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Carbonyl(5-carboxypyridine-2-carboxylato-κ^2N,O^2)chlorobis(triphenylphosphine-κP)ruthenium(II) 0.345-hydrate benzene sesquisolvate

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.041
wR factor = 0.102
Data-to-parameter ratio = 18.8

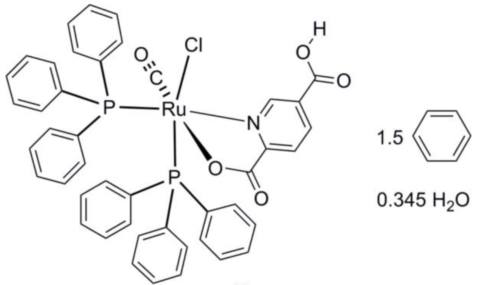
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound $[Ru(C_7H_4NO_4)Cl(C_{18}H_{15}P)_2(CO)]\cdot 1.5C_6H_6\cdot 0.345H_2O$, exhibits pairs of chains of hydrogen-bonded complex molecules that run parallel to the *a* axis with two different orientations, A and B, for the isocinchomeranic acid (pyridine-2,5-dicarboxylic acid) ligand as a result of disorder; the minor orientation B may occur in either strand, and is hydrogen bonded *via* a water molecule to a parallel chain of type A. 69% of the pairs of chains are of type A–B; the rest consist of chains in the combination A–A with no bridging water molecules.

Comment

Mixed-valence transition metal complexes are a fascinating tool for the investigation of electron-transfer processes and metal–metal interactions (Baitalik *et al.*, 2002; Ceccon *et al.*, 2004; Rocha & Toma, 2001) and, as such, they are also promising building blocks for the construction of redox-active molecular devices (Jones *et al.*, 2001; Amendola *et al.*, 2006; Kim & Lieber 1989; Constable & Thomson 1992; Toma *et al.*, 2001).

As part of our ongoing studies on the synthesis of binuclear redox-active metal complexes, we are especially interested in the synthesis of binuclear ruthenium compounds with various spacers such as *N*-hetero aromatic carboxylic acids that are planar, rigid and at the same time able to attach to the two metal centers in various coordination modes. To be able to prepare binuclear complexes of this type with different metal caps, we first reacted one of those ligands, 2,5-pyridinedicarboxylic acid, H_2dpc, with the ruthenium hydride $[RuHCl(CO)(PPh_3)_3]$ in a 1:1 ratio. Refluxing in ethanol yielded the title compound, (I), in 75% yield, and single crystals were grown from a benzene–ethanol mixture.



(I)

The description of the structure is complicated by the presence of two solvent benzene molecules (one of them on an inversion center), a site partially occupied with a water molecule disordered around another inversion center, and a slip-disorder of the 2,5-dicarboxypyridine ligand (Fig. 1). A close

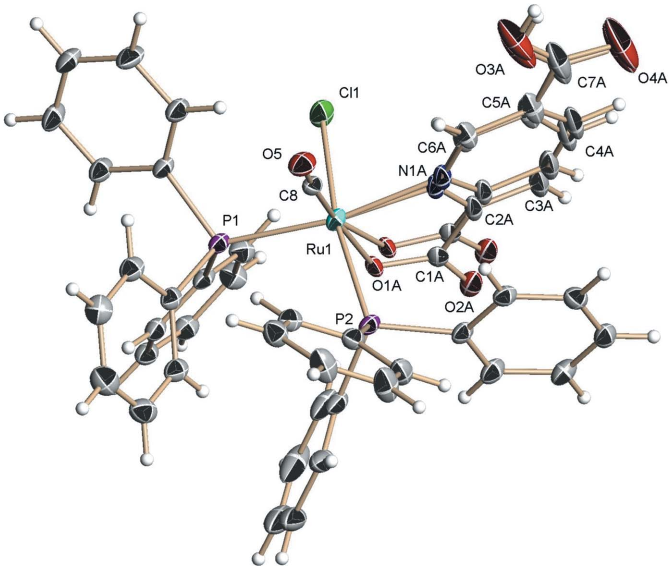


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and labels for the minor carboxylate ligand as well as the phenyl C atoms have been omitted for clarity. Both disorder components are shown.

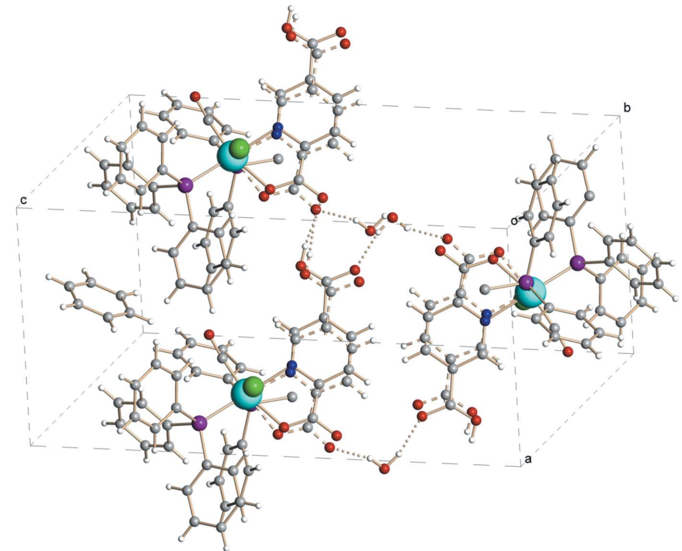


Figure 2
A depiction of the hydrogen-bonding interactions (dotted lines) between parallel chains. Dashed lines indicate the major component ligand A. Some benzene solvent molecules and phenyl substituents have been omitted for clarity.

inspection of the refined occupancies for both the water molecules and the disordered ligand, as well as an analysis of the intermolecular distances, contacts and possible hydrogen bonds, revealed that the two disorder features are systematically linked. The metal complexes are arranged in chains along the *a* axis that are connected *via* hydrogen bonds between the protonated and the unprotonated carboxylate groups of neighboring molecules. Within each chain, the ligands are all in either the major orientation A or the minor orientation B. Any combination of two neighboring ligands of different orientations would result in either very long or extremely short hydrogen-bonding interactions ($H\cdots O = 1.62$ and 2.50 Å for combinations of different orientations *versus* 1.91 and 2.25 Å for pairs from the same orientation). Combinations of A and B molecules within one chain thus seem to be unfavorable and may be present only as defects within the larger ordered chains of only A or B molecules.

Each of the chains of molecules is parallel to another chain of hydrogen-bonded ruthenium complexes running in the opposite direction. The site partially occupied by the disordered water molecule is located between the carboxylate groups of these parallel chains. The occupancy factors for this water molecule and the minor component ligand do refine to basically the same value and were treated as being identical (see refinement section for details). A close inspection of possible close contacts between the water molecule and the carboxylate O atoms reveals that the parallel chains cannot both consist of complexes with two ligands of the minor orientation B as this would result in a very close contact of atom O4*B* with the water molecule (1.87 Å). No such unfavorable interactions with the water molecules are observed for combinations of A and B chains.

The coordination environment of the metal center is as expected for an octahedral ruthenium complex and very similar for both of the ligand orientations. Selected bond lengths and angles are listed in Table 1, hydrogen-bonding parameters in Table 2, and an overview picture showing the hydrogen-bonding interactions and the arrangements of the A and B chains is shown in Fig. 2.

Therefore, the findings can be summarized in the following way. Pairs of chains of hydrogen-bonded complex molecules run parallel to the *a* axis. Only one of each pair of the strands can have ligands in the minor orientation B. If such a chain is present then it is hydrogen bonded *via* a water molecule to the parallel chain with ligands in the major orientation A. These A–B and B–A combinations make up 69% [2 × 34.5 (3)%] of the pairs of chains present. The remaining 31% consist of chains in the combination A–A. Whether it is the presence of the water molecules that induces the formation of the B chains or whether the presence of a B chain is the cause for the incorporation of the water molecules cannot be answered based only on the X-ray diffraction data. Nevertheless, the systematic combination of A–B pairs of chains with the presence of water molecules points towards a concerted effect of B chains and inclusion of water favoring each other, and whether a certain pair of chains is found as A–B or A–A might very well depend only on the accidental starting point for nucleation or an occasional defect within the chain.

Experimental

A benzene (20 ml) solution of $[RuHCl(CO)(PPh_3)_3]$ (Ahmad *et al.*, 1974) (0.095 g, 0.1 mmol) was added to a refluxing solution of isocinchomeranic acid (2,5-pyridine-dicarboxylic acid, H_2pdc) (0.018 g, 0.1 mmol) in ethanol (20 ml). The mixture was heated under reflux for 6 h. The solution was filtered while hot, reduced to half of its volume and left for slow evaporation. The crystalline product that separated out was filtered off, washed with ethanol and dichloromethane, and dried under vacuum. The product was recrystallized

m136 Sukanya *et al.* • $[Ru(C_7H_4NO_4)Cl(C_{18}H_{15}P)_2(CO)]\cdot 1.5C_6H_6$ *Acta Cryst.* (2007). E**63**, m135–m137

from a benzene/ethanol mixture to give pale-yellow crystals suitable for X-ray diffraction. Yield 75%. Analysis calculated for $C_{44}H_{34}NO_5ClP_2Ru$: C 61.79, H 4.00, N 1.63%; found: C 61.54, H 4.23, N 1.58%.

Crystal data

$[Ru(C_7H_4NO_4)Cl(C_{18}H_{15}P)_2(CO)]\cdot 1.5C_6H_6\cdot 0.345H_2O$
$M_r = 978.55$
Triclinic, $P\overline{1}$
$a = 9.9570$ (7) Å
$b = 11.0361$ (7) Å
$c = 22.9009$ (16) Å
$\alpha = 90.678$ (1)°
$\beta = 96.295$ (1)°
$\gamma = 115.790$ (1)°
$V = 2247.2$ (3) Å^3
$Z = 2$
$D_x = 1.446$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.53$ mm^{-1}
$T = 100$ (2) K
Block, pale yellow
0.39 × 0.39 × 0.29 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 2003)
$T_{min} = 0.739$, $T_{max} = 0.857$
23291 measured reflections
11106 independent reflections
10487 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 28.3$°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.102$
$S = 1.03$
11106 reflections
592 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 4.5218P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.42$ e Å^{-3}
$\Delta\rho_{min} = -1.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—Ru1	2.134 (4)	C8—Ru1	1.831 (2)
N1*A*—Ru1	2.050 (3)	Cl1—Ru1	2.4241 (6)
O1*B*—Ru1	2.119 (8)	P1—Ru1	2.3668 (6)
N1*B*—Ru1	2.239 (6)	P2—Ru1	2.3505 (6)
C8—Ru1—N1*A*	97.39 (15)	N1*A*—Ru1—P1	166.90 (19)
C8—Ru1—O1*B*	165.74 (19)	O1*B*—Ru1—P1	104.2 (2)
C8—Ru1—O1*A*	172.39 (13)	O1*A*—Ru1—P1	95.57 (9)
N1*A*—Ru1—O1*A*	78.48 (16)	N1*B*—Ru1—P1	167.9 (4)
C8—Ru1—N1*B*	91.8 (3)	P2—Ru1—P1	99.94 (2)
O1*B*—Ru1—N1*B*	73.9 (3)	C8—Ru1—Cl1	96.73 (7)
C8—Ru1—P2	91.50 (7)	N1*A*—Ru1—Cl1	80.5 (2)
N1*A*—Ru1—P2	90.9 (2)	O1*B*—Ru1—Cl1	80.9 (2)
O1*B*—Ru1—P2	89.2 (2)	O1*A*—Ru1—Cl1	88.93 (10)
O1*A*—Ru1—P2	82.24 (10)	N1*B*—Ru1—Cl1	80.1 (4)
N1*B*—Ru1—P2	92.0 (4)	P2—Ru1—Cl1	168.75 (2)
C8—Ru1—P1	89.74 (7)	P1—Ru1—Cl1	87.79 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*B*—H3*B*1···O2*B*^{i}	0.84	2.25	3.07 (2)	165
O3*A*—H3*A*1···O2*A*^{i}	0.84	1.91	2.747 (10)	173
O6—H6*C*···O4*B*	0.86	1.87	2.706 (11)	165
O6—H6*D*···O2*B*^{ii}	0.87	1.93	2.802 (12)	177
O6—H6*D*···O2*A*^{ii}	0.87	1.83	2.648 (9)	156

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

Two solvent benzene molecules are found in the asymmetric unit, one of which is located on an inversion center. Disordered around the other inversion center is a partially occupied water molecule. Associated with the presence (or absence) of this water molecule is a disorder of the 2,5-dicarboxypyridine ligand, which is shifted towards this water molecule *via* hydrogen bonding over both carboxylate groups. The occupancy factor for the water molecule was constrained to be identical with the occupancy factor for the minor component of the disordered ligand and refined to 0.345 (3); the remaining occupancy for the ligand in the absence of water is thus 0.655 (3). The combined occupancy for the water molecule site (disordered around the inversion center) is thus 0.690 (3) [2 × 0.345 (3)]. The disordered 2,5-dicarboxypyridine ligand was modeled in the following way. In both components the aromatic rings were constrained to be ideal hexagons with a side length of 1.39 Å. The remaining bond distances were restrained to be identical for both orientations (within a standard deviation of 0.02 Å). All atoms equivalent by chemical symmetry within the disordered moiety were constrained to have identical anisotropic displacement parameters, and were also restrained to be isotropic within a standard deviation of 0.01 Å^2. The carboxylate groups were further restrained to be flat within a standard deviation of 0.1 Å.

All H atoms were placed in calculated positions (C—H = 0.95 Å, O—H = 0.84–0.87 Å) and were refined as riding with $U_{iso}(H) = 1.5U_{eq}(O)$ or $1.2U_{eq}(C)$. The water H atoms could not be reliably located in the difference Fourier map and thus their placement was based on the most likely hydrogen-bonding interactions, using distance restraints. Methyl and carboxylic acid OH groups were allowed to rotate to better fit the observed electron density. The s.u. values of the cell parameters are taken from the software recognizing that the values are unreasonably small (Herbstein, 2000). The highest peak was found at 0.62 Å from O4*A* and the deepest hole 0.65 Å from Ru1.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Acta Cryst. (2007). E**63**, m135–m137 Sukanya *et al.* • $[Ru(C_7H_4NO_4)Cl(C_{18}H_{15}P)_2(CO)]\cdot 1.5C_6H_6$ **m137**