

Structure of Bis(2,2'-bipyridine)[3,5-bis(2-pyridyl)-1,2,4-triazole]ruthenium(II) Hexafluorophosphate Hemihydrate

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Abstract. $[\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_{12}\text{H}_8\text{N}_5)]\text{PF}_6 \cdot 0.5\text{H}_2\text{O}$, $M_r = 789.65$, monoclinic, $P2_1/n$, $a = 11.033$ (3), $b = 14.235$ (9), $c = 21.847$ (5) Å, $\beta = 103.7$ (2)°, $V = 3333.5$ Å³, $Z = 4$, $D_m = 1.57$ (1), $D_x = 1.57$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 5.78$ cm⁻¹, $F(000) = 1576.4$, $T = 298$ K, $R(wR) = 0.052$ (0.056) for 2435 unique observed reflections [$I > 2\sigma(I)$] and 0.133 (0.054) for all 5456 unique reflections. The planar bis(pyridyl)triazole ligand is coordinated to the central metal atom *via* N(2) and N(13). The Ru–N distances of 2.03 (2)–2.11 (12) Å are unexceptional. A water molecule may participate in weak hydrogen bonding with N(4) and N(7) of the bis(pyridyl)triazole ligand.

Introduction. Ruthenium(II) compounds with 2,2'-bipyridine-like ligands have been studied in great detail because of their possible application in the photochemical decomposition of water (Seddon, 1982; Kalyanasundaram, Grätzel & Pelizzetti, 1986). The crystal structures of a number of ruthenium(II) compounds containing bipyridine have been reported recently, and in these structures an Ru–N distance of about 2.06 Å is observed (Rillema, Jones & Levy, 1979; Eggleston, Goldsby, Hodgson & Meyer, 1985; Thummel, Lefoulon & Korp, 1987). 3,5-Bis(2-pyridyl)-1,2,4-triazole (bpt) has two coordination modes [N(13) and N(2) or N(13) and N(4)], see Fig. 1. Recently, it was shown that the coordination mode of NH₂bpt in $[\text{Rh}(\text{NH}_2\text{bpt})(\text{CO})_2]\text{ClO}_4$ is *via* N(2) of the triazole ring (Garcia, Manero, Oro, Aprea, Cano, Foces-Foces, Haasnoot, Prins & Reedijk, 1986).

On the basis of NMR data, it was predicted that deprotonated bpt also coordinates through N(2) and N(13) to the ruthenium(II) ion (Hage, Dijkhuis, Haasnoot, Prins, Reedijk, Buchanan & Vos, 1988). However, a related ligand, 1-methyl-3-(2-pyridyl)-1,2,4-triazole, binds *via* N(4) of the triazole ring to ruthenium(III) (Hage, Prins, de Graaff, Haasnoot, Reedijk & Vos, 1988). Apparently, steric effects result

in different coordination modes for pyridyltriazole derivatives.

Experimental. The complex was synthesized as reported previously (Hage, Dijkhuis, Haasnoot, Prins, Reedijk, Buchanan & Vos, 1988). After crystallization from acetone/water, a bar-shaped single crystal of dimensions 0.50 × 0.07 × 0.10 mm was selected for crystal structure determination. D_m was determined by flotation, using dibromopropane and heptane. Intensity data were collected at room temperature using an Enraf-Nonius CAD-4 diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. Cell parameters were obtained from 24 reflections with $10 < \theta < 12^\circ$. Data were collected within $2 < \theta < 24^\circ$ (using the ω -scan method) and were corrected for Lorentz and polarization effects. Corrections for absorption were not applied. The range for h was -12 to 12 , for k 0 to 16 and for l 0 to 25 . The intensity variation of the standard reflections was 14% from the mean value. The principal computer programs used in the crystallographic calculations were written or modified by Mrs E. Rutten-Keulemans and Dr R. A. G. de Graaff. Of the 5618 reflections measured, 5456 were independent of which 2435 were significant [$I > 2\sigma(I)$]; $R_{\text{int}} = 0.036$. The structure was solved by standard heavy-atom techniques and refined by full-matrix least squares based on F with weights $w = [\sigma^2(F_o)]^{-1}$ using all 5456 independent reflections. The non-H atoms were refined anisotropically, except for the water O atom for which isotropic temperature factors were refined. Water H atoms were not located. The PF₆ group is disordered over three different positions with occupancies 0.40, 0.09 and 0.51. Waser constraints (P–F = 1.550 Å, F–P–F = 90.0° with respective standard deviations 0.002 Å and 0.002°) were used. For H atoms the positional parameters and one common isotropic thermal parameter were refined. The final difference Fourier synthesis had a minimum value of $-0.85 \text{ e } \text{Å}^{-3}$, and a maximum value of $1.11 \text{ e } \text{Å}^{-3}$ at a noise level of $0.31 \text{ e } \text{Å}^{-3}$. Scattering factors were taken from

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International Tables for X-ray Crystallography (1974); shift-to-e.s.d. ratio in final cycle <0.1.

Discussion. Atomic fractional coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.* Fig. 1. shows a projection of the cation with the atomic numbering scheme. Selected bond distances and bond angles are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51481 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

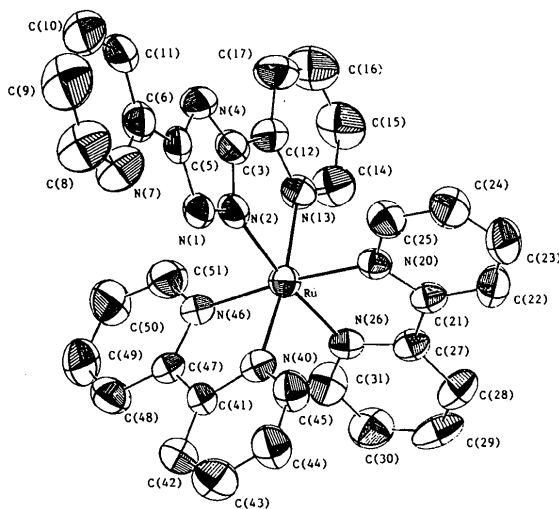


Fig. 1. The structure of the bis(2,2'-bipyridine)[3,5-bis(2-pyridyl)-1,2,4-triazole]ruthenium(II) cation. Thermal ellipsoids are shown at 50% probability. H atoms have been omitted for reasons of clarity.

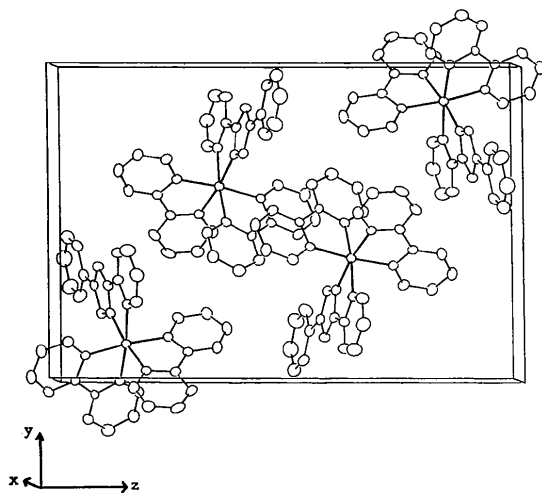


Fig. 2. Projection of the unit cell showing only the cation positions.

Table 1. Fractional atomic coordinates ($\times 10^4$ for Ru; $\times 10^3$ for C, N, P, F and O) and isotropic thermal parameters ($\times 10^2$ for Ru; $\times 10$ for C and N)

$$B_{\text{iso}} = (8\pi^2/3) \text{ trace } U.$$

	x	y	z	$B_{\text{iso}}(\text{\AA}^2)$
Ru	2379 (2)	-3822 (2)	3521 (1)	336 (6)
N(1)	494 (2)	-283 (2)	412 (1)	39 (7)
N(2)	369 (2)	-284 (2)	389 (1)	39 (8)
N(4)	417 (3)	-135 (2)	416 (1)	44 (8)
N(7)	736 (3)	-223 (2)	464 (1)	61 (10)
N(13)	129 (2)	-259 (2)	346 (1)	38 (8)
N(20)	247 (2)	-360 (2)	261 (1)	34 (7)
N(26)	98 (2)	-469 (2)	305 (1)	34 (7)
N(40)	354 (2)	-497 (2)	369 (1)	36 (7)
N(46)	225 (2)	-419 (2)	441 (1)	37 (7)
C(5)	519 (3)	-193 (2)	428 (1)	43 (10)
C(3)	327 (3)	-196 (2)	392 (1)	41 (10)
C(6)	645 (3)	-159 (3)	454 (1)	48 (11)
C(11)	671 (4)	-65 (3)	468 (2)	61 (13)
C(9)	883 (4)	-104 (4)	501 (2)	88 (19)
C(8)	853 (4)	-193 (3)	488 (2)	78 (16)
C(12)	194 (3)	-181 (2)	368 (1)	45 (10)
C(17)	135 (4)	-95 (2)	365 (2)	60 (13)
C(16)	9 (4)	-90 (3)	342 (2)	76 (16)
C(15)	-55 (3)	-169 (3)	320 (2)	65 (14)
C(14)	7 (3)	-252 (3)	323 (2)	55 (12)
C(25)	323 (3)	-299 (2)	241 (2)	46 (10)
C(24)	318 (3)	-285 (2)	179 (2)	53 (11)
C(23)	234 (3)	-333 (3)	134 (2)	60 (13)
C(22)	156 (3)	-395 (2)	153 (1)	51 (11)
C(21)	161 (3)	-408 (2)	216 (1)	35 (9)
C(31)	26 (3)	-524 (2)	331 (2)	51 (11)
C(30)	-60 (3)	-585 (2)	297 (2)	58 (12)
C(29)	-73 (3)	-591 (2)	233 (2)	60 (13)
C(28)	-2 (3)	-534 (2)	205 (2)	50 (10)
C(27)	83 (3)	-472 (2)	242 (1)	37 (9)
C(10)	794 (5)	-37 (3)	491 (2)	81 (16)
C(45)	419 (3)	-532 (2)	330 (2)	48 (10)
C(44)	494 (3)	-609 (3)	344 (2)	56 (11)
C(43)	503 (3)	-653 (2)	400 (2)	61 (12)
C(42)	438 (3)	-620 (2)	441 (1)	49 (10)
C(41)	363 (3)	-541 (2)	424 (1)	36 (9)
C(51)	157 (3)	-377 (3)	476 (2)	52 (10)
C(50)	149 (3)	-408 (3)	533 (2)	62 (14)
C(49)	210 (4)	-488 (3)	557 (2)	64 (13)
C(48)	282 (3)	-535 (2)	522 (2)	52 (11)
C(47)	289 (3)	-498 (2)	464 (1)	38 (9)
P(1A)	227 (4)	-179 (3)	-349 (2)	61 (6)
F(1A)	195 (8)	-73 (4)	-355 (3)	12 (2)
F(1B)	104 (9)	-96 (7)	-362 (5)	12 (1)
F(2A)	261 (7)	-177 (5)	-413 (2)	10 (2)
F(2B)	222 (9)	-169 (7)	-420 (5)	10 (2)
F(3A)	193 (6)	-181 (5)	-284 (2)	10 (2)
F(3B)	148 (9)	-211 (7)	-289 (5)	10 (2)
F(4A)	364 (5)	-155 (5)	-316 (4)	12 (2)
F(4B)	285 (9)	-142 (7)	-324 (5)	12 (2)
F(5A)	90 (5)	-203 (7)	-381 (4)	15 (3)
F(5B)	85 (9)	-238 (7)	-385 (5)	15 (3)
F(6A)	259 (7)	-285 (3)	-343 (3)	11 (1)
F(6B)	266 (9)	-285 (7)	-346 (5)	11 (1)
P(1B)	185 (9)	-190 (7)	-354 (5)	61 (6)
P(1C)	226 (2)	-159 (2)	-345 (1)	61 (6)
F(1C)	195 (5)	-55 (3)	-363 (2)	12 (2)
F(2C)	289 (5)	-129 (4)	-277 (1)	10 (2)
F(3C)	353 (2)	-148 (3)	-364 (2)	10 (2)
F(4C)	100 (2)	-170 (4)	-327 (3)	12 (2)
F(5C)	164 (5)	-189 (4)	-414 (2)	15 (3)
F(6C)	258 (4)	-263 (2)	-327 (3)	11 (1)
O(60)	-185 (6)	150 (5)	165 (3)	12 (1)

As can be seen from Fig. 1, bis(pyridyl)triazole coordinates through N(2) and N(13) in agreement with the NMR spectra (Hage, Dijkhuis, Haasnoot, Prins, Reedijk, Buchanan & Vos, 1988). The Ru-N(bpy) distances of 2.04–2.06 Å are similar to those found in [Ru(bpy)₃]²⁺ (Rillema, Jones & Levy, 1979). The rather long Ru-N(13) bond may be caused by diminished π back-bonding in this system (Eggleston, Goldsby, Hodgson & Meyer, 1985). The bite angles of

Table 2. Selected bond distances (Å) and bond angles (°)

Ru—N(2)	2.03 (2)	N(7)—C(6)	1.34 (4)
Ru—N(13)	2.11 (2)	N(7)—C(8)	1.34 (4)
Ru—N(20)	2.04 (2)	C(8)—C(9)	1.32 (5)
Ru—N(26)	2.05 (2)	C(9)—C(10)	1.35 (5)
Ru—N(40)	2.06 (2)	C(10)—C(11)	1.39 (5)
Ru—N(46)	2.04 (2)	C(6)—C(11)	1.38 (4)
N(1)—N(2)	1.35 (3)	N(13)—C(12)	1.35 (4)
N(1)—C(5)	1.34 (3)	N(13)—C(14)	1.33 (4)
N(2)—C(3)	1.34 (4)	C(14)—C(15)	1.36 (4)
N(4)—C(5)	1.36 (4)	C(15)—C(16)	1.35 (4)
N(4)—C(3)	1.33 (3)	C(16)—C(17)	1.36 (5)
C(5)—C(6)	1.46 (4)	C(17)—C(12)	1.38 (4)
C(3)—C(12)	1.45 (4)		
N(1)...O(60)	3.14 (7)	N(7)...O(60)	3.29 (7)
N(2)—Ru—N(13)	78 (1)	N(20)—Ru—N(40)	97.2 (9)
N(2)—Ru—N(20)	95 (1)	N(26)—Ru—N(40)	88.6 (9)
N(2)—Ru—N(40)	97.0 (9)	N(26)—Ru—N(46)	97.3 (9)
N(2)—Ru—N(46)	90.4 (9)	N(40)—Ru—N(46)	79 (1)
N(13)—Ru—N(20)	88.2 (9)	N(2)—Ru—N(26)	172.0 (9)
N(13)—Ru—N(26)	96.9 (9)	N(13)—Ru—N(40)	173 (1)
N(13)—Ru—N(46)	96.0 (9)	N(20)—Ru—N(46)	174 (1)
N(20)—Ru—N(26)	79 (1)		

the two bipyridine ligands and the bpt ligand are 78.8, 79.2 and 77.9°, respectively, in agreement with other ruthenium bipyridine compounds (Rillema, Jones & Levy, 1979; Heeg, Kroener & Deutsch, 1985).

The packing of the cations (Fig. 2) is such that bipyridyl ligands in adjacent molecules are roughly

parallel; the shortest C...C contact between such parallel bpy ligands is 3.64 Å. The shortest intermolecular distance in the structure is 2.05 Å between F(1B) and H(16), and the shortest H...H contact is 2.43 Å involving H(15) and H(29).

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Structure of (Methyl 5-deoxy-β-D-ribofuranos-5-yl)(pyridine)cobaloxime Monohydrate

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Abstract. C₁₉H₃₀CoN₅O₈·H₂O, $M_r = 533.4$, monoclinic, $P2_1$, $a = 8.519(1)$, $b = 17.012(3)$, $c = 9.135(1)$ Å, $\beta = 117.04(1)^\circ$, $V = 1179.2$ Å³, $Z = 2$, $D_x = 1.502$ Mg m⁻³, $F(000) = 560$, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.78$ mm⁻¹, $R = 0.026$ for 4022 unique observed reflections, absolute structure determined from anomalous-scattering effects. Co is octahedrally coordinated by two dimethylglyoximate [2,3-butanedione dioximato(1-)], one pyridine and the ribosyl ligands. The Co—C bond length of 2.015(2) Å and Co—C—C angle of 123.0(2)° closely resemble those of the vitamin B₁₂ coenzyme adenosylcobalamin, for which this simpler complex is a model.

Introduction. Attempts to elucidate the mechanism of action of vitamin B₁₂ have involved various model

compounds, mainly cobalamins and cobaloximes (Zagalak & Friedrich, 1979; Dolphin, 1982; Golding & Rao, 1987). Among the structural investigations, a coenzyme form of vitamin B₁₂, adenosylcobalamin (AdoCbl), shows a Co—C—C angle of 124° (Lenhert, 1968; Savage, Lindley, Finney & Timmins, 1987). This is rather larger than for other alkylcobalamins, and has been considered to be exceptional, and a sign of strain in the molecule, facilitating cleavage of the Co—C bond in the biological action of the coenzyme (Alcock, Dixon & Golding, 1985; Pett, Liebman, Murray-Rust, Prasad & Glusker, 1987). On the other hand, a wide range of values for the Co—C—C angle is found in alkylcobaloximes, and the variation has been ascribed to steric repulsions between the alkyl substituents and the dimethylglyoximate (dmg) ligands (Bresciani-Pahor,