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Comparison of the Crystal Structures of Tris Heterocyclic Ligand Complexes of Ruthenium(II)

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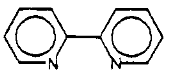
The structures of $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2′-bipyridine) and $[Ru(bpm)_3](PF_6)_2{\cdot}CH_3CN$ (bpm = 2,2′-bipyrimidine) have been determined by single-crystal X-ray diffraction. $[Ru(bpy)_3](PF_6)_2$ crystallized in the hexagonal space group $P\bar{3}c1$ with cell dimensions $a = 10.760$ (1) Å, $b = 10.760$ (1) Å, $c = 16.391$ (3) Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $Z = 2$, and $d_{calcd} = 1.74$ g cm^{-3}. Of the 1411 unique reflections (Mo Kα, $1° \leq 2\theta \leq 57°$), 1081 reflections with $I > \sigma(I)$ were used in full-matrix least-squares refinement. Final residuals were $R_F = 0.044$. $[Ru(bpm)_3](PF_6)_2{\cdot}CH_3CN$ crystallized in the triclinic space group $P\bar{1}$ with cell dimensions $a = 10.552$ (2) Å, $b = 11.635$ (1) Å, $c = 14.231$ (2) Å, $\alpha = 74.47$ (1)°, $\beta = 81.41$ (1)°, $\gamma = 75.08$ (1)°, $Z = 2$, and $d_{calc} = 1.852$ g cm^{-3}. Of the 4269 unique reflections (Mo Kα, $3.5° \leq 2\theta \leq 45°$), 3941 reflections with $|F| > 4.0\sigma(F)$ were used in full-matrix least-squares refinement. Final residuals were $R_F = 0.028$. Ru–N bond distances in $[Ru(bpy)_3]^{2+}$ were 2.056 (2) Å and average 2.067 (4) Å in $[Ru(bpm)_3]^{2+}$. Other bond distances and angles lead to the conclusion that the structures of the $[Ru(bpy)_3]^{2+}$ and $[Ru(bpm)_3]^{2+}$ cations are basically the same.

Introduction

The discovery of electron transfer from photoexcited $Ru(bpy)_3^{2+}$, where bpy is 2,2′-bipyridine, has prompted the examination of a large number of ruthenium(II) complexes for similar behavior.[1] Among these are ruthenium(II) complexes based on analogous ligands, 2,2′-bipyrimidine (bpm)[2-4] and 2,2′-bipyrazine (bpz).[4,5] The bpy, bpm and bpz ligands differ in their σ- and π-bonding character. The pK_a values of the ligands, 5.2 for pyridine,[6] 1.3 for pyrimidine,[7] and 0.8 for pyrazine,[8] vary by a factor of 5; thus, one might expect the Ru–N bond distance to increase in the series Ru–N(bpy) < Ru–N(bpm) < Ru–N(bpz) if only σ bonding were important. The π-bonding differences of ligands can be predicted on the basis of electrochemical reductions since reductions are assinged to addition of electrons to the empty π^* energy levels. The $E_{1/2}$ values for the $L^{0/-}$ couple (L = bpy, bpm, or bpz) follow the sequence (−1.76 V) bpz[5b] > (−1.80) bpm[9] > (−2.20) bpy[10] as well as for the $RuL^{2+/+}$ couples[4b] (−0.68) $Ru(bpz)_3^{2+/+}$ > (−0.91) $Ru(bpm)_3^{2+/+}$ > (−1.31) $Ru(bpy)_3^{2+/+}$. On this basis, the interaction of the dπ orbitals of ruthenium(II) with the π^* ligand orbitals is expected to be greatest with bpz, next greatest with bpm, and least with bpy. On the basis of π-bonding arguments, the Ru–N bond distances are expected to increase in the sequence Ru–N(bpz) < Ru–N(bpm) < Ru–N(bpy). Thus, σ and π bonding are opposed to one another and the net result is difficult to predict.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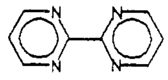
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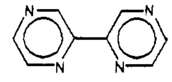
bpz

In an earlier communication, we reported[11] preliminary data on the X-ray structure of $Ru(bpy)_3^{2+}$. In this paper the final structure parameters for the $Ru(bpy)_3^{2+}$ cation are reported along with the structure of the $Ru(bpm)_3^{2+}$ cation. Both structures are compared to the one for the $Ru(bpz)_3^{2+}$ cation which was recently reported.[12]

Experimental Section

Table I. Crystallographic Data

	bpy	bpm
chem formula	$RuN_6C_{30}H_{24}P_2F_{12}$	$RuN_{12}C_{24}H_{18}P_2F_{12}{\cdot}CH_3CN$
a, Å	10.760 (1)	10.552 (2)
b, Å	10.760 (1)	11.635 (1)
c, Å	16.391 (3)	14.231 (2)
α, deg	90	74.47 (1)
β, deg	90	81.41 (1)
γ, deg	120	75.08 (1)
V, Å^3	1644 (1)	1620.4 (4)
Z	2	2
fw	859.56	906.5
space group	$P\bar{3}c1$ (No. 165)	$P\bar{1}$ (No. 2)
T, K	294	143
ρ_{calcd}, g cm^{-3}	1.74	1.852
λ, Å	0.709 26	0.709 26
μ, cm^{-1}	6.64	6.81
$R(F_o)^a$	0.044	0.028

^{a} $R(F_o) = (\sum||F_{obs}| - |F_{calc}||)/\sum|F_{obs}|$.

X-ray Data Collection, Structure Solution, and Refinement. Crystals of $[Ru(bpm)_3](PF_6)_2{\cdot}CH_3CN$ were obtained from acetonitrile/toluene solution. Accurate unit cell dimensions and a crystal orientation matrix were obtained by least-squares refinement of the diffractometer setting angles of 48 high-angle reflections. The diffraction data were collected at 143 K on a Siemens R3m/V diffractometer equipped with a graphite monochromator and a LT-2 low-temperature apparatus. The intensities of three standard reflections were monitored every 97 reflections, and no significant variations in the intensities of the standards were observed; thus the standards were treated as normal data during structure solution

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Table II. Fractional Coordinates and Isotropic Thermal Parameters, with Estimated Standard Deviations in Parentheses, for $[Ru(bpy)_3](PF_6)_2$[a]

atom	*x*	*y*	*z*	*U*, Å^2
Ru	0.0	0.0	0.2500	0.033
N	0.1893 (2)	0.1063 (2)	0.1860 (1)	0.041
C(1)	0.2839 (3)	0.2401 (3)	0.2126 (2)	0.042
C(2)	0.4079 (4)	0.3249 (4)	0.1704 (2)	0.056
C(3)	0.4382 (4)	0.2745 (4)	0.1005 (2)	0.062
C(4)	0.3463 (4)	0.1396 (4)	0.0755 (2)	0.063
C(5)	0.2235 (4)	0.0575 (4)	0.1184 (2)	0.052
P	0.33333	0.66667	0.12953 (8)	0.067
F(1)	0.3520 (4)	0.5584 (4)	0.0740 (2)	0.162
F(2)	0.2239 (3)	0.5418 (3)	0.1837 (2)	0.119
H(2)	0.461 (4)	0.403 (3)	0.186 (2)	0.05 (2)
H(3)	0.515 (4)	0.329 (4)	0.075 (2)	0.07 (2)
H(4)	0.355 (3)	0.102 (3)	0.029 (2)	0.06 (2)
H(5)	0.163 (4)	−0.032 (3)	0.105 (2)	0.05 (2)

[a] Thermal parameters without standard deviations are equivalent parameters. The temperature factor has the form $\exp[-8\pi^2 U((\sin^2\theta)/\lambda^2)]$.

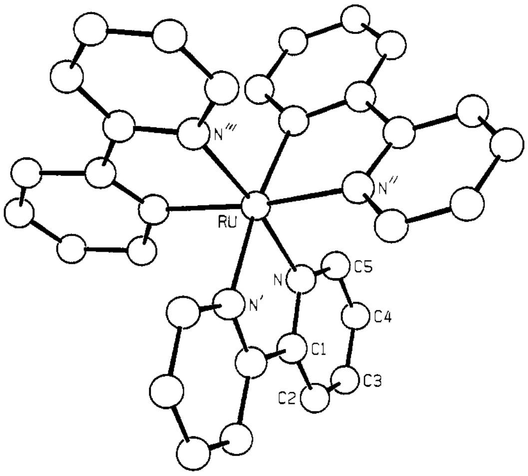


Figure 1. ORTEP diagram of $Ru(bpy)_3^{2+}$ showing the atom-labeling scheme.

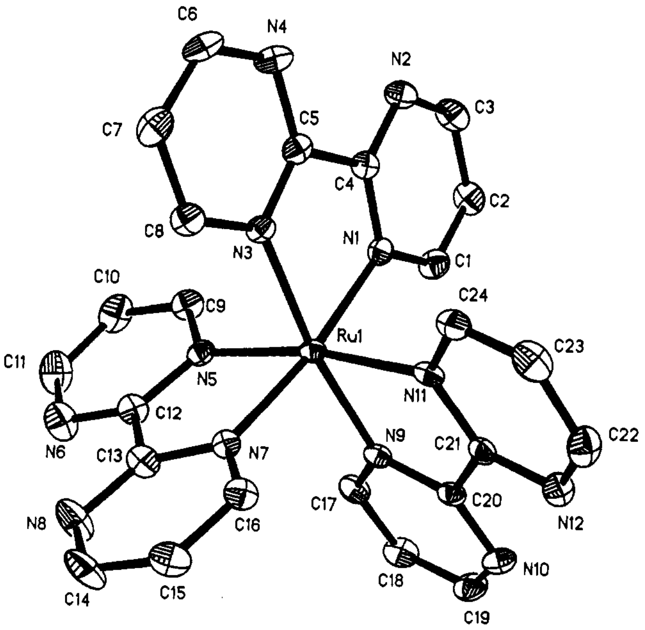


Figure 2. ORTEP diagram of $Ru(bpm)_3^{2+}$ showing the atom-labeling scheme.

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\times 10^3$) for $[Ru(bpm)_3](PF_6)_2$

atom	*x*	*y*	*z*	*U*(eq),[a] Å^2
Ru(1)	82 (1)	3041 (1)	2797 (1)	13 (1)
N(1)	−1445 (2)	2524 (2)	3780 (2)	16 (1)
N(2)	−2210 (2)	775 (2)	4747 (2)	20 (1)
N(3)	603 (2)	1159 (2)	3034 (2)	15 (1)
N(4)	−26 (2)	−682 (2)	3940 (2)	21 (1)
N(5)	−731 (2)	3126 (2)	1539 (2)	16 (1)
N(6)	−305 (3)	3539 (3)	−200 (2)	29 (1)
N(7)	1596 (2)	3389 (2)	1741 (2)	15 (1)
N(8)	2176 (3)	3756 (3)	28 (2)	30 (1)
N(9)	−503 (2)	4892 (2)	2743 (2)	15 (1)
N(10)	−142 (3)	6449 (2)	3397 (2)	21 (1)
N(11)	1083 (2)	3177 (2)	3892 (2)	15 (1)
N(12)	1685 (2)	4640 (2)	4535 (2)	19 (1)
C(1)	−2512 (3)	3263 (3)	4126 (2)	22 (1)
C(2)	−3457 (3)	2788 (3)	4774 (2)	24 (1)
C(3)	−3271 (3)	1537 (3)	5067 (2)	24 (1)
C(4)	−1358 (3)	1300 (3)	4109 (2)	16 (1)
C(5)	−191 (3)	526 (3)	3683 (2)	17 (1)
C(6)	1037 (3)	−1318 (3)	3501 (3)	22 (1)
C(7)	1884 (3)	−759 (3)	2812 (3)	23 (1)
C(8)	1646 (3)	487 (3)	2593 (3)	20 (1)
C(9)	−1903 (3)	2909 (3)	1456 (3)	22 (1)
C(10)	−2292 (3)	2979 (3)	564 (3)	29 (1)
C(11)	−1478 (3)	3326 (4)	−253 (3)	33 (2)
C(12)	24 (3)	3406 (3)	689 (2)	20 (1)
C(13)	1348 (3)	3540 (3)	804 (2)	21 (1)
C(14)	3380 (3)	3815 (4)	188 (3)	31 (1)
C(15)	3730 (3)	3678 (3)	1102 (3)	23 (1)
C(16)	2812 (3)	3464 (3)	1870 (3)	19 (1)
C(17)	−1389 (3)	5739 (3)	2171 (2)	20 (1)
C(18)	−1685 (3)	6941 (3)	2217 (3)	23 (1)
C(19)	−1034 (3)	7265 (3)	2831 (3)	24 (1)
C(20)	74 (3)	5296 (3)	3339 (2)	15 (1)
C(21)	1003 (3)	4332 (3)	3973 (2)	16 (1)
C(22)	2558 (3)	3723 (3)	5040 (2)	23 (1)
C(23)	2707 (3)	2522 (3)	5018 (3)	25 (1)
C(24)	1927 (3)	2263 (3)	4450 (2)	19 (1)
P(1)	5353 (1)	4173 (1)	7406 (1)	23 (1)
F(1)	4592 (2)	4303 (2)	6485 (2)	53 (1)
F(2)	4061 (2)	4969 (2)	7869 (2)	42 (1)
F(3)	6628 (2)	3398 (2)	6936 (2)	57 (1)
F(4)	6080 (2)	4047 (2)	8348 (2)	57 (1)
F(5)	5807 (2)	5403 (2)	6885 (2)	46 (1)
F(6)	4879 (3)	2957 (2)	7950 (2)	57 (1)
P(2)	4217 (1)	−578 (1)	7286 (1)	32 (1)
F(7)	4105 (3)	778 (2)	7347 (2)	73 (1)
F(8)	5765 (2)	−863 (2)	7314 (2)	72 (1)
F(9)	2661 (2)	−302 (2)	7240 (2)	52 (1)
F(10)	4317 (2)	−1937 (2)	7202 (2)	42 (1)
F(11)	4038 (3)	−1046 (3)	8441 (2)	70 (1)
F(12)	4395 (2)	−145 (2)	6125 (2)	52 (1)
C(25)	−182 (11)	−189 (10)	10807 (8)	70 (3)
C(26)	−819 (11)	−381 (11)	10087 (9)	75 (3)
N(13)	−1396 (12)	−704 (11)	9627 (9)	104 (3)
C(27)	5117 (13)	260 (11)	9785 (8)	73 (3)
C(28)	3845 (11)	483 (10)	10092 (8)	64 (3)
N(14)	2730 (10)	824 (9)	10287 (7)	80 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

and refinement. The data were corrected for Lorentz and polarization effects but not for absorption. The absorption coefficient was found to be 6.8 cm^{-1}. The structure was solved by Patterson and difference Fourier methods.[12] The asymmetric unit consists of one cation, two PF_6^- ions, and two acetonitrile sites, each with 50% occupancy; thus, there is one acetonitrile molecule for each formula unit of $[Ru(bpm)_3](PF_6)_2$. The acetonitrile molecules were refined isotropically with all atoms in the acetonitrile molecules assigned a site occupation number of 0.50. All other non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference maps after all non-hydrogen atoms had been assigned, and the hydrogen atoms were refined isotropically during the final refinements. The single-crystal data are listed in Table I.

Red crystals of $[Ru(bpy)_3](PF_6)_2$ were obtained from a 50/50 mixture of acetonitrile and ethyl alcohol; the crystal chosen for data collection was a hexagonal plate. Systematic absences on precession and Weissenberg photographs were characteristic of space group $P3c1$ or $P\bar{3}c1$. The diffraction data were collected at the Oak Ridge National Laboratory on a computer-controlled Picker diffractometer utilizing Nb-filtered

Table IV. Bond Distances (Å) and Bond Angles (deg), with Estimated Standard Deviations in Parentheses, for $[Ru(bpy)_3](PF_6)_2$

Bond Distances			
Ru–N	2.056 (2)	C(4)–C(5)	1.362 (5)
N–C(1)	1.354 (3)	C(3)–H(3)	0.85 (4)
N–C(5)	1.354 (4)	C(4)–H(4)	0.88 (3)
C(1)–C(2)	1.369 (4)	C(5)–H(5)	0.88 (3)
C(1)–C(1′)	1.474 (5)	P–F(1)	1.568 (3)
C(2)–C(3)	1.374 (5)	P–F(2)	1.549 (3)
C(3)–C(4)	1.348 (5)		
Bond Angles			
F(2)–P–F(2′)	90.4 (2)	F(2)–P–F(1″)	89.2 (2)
F(2)–P–F(1)	90.7 (2)	F(1)–P–F(1′)	89.7 (2)
F(2)–P–F(1′)	178.8 (2)		
N–Ru–N′	78.7 (1)	C(3)–C(4)–C(5)	119.5 (3)
N–Ru–N″	89.1 (1)	C(4)–C(5)–N	122.4 (3)
N–Ru–N‴	173.0 (1)	C(5)–N–C(1)	118.0 (2)
N′–Ru–N″	96.3 (1)	C(1)–C(2)–H(2)	120 (2)
Ru–N–C(1)	115.9 (2)	C(3)–C(2)–H(2)	120 (2)
Ru–N–C(5)	126.0 (2)	C(2)–C(3)–H(3)	118 (2)
N–C(1)–C(1′)	114.6 (1)	C(4)–C(3)–H(3)	122 (2)
N–C(1)–C(2)	120.7 (2)	C(3)–C(4)–H(4)	124 (2)
C(1)–C(2)–C(3)	120.2 (3)	C(5)–C(4)–H(4)	116 (2)
C(1′)–C(1)–C(2)	124.7 (2)	C(4)–C(5)–H(5)	122 (2)
C(2)–C(3)–C(4)	119.2 (3)	N–C(5)–H(5)	116 (2)

Mo radiation at ambient temperature (20.5 ± 1.0 °C). Data were collected using the θ–2θ scan technique; all data in the range $2\theta \leq 57°$ were obtained. Three standards were collected after every 30 reflections; no significant variations in intensity were noted. The data were corrected for Lorentz and polarization effects and for absorption. The structure was solved using the MULTAN direct methods program.[14] Subsequent refinement (program ORXFLS4)[15] showed the space group to be $P\bar{3}c1$; the Ru atom is on a special position with 32 site symmetry, while the P atom of the PF_6^- group is on a special position with site symmetry 3. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions, and their position and thermal parameters were then allowed to vary. The refinement converged to an R_F value of 0.044 (R_{F^2} of 0.076) for 1081 reflections having $I > \sigma(I)$. The single-crystal data are listed in Table I.

Results

The single-crystal X-ray crystallographic analysis positional parameters are given in Tables II and III. Figures 1 and 2 show ORTEP[16] drawings of $Ru(bpy)_3^{2+}$ and $Ru(bpm)_3^{2+}$ cations, and Tables IV and V contain a listing of bond distances and angles. The hexafluorophosphate salt of $Ru(bpy)_3^{2+}$ crystallized in the hexagonal centrosymmetric space group $P\bar{3}c1$. The cation contains crystallographically rigorous C_2 and C_3 symmetry axes, indicative of the expected symmetry of the $Ru(bpy)_3^{2+}$ cation. The hexafluorophosphate salt of $Ru(bpm)_3^{2+}$ crystallized in the triclinic space group $P\bar{1}$. Apparently this resulted from inclusion of CH_3CN in the crystal lattice. This causes nonequivalence in the bond distances and bond angles of similarly bonded atoms in the structure. These differences are on the order of experimental error, and the $Ru(bpm)_3^{2+}$ cation in practical terms has the same structure as the $Ru(bpy)_3^{2+}$ cation.

Table V. Bond Lengths (Å) and Bond Angles (deg) for $[Ru(bpm)_3](PF_6)_2$

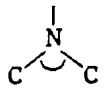
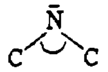
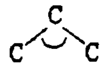
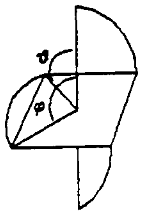
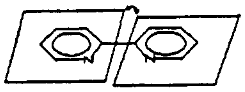
Bond Distances							
Ru(1)–N(1)	2.072 (2)	Ru(1)–N(3)	2.062 (3)	C(4)–C(5)	1.482 (4)	C(6)–C(7)	1.371 (5)
Ru(1)–N(5)	2.067 (3)	Ru(1)–N(7)	2.065 (2)	C(7)–C(8)	1.363 (5)	C(9)–C(10)	1.366 (6)
Ru(1)–N(9)	2.065 (3)	Ru(1)–N(11)	2.069 (3)	C(10)–C(11)	1.372 (5)	C(12)–C(13)	1.482 (5)
N(1)–C(1)	1.346 (4)	N(1)–C(4)	1.358 (4)	C(14)–C(15)	1.362 (5)	C(15)–C(16)	1.363 (4)
N(2)–C(3)	1.340 (4)	N(2)–C(4)	1.322 (4)	C(17)–C(18)	1.370 (5)	C(18)–C(19)	1.366 (6)
N(3)–C(5)	1.349 (4)	N(3)–C(8)	1.352 (4)	C(20)–C(21)	1.479 (4)	C(22)–C(23)	1.374 (6)
N(4)–C(5)	1.325 (4)	N(4)–C(6)	1.344 (4)	C(23)–C(24)	1.369 (6)	P(1)–F(1)	1.591 (3)
N(5)–C(9)	1.352 (5)	N(5)–C(12)	1.356 (4)	P(1)–F(2)	1.600 (2)	P(1)–F(3)	1.580 (2)
N(6)–C(11)	1.339 (5)	N(6)–C(12)	1.320 (5)	P(1)–F(4)	1.598 (3)	P(1)–F(5)	1.583 (2)
N(7)–C(13)	1.354 (4)	N(7)–C(16)	1.350 (4)	P(1)–F(6)	1.586 (3)	P(2)–F(7)	1.577 (3)
N(8)–C(13)	1.313 (4)	N(8)–C(14)	1.346 (5)	P(2)–F(8)	1.585 (3)	P(2)–F(9)	1.598 (2)
N(9)–C(17)	1.354 (4)	N(9)–C(20)	1.352 (5)	P(2)–F(10)	1.592 (3)	P(2)–F(11)	1.586 (3)
N(10)–C(19)	1.339 (4)	N(10)–C(20)	1.325 (4)	P(2)–F(12)	1.591 (3)	C(25)–C(26)	1.400 (19)
N(11)–C(21)	1.360 (4)	N(11)–C(24)	1.351 (4)	C(26)–N(13)	1.144 (21)	C(27)–C(28)	1.330 (16)
N(12)–C(21)	1.321 (5)	N(12)–C(22)	1.335 (4)	C(28)–N(14)	1.157 (14)		
C(1)–C(2)	1.374 (5)	C(2)–C(3)	1.372 (5)				
Bond Angles							
N(1)–Ru(1)–N(3)	78.0 (1)	N(1)–Ru(1)–N(5)	96.9 (1)	N(5)–C(12)–N(6)	126.2 (3)	N(5)–C(12)–C(13)	114.8 (3)
N(3)–Ru(1)–N(5)	89.0 (1)	N(1)–Ru(1)–N(7)	173.1 (1)	N(6)–C(12)–C(13)	118.9 (3)	N(7)–C(13)–N(8)	125.7 (3)
N(3)–Ru(1)–N(7)	96.5 (1)	N(5)–Ru(1)–N(7)	78.6 (1)	N(7)–C(13)–C(12)	114.7 (3)	N(8)–C(13)–C(12)	119.6 (3)
N(1)–Ru(1)–N(9)	96.6 (1)	N(3)–Ru(1)–N(9)	172.9 (1)	N(8)–C(14)–C(15)	122.4 (3)	C(14)–C(15)–C(16)	117.6 (3)
N(5)–Ru(1)–N(9)	96.3 (1)	N(7)–Ru(1)–N(9)	89.1 (1)	N(7)–C(16)–C(15)	121.8 (3)	N(9)–C(17)–C(18)	120.6 (3)
N(1)–Ru(1)–N(11)	92.5 (1)	N(3)–Ru(1)–N(11)	97.2 (1)	C(17)–C(18)–C(19)	118.3 (3)	N(10)–C(19)–C(18)	122.5 (3)
N(5)–Ru(1)–N(11)	169.6 (1)	N(7)–Ru(1)–N(11)	92.4 (1)	N(9)–C(20)–N(10)	125.5 (3)	N(9)–C(20)–C(21)	114.9 (3)
N(9)–Ru(1)–N(11)	78.3 (1)	Ru(1)–N(1)–C(1)	127.4 (2)	N(10)–C(20)–N(21)	119.6 (3)	N(11)–C(21)–N(12)	125.9 (2)
Ru(1)–N(1)–C(4)	116.1 (2)	C(1)–N(1)–C(4)	116.5 (3)	N(11)–C(21)–C(20)	114.3 (3)	N(12)–C(21)–C(20)	119.7 (3)
C(3)–N(2)–C(4)	116.0 (3)	Ru(1)–N(3)–C(5)	116.9 (2)	N(12)–C(22)–C(23)	122.7 (4)	C(22)–C(23)–C(24)	118.3 (3)
Ru(1)–N(3)–C(8)	126.9 (2)	C(5)–N(3)–C(8)	116.2 (3)	N(11)–C(24)–C(23)	120.4 (3)	F(1)–P(1)–F(2)	89.6 (1)
C(5)–N(4)–C(6)	115.8 (3)	Ru(1)–N(5)–C(9)	128.4 (2)	F(1)–P(1)–F(3)	89.9 (1)	F(2)–P(1)–F(3)	179.3 (1)
Ru(1)–N(5)–C(12)	115.7 (2)	C(9)–N(5)–C(12)	115.8 (3)	F(1)–P(1)–F(4)	178.4 (1)	F(2)–P(1)–F(4)	89.0 (1)
C(11)–N(6)–C(12)	116.1 (3)	Ru(1)–N(7)–C(13)	116.0 (2)	F(3)–P(1)–F(4)	91.5 (1)	F(1)–P(1)–F(5)	90.3 (1)
Ru(1)–N(7)–C(16)	128.0 (2)	C(13)–N(7)–C(16)	115.9 (3)	F(2)–P(1)–F(5)	88.6 (1)	F(3)–P(1)–F(5)	90.9 (1)
C(13)–N(8)–C(14)	116.5 (3)	Ru(1)–N(9)–C(17)	127.1 (3)	F(4)–P(1)–F(5)	90.4 (1)	F(1)–P(1)–F(6)	90.5 (1)
Ru(1)–N(9)–C(20)	116.1 (2)	C(17)–N(9)–C(20)	116.8 (3)	F(2)–P(1)–F(6)	90.1 (1)	F(3)–P(1)–F(6)	90.4 (1)
C(19)–N(10)–C(20)	116.4 (3)	Ru(1)–N(11)–C(21)	115.9 (2)	F(4)–P(1)–F(6)	88.9 (1)	F(5)–P(1)–F(6)	178.5 (1)
Ru(1)–N(11)–C(24)	126.9 (2)	C(21)–N(11)–C(24)	116.6 (3)	F(7)–F(2)–F(8)	90.2 (2)	F(7)–F(2)–F(9)	90.5 (2)
C(21)–N(12)–C(22)	115.9 (3)	N(1)–C(1)–C(2)	121.0 (3)	F(8)–P(2)–F(9)	178.9 (2)	F(7)–P(2)–F(10)	178.8 (2)
C(1)–C(2)–C(3)	117.9 (3)	N(2)–C(3)–C(2)	122.6 (3)	F(8)–P(2)–F(10)	90.4 (1)	F(9)–P(2)–F(10)	88.9 (1)
N(1)–C(4)–N(2)	126.0 (3)	N(1)–C(4)–C(5)	114.5 (2)	F(7)–P(2)–F(11)	92.4 (2)	F(8)–P(2)–F(11)	90.6 (2)
N(2)–C(4)–C(5)	119.5 (3)	N(3)–C(5)–N(4)	126.2 (3)	F(9)–P(2)–F(11)	90.2 (2)	F(10)–P(2)–F(11)	88.7 (2)
N(3)–C(5)–C(4)	114.4 (3)	N(4)–C(5)–C(4)	119.4 (3)	F(7)–P(2)–F(12)	89.2 (2)	F(8)–P(2)–F(12)	89.6 (2)
N(4)–C(6)–C(7)	122.5 (3)	C(6)–C(7)–C(8)	118.0 (3)	F(9)–P(2)–F(12)	89.6 (1)	F(10)–P(2)–F(12)	89.7 (1)
N(3)–C(8)–C(7)	121.3 (3)	N(5)–C(9)–C(10)	121.4 (3)	F(11)–P(2)–F(12)	178.5 (2)	C(25)–C(26)–N(13)	167.9 (12)
C(9)–C(10)–C(11)	117.9 (4)	N(6)–C(11)–C(10)	122.4 (4)	C(27)–C(28)–N(14)	171.4 (12)		

Table VI. Bond Length (Å) Comparisons[a]

bond length	$Ru(bpy)_3(PF_6)_2$	$Ru(bpm)_3(PF_6)_2$	$Ru(bpz)_3(PF_6)_2$
Ru–N	2.056 (2)	2.067 (4)	2.05 (1)
–C–N–	1.354 (4)	1.351 (4)	1.37 (2)
–C–N|		1.341 (4)	1.33 (2)
–C–C–	1.369 (4)	1.369 (4)	1.40 (4)
>C–N–	1.354 (3)	1.355 (4)	1.33 (3)
>C–N|		1.321 (4)	
>C–C–	1.369 (4)		1.42 (3)
>C–C<	1.474 (5)	1.481 (4)	1.48 (4)

[a] –N– (bonding to Ru), –N| (nonbonding to Ru), –C– (ring), >C– (bridgehead carbons).

Table VII. Bond Angle (deg) Comparisons

	$Ru(bpy)_3$-$(PF_6)_2$	$Ru(bpm)_3(PF_6)_2$	$Ru(bpz)_3$-$(PF_6)_2$
	173.0 (1)	172 (2)	172.3 (4)
	118.0 (2)	116.3 (4)	118 (2)
		116.1 (3)	118 (2)
	119.6 (5)	118.0 (3)	
	78.7 (1)	78.3 (3)	78.6 (4)
	89.1 (1)	90 (2)	90 (2)
	96.3 (1)	96 (2)	96 (1)
	2.2 (1)	5 (1)	4 (1)

Discussion

Comparison of $Ru(bpy)_3^{2+}$, $Ru(bpm)_3^{2+}$, and $Ru(bpz)_3^{2+}$ Structures. Bond lengths and bond angles of similarly attached atoms are compared in Tables VI and VII. Entries were averaged in cases where there was more than one equivalent bond distance or angle for a given cation. The Ru–N bond distances in $Ru(bpy)_3^{2+}$, $Ru(bpm)_3^{2+}$, and $Ru(bpz)_3^{2+}$ are essentially the same. Replacement of C by N in the aromatic ring causes little variation in bond length or in bond angle nor does it affect the bridging C–C distance connecting the two aromatic heterocyclic rings. For all intents and purposes the structures of the cations are the same. The weaker σ bonding in the series bpy > bpm > bpz is balanced by the stronger π bonding in the series bpz > bpm > bpy such that the interatomic Ru–N distance is constant.

The distance of 2.05–2.06 Å may be the limiting distance of ligand approach in symmetrical ruthenium(II) complexes. Metalloporphyrin complexes, for example, display Ru–N bond distances of 2.052 (9) Å for [(TPP)Ru(CO)(py)][17] and 2.050 Å in (TDCPP)Ru(CO)(styrene oxide),[18] where TPP is tetraphenylporphyrin and TDCPP is tetrakis(2,6-dichlorophenyl)porphyrin. In these structures the ruthenium(II) atom is displaced from the porphyrin plane toward CO by 0.079 and 0.11 Å, respectively. The Ru–N bond distances are similar to those of the tris heterocycles above, even though shorter bond distances are possible by movement of ruthenium(II) into the plane of the porphyrin ring. In asymmetric ruthenium(II) heterocycles, Ru–N bond distances as short as 2.03 Å have been reported in pyridine–triazole complexes of $Ru(bpy)_2^{2+}$.[19]

In summary, the similarity of the structures has significance for theoretical and photophysical chemists. It may be possible to theoretically evaluate the degree of σ and π bonding in the complexes and provide a quantitative understanding of the bonding differences that exist among ruthenium(II) heterocycles. For the photophysical chemist, the similarity in bond distances implies that the potential energy surfaces are similar and one is justified in utilizing a common description for their excited-state behavior.

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Registry No. $[Ru(bpy)_3](PF_6)_2$, 60804-74-2; $[Ru(bpm)_3](PF_6)_2 \cdot CH_3CN$, 140874-38-0.

Supplementary Material Available: Tables of details of crystal data and refinement parameters for $[Ru(bpy)_3](PF_6)_2$, $[Ru(bpm)_3](PF_6)_2 \cdot CH_3CN$, and $[Ru(bpz)_3](PF_6)_2 \cdot DMF \cdot H_2O$ (Table S5) thermal parameters for $[Ru(bpy)_3](PF_6)_2$ (Table S1), and thermal parameters (Table S2) and hydrogen atomic coordinates (Table S3) for $[Ru(bpm)_3](PF_6)_2 \cdot CH_3CN$ (4 pages); a table of calculated and observed structure factors for $[Ru(bpm)_3](PF_6)_2 \cdot CH_3CN$ (Table S4) (16 pages). Ordering information is given on any current masthead page.

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