

Structure of *cis*-Bis(acetonitrile)bis(2,2'-bipyridine)ruthenium(II) Hexafluorophosphate, [Ru(C₂H₃N)₂(C₁₀H₈N₂)₂](PF₆)₂

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Abstract. $M_r = 785.48$, monoclinic, $P2_1/n$, $a = 16.726$ (9), $b = 10.539$ (4), $c = 17.322$ (9) Å, $\beta = 95.98$ (3)°, $V = 3037$ (3) Å³, $Z = 4$, $D_x = 1.718$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 6.6$ cm⁻¹, $F(000) = 1560$, $T = 298$ K, $R = 0.064$ for 3770 observed reflections. The Ru atom is octahedrally coordinated to six N atoms. Three types of Ru–N bonds are observed in this structure: Ru–N(bpy) *trans* to bpy 2.065 (6) Å; Ru–N(bpy) *trans* to acetonitrile 2.043 (6) Å; Ru–N(acetonitrile) 2.033 (6) Å. The dihedral angle between the two best bpy planes is 72.5 (1)°.

Introduction. Reactions of Ru–bipyridine complexes are important because of the redox properties of the photoinduced excited state Ru(bpy)₃^{2+*} and the resulting implications for solar-generated energy. The structure determination of *cis*-[Ru(bpy)₂(NCCCH₃)₂]²⁺ was undertaken to identify an unknown side-product of the reaction of *cis*-Ru(bpy)₂Cl₂ with other conjugated ligands. The *cis*-[bis(acetonitrile)bis(2,2'-bipyridine)Ru^{II}]²⁺ complex has been previously prepared by a more straightforward synthetic route (Brown, Callahan & Meyer, 1975). The structure analysis reported herein definitively identifies and characterizes this complex, and contributes to the body of information on structural *trans*-effects in Ru complexes.

Experimental. Red tabular crystals 0.20 × 0.22 × 0.43 mm; Nonius CAD-4 diffractometer, monochromated Mo $K\alpha$, $\theta/2\theta$ scan; $2^\circ \leq 2\theta \leq 50^\circ$; lattice parameters from 48 high-angle reflections measured at $\pm 2\theta$; Gaussian integration absorption corrections applied with transmission coefficients ranging 0.80 to 0.91; h 0→19, k 0→12, l -20→+20; 3 intensity monitors varied 2%; 5755 total reflections, 5630 unique, 3770 with $I \geq 2\sigma(I)$; $R_{\text{int}} = 0.035$; $I = S - rB$ where S = scan counts, r = scan time/background ratio,

B = sum background counts; $\sigma_f^2 = S + r^2B + (pI)^2$ where $p = 0.04$; structure solved by Patterson methods; H atoms which were placed were done so in calculated positions with $U = 0.08$ Å² and held invariant; the six H atoms of the methyl groups were not found and are not included in the model; full-matrix anisotropic refinement on F yielded $R = 0.064$, $wR = 0.075$, $S = 2.2$; $w = (\sigma_F)^{-2}$; max. Δ/σ in final cycle = 0.08; final ΔF map showed ± 0.8 e Å⁻³ near Ru atom; no correction for secondary extinction; neutral-atom scattering factors and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974); calculations performed with local modifications of *SHELX76* crystallographic programs (Sheldrick, 1976).

Discussion. The atomic coordinates are given in Table 1, ‡ and bond lengths and angles in this *cis*-[Ru^{II}(bpy)₂(NCCCH₃)₂]²⁺ cation are shown in Table 2. Fig. 1 illustrates the geometry and labeling of the cation. The ligands form an approximately octahedral coordination sphere about the Ru atom, with the bipyridine groups exhibiting their usual acute 'bite' angles [79.4 (2) and 78.7 (2)°]. The bipyridines are nearly planar (average r.m.s.d. from calculated plane = 0.06 Å) but show a slight curvature through the length of the ligand placing the central six atoms (consisting of the bridge C atoms and the two atoms bound to each) opposite the six outer C atoms with respect to the best calculated plane. The dihedral angle between the two bpy best planes is 72.5 (1)°.

The Ru–N bond lengths in this complex occur in three distinct sets. The Ru–N(bpy) *trans* to N(bpy) averages 2.065 (6) Å and is in the range of values reported for other Ru^{II} and Ru^{III} complexes: 2.056 (6)

‡ Lists of structure amplitudes, anisotropic thermal parameters, bond lengths and angles in the anion and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39958 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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for $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ (Rillema, Jones & Levy, 1979), 2.071 (7) Å for $[(\text{bpy})_2(\text{NO}_2)\text{Ru}^{\text{III}}-\text{O}-\text{Ru}^{\text{III}}(\text{NO}_2)(\text{bpy})_2]^{2+}$ (Phelps, Kahn & Hodgson, 1975). The Ru–N(bpy) bonds *trans* to acetonitrile are somewhat shorter [average 2.043 (6) Å]. This shortening is attributed to the effect of changing *trans*-coordinated ligands; within the *cis*- $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{NCCH}_3)_2]^{2+}$ complex the bpy ligands are apparently stronger π -acids than are the acetonitrile ligands, and thus the shorter Ru–N(bpy) bond occurs when bpy is *trans* to acetonitrile. The Ru–N(acetonitrile) lengths are also shorter than Ru–N(bpy) *trans* to N(bpy) due at least partially to the smaller radius of N(*sp*) in acetonitrile over N(*sp*²) in bpy. The bond lengths and angles within both bpy and NCCH₃ groups are normal.

The two PF_6^- anions display a not atypical disorder in the crystal lattice which is evidenced by the large temperature factors for the F atoms and a number of 'alternative' F positions appearing up to 0.75 e Å⁻³ in a difference Fourier map. The P–F bond length averages 1.509 (42) Å and ranges 1.46–1.56 Å. Anionic bond lengths and angles have been deposited.

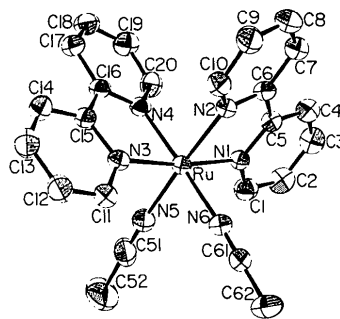
Table 1. Atomic parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Ru(1)	0.75236 (3)	-0.02293 (5)	0.50807 (3)	0.0498 (2)
P(1)	0.8776 (2)	0.4755 (3)	0.3381 (2)	0.093 (1)
P(2)	0.1256 (1)	-0.0137 (2)	0.1531 (1)	0.081 (1)
N(1)	0.8516 (3)	-0.0219 (6)	0.4466 (3)	0.053 (2)
N(2)	0.8138 (3)	0.1287 (5)	0.5576 (3)	0.051 (2)
N(3)	0.6513 (3)	0.0008 (5)	0.5657 (3)	0.056 (2)
N(4)	0.6888 (4)	0.1065 (5)	0.4384 (3)	0.054 (2)
C(1)	0.8700 (5)	-0.1091 (8)	0.3955 (5)	0.072 (3)
C(2)	0.9355 (6)	-0.0965 (9)	0.3535 (5)	0.082 (4)
C(3)	0.9827 (6)	-0.012 (1)	0.3630 (5)	0.085 (4)
C(4)	0.9639 (5)	0.1001 (8)	0.4168 (5)	0.075 (3)
C(5)	0.8990 (4)	0.0785 (7)	0.4580 (4)	0.056 (3)
C(6)	0.8774 (4)	0.1660 (7)	0.5221 (4)	0.060 (3)
C(7)	0.9212 (5)	0.2743 (8)	0.5441 (5)	0.077 (3)
C(8)	0.8975 (6)	0.3446 (8)	0.6065 (6)	0.087 (4)
C(9)	0.8349 (5)	0.3028 (9)	0.6428 (5)	0.083 (4)
C(10)	0.7952 (5)	0.1956 (8)	0.6179 (5)	0.071 (3)
C(11)	0.6309 (5)	-0.0687 (7)	0.6270 (5)	0.069 (3)
C(12)	0.5635 (5)	-0.0438 (9)	0.6634 (5)	0.076 (3)
C(13)	0.5142 (5)	0.0533 (9)	0.6364 (5)	0.079 (4)
C(14)	0.5322 (5)	0.1231 (8)	0.5716 (5)	0.078 (3)
C(15)	0.6000 (4)	0.0952 (7)	0.5382 (4)	0.057 (3)
C(16)	0.6228 (4)	0.1550 (7)	0.4673 (4)	0.058 (3)
C(17)	0.5801 (5)	0.2543 (7)	0.4300 (5)	0.073 (3)
C(18)	0.6019 (6)	0.2999 (8)	0.3608 (6)	0.081 (4)
C(19)	0.6675 (5)	0.2500 (8)	0.3325 (5)	0.077 (3)
C(20)	0.7089 (5)	0.1519 (8)	0.3713 (4)	0.071 (3)
N(5)	0.6990 (4)	-0.1753 (6)	0.4523 (4)	0.072 (3)
C(51)	0.6725 (5)	-0.264 (1)	0.4258 (7)	0.105 (5)
C(52)	0.6383 (7)	-0.385 (1)	0.3923 (9)	0.172 (7)
N(6)	0.8090 (4)	-0.1463 (6)	0.5858 (4)	0.062 (2)
C(61)	0.8358 (4)	-0.2161 (8)	0.6320 (5)	0.068 (3)
C(62)	0.8717 (6)	-0.3068 (9)	0.6922 (6)	0.103 (4)
F(1)	0.8288 (4)	0.3859 (8)	0.3873 (5)	0.191 (4)
F(2)	0.9294 (4)	0.5633 (9)	0.2904 (5)	0.174 (4)
F(3)	0.9560 (5)	0.415 (1)	0.3711 (8)	0.238 (7)
F(4)	0.891 (1)	0.565 (1)	0.4032 (8)	0.296 (9)
F(5)	0.8034 (6)	0.535 (2)	0.3045 (9)	0.38 (1)
F(6)	0.867 (1)	0.395 (1)	0.2697 (8)	0.36 (1)
F(7)	0.1846 (5)	0.0237 (9)	0.2244 (5)	0.190 (5)
F(8)	0.0678 (6)	-0.046 (1)	0.0821 (5)	0.243 (6)
F(9)	0.1948 (6)	-0.069 (1)	0.1200 (8)	0.299 (8)
F(10)	0.1442 (6)	0.1076 (8)	0.1167 (6)	0.210 (5)
F(11)	0.0974 (8)	-0.1334 (9)	0.1959 (7)	0.263 (8)
F(12)	0.0558 (5)	0.042 (1)	0.1900 (6)	0.237 (7)

Table 2. Bond lengths (Å) and angles (°)

Ru(1)–N(1)	2.063 (5)	C(5)–C(6)	1.52 (1)
Ru(1)–N(2)	2.040 (5)	C(6)–C(7)	1.39 (1)
Ru(1)–N(3)	2.067 (6)	C(7)–C(8)	1.40 (1)
Ru(1)–N(4)	2.045 (6)	C(8)–C(9)	1.35 (1)
Ru(1)–N(5)	2.033 (7)	C(9)–C(10)	1.36 (1)
Ru(1)–N(6)	2.033 (6)	C(11)–C(12)	1.37 (1)
N(1)–C(1)	1.334 (9)	C(12)–C(13)	1.37 (1)
N(1)–C(5)	1.325 (9)	C(13)–C(14)	1.40 (1)
N(2)–C(6)	1.343 (9)	C(14)–C(15)	1.36 (1)
N(2)–C(10)	1.323 (9)	C(15)–C(16)	1.465 (9)
N(3)–C(11)	1.361 (9)	C(16)–C(17)	1.39 (1)
N(3)–C(15)	1.367 (9)	C(17)–C(18)	1.38 (1)
N(4)–C(16)	1.359 (9)	C(18)–C(19)	1.35 (1)
N(4)–C(20)	1.331 (9)	C(19)–C(20)	1.38 (1)
C(1)–C(2)	1.38 (1)	N(5)–C(51)	1.11 (1)
C(2)–C(3)	1.39 (1)	C(51)–C(52)	1.49 (2)
C(3)–C(4)	1.37 (1)	N(6)–C(61)	1.14 (1)
C(4)–C(5)	1.38 (1)	C(61)–C(62)	1.49 (1)
Ru(1)–N(1)–C(1)	126.4 (5)	N(3)–C(15)–C(16)	113.4 (6)
Ru(1)–N(1)–C(5)	115.4 (4)	N(4)–Ru(1)–N(5)	94.0 (2)
Ru(1)–N(2)–C(6)	115.2 (4)	N(4)–Ru(1)–N(6)	174.4 (2)
Ru(1)–N(2)–C(10)	126.8 (5)	N(4)–C(16)–C(15)	116.1 (6)
Ru(1)–N(3)–C(11)	126.5 (5)	N(4)–C(16)–C(17)	120.7 (6)
Ru(1)–N(3)–C(15)	115.8 (4)	N(4)–C(20)–C(19)	122.4 (7)
Ru(1)–N(4)–C(16)	115.2 (4)	C(1)–N(1)–C(5)	118.2 (6)
Ru(1)–N(4)–C(20)	126.3 (5)	C(1)–C(2)–C(3)	119.2 (8)
Ru(1)–N(5)–C(51)	174.9 (7)	C(2)–C(3)–C(4)	117.9 (8)
Ru(1)–N(6)–C(61)	175.1 (6)	C(3)–C(4)–C(5)	119.2 (8)
N(1)–Ru(1)–N(2)	79.4 (2)	C(4)–C(5)–C(6)	122.6 (7)
N(1)–Ru(1)–N(3)	172.5 (2)	C(5)–C(6)–C(7)	122.8 (7)
N(1)–Ru(1)–N(4)	95.1 (2)	C(6)–N(2)–C(10)	117.9 (6)
N(1)–Ru(1)–N(5)	95.5 (2)	C(6)–C(7)–C(8)	117.5 (7)
N(1)–Ru(1)–N(6)	90.1 (2)	C(7)–C(8)–C(9)	118.8 (8)
N(1)–C(1)–C(2)	122.2 (8)	C(8)–C(9)–C(10)	120.1 (8)
N(1)–C(5)–C(6)	123.1 (7)	C(11)–N(3)–C(15)	117.8 (6)
N(1)–C(5)–C(10)	114.2 (6)	C(11)–C(12)–C(13)	118.8 (7)
N(2)–Ru(1)–N(3)	95.9 (2)	C(12)–C(13)–C(14)	119.6 (7)
N(2)–Ru(1)–N(4)	86.2 (2)	C(13)–C(14)–C(15)	119.2 (8)
N(2)–Ru(1)–N(5)	174.9 (2)	C(14)–C(15)–C(16)	124.5 (7)
N(2)–Ru(1)–N(6)	92.4 (2)	C(15)–C(16)–C(17)	123.2 (7)
N(2)–C(6)–C(5)	114.7 (6)	C(16)–N(4)–C(20)	118.4 (6)
N(2)–C(6)–C(7)	122.4 (6)	C(16)–C(17)–C(18)	119.9 (7)
N(2)–C(10)–C(9)	123.1 (7)	C(17)–C(18)–C(19)	118.6 (8)
N(3)–Ru(1)–N(4)	78.7 (2)	C(18)–C(19)–C(20)	119.9 (7)
N(3)–Ru(1)–N(5)	89.1 (2)	N(5)–Ru(1)–N(6)	87.8 (3)
N(3)–Ru(1)–N(6)	96.1 (2)	N(5)–C(51)–C(52)	178 (1)
N(3)–C(11)–C(10)	122.6 (7)	N(6)–C(61)–C(62)	179.4 (7)
N(3)–C(15)–C(16)	122.0 (7)		

Fig. 1. Drawing by ORTEP (Johnson, 1965) illustrating a view of the $[\text{Ru}(\text{bpy})_2(\text{NCCH}_3)_2]^{2+}$ cation down the crystallographic z axis.

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Solid-State Structure of Ferrocenecarboxylic Acid, [Fe(C₅H₄CO₂H)(C₅H₅)]

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Abstract. $M_r = 230.05$, monoclinic, $P2_1/n$, $a = 5.797$ (1), $b = 12.896$ (3), $c = 12.586$ Å, $\beta = 96.96$ (1)°, $V = 934.1$ (3) Å³, $Z = 4$, $D_x = 0.818$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 7.889$ cm⁻¹, $F(000) = 236.0$, $T = 296$ K, $R = 0.053$ for 885 observed reflections. The structure consists of hydrogen-bonded pairs of molecules located so that the geometric center of the hydrogen-bonding framework coincides with a crystallographic center of inversion. The O...O distance is 2.714 (14) Å and the (C₅H₅)(C₅H₄)Fe moieties are eclipsed. Comparisons are made between this structural determination and the study of ferrocene-1,1'-dicarboxylic acid reported by Takusagawa & Koetzie [*Acta Cryst.* (1979), **B35**, 2888–2896].

Introduction. The study of the chemistry of ferrocene and other metallocenes has become one of the largest areas of interest in the whole of organometallic chemistry since the first reports of this revolutionary compound and its congeners (Kealy & Pauson, 1951). One of the earliest evidences of the aromatic nature of ferrocene (Wilkinson, Rosenblum, Whiting & Woodward, 1952) was the dissociation constant of ferrocenecarboxylic acid (FCAH), after the determination of which studies of electrophilic substitution reactions and derivatizations followed rapidly (Pauson, 1977, and references therein). Despite the early recognition of the importance of the title compound (Benkesen, Goggin & Scholl, 1954), its structure in the single crystal has never been reported.

We have recently undertaken an exploration of the anion of the title compound as a ligand for the synthesis of mixed-metal species containing both iron and dimeric units made up of the Group VI transition elements (Cotton, Reid & Tocher, 1984). It was of interest to us to be able to make direct comparisons between the structure of the free acid and the structure of its anion upon ligation to such a dimetal unit. We have therefore

carried out a single-crystal X-ray study of the free acid, the results of which we report here.

Experimental. Material studied was a recrystallized (tetrahydrofuran–hexane) commercial (Aldrich Chemical Company) sample. Well formed crystal, 0.40 × 0.15 × 0.15 mm, Enraf–Nonius CAD-4 automated diffractometer, graphite monochromator, automatic search routine located and centered 25 intense reflections, $12 < 2\theta < 37^\circ$, from which unit-cell dimensions derived; systematic absences uniquely defined space group as $P2_1/n$; 1214 unique reflections, $5 < 2\theta < 50^\circ$, 885 ($I > 3\sigma$) collected, $0 < h < 7$, $0 < k < 12$, $-12 < l < 12$, three intensity standards checked every hour of exposure time; no decay, random fluctuations of ca 3% during collection; empirical absorption correction, ψ scan for each of nine reflections near $\chi = 90^\circ$ measured, each reflection measured at 10° intervals from $\psi = 0$ to $\psi = 360^\circ$, normalized transmission factors 0.98 to 0.82; structure solved by conventional heavy-atom methods (Bino, Cotton & Fanwick, 1979). All nonhydrogen atoms refined by full-matrix least squares using anisotropic and, for C(1'), isotropic thermal parameters, carboxylate hydrogen atom (from $F_o - F_c$ map) also with isotropic thermal parameter, $\sum w||F_o| - |F_c|| / \sum |F_o|$ minimized; $R = 0.053$, $wR = 0.064$, $w = 1/\sigma^2(|F_o|)$, scale factor = 0.971 (2), $\Delta_{\text{max}}/\sigma = 0.21$, $\Delta\rho$ excursion in final difference Fourier map 0.583 e Å⁻³; neutral atomic scattering factors and f' , f'' values from *International Tables for X-ray Crystallography* (1974). All computations carried out on the departmental VAX-11/780 with Enraf–Nonius (1981) VAX-SDP software.

Discussion. The positional parameters and equivalent isotropic thermal parameters are given in Table 1. The structure of the molecule is given in Fig. 1, together with the numbering scheme used. Fig. 2 is an *ORTEP*