

# *trans*-Dichloridotetrakis(pyridine- $\kappa$ N)rhodium(III) chloride methanol tetrasolvate

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Received 17 October 2018

Accepted 19 October 2018

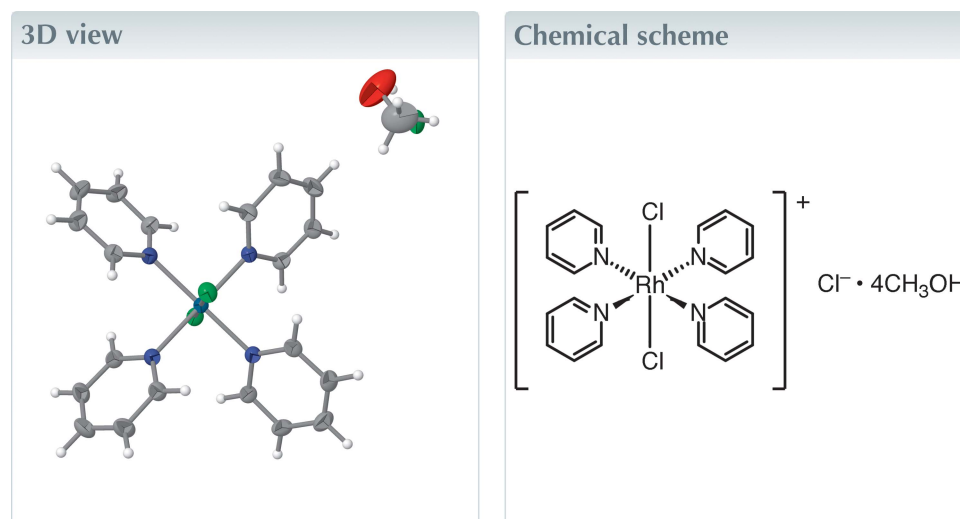
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; rhodium(III) complex; pyridine complex; hydrogen bonds.

CCDC reference: 1874254

Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

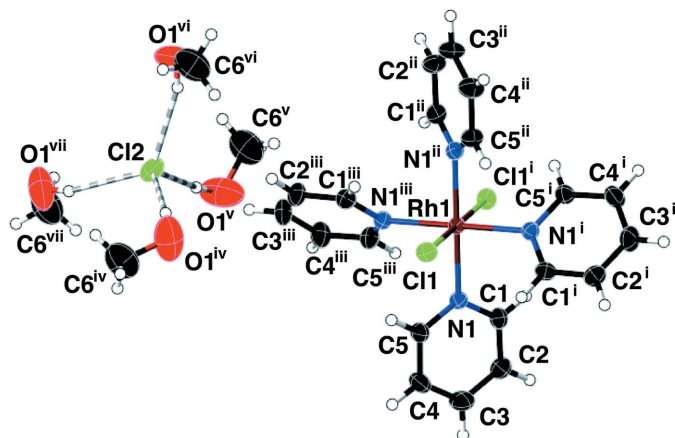
In the solvated title salt,  $[\text{RhCl}_2(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}\cdot 4\text{CH}_3\text{OH}$ , the  $\text{Rh}^{\text{III}}$  atom lies on a special position of 2.22 site symmetry. Consequently, the cationic complex has molecular  $D_2$  symmetry with a *trans* disposition for two equivalent  $\text{Cl}^-$  and four equivalent pyridine ligands. The  $\text{Rh}-\text{Cl}$  and  $\text{Rh}-\text{N}$  bond lengths are 2.3452 (7) and 2.064 (2) Å, respectively. The planes of the coordinating pyridine ligands are tilted synchronously, with a dihedral angle of 40.76 (9)° between the least-squares pyridine plane and the coordination plane defined by the  $\text{Rh}^{\text{III}}$  and four pyridine N atoms. The chloride counter-anion is located on a crystallographic  $\bar{4}$ . site, and is surrounded by four methanol molecules to which it is bound in a pseudo-tetrahedral arrangement by  $\text{O}-\text{H}\cdots\text{Cl}$  hydrogen bonds.



## Structure description

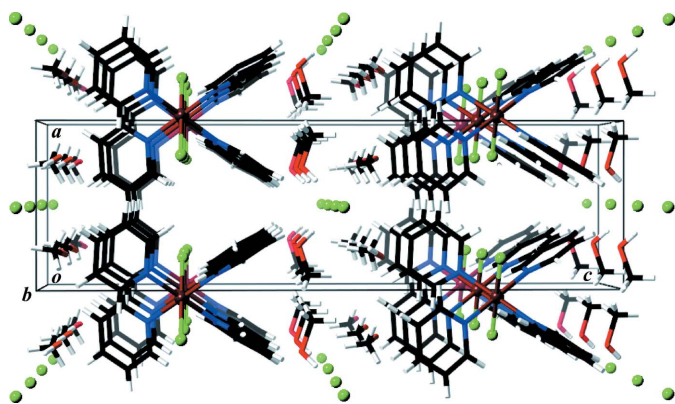
Mixed-ligand rhodium(III) complexes with chlorido and pyridine ligands have been known since the 1880s (Jørgensen, 1883). Their composition, structures and properties were reexamined very carefully by Gillard & Wilkinson (1964). They concluded that the highest stable species is the *trans*-dichloridotetrakis(pyridine)rhodium(III) cation. Up to now, several crystal structures of this complex with different counter-anions have been reported: hydrogen dinitrate (Dobinson *et al.*, 1967), dinitratoargentate(I) (Gillard *et al.*, 1990), perchlorate, perrhenate (Vasilchenko *et al.*, 2009), thiocyanate and 2-hydroxybenzoate (Vasil'chenko *et al.*, 2015). However, one of the most simple complex salts, the chloride, has not been reported so far.

The title complex salt, *trans*- $[\text{RhCl}_2(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}$ , crystallizes with four molecules of methanol in the space group  $P\bar{4}c2$ . The  $\text{Rh}^{\text{III}}$  atom lies on a special position of 2.22 site symmetry (Wyckhoff position 2a), the chlorido ligand (Cl1) on a position with ..2 symmetry (4f), and the non-coordinating  $\text{Cl}^-$  anion (Cl2) is located on a  $\bar{4}$ . site (2d). In addition, the asymmetric unit contains a molecule of pyridine (py) and a molecule of



**Figure 1**  
View of the molecular components of the solvated title salt, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are shown as an ideal sphere with a radius of 0.15 Å. The striped bonds indicate hydrogen bonds between Cl and H atoms. [Symmetry codes: (i)  $-x, -y, z$ ; (ii)  $-y, -x, -z + \frac{1}{2}$ , (iii)  $y, x, -z + \frac{1}{2}$ ; (iv)  $-x + 1, y + 1, z$ ; (v)  $-y + 1, x, -z$ ; (vi)  $y, x + 1, -z$ .]

methanol, both in general sites. Expanding the symmetry operations gives molecular units of a cationic  $\text{Rh}^{\text{III}}$  complex,  $\text{trans-}[\text{RhCl}_2(\text{py})_4]^+$ , and a tetra(methanol) solvated  $\text{Cl}^-$  anion (Fig. 1). The resulting cationic complex exhibits molecular  $D_2$  symmetry. The Rh–Cl and Rh–N bond lengths are 2.3452 (7) and 2.064 (2) Å, respectively. The Cl–Rh–N and N–Rh–N bond angles are close, but not strictly equal, to  $90^\circ$ . Similar to previously reported structures (Dobinson *et al.*, 1967; Gillard *et al.*, 1990; Vasilchenko *et al.*, 2009; Vasilchenko *et al.*, 2015), the planes of the coordinating pyridine are tilted synchronously with respect to the  $\text{RhN}_4$  coordination plane. The dihedral angle between the least-squares pyridine plane and the coordination plane defined by the Rh and four N atoms is  $40.76(9)^\circ$ . The hydrogen-bonded anionic  $[\text{Cl}(\text{CH}_3\text{OH})_4]^-$  unit exhibits a pseudo-tetrahedral arrangement (Fig. 1, Table 1). The packing of the molecular entities in the crystal structure is shown in Fig. 2.



**Figure 2**  
A packing diagram of the solvated title salt, in a view along the *b* axis. Colour code: purple, Rh; green, Cl; red, O; blue, N; black, C; and white, H.

**Table 1**  
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–H1···Cl2	0.84	2.32	3.110 (4)	156

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$[\text{RhCl}_2(\text{C}_5\text{H}_5\text{N})_4]\text{Cl}\cdot 4\text{CH}_3\text{O}$
$M_r$	653.83
Crystal system, space group	Tetragonal, $P4c2$
Temperature (K)	163
<i>a</i> , <i>c</i> (Å)	7.6130 (7), 26.461 (3)
<i>V</i> (Å <sup>3</sup> )	1533.7 (3)
<i>Z</i>	2
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.85
Crystal size (mm)	0.70 × 0.60 × 0.30
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Numerical ( <i>NUMABS</i> ; Higashi, 1999)
$T_{\text{min}}$ , $T_{\text{max}}$	0.611, 0.775
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	13753, 1749, 1605
$R_{\text{int}}$	0.038
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , <i>S</i>	0.022, 0.047, 1.03
No. of reflections	1749
No. of parameters	85
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.22, -0.48
Absolute structure	Flack <i>x</i> determined using 652 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.043 (19)

Computer programs: *RAPID-AUTO* (Rigaku, 2006), *SIR2014* (Burla *et al.*, 2012), *SHELXL2014* (Sheldrick, 2015) and *CrystalMaker* (Palmer *et al.*, 2017).

## Synthesis and crystallization

The hydrated complex chloride,  $\text{trans-}[\text{RhCl}_2(\text{py})_4]\text{Cl}\cdot 5\text{H}_2\text{O}$ , was prepared from  $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$  and pyridine in refluxing water, according to the method described in our previous paper (Suzuki *et al.*, 1995). The product was recrystallized from methanol, affording yellow platelet methanol tetrasolvate crystals of the title compound.

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## Funding information

Funding for this research was provided by: Grant-in-Aid for Scientific Research No. 18K05146 from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

## References

- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Mallamo, M., Mazzone, A., Polidori, G. & Spagna, R. (2012). *J. Appl. Cryst.* **45**, 357–361.
- Dobinson, G. C., Mason, R. & Russell, D. R. (1967). *Chem. Commun. (London)*, pp. 62–63.
- Gillard, R. D., Hanton, L. R. & Mitchell, S. H. (1990). *Polyhedron*, **9**, 2127–2133.
- Gillard, R. D. & Wilkinson, G. (1964). *J. Chem. Soc.* pp. 1224–1228.
- Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
- Jørgensen, S. M. (1883). *J. Prakt. Chem.* **27**, 433–489.
- Palmer, D., Conley, M., Parsonson, L., Rimmer, L. & Stenson, I. (2017). *CrystalMaker*. CrystalMaker Software Ltd, Bicester, England.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Rigaku (2006). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Suzuki, T., Isobe, K. & Kashiwabara, K. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3609–3616.
- Vasilchenko, D. B., Baidina, I. A., Filatov, E. Y. & Korenev, S. V. (2009). *J. Struct. Chem.* **50**, 335–342.
- Vasil'chenko, D. B., Venediktov, A. B., Baidina, I. A. & Korenev, S. V. (2015). *J. Struct. Chem.* **56**, 310–316.

## full crystallographic data

*IUCrData* (2018). 3, x181482 [https://doi.org/10.1107/S2414314618014827]

***trans*-Dichloridotetrakis(pyridine- $\kappa$ N)rhodium(III) chloride methanol tetrasolvate**

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*trans*-Dichloridotetrakis(pyridine- $\kappa$ N)rhodium(III) chloride methanol tetrasolvate

*Crystal data*

[RhCl<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>]Cl·4CH<sub>3</sub>O

$M_r = 653.83$

Tetragonal,  $P4c2$

$a = 7.6130$  (7) Å

$c = 26.461$  (3) Å

$V = 1533.7$  (3) Å<sup>3</sup>

$Z = 2$

$F(000) = 672$

$D_x = 1.416$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71075$  Å

Cell parameters from 13381 reflections

$\theta = 3.1$ – $27.5^\circ$

$\mu = 0.85$  mm<sup>-1</sup>

$T = 163$  K

Platelet, yellow

$0.70 \times 0.60 \times 0.30$  mm

*Data collection*

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.00 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: numerical

(NUMABS; Higashi, 1999)

$T_{\min} = 0.611$ ,  $T_{\max} = 0.775$

13753 measured reflections

1749 independent reflections

1605 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 3.1^\circ$

$h = -9 \rightarrow 9$

$k = -8 \rightarrow 9$

$l = -34 \rightarrow 34$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.047$

$S = 1.03$

1749 reflections

85 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2 + 0.2836P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.22$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.47$  e Å<sup>-3</sup>

Absolute structure: Flack  $x$  determined using

652 quotients  $[(I^+)-(I^-)]/[(I^+)+(I^-)]$  (Parsons *et al.*, 2013)

Absolute structure parameter:  $-0.043$  (19)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** The H atom of the methanol hydroxy group was located from a difference Fourier map. Afterwards it was refined using a riding model, with O—H = 0.84 Å. For other H atoms, C—H = 0.95 (aromatic) or 0.98 (methyl) Å, with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{O})$  were applied.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Rh1	0.0000	0.0000	0.2500	0.02029 (9)
Cl1	0.21783 (6)	−0.21783 (6)	0.2500	0.02777 (16)
Cl2	0.5000	0.5000	0.0000	0.0462 (3)
O1	0.7689 (6)	0.2828 (5)	0.06260 (15)	0.0971 (16)
H1	0.7245	0.3530	0.0417	0.116*
N1	0.1360 (4)	0.1368 (4)	0.19521 (6)	0.0238 (3)
C1	0.0516 (4)	0.2088 (4)	0.15529 (10)	0.0285 (6)
H1A	−0.0724	0.1973	0.1529	0.034*
C2	0.1408 (4)	0.2984 (4)	0.11805 (11)	0.0347 (6)
H2	0.0782	0.3457	0.0901	0.042*
C3	0.3185 (6)	0.3196 (6)	0.12101 (9)	0.0406 (6)
H3	0.3802	0.3823	0.0956	0.049*
C4	0.4079 (4)	0.2473 (4)	0.16217 (12)	0.0376 (7)
H4	0.5316	0.2598	0.1653	0.045*
C5	0.3125 (4)	0.1571 (4)	0.19829 (10)	0.0296 (6)
H5	0.3730	0.1075	0.2263	0.035*
C6	0.7411 (7)	0.1140 (7)	0.0467 (2)	0.0807 (15)
H6A	0.7246	0.1127	0.0100	0.097*
H6B	0.6359	0.0669	0.0632	0.097*
H6C	0.8429	0.0415	0.0556	0.097*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Rh1	0.02015 (11)	0.02015 (11)	0.02056 (14)	0.00233 (13)	0.000	0.000
Cl1	0.0266 (2)	0.0266 (2)	0.0301 (3)	0.0081 (3)	0.0019 (6)	0.0019 (6)
Cl2	0.0557 (4)	0.0557 (4)	0.0273 (5)	0.000	0.000	0.000
O1	0.095 (3)	0.082 (3)	0.115 (3)	0.028 (3)	−0.058 (3)	−0.027 (2)
N1	0.0238 (19)	0.0239 (19)	0.0236 (8)	0.0016 (7)	0.0009 (14)	−0.0002 (13)
C1	0.0256 (13)	0.0294 (14)	0.0305 (13)	0.0026 (10)	−0.0050 (10)	0.0010 (11)
C2	0.0383 (16)	0.0362 (16)	0.0297 (13)	0.0023 (13)	−0.0047 (12)	0.0102 (13)
C3	0.044 (3)	0.039 (3)	0.0387 (12)	−0.0061 (11)	0.006 (2)	0.014 (2)
C4	0.0258 (16)	0.0442 (19)	0.0428 (15)	−0.0060 (13)	−0.0012 (13)	0.0104 (14)
C5	0.0243 (14)	0.0344 (15)	0.0300 (12)	0.0014 (11)	−0.0031 (11)	0.0063 (11)
C6	0.072 (3)	0.059 (3)	0.111 (4)	0.013 (3)	−0.009 (3)	0.002 (3)

## Geometric parameters (Å, °)

Rh1—N1	2.0638 (17)	C1—H1A	0.9500
Rh1—N1 <sup>i</sup>	2.0638 (17)	C2—C3	1.365 (5)
Rh1—N1 <sup>ii</sup>	2.0638 (17)	C2—H2	0.9500
Rh1—N1 <sup>iii</sup>	2.0638 (17)	C3—C4	1.397 (5)
Rh1—Cl1	2.3452 (7)	C3—H3	0.9500
Rh1—Cl1 <sup>ii</sup>	2.3452 (7)	C4—C5	1.383 (4)
O1—C6	1.368 (6)	C4—H4	0.9500
O1—H1	0.8400	C5—H5	0.9500
N1—C5	1.355 (4)	C6—H6A	0.9800
N1—C1	1.352 (4)	C6—H6B	0.9800
C1—C2	1.377 (4)	C6—H6C	0.9800
N1—Rh1—N1 <sup>i</sup>	89.26 (10)	N1—C1—H1A	119.2
N1—Rh1—N1 <sup>ii</sup>	90.74 (10)	C2—C1—H1A	119.2
N1 <sup>i</sup> —Rh1—N1 <sup>ii</sup>	179.7 (2)	C3—C2—C1	120.4 (3)
N1—Rh1—N1 <sup>iii</sup>	179.7 (2)	C3—C2—H2	119.8
N1 <sup>i</sup> —Rh1—N1 <sup>iii</sup>	90.74 (10)	C1—C2—H2	119.8
N1 <sup>ii</sup> —Rh1—N1 <sup>iii</sup>	89.26 (10)	C2—C3—C4	118.8 (2)
N1—Rh1—Cl1	90.13 (12)	C2—C3—H3	120.6
N1 <sup>i</sup> —Rh1—Cl1	89.87 (12)	C4—C3—H3	120.6
N1 <sup>ii</sup> —Rh1—Cl1	89.87 (12)	C5—C4—C3	118.6 (3)
N1 <sup>iii</sup> —Rh1—Cl1	90.13 (12)	C5—C4—H4	120.7
N1—Rh1—Cl1 <sup>ii</sup>	89.87 (12)	C3—C4—H4	120.7
N1 <sup>i</sup> —Rh1—Cl1 <sup>ii</sup>	90.13 (12)	N1—C5—C4	122.4 (3)
N1 <sup>ii</sup> —Rh1—Cl1 <sup>ii</sup>	90.13 (12)	N1—C5—H5	118.8
N1 <sup>iii</sup> —Rh1—Cl1 <sup>ii</sup>	89.87 (12)	C4—C5—H5	118.8
Cl1—Rh1—Cl1 <sup>ii</sup>	180.0	O1—C6—H6A	109.5
C6—O1—H1	109.5	O1—C6—H6B	109.5
C5—N1—C1	118.2 (2)	H6A—C6—H6B	109.5
C5—N1—Rh1	120.8 (2)	O1—C6—H6C	109.5
C1—N1—Rh1	121.0 (2)	H6A—C6—H6C	109.5
N1—C1—C2	121.7 (3)	H6B—C6—H6C	109.5
C5—N1—C1—C2	1.0 (5)	C2—C3—C4—C5	0.0 (6)
Rh1—N1—C1—C2	-179.1 (2)	C1—N1—C5—C4	-0.3 (5)
N1—C1—C2—C3	-1.2 (6)	Rh1—N1—C5—C4	179.7 (2)
C1—C2—C3—C4	0.7 (6)	C3—C4—C5—N1	-0.2 (5)

Symmetry codes: (i)  $y, x, -z+1/2$ ; (ii)  $-x, -y, z$ ; (iii)  $-y, -x, -z+1/2$ .

## Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ Cl2	0.84	2.32	3.110 (4)	156