

## Aquabis(3-methoxy-2-pyridonato)- (2,2':6',2''-terpyridine)ruthenium(II)– acetonitrile–water (1/1/1)

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Received 14 December 2006

Accepted 25 January 2007

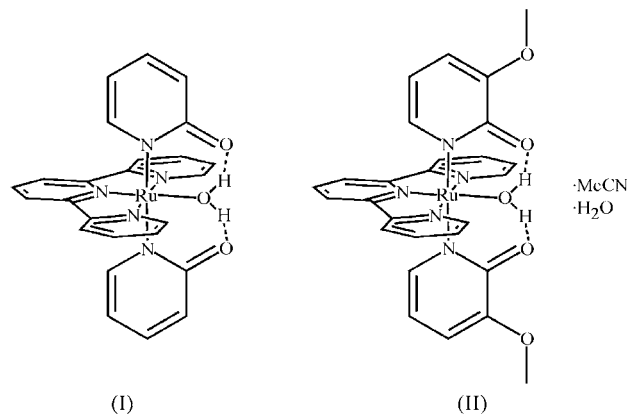
Online 17 February 2007

The title compound,  $[\text{Ru}(\text{C}_6\text{H}_6\text{NO}_2)_2(\text{C}_{15}\text{H}_{11}\text{N}_3)(\text{H}_2\text{O})] \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ , is a transfer hydrogenation catalyst supported by nitrogen-donor ligands. This octahedral  $\text{Ru}^{\text{II}}$  complex features rare monodentate coordination of 3-methoxy-2-pyridonate ligands and interligand  $S(6)S(6)$  hydrogen bonding. Comparison of the title complex with a structural analog with unsubstituted 2-pyridonate ligands reveals subtle differences in the orientation of the ligand planes.

### Comment

Transition metal catalysts for the transfer hydrogenation of alkanes and ketones have attracted considerable interest as a safe and economical alternative to traditional hydrogenation catalysts. Much of the effort devoted to developing these catalysts has focused on ligand design in  $\text{Ru}^{\text{II}}$  complexes (Fan *et al.*, 2002; Naota *et al.*, 1998; Noyori & Hashiguchi, 1997; Zassinovich *et al.*, 1992). A vast majority of the reported systems are organometallic with inconvenient air (and often water) sensitivity. Nearly all reported transfer hydrogenation catalysts also require strong base co-catalysts for significant turnover rates. These base co-catalysts currently limit the application of these catalytic systems. Our laboratory has developed the only examples of well defined polypyridyl-supported  $\text{Ru}^{\text{II}}$  transfer hydrogenation catalysts that tolerate air and water. The structure and reactivity of one of these complexes,  $[\text{Ru}^{\text{II}}(\text{pyO})_2(\text{terpy})(\text{H}_2\text{O})]$  (pyO is 2-pyridonate and terpy is 2,2':6',2''-terpyridine), (I), has been reported (Kelson & Phengsy, 2000). Complex (I) features rare monodentate pyO ligands stabilized by hydrogen bonding between their carbonyl groups and an adjacent aqua ligand. Our mechanistic studies on complex (I) suggest that the intramolecular hydrogen bonding is important to the formation of catalytic intermediates and proton transfer in the catalytic reaction. As part of our continuing development of the  $[\text{Ru}^{\text{II}}(\text{pyO})_2(\text{terpy})(\text{H}_2\text{O})]$  system, the work presented here was concerned with the crystal structure of the newly synthesized complex of formula  $[\text{Ru}^{\text{II}}(\text{MeOpyO})_2(\text{terpy})$

$(\text{H}_2\text{O})] \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  (where MeOpyO is 3-methoxy-2-pyridonate), (II), obtained from the reaction of  $\text{Ru}^{\text{III}}\text{Cl}_3$  with 3-methyl-2-pyridone. The addition of the 3-methoxy substituent to the structure of complex (I) was expected to increase the basicity of the 2-pyridonate ligand and increase catalytic activity. However, complex (II) actually exhibits about half the activity of complex (I) toward the transfer hydrogenation of 2-adamantanone in 2-propanol, and no significant difference was observed in the  $pK_b$  values of compounds (I) and (II) [8.76 (11) and 8.57 (14), respectively]. The crystal structures of (I) and (II) were compared to determine the structural influence of the 3-methoxy substitution on the catalysts.



Our analysis found that the structure of compound (II) consists of one molecule of  $[\text{Ru}^{\text{II}}(\text{MeOpyO})_2(\text{terpy})(\text{H}_2\text{O})]$ , one uncoordinated molecule of water and one uncoordinated molecule of acetonitrile. In the complex molecule, the Ru atom is surrounded by a distorted octahedral arrangement of donors from one tridentate terpy ligand, two MeOpyO ligands coordinated *trans* with respect to each other through their N atoms, and an aqua ligand (Fig. 1 and Table 1). The Ru–N and Ru–O<sub>aqua</sub> distances typical for polypyridyl  $\text{Ru}^{\text{II}}$  complexes and the two easily located aqua H atoms confirm the  $\text{Ru}^{\text{II}}$ –aqua oxidation–protonation state of this complex (Hecker *et al.*, 1991; Rasmussen *et al.*, 1995; Grover *et al.*, 1992). The geometry of the terpy ligand and its coordination are as expected. The alternating long–short C–C bond distances around the MeOpyO rings and the relatively short C16,C22–O distances are consistent with the pyridonate (*versus* the hydroxypyridinate) resonance form of MeOpyO. The solvent acetonitrile and disordered water molecules exhibit only weak interactions with other molecules within the unit cell and have no apparent impact on the structure of the complex. The lack of lattice interactions with the water molecule may be responsible for its disorder into three positions of 44.7 (12), 38.2 (11) and 17.1 (6)% occupation.

Interligand hydrogen bonds between the MeOpyO carbonyl O atoms and the aqua ligands (Table 2) close a pair of fused six-membered metallocycles. This concerted  $S(6)S(6)$  interaction appears to be responsible for stabilizing the rare monodentate coordination of the MeOpyO ligands and aligning their planes to a nearly eclipsed dihedral angle of 12.66 (4) Å. The strong hydrogen bonds to the aqua ligand

also appear to tip the MeOpyO planes toward the hydrogen-bond vectors, resulting in a mean dihedral angle of  $84.33(6)^\circ$  with the equatorial plane. Compounds (I) and (II) appear to be rare examples of clean  $S(6)S(6)$  interligand hydrogen bonding in transition metal complexes. Among the few monodentate pyO complexes reported only [Pt(NH<sub>3</sub>)<sub>2</sub>(pyO)-Cl<sub>3</sub>] has  $S(6)$  intramolecular hydrogen bonding confirmed crystallographically, but this interaction is considered secondary to intermolecular hydrogen bonding to donors in adjacent molecules (Hollis & Lippard, 1983). Intramolecular hydrogen bonds are also implied by short N—O distances within *trans*-[(CH<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>Pt(pyO)(pyOH)](NO<sub>3</sub>), but the protons were not located and the structure is dominated by intermolecular hydrogen bonding between ambiguously averaged pyO and pyOH ligands (Schreiber *et al.*, 1994). Interligand  $S(6)$  hydrogen bonding has also been reported in a tetraacetate ruthenium(III) dimer where capping 7-azaindole ligands interact through N—H bonds with proximal acetate O atoms (Bland *et al.*, 2005). Again, these intramolecular interactions are considered secondary to intermolecular hydrogen bonds to PF<sub>6</sub><sup>-</sup> counter-ions.

Though bond distances and angles are experimentally indistinguishable between the structure of complex (II) and that reported for complex (I), the two compounds exhibit significant differences in the orientations of the pyO and MeOpyO rings. The MeOpyO ligands of complex (II) are rotated by a mean angle of  $39.6(2)^\circ$  away from the pseudo-plane bisecting the terpy ligand, as compared with the slightly smaller mean angle of  $35.1(2)^\circ$  for the pyO ligands of complex (I). The MeOpyO ligands of complex (II) are also tipped slightly further from perpendicularity with the equatorial plane than the pyO ligands of complex (I) [ $84.33(6)$  *versus*

$85.41(5)^\circ$ , respectively]. The ligand conformation differences may reflect a stronger  $S(6)S(6)$  interaction in complex (II) owing to greater basicity of the MeOpyO *versus* pyO ligands. The ligand conformations may also have electronic consequences on the complex. The larger rotation angle for the MeOpyO ligand could subtly shift ligand–metal  $\pi$ -interactions from one coordinate axis toward the other, and the larger tip in the MeOpyO plane could encourage stronger orbital overlap between the ligand  $\pi$ -system and the ruthenium center. An *ab initio* investigation is underway to confirm the electronic significance of the ligand conformations and their importance to the catalytic reaction.

## Experimental

The title compound was prepared by refluxing Ru<sup>III</sup>Cl<sub>3</sub>(terpy) (0.10 g) with 3-methoxy-2-pyridinol (0.13 g) in a mixture of ethanol (38 ml) and 0.30 M aqueous sodium hydroxide (19 ml) for 1 h followed by crystallization upon rotoevaporation to 6 ml volume. <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  9.34 (2H, *d*, 5.6 Hz), 8.50 (2H, *d*, 8.4 Hz), 8.44 (2H, *d*, 8.0 Hz), 7.90 (2H, *m*), 7.80 (1H, *t*, 8.0 Hz), 7.64 (2H, *t*, 6.0 Hz), 6.32 (2H, *dd*, 7.2, 1.6 Hz), 5.42 (2H, *m*), 5.36 (2H, *m*), 3.47 (6H, *s*). Addition of hexane to an acetonitrile solution of the product afforded black irregular crystals of the title compound that grew over several days at room temperature.

### Crystal data

[Ru(C <sub>6</sub> H <sub>6</sub> NO <sub>2</sub> ) <sub>2</sub> (C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> )(H <sub>2</sub> O)]·C <sub>2</sub> H <sub>5</sub> N·H <sub>2</sub> O	$V = 2894.1(6) \text{ \AA}^3$
	$Z = 4$
$M_r = 659.66$	$D_x = 1.514 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.5695(10) \text{ \AA}$	$\mu = 0.60 \text{ mm}^{-1}$
$b = 13.8950(16) \text{ \AA}$	$T = 100 \text{ K}$
$c = 22.229(3) \text{ \AA}$	Irregular, black
$\beta = 101.720(9)^\circ$	$0.4 \times 0.2 \times 0.1 \text{ mm}$

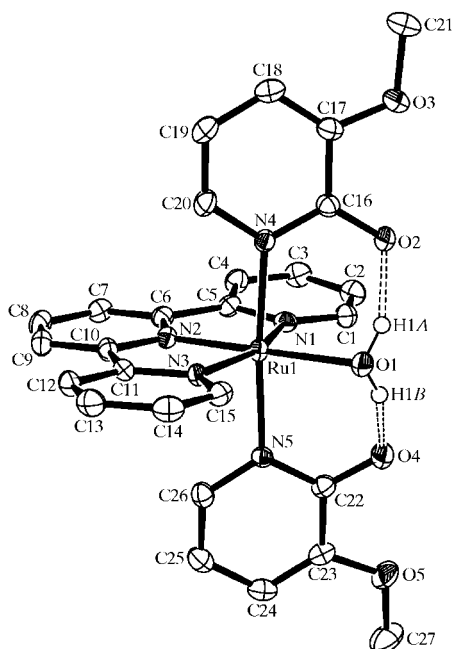
### Data collection

Oxford Diffraction Sapphire-3 CCD diffractometer	55112 measured reflections
$\varphi$ and $\omega$ scans	8112 independent reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	7939 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.863$ , $T_{\max} = 0.944$	$R_{\text{int}} = 0.036$
	$\theta_{\max} = 30^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0261P)^2 + 10.7726P]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.10$	$\Delta\rho_{\max} = 1.87 \text{ e \AA}^{-3}$
8112 reflections	$\Delta\rho_{\min} = -0.76 \text{ e \AA}^{-3}$
394 parameters	
H atoms treated by a mixture of independent and constrained refinement	

H atoms bound to carbon were positioned with idealized geometry ( $Csp^2-H = 0.93 \text{ \AA}$  and  $Csp^3-H = 0.96 \text{ \AA}$ ) and assigned isotropic displacement parameters equal to  $1.2U_{\text{eq}}$  or  $1.5U_{\text{eq}}$  of the parent  $Csp^2$  or  $Csp^3$  atoms, respectively. H atoms on the aqua ligand and solvent water molecule were found in a difference Fourier synthesis and were first refined without restraints, which resulted in a large electron-density peak (approximately  $2.60 \text{ e \AA}^{-3}$ ) located  $0.88 \text{ \AA}$  from the solvent water O atom. The solvent water molecule was remodeled as disordered between two orientations, where the H atoms for the new position were initially located by Fourier synthesis. To obtain satis-



**Figure 1**

A view of the title ruthenium complex, (II), drawn with 50% probability displacement ellipsoids. Solvent molecules are not shown. The hydrogen bonds are depicted with dashed lines.

**Table 1**

Selected geometric parameters (Å, °).

Ru1—O1	2.163 (2)	N4—C20	1.365 (3)
Ru1—N1	2.084 (3)	N5—C22	1.372 (4)
Ru1—N2	1.933 (2)	N5—C26	1.360 (4)
Ru1—N3	2.043 (2)	C16—C17	1.443 (4)
Ru1—N4	2.124 (2)	C17—C18	1.366 (4)
Ru1—N5	2.131 (2)	C18—C19	1.411 (5)
O2—C16	1.281 (3)	C19—C20	1.362 (5)
O3—C17	1.370 (4)	C22—C23	1.445 (4)
O4—C22	1.283 (4)	C23—C24	1.360 (5)
O5—C23	1.371 (4)	C24—C25	1.410 (5)
N4—C16	1.370 (4)	C25—C26	1.366 (4)
<hr/>			
N1—Ru1—N2	80.47 (10)	N2—Ru1—N3	80.81 (10)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1A...O2	0.837 (19)	1.78 (3)	2.561 (3)	155 (5)
O1—H1B...O4	0.831 (19)	1.76 (3)	2.550 (3)	159 (5)

factory behavior for the two disordered solvent water positions, the O—H bond lengths were fixed at 0.83 (2) Å, 1,3 H...H distances were fixed at 1.31 (4) Å, isotropic O-atom displacement parameters were allowed to refine, and isotropic H-atom displacement parameters were assigned equal to 1.5 $U_{eq}$  of the corresponding O atom. The model converged to a 71 (2)/29 (2)% occupation of the two orientations, with a large residual electron-density peak (approximately 1.33 e Å<sup>-3</sup>) located 0.08 Å from a solvent water H atom. The solvent water molecule was then remodeled as disordered between the two existing orientations and a third O atom, positioned on the large residual electron-density peak. Attempts to refine the isotropic displacement parameter on the third solvent water O atom and locate its H atoms were unsuccessful and one H atom on O1WB refined impossibly close to H2SC of the acetonitrile solvent molecule. The three solvent water O-atom positions were finally refined without their H atoms and with a single isotropic displacement parameter. The model converged to a 46.5 (11)/37.8 (11)/15.8 (7)% occupation of the three orientations. The final difference map was relatively flat, with its residual maximum and minimum in close proximity (0.71 and 0.65 Å, respectively) to atom Ru1.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

This material is based on work supported by the National Science Foundation under grant No. 0321389. The authors gratefully acknowledge the Petroleum Research Fund administered by the American Chemical Society, the Camille and Henry Dreyfus Foundation, and NIH SCORE (S06 GM48680) for financial support for this research.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3063). Services for accessing these data are described at the back of the journal.

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