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Structure of *mer*-(Acetonitrile)trichloro[1-methyl-3-(2-pyridyl)-1,2,4-triazole]ruthenium(III)

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Abstract. [$RuCl_3(C_2H_3N)(C_8H_8N_4)$], $M_r = 408.63$, monoclinic, $P2_1/c$, $a = 11.929$ (1), $b = 7.472$ (1), $c = 16.486$ (3) Å, $\beta = 95.11$ (2)°, $V = 1463.7$ Å^3, $Z = 4$, $D_x = 1.85$ (1), $D_m = 1.81$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7145 Å, $\mu = 1.586$ mm^{-1}, $F(000) = 804$, $T = 298$ K, $R = 0.018$ for 1337 unique reflections [$I > 2\sigma(I)$]. The planar pyridyltriazole ligand is coordinated to the central metal atom *via* N(1') and N(4). No water molecules leading to hydrogen bonding have been detected. The Ru—Cl distances of 2.33–2.34 Å are in the range expected for ruthenium(III) compounds.

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; Kalyanasandaram, 1982). However, less attention has been paid to ruthenium(III) compounds; no crystal structures have been reported for ruthenium(III) compounds with asymmetric chelating N-donor ligands. Recently it was predicted, on the basis of ^{1}H NMR data, that 1-methyl-3-(2-pyridyl)-1,2,4-triazole (1Mepyrtr) would coordinate *via* N(1') and N(4) to ruthenium(II) (Hage, Haasnoot, Reedijk & Vos, 1986). The ligand has two coordination modes [N(1') and N(2) or N(1') and N(4); see Fig. 1]. Until now no

crystal structures of compounds containing this ligand have been reported. The crystal structure of a ruthenium(III) compound containing both 1Mepyrtr and acetonitrile is described in this paper.

Experimental. Bright red crystals of the title compound were obtained after heating $RuCl_3$ and 1Mepyrtr in acetonitrile. A hexagonal single crystal of dimensions $0.12 \times 0.09 \times 0.06$ mm was selected for crystal-structure determination. D_m was determined by flotation. Intensity data were collected at room temperature by using an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71745$ Å) was used. Cell parameters were obtained by least-squares methods for 24 reflections; the
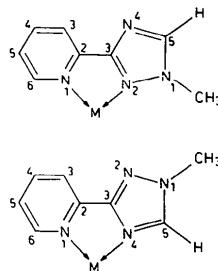

Fig. 1. Atomic numbering and coordination modes of 1-methyl-3-(2-pyridyl)-1,2,4-triazole.

Table 1. *Fractional atomic coordinates* ($\times 10^5$ *for* Ru; $\times 10^4$ *for* C, N *and* Cl; $\times 10^3$ *for* H) *and isotropic thermal parameters* $\{\times 10^3$ *for* Ru; $\times 10^2$ *for* C [*except* C(51)], N *and* Cl; $\times 10$ *for* C(51) *and* H$\}$

$B_{eq} = 8\pi^2/3$ trace U.

	x	y	z	$B_{eq}(\text{Å}^2)$
Ru(1)	21048 (3)	42577 (4)	10881 (2)	2310 (9)
C(5)	1781 (3)	4596 (5)	−853 (2)	289 (11)
N(4)	2291 (2)	4798 (4)	−113 (2)	245 (8)
C(3)	3169 (3)	5905 (5)	−230 (2)	254 (9)
N(2)	3228 (2)	6378 (4)	−987 (2)	299 (9)
N(1)	2321 (3)	5519 (4)	−1375 (2)	302 (8)
C(51)	2027 (6)	5765 (9)	−2248 (3)	46 (2)
C(32)	3898 (3)	6447 (5)	482 (2)	251 (9)
C(33)	4833 (3)	7486 (5)	457 (3)	352 (12)
C(34)	5469 (3)	7881 (6)	1175 (3)	415 (13)
C(35)	5137 (3)	7225 (6)	1885 (3)	394 (13)
C(36)	4184 (3)	6208 (5)	1881 (2)	328 (11)
N(31)	3556 (2)	5798 (4)	1187 (2)	251 (7)
Cl(1)	2015 (1)	3919 (1)	2494 (1)	347 (3)
Cl(2)	3164 (1)	1661 (1)	988 (1)	359 (3)
Cl(3)	1022 (1)	6876 (1)	1085 (1)	320 (2)
N(11)	691 (2)	2729 (4)	927 (2)	278 (8)
C(12)	−56 (3)	1797 (5)	851 (2)	274 (10)
C(13)	−1007 (4)	595 (7)	738 (3)	368 (13)
H(33)	502 (2)	783 (4)	0 (2)	18 (7)
H(34)	611 (3)	854 (5)	117 (2)	42 (9)
H(35)	550 (3)	743 (5)	233 (2)	46 (10)
H(36)	391 (3)	575 (4)	235 (2)	28 (8)
H(131)	−142 (4)	67 (7)	21 (3)	10 (1)
H(132)	−141 (4)	71 (7)	107 (3)	60 (14)
H(133)	−70 (5)	−47 (7)	81 (3)	8 (1)
H(51)	115 (3)	403 (4)	−99 (2)	18 (7)
H(11)	130 (3)	520 (5)	−240 (2)	46 (10)
H(12)	248 (5)	525 (8)	−250 (3)	8 (2)
H(13)	188 (4)	688 (7)	−231 (3)	57 (14)

θ-angle limit of these reflections was 12°. Data were collected within $2 < \theta < 22°$ (using the ω-scan method) and have been corrected for Lorentz and polarization effects. Corrections for absorption were not applied. The range for h was -12 to 12, for k 0 to 7 and for $l -17$ to 17. The intensity variation of the standard reflections was 17%. The number of reflections was reduced by selecting those for which $I > 2\sigma(I)$. 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 3923 reflections measured, 1964 were independent, of which 1337 were observed $[I > 2\sigma(I)]$ and were used in the refinement; $R_{int} = 0.03$. The structure was solved by standard Patterson techniques and refined using full-matrix least-squares refinements based on F with weights $w = [\sigma^2(F_o)]^{-1}$. The non-hydrogen atoms were refined anisotropically. All H atoms were located in successive difference Fourier maps and were refined with isotropic thermal parameters. The final Fourier synthesis had a minimum value of -0.27 and a maximum value of $0.23\,\text{e}\,\text{Å}^{-3}$ at a noise level of $0.10\,\text{e}\,\text{Å}^{-3}$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974); shift-to-e.s.d. ratio in final cycle <0.1. Final $R = 0.018$, $wR = 0.019$.

Discussion. Atomic fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 1.* Fig. 2 shows a projection of the molecule together with the atomic numbering scheme. Relevant bond distances and bond angles are listed in Table 2. As can be seen from Fig. 2 the coordination mode of the planar ligand 1Mepyrtr is *via* N(4) and N(1′). This is in agreement with the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44359 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
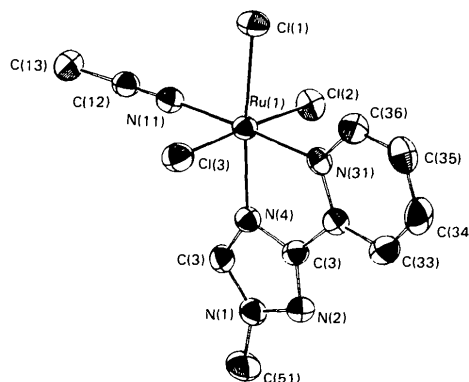

Fig. 2. The molecular structure of *mer*-Ru(1Mepyrtr)(CH$_3$CN)Cl$_3$. Thermal ellipsoids are shown at 50% probability.

Table 2. *Bond distances* (Å) *and bond angles* (°)

Ru(1)−N(4)	2·053 (3)	C(34)−C(35)	1·359 (6)
Ru(1)−N(31)	2·073 (3)	C(35)−C(36)	1·367 (5)
Ru(1)−Cl(1)	2·343 (1)	C(36)−N(31)	1·345 (4)
Ru(1)−Cl(2)	2·330 (1)	N(11)−C(12)	1·130 (4)
Ru(1)−Cl(3)	2·345 (1)	C(12)−C(13)	1·446 (6)
Ru(1)−N(11)	2·034 (3)	C(5)−H(51)	0·879 (3)
C(5)−N(4)	1·321 (4)	C(51)−H(11)	0·97 (4)
C(5)−N(1)	1·315 (5)	C(51)−H(12)	0·81 (5)
N(4)−C(3)	1·362 (4)	C(51)−H(13)	0·86 (5)
C(3)−N(2)	1·305 (4)	C(33)−H(33)	0·84 (3)
C(3)−C(32)	1·455 (5)	C(34)−H(34)	0·91 (4)
N(2)−N(1)	1·367 (4)	C(35)−H(35)	0·84 (4)
N(1)−C(51)	1·462 (5)	C(36)−H(36)	0·92 (3)
C(32)−C(33)	1·363 (5)	C(13)−H(131)	0·97 (5)
C(32)−N(31)	1·356 (4)	C(13)−H(132)	0·76 (5)
C(33)−C(34)	1·380 (5)	C(13)−H(133)	0·88 (5)
N(4)−Ru(1)−N(31)	78·8 (1)	C(3)−NA(2)−N(1)	102·3 (3)
N(4)−Ru(1)−N(11)	98·3 (1)	N(2)−C(3)−N(4)	114·0 (3)
N(11)−Ru(1)−Cl(1)	87·61 (8)	N(4)−C(3)−C(32)	117·9 (3)
N(31)−Ru(1)−Cl(1)	95·35 (8)	C(5)−N(4)−C(3)	103·6 (2)
Cl(1)−Ru(1)−Cl(2)	93·05 (3)	N(4)−C(5)−N(1)	109·4 (4)
N(4)−Ru(1)−Cl(2)	89·38 (8)	C(32)−N(31)−C(36)	117·4 (3)
N(11)−Ru(1)−Cl(2)	88·39 (9)	N(31)−C(32)−C(33)	122·7 (3)
N(31)−Ru(1)−Cl(2)	90·78 (8)	C(32)−C(33)−C(34)	119·0 (4)
Cl(1)−Ru(1)−Cl(3)	91·06 (3)	C(33)−C(34)−C(35)	118·8 (4)
N(4)−Ru(1)−Cl(3)	86·61 (8)	C(34)−C(35)−C(36)	120·1 (4)
N(11)−Ru(1)−Cl(3)	91·03 (9)	C(35)−C(36)−N(31)	122·1 (4)
N(31)−Ru(1)−Cl(3)	89·59 (8)	Ru(1)−N(11)−C(12)	176·0 (3)
N(2)−N(1)−C(51)	120·8 (4)	N(11)−C(12)−C(13)	178·8 (4)
C(5)−N(1)−N(2)	110·6 (3)		

interpretation of the NMR spectra of related ruthenium(II) compounds containing this ligand (Hage, Haasnoot, Reedijk & Vos, 1986). The Ru^{III}—N(1') distance of 2·073 Å is slightly longer than the metal–nitrogen bonds observed in [Ru(bpy)₂Cl₂]$^+$ (average 2·05 Å). This might originate from the presence of acetonitrile *trans* to the pyridine group. The Ru—N(11) distance of 2·034 Å is the shortest metal–ligand bond in the molecule.

The octahedral geometry is not regular, because of the bite angle of the ligand (78·8°). Interestingly, this angle is the same as that observed for bpy in [Ru(bpy)₂Cl₂]$^+$ (Eggleston, Goldsby, Hogson & Meyer, 1985). The Cl atoms constitute a mutual meridional arrangement around the central Ru atom. The Ru^{III}—Cl bond lengths of 2·330, 2·343 and 2·345 Å are up to 0·024 Å longer than the Ru—Cl distances in the structure of [Ru(bpy)₂Cl₂]Cl.H₂O (Eggleston, Goldsby, Hogson & Meyer, 1985), approximately equal to the Ru—Cl distance in [Ru(NH₃)₅-Cl]Cl₂ (Prout & Powell. 1962) and 0·01–0·04 Å shorter than the Ru—Cl distances in the structure of [RuCl₃(NO){P(C₆H₅)₃}₂] (Haymore & Ibers, 1975).

The differences in the Ru—Cl distances for the various ruthenium compounds can be attributed to bipyridine and especially NO$^+$ and PPh₃ having stronger π-acceptor properties than 1Mepyrtr. Acetonitrile, which has rather strong σ-donor properties, is also expected to influence the Ru—Cl distances.

A projection of the unit cell is given in Fig. 3. No stacking between the molecules is observed. The shortest intermolecular distance found in this structure
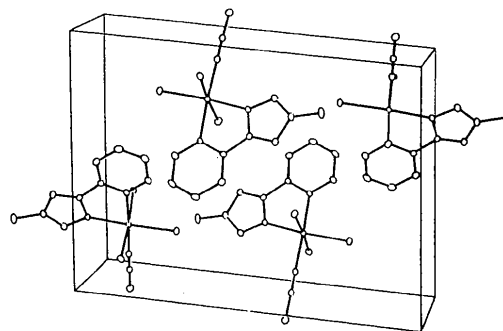

Fig. 3. Projection of the unit cell of *mer*-Ru(1mepyrtr)(CH₃-CN)Cl₃.

is between H(35) and H(36) and is 2·62 Å. Also, a number of short chlorine-hydrogen distances in the range 2·67–3·16 Å are observed in this structure.

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Structure of 4,4,6,6-Tetrachloro-2-[ferrocenyl(hydroxy)methyl]-2-isopropyl-1,3,5,2λ⁵,4λ⁵,6λ⁵-triazatriphosphorine

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Abstract. C₁₄H₁₈Cl₄FeN₃OP₃, $M_r = 534·9$, monoclinic, *I*2/*a*, $a = 21·72$ (1), $b = 8·581$ (1), $c = 23·377$ (4) Å, $\beta = 101·68$ (3)°, $V = 4267$ (2) Å³, $Z = 8$, $D_x = 1·665$ g cm⁻³, Mo $K\bar{\alpha}$, $\lambda = 0·71073$ Å, $\mu = 14·4$ cm⁻¹, $F(000) = 2160$, $T = 130$ K, $R = 0·029$ for 3759 observed reflections with $I > 2·5\sigma(I)$. The N₃P₃ six-membered ring has an envelope conformation. The ferrocenyl group is attached to the isopropyl-substituted

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