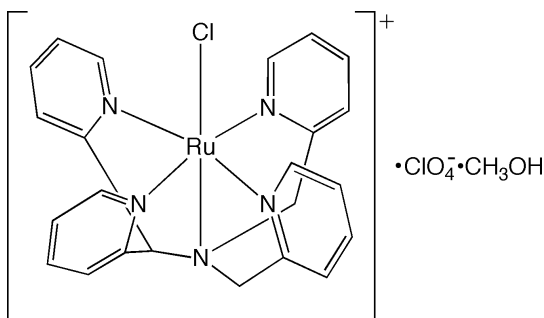


Takahiko Kojima,<sup>a\*</sup> David M.  
Weber<sup>b</sup> and Christin T. Choma<sup>b\*</sup><sup>a</sup>Department of Chemistry, Faculty of Sciences,  
Kyushu University, 6-10-1 Hakozaki, Higashi-  
Ku, Fukuoka 812-8581, Japan, and <sup>b</sup>Department  
of Chemistry, Rensselaer Polytechnic Institute,  
Troy, NY 12180-3590, USACorrespondence e-mail:  
cosyscc@mbox.nc.kyushu-u.ac.jp

## Key indicators

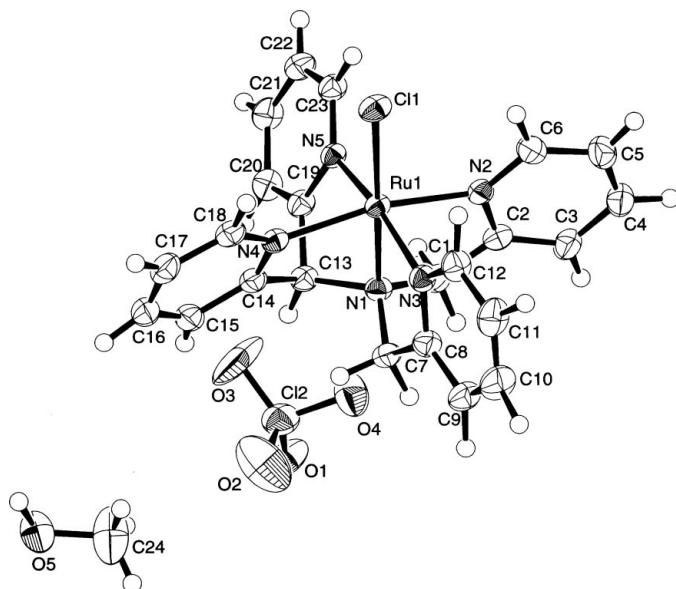
Single-crystal X-ray study  
*T* = 113 K  
Mean  $\sigma(\text{C}-\text{C})$  = 0.006 Å  
*R* factor = 0.044  
*wR* factor = 0.119  
Data-to-parameter ratio = 17.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**{*N*-[Bis(2-pyridyl)methyl]-*N,N*-bis(2-pyridyl-  
methyl)amine- $\kappa^5 N$ ]chlororuthenium(II) perchlorate  
methanol solvate**The structure of the title compound,  $[\text{RuCl}(\text{C}_{23}\text{H}_{21}\text{N}_5)]\text{-ClO}_4\cdot\text{CH}_4\text{O}$ , has been determined at 113 K, revealing a mononuclear six-coordinate structure with a 0.263 (2) Å displacement of the  $\text{Ru}^{\text{II}}$  atom from the  $\text{N}_4$  equatorial plane.

## Comment

Ruthenium complexes with multidentate pyridylamine derivatives as ligands have been shown to perform catalytic hydrocarbon oxygenation with use of various terminal oxidants. Among these, we and other groups have reported catalytic alkane oxygenation by ruthenium complexes with tris(2-pyridylmethyl)amine (TPA) and its derivatives as ligands (Kojima, 1996; Yamaguchi *et al.*, 1997; Kojima & Matsuda, 1999; Kojima, Matsuo & Matsuda, 2000; Jitsukawa *et al.*, 2001; Yamaguchi *et al.*, 2004). Recently, Yamaguchi and co-workers have reported on those reactions of a  $\text{Ru}^{\text{II}}$  complex with *N*-[tris(2-pyridyl)methyl]-*N,N*-tris(2-pyridyl)methylamine ( $\text{N}_4\text{py}$ ) (Lubben *et al.*, 1995; Roelfes *et al.*, 1997) in  $\text{CHCl}_3$  with *m*-chloroperbenzoic acid (Yamaguchi *et al.*, 2002). However, no crystal structure has been reported of the catalyst,  $[\text{RuCl}(\text{N}_4\text{py})]^+$ . In order to set up a baseline to consider the reactivity and properties of the title complex, (I), we determined the crystal structure of its perchlorate salt.

(I)

Compound (I) is depicted in Fig. 1, showing the atomic numbering scheme, and selected bond lengths and angles are given in Table 1. The  $\text{Ru}^{\text{II}}$  center in (I) exhibits a distorted octahedral geometry, with a displacement of 0.263 (2) Å toward the chloro ligand from the equatorial least-squares plane consisting of atoms  $\text{N}2-\text{N}5$ . This value is smaller than that in  $[\text{ZnCl}(\text{N}_4\text{py})]\text{ClO}_4\cdot\text{H}_2\text{O}$  [0.502 (2) Å; Kojima, Weber & Choma, 2004]. The bond lengths around the  $\text{Ru}^{\text{II}}$  center are comparable to those observed for other  $\text{Ru}^{\text{II}}$ -TPA complexes reported so far (Kojima *et al.*, 1998, 2003; Kojima, Hayashi & Matsuda, 2000, 2004; Kojima & Matsuda, 2001; Kojima, Sakamoto & Matsuda, 2004; Kojima, Miyazaki *et al.*, 2004).



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The dihedral angles of the planes of the pyridine rings relative to the equatorial mean plane were estimated to be  $96.0(1)^\circ$  for the pyridine ring containing N2,  $83.0(1)^\circ$  for that with N3,  $110.3(1)^\circ$  for that with N4, and  $64.4^\circ$  for that with N5. The pyridine ring containing N5, which is connected to a methine C atom of N<sub>4</sub>py, undergoes severe distortion from an ideal orientation (*ca*  $90^\circ$ ) toward the equatorial plane. In the crystal structure, an intermolecular hydrogen bond was observed between the chloro ligand and the OH group of the methanol molecule [ $3.158(3)$  Å; Table 2].

## Experimental

$[\text{RuCl}(\text{N}_4\text{py})]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$  was prepared by refluxing  $[\text{RuCl}_2(\text{DMSO})_4]$  (90 mg,  $1.9 \times 10^{-4}$  mol) with  $\text{N}_4\text{py} \cdot \text{HClO}_4$  (87 mg,  $1.9 \times 10^{-4}$  mol) in methanol (10 ml) for 24 h. After filtration, the solvent was removed by a rotary evaporator. The crude product was recrystallized from methanol with vapor diffusion of diethyl ether to give red crystals of the title compound.

### Crystal data

$[\text{RuCl}(\text{C}_{23}\text{H}_{21}\text{N}_5)]\text{ClO}_4 \cdot \text{CH}_4\text{O}$	$D_x = 1.650 \text{ Mg m}^{-3}$
$M_r = 635.47$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 31 496 reflections
$a = 14.768(2) \text{ \AA}$	$\theta = 2.2\text{--}27.5^\circ$
$b = 13.048(2) \text{ \AA}$	$\mu = 0.87 \text{ mm}^{-1}$
$c = 15.084(2) \text{ \AA}$	$T = 113.2 \text{ K}$
$\beta = 118.349(3)^\circ$	Block, red
$V = 2558.0(5) \text{ \AA}^3$	$0.48 \times 0.45 \times 0.20 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer	5745 independent reflections
$\omega$ scans	4780 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.042$
$T_{\text{min}} = 0.444$ , $T_{\text{max}} = 0.841$	$\theta_{\text{max}} = 27.5^\circ$
17 293 measured reflections	$h = -19 \rightarrow 19$
	$k = -16 \rightarrow 16$
	$l = -19 \rightarrow 19$

### Refinement

Refinement on $F^2$	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + [0.06(\max(F_o^2, 0) + 2F_c^2/3)]^2]$
$wR(F^2) = 0.120$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.32$	$\Delta\rho_{\text{max}} = 1.18 \text{ e \AA}^{-3}$
5743 reflections	$\Delta\rho_{\text{min}} = -1.24 \text{ e \AA}^{-3}$
334 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Ru1—Cl1	2.4162 (8)	Ru1—N3	2.062 (3)
Ru1—N1	2.036 (3)	Ru1—N4	2.059 (3)
Ru1—N2	2.060 (3)	Ru1—N5	2.047 (3)
Cl1—Ru1—N1	179.28 (8)	N1—Ru1—N5	82.0 (1)
Cl1—Ru1—N2	97.27 (8)	N2—Ru1—N3	85.0 (1)
Cl1—Ru1—N3	96.94 (8)	N2—Ru1—N4	165.6 (1)
Cl1—Ru1—N4	97.16 (8)	N2—Ru1—N5	93.3 (1)
Cl1—Ru1—N5	97.85 (7)	N3—Ru1—N4	93.7 (1)
N1—Ru1—N2	83.4 (1)	N3—Ru1—N5	165.2 (1)
N1—Ru1—N3	83.2 (1)	N4—Ru1—N5	84.25 (10)
N1—Ru1—N4	82.1 (1)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
$\text{O5—H25} \cdots \text{Cl1}^i$	0.93	2.23	3.158 (3)	174

Symmetry code: (i)  $-x + 1, +y + \frac{1}{2}, -z + \frac{3}{2}$ .

All H atoms were placed at ideal positions ( $\text{C—H} = 0.95 \text{ \AA}$ ), except H25, which was located in a difference Fourier map, and were refined as riding [ $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ ]. The maximum residual peak in the final Fourier map was found in the vicinity of the Ru ion.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* Version 1.11 (Molecular Structure Corporation & Rigaku Corporation, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN* Version 1.10 (Molecular Structure Corporation, 1985–1999); molecular graphics: *TEXSAN* Version 1.11; software used to prepare material for publication: *TEXSAN* Version 1.11.

We are grateful to Professor Ken Sakai (Department of Chemistry, Faculty of Sciences, Kyushu University) for his help in preparing this manuscript.

## References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A. & Polidoli, G. (1994). *J. Appl. Cryst.* **27**, 435.  
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.  
 Jitsukawa, K., Oka, Y., Einaga, H. & Masuda, H. (2001). *Tetrahedron Lett.* **42**, 3467–3469.  
 Kojima, T. (1996). *Chem. Lett.* pp. 121–122.  
 Kojima, T., Amano, T., Ishii, Y., Ohba, M., Okaue, Y. & Matsuda, Y. (1998). *Inorg. Chem.* **37**, 4076–4085.  
 Kojima, T., Hayashi, K. & Matsuda, Y. (2000). *Chem. Lett.* pp. 1008–1009.  
 Kojima, T., Hayashi, K. & Matsuda, Y. (2004). *Inorg. Chem.* **43**, 6793–6804.  
 Kojima, T. & Matsuda, Y. (1999). *Chem. Lett.* pp. 81–82.  
 Kojima, T. & Matsuda, Y. (2001). *J. Chem. Soc. Dalton Trans.* pp. 958–960.  
 Kojima, T., Matsuo, H. & Matsuda, Y. (2000). *Inorg. Chim. Acta*, **300–302**, 661–667.  
 Kojima, T., Miyazaki, S., Hayashi, K., Shimazaki, Y., Tani, F., Naruta, Y. & Matsuda, Y. (2004). *Chem. Eur. J.* **10**, 6402–6410.  
 Kojima, T., Sakamoto, T. & Matsuda, Y. (2004). *Inorg. Chem.* **43**, 2243–2245.

- Kojima, T., Sakamoto, T., Matsuda, Y., Ohkubo, K. & Fukuzumi, S. (2003). *Angew. Chem. Int. Ed.* **43**, 4951–4954.
- Kojima, T., Weber, D. M. & Choma, C. T. (2004). *Acta Cryst.* **E60**, m1291–m1292.
- Lubben, M., Meetsma, A., Wilkinson, E. C., Feringa, B. L. & Que, L. Jr (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1512–1514.
- Molecular Structure Corporation (1985–1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Molecular Structure Corporation & Rigaku Corporation (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku, 3-9-12 Akishima, Tokyo, Japan.
- Roelfes, G., Lubben, M., Leppard, S. W., Schudde, E. P., Hermant, R. M., Hage, R., Wilkinson, E. C., Que, L. Jr & Feringa, B. L. (1997). *J. Mol. Cat. A*, **117**, 223–227.
- Rigaku Corporation (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Yamaguchi, M., Ichii, Y., Kosaka, S., Masui, D. & Yamagishi, T. (2002). *Chem. Lett.* pp. 434–435.
- Yamaguchi, M., Kousaka, H. & Yamagishi, T. (1997). *Chem. Lett.* pp. 769–770.
- Yamaguchi, M., Kumano, T., Masui, D. & Yamagishi, T. (2004). *Chem. Commun.* pp. 798–799.