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Di-μ-acetato-κ^4*O*:*O′*-tetracarbonylbis(pyridyl-2-yl-κ*N*-amine)diruthenium(**I**)(*Ru*—*Ru*)

Reto Dorta,‡ Georg Süss-Fink and Helen Stoeckli-Evans*

Institut de Chimie, Université de Neuchâtel,
Avenue de Bellevaux 51, CH-2000 Neuchâtel,
Switzerland

‡ Present address: The Arnold and Mabel
Beckman Laboratories of Chemical Synthesis,
California Institute of Technology, Pasadena,
California 91125, USA.

Correspondence e-mail:
helen.stoeckli-evans@unine.ch

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The structure of the title compound, $[Ru_2(C_2H_3O_2)_2(C_5H_6N_2)_2(CO)_4]$, consists of a ‘sawhorse’ diruthenium complex with two acetate bridges and two 2-aminopyridine ligands in the axial positions, coordinating *via* the pyridine N atoms. A double-stranded hydrogen-bonded chain is formed *via* intra- and intermolecular hydrogen bonds involving the amine groups, one O atom of both acetate groups and two carbonyl O atoms.

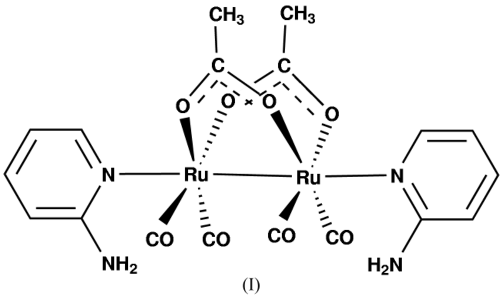
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.025
wR factor = 0.058
Data-to-parameter ratio = 13.4

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

Comment

Binuclear ruthenium(I) ‘sawhorse’ complexes of the type $[Ru_2(CO)_4(\mu_2,\eta^2\text{-}OOCR)_2L_2]$ were first discovered by Crooks *et al.* (1969). These complexes were prepared by refluxing $[Ru_3(CO)_{12}]$ with the corresponding acid (RCO_2H), which led first to the formation of the polymer $[Ru_2(CO)_4(\mu_2,\eta^2\text{-}OOCR)_2]_n$. The latter was then dissolved in a coordinating solvent (L), such as tetrahydrofuran (THF) or CH_3CN, to give the binuclear complex $[Ru_2(CO)_4(\mu_2,\eta^2\text{-}OOCR)_2(L)_2]$. It was shown later by Rheinwald (1994) that complexes of the type $[Ru_2(CO)_4(\mu_2,\eta^2\text{-}OOCR)_2(THF)_2]$ could be synthesized directly, and almost quantitatively, by the reaction of $[Ru_3(CO)_{12}]$ with the corresponding acid in THF at 393 K by using a pressure Schlenk tube. Reaction of the bisacetate derivative with 2-aminopyridine in THF led to the formation of the title compound, (I).



(I)

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are given in Table 1. In this binuclear ruthenium(I) ‘sawhorse’ complex, the two aminopyridine molecules occupy the axial positions and are coordinated *via* the pyridine N atoms. The pyridine rings do not lie in the same plane but are inclined with respect to one another by 75.45 (17)°. Amine atom N4 is intramolecularly hydrogen bonded to acetate atom O4 (details are given in Fig. 2 and Table 2). The pyridine rings are displaced away from the carbonyl groups with N1—Ru1—Ru2 and N3—Ru2—Ru1 angles of 160.31 (7) and 164.55 (7)°, respectively. This arrangement was also seen in the pyridine analogue (Kepert *et*

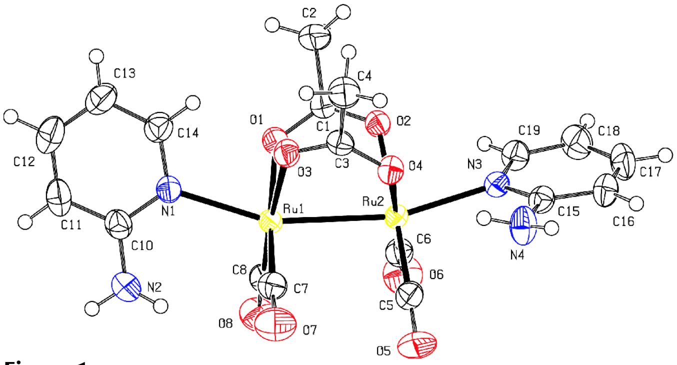


Figure 1
A perspective view of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

al., 2000) and the di(2-pyridyl)amine analogue (Kepert *et al.*, 2003), both of which possess C_2 symmetry.

The overall geometry of the diruthenium(I) ‘sawhorse’ moiety is also similar to that in the above-mentioned complexes. The Ru1—Ru2 distance is 2.6756 (7) Å, and the Ru1—N1 and Ru2—N3 distances are 2.267 (3) and 2.243 (3) Å, respectively. The Ru—N1 distance is slightly longer than that observed previously. The acetate groups are slightly twisted with respect to the Ru1—Ru2 bond (by *ca* 15°), as shown by the O1—Ru1—Ru2—O2 and O3—Ru1—Ru2—O4 torsion angles (Table 1).

Amine atom N2 is intermolecularly hydrogen bonded to carbonyl atoms O8^{i} and O5^{ii} (see Table 2 for symmetry codes and details). In this way, a polymer chain is built up, as illustrated in Fig. 2. The aminopyridine ligand involving amine atom N4 is also involved in an intermolecular hydrogen bond to acetate atom O1^{iii}. This results in the formation of a double-stranded hydrogen-bonded chain, extending in the *a* direction. This situation is illustrated in Fig. 3 and full details of the hydrogen bonding are given in Table 2.

Experimental

Using a pressure Schlenk tube, 2-aminopyridine (67 mg, 0.712 mmol) was added, under argon and with stirring, to an orange solution of [$Ru_2(CO)_4(\mu_2,\eta^2\text{-}OOCCH_3)_2(THF)_2$] (200 mg, 0.346 mmol) in THF (50 ml). The solution became yellow and was stirred at room temperature for 30 min. The solvent was evacuated under vacuum, and the resulting residue was redissolved in CH_2Cl_2(10 ml) and then purified by thin-layer chromatography (CH_2Cl_2/cyclohexane 2:1). The yellow band, containing the title compound, (I), was extracted with CH_2Cl_2 and dried *in vacuo*, giving a yellow crystalline solid. Yield 33 mg (86%). The elemental and spectroscopic analyses agreed with the structure deduced by X-ray crystallography.

Crystal data

[$Ru_2(C_2H_3O_2)_2(C_5H_6N_2)_2(CO)_4$]
M_r = 620.50
Triclinic, $P\overline{1}$
a = 9.3027 (15) Å
b = 9.952 (2) Å
c = 12.474 (3) Å
α = 83.82 (2)°
β = 78.925 (17)°
γ = 76.881 (15)°
V = 1101.3 (4) Å^3
Z = 2
D_x = 1.871 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
θ = 14.0–16.8°
μ = 1.42 mm^{-1}
T = 293 (2) K
Block, yellow
0.34 × 0.34 × 0.19 mm

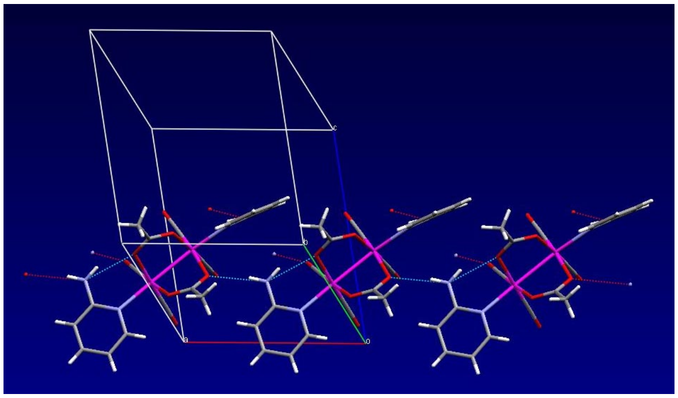


Figure 2
A view of part of the crystal packing of (I), showing the formation of the hydrogen-bonded chain along the *a* axis (hydrogen bonds are represented by dashed blue lines).

Data collection

Stoe AED-2 four-circle diffractometer
2θ/ω scans
Absorption correction: refined from ΔF (DELrefABS in *PLATON*; Spek, 2003)
T_{min} = 0.363, T_{max} = 0.764
4092 measured reflections
4092 independent reflections
3678 reflections with $I > 2\sigma(I)$
θ_{max} = 25.5°
h = −10 → 11
k = −11 → 12
l = 0 → 15
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.058
S = 1.12
4092 reflections
305 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 1.3224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—C8	1.833 (3)	Ru2—C6	1.830 (3)
Ru1—C7	1.834 (4)	Ru2—C5	1.837 (4)
Ru1—O1	2.131 (2)	Ru2—O2	2.127 (2)
Ru1—O3	2.132 (2)	Ru2—O4	2.133 (2)
Ru1—N1	2.267 (3)	Ru2—N3	2.243 (3)
Ru1—Ru2	2.6756 (7)		
C8—Ru1—C7	90.59 (15)	C6—Ru2—C5	88.00 (16)
C8—Ru1—O1	95.02 (12)	C6—Ru2—O2	94.91 (13)
C7—Ru1—O1	173.35 (12)	C5—Ru2—O2	176.54 (13)
C8—Ru1—O3	175.45 (12)	C6—Ru2—O4	176.91 (12)
C7—Ru1—O3	91.21 (12)	C5—Ru2—O4	95.01 (13)
O1—Ru1—O3	82.94 (9)	O2—Ru2—O4	82.06 (9)
C8—Ru1—N1	98.68 (12)	C6—Ru2—N3	93.14 (13)
C7—Ru1—N1	102.03 (13)	C5—Ru2—N3	98.45 (13)
O1—Ru1—N1	80.68 (9)	O2—Ru2—N3	83.27 (9)
O3—Ru1—N1	85.03 (9)	O4—Ru2—N3	87.11 (9)
C8—Ru1—Ru2	93.73 (10)	C6—Ru2—Ru1	94.75 (11)
C7—Ru1—Ru2	93.02 (11)	C5—Ru2—Ru1	95.08 (11)
O1—Ru1—Ru2	83.07 (6)	O2—Ru2—Ru1	82.83 (6)
O3—Ru1—Ru2	82.01 (6)	O4—Ru2—Ru1	84.31 (6)
N1—Ru1—Ru2	160.31 (7)	N3—Ru2—Ru1	164.55 (7)
O1—Ru1—Ru2—O2	16.05 (9)	O3—Ru1—Ru2—O4	14.93 (9)

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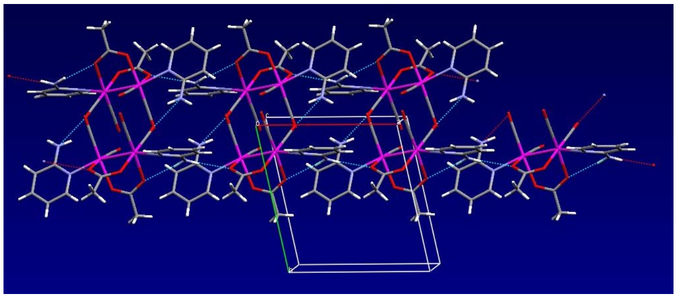

Figure 3
A view of the formation of the double-stranded hydrogen-bonded chain in (I), extending in the *a* direction (hydrogen bonds are represented by dashed blue lines).

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H21$\cdots$O8^{i}	0.880 (19)	2.60 (2)	3.461 (4)	166 (4)
N2—H22$\cdots$O5^{ii}	0.865 (19)	2.39 (3)	3.031 (5)	132 (3)
N4—H41$\cdots$O1^{iii}	0.874 (18)	2.17 (2)	3.032 (4)	171 (3)
N4—H42$\cdots$O4	0.882 (19)	2.24 (3)	3.050 (4)	152 (3)

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

The amine H atoms were located in a difference map and were refined isotropically, with the N—H distance restrained to 0.88 (2) Å. The remaining H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for CH_3 atoms, and C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms.

Data collection: *STADI*4 (Stoe & Cie, 1997); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL*97.

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