also observed in the Pt(bpy-*N*,*N*′)$_2^{2+}$ NMR spectrum where, on going from square-planar to a cis conformation, half of the H6 protons become sheilded by an adjacent aromatic ring.[20] The fact that the δ 7.12 multiplet in Figure 4 becomes a doublet when the δ 6.8 doublet is selectively decoupled implies that the multiplet is due to the H5 of the same C-coordinating ring. These two high-field signals are not observed in aqueous acid where all relative shifts are smaller and all signals overlap. This smaller separation also occurs when free bpy is protonated.

The ultraviolet spectra of the tris complexes are noteworthy in that the ratios of the intensities of the highest and lowest energy bands decrease with change from N,N′ to C,N′ coordination.[25] This together with the absolute intensities of the bands can be used for easy identification of the four complexes listed in Table VI. Thus, we find that the absorption spectrum for the orange compound given in ref 4 is that of Watts' complex together with unreacted bpy. The analysis given in this reference was, however, presumably for a bpy free sample. Although the formula given in the paper[4] is that of the anhydrous Ir(bpy)$_3$(ClO_4)$_3$, the analysis better corresponds to a monohydrate of this, i.e., Watts' salt. The presence of a small amount of the title compound required to give the orange color is explained by the acid–base equilibrium given in the scheme. This synthesis scheme also illustrates that an Ir–C bond is formed when the coordinated ligand reacts with a good proton base in a poorly hydrogen-bonding solvent and that dehydration of Watts' complex in solution with dimethyl sulfoxide also is accompanied by deprotonation.

As pointed out by Serpone,[7] Ir–C bonds are not unusual. However, the title complex is unusual in that the change from Ir–N to Ir–C is not accompanied by degradation of the C–N skeleton of the ligand and that when treated with aqueous acid it yields crystals the empirical formula of which differs only from that of the normal tris-*N*,*N*′ dihydrate by one water molecule. If, in accordance with our assignment for this complex, the presence of signals in the ^1H NMR spectra that are at higher fields than those of the uncoordinated ligand is diagnostic of a metal–C-bonded bpy ring, then two other compounds have been reported in which this occurs although the molecular formula for neither has been established. The ^1H NMR spectrum of a compound produced from $IrCl_3 \cdot xH_2O$ and 1,10-phenanthroline by the methods of ref 3 and 5 is given in ref 6. Whereas bpy is very resistant to oxidation in basic solution, 1,10-phenanthroline is not[26] and can be oxidized to several products including 2,2′-bipyridine-3,3′-dicarboxylic acid. The analysis of the compound given by the authors[6] accords with a compound in which partial ligand oxidation has occurred.[27] The other high-field signal was reported for a Pt(II) complex by Gillard and co-workers.[28] These authors have wrongly stated[5] that the high-field signals in Figure 3 and also of ref 28 are diagnostic of an adduct in which OH is attached to a carbon of the ligand ring. The spectrum in ref 28 was produced from a dimethyl sulfoxide solution of Pt(bpy-*N*,*N*′)(CN)$_2$, but it has later been found[29] that this spectrum cannot be reversibly formed by heating and cooling the solution as was stated by the authors of ref 28; disruption of the complex must occur. However, by more drastic treatment, they may well have produced a different Pt(bpy) complex containing a Pt–C bond.[30]

The mechanistic significance of the title complex and its hydrated acid form for reactions of metal–bpy complexes in general is difficult to assess at present. However, since such metal–C bonds (like the HO–C bonds postulated in ref 5 and 28) once formed would be expected to persist, we do not think it likely that these complexes are good models for reactive intermediates as has been suggested.[3,5] It seems to us that the title complex is best considered as the end product of a reaction series in which the kinetically unexplored and mechanistically interesting step is the proton loss from the C3 of an N,N′-coordinated bipyridine.

Registry No. $IrCl_3$, 10025-83-9; [Ir(bpy-*N*,*N*′)$_2$$Cl_2$]Cl, 22710-60-7; [Ir(bpy-*N*,*N*′)$_3$](ClO_4)$_3$, 52155-02-9; [Ir(bpy-*N*,*N*′)$_2$(bpy-*C*,*N*′)](ClO_4)$_2$·$^1/_3H_2O$, 87137-20-0.

Supplementary Material Available: Listings of hydrogen atom coordinates, anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure amplitudes (18 pages). Ordering information is given on any current masthead page.

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[23] Clear, J. M.; Kelly, J. M.; O'Connell, C. M.; Cardin, C. J.; Costa, S. R.; Edwards, A. J. *J. Chem. Soc., Chem. Commun.* **1980**, 750.

[24] Swallow, A. G.; Truter, M. R. *Proc. R. Soc.* London, Ser. *A* **1962**, *A266*, 527.

[25] The two lowest energy maxima (of nearly equal intensity) are derived from the long-axis-polarized π–π^* ligand transition: Bosnich, B. *Acc. Chem. Res.* **1969**, *2*, 266.

[26] Eckard, I. F.; Sumers, L. A. *Aust. J. Chem.* **1973**, *26*, 2727 and references therein.

[27] The empirical formula that best fits the analytical data is $IrC_{36}N_8H_{29}O_{12}$, which may be a mixture but could correspond to the anhydrous bis(nitrate) of a complex in which Ir(III) is coordinated to partially oxidized ligands one of which is both deprotonated and bonded to Ir(III) at the C3′ position. The pentahydrated tris complex postulated by the authors has the empirical formula $IrC_{36}N_8H_{35}O_{12}$, and this requires an error in the H determination that is very much larger than that found for the other complexes reported.[6] The above complex is also the only one in ref 6 for which the ^{13}C NMR spectrum is not given and also for which the ^1H NMR spectrum is poorly resolved.

[28] Gillard, R. D.; Kane-Maguire, L. A.; Williams, P. A. *Transition Met. Chem.* (*Weinheim, Ger.*) **1976**, *1*, 247.

[29] Nord, G.; Agarwala, B. V. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 231.

[30] For example were this found to be a *cis*-(bpy)$_2$ complex then the high-field signal and the observed Pt coupling to this would be explained by an assignment as the H4 proton of a C-bonded ligand.