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Di-μ-benzoato-bis[dicarbonyl(pyridine)ruthenium(I)] (new polymorph) and di-μ-trifluoroacetato-bis[dicarbonyl(pyridine)ruthenium(I)]

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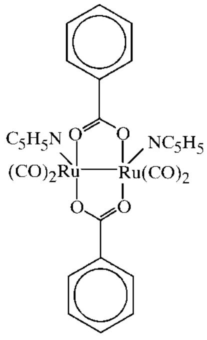
The syntheses and crystal structure determinations of a pair of 'sawhorse' dimers are reported, *viz*. $[Ru_2(C_6H_5CO_2)_2(C_5H_5N)_2(CO)_4]$ [a new polymorph, *cf*. Kepert, Deacon, Spiccia, Fallon, Skelton & White (2000). *J. Chem. Soc. Dalton Trans*. pp. 2867–2874] and $[Ru_2(CF_3CO_2)_2(C_5H_5N)_2(CO)_4]$. The Ru$\cdots$Ru distances are 2.6724 (2) and 2.7122 (5) Å, respectively.

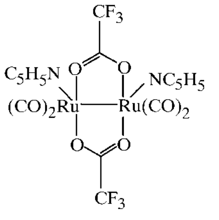
Comment

An earlier report (Kepert *et al.*, 2000) records the syntheses and chemical and structural characterizations of a number of binuclear ruthenium(I) 'sawhorse' complexes, *viz*. $[Ru(RCO_2)(CO)_2L]_2$ [R = Me, Et, ^{t}Bu and Ph; L is pyridine (py) or 3-methylpyridine (mpy)]. Despite the diversity of the carboxylate substituents, the core geometry of the binuclear array proved remarkably resistant to any form of systematic substituent variation across the array. A counterpart complex, with an electronically more significantly varied substituent (R = CF_3 and L = py), (II), has since been crystallized and examined structurally as an extension of the series, and is reported here; also reported is the structure of a second monoclinic polymorph, (I), this time in space group $P2_1/c$ rather than $C2/c$, of the previously studied Ph/py complex. Both (I) and (II) were obtained as unsolvated crystals; a further phase of the Ph/py complex is a toluene hemisolvate (triclinic, $P\bar{1}$, $Z = 2$; Xu & Sasaki, 1999). There are no coordinates in the Cambridge Structural Database (Allen, 2002) deposition for this form; the limited data in that report, in particular, the Ru—Ru distance of 2.6809 (7) Å and the mean Ru—O distance of 2.121 (4) Å, agree with the following comments.

In both phases of (I), $[Ru(PhCO_2)(CO)_2(py)]_2$, one binuclear molecule, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The geometric parameters of the present phase (Table 1 and Fig. 1) are generally similar to those of the other phase insofar as bond lengths and angles are concerned. There is a significant difference, however, in the dihedral angle between the pair of C_2O_2 carboxylate planes, the present value of 78.20 (7)° being more nearly comparable to the values of 67.5 (1), 71 (1)/76 (1), 73.1 (4) and 70.8 (1)° reported previously for the analogues in which R/L is Me/py, Me/mpy (two molecules), Et/py and ^{t}Bu/py, all of which are very much less than the value found for the $C2/c$ Ph/py phase [84.9 (2)°]. The molecule of the present phase has quasi-*mm* symmetry, the pyridine ligands lying in one putative mirror plane ('upright'), the other plane containing the C—C bonds of the carboxylates and the Ru—Ru bisector; this symmetry is also compatible with the pyridine ligands lying normal to the first mirror plane ('flat'), as reported for the Me/py adduct. The previous Ph/py ($C2/c$) molecule is unusual in that the pyridine ligands have a one-upright/one-flat combination, reducing the putative molecular symmetry to *m*. It seems unlikely that this conformation (rather than, for example, 'packing forces') is responsible for the considerably greater splaying of the carboxylate ligands in the less symmetrical form; the disparity in, for example, the angles about the two Ru atoms is less than that in the present, more symmetric, array. The C_6/CO_2 interplanar dihedral angles of the carboxylate ligands of the $C2/c$ form are 15.7 (2) and 10.2 (1)° [*cf*. the present values of 4.62 (7) and 6.55 (6)°]; the Ru-atom deviations from the CCO_2 planes are 0.148 (6) and 0.131 (6) Å for atom Ru1, and 0.228 (6) and 0.254 (5) Å for atom Ru2.



(I)



(II)

In the trifluoroacetate/pyridine counterpart, $[Ru(F_3CCO_2)(CO)_2(py)]_2$, (II), one complete binuclear neutral molecule again composes the asymmetric unit of the structure; the putative symmetry is again quasi-*mm*, with a pair of 'upright' pyridine ligands. That symmetry is broken, however, by the pair of CF_3 substituents, whose mutual orientations are 'geared'. Again, much of the geometry of the core of the dimer (Table 2 and Fig. 2) is similar to that found in the related complexes. Worthy of note as being different, however, are the Ru—O distances, with a mean value of 2.144 (8) Å [*cf*. the mean value of 2.13 (1) Å for the $C2/c$ and $P2_1/c$ benzoates], in

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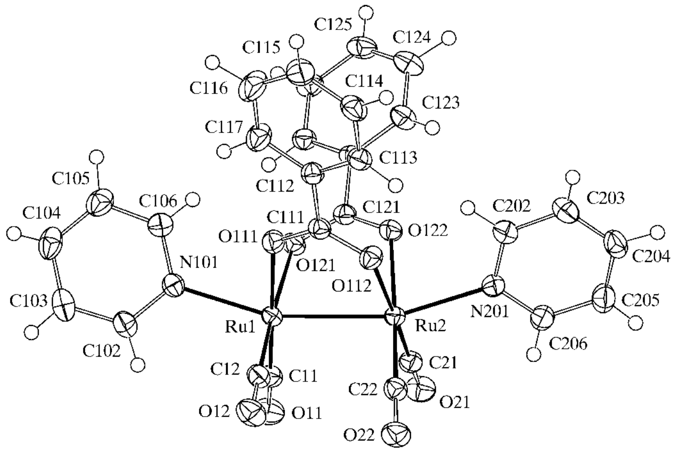

Figure 1
The molecular structure of (I), with the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are represented as circles with arbitrary radii 0.1 Å.

keeping with the diminished basicity of the ligand and with the more pronounced concomitant changes in the Ru—Ru distance. The latter is the longest observed (*cf.* all of the other complexes) by more than 0.03 Å. [The Ru—Ru distances in all other complexes (Kepert *et al.*, 2000; Xu & Sasaki, 1999) are remarkably constant, lying between 2.672 (1) and 2.6780 (4) Å.] The mean O—C—O angle is 129.9 (1)° [*cf.* the mean angle of 125.3 (1)° for the benzoates] and the mean interplanar dihedral angle between the CCO_2 planes is 68.0 (2)°; all other angles lie above 70°, except that of the complex where *R*/*L* is Me/py, in which the angle is 67.5 (1)°. Atoms Ru1 and Ru2 deviate from the CCO_2 planes by 0.325 (7) and 0.289 (7) Å (plane 11*n*), and 0.223 (7) and 0.256 (7) Å (plane 12*n*), and from the C_5N planes, 10*n* and 20*n*, by 0.044 (6) and 0.132 (7) Å, respectively.

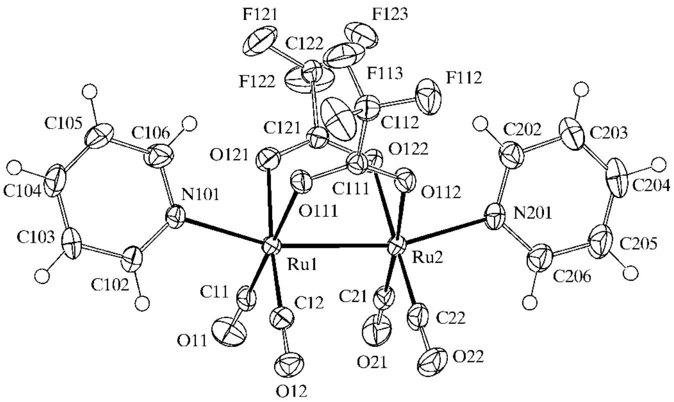

Figure 2
The molecular structure of (II), with the atom-numbering scheme and displacement ellipsoids at the 50% probability level. H atoms are represented as small circles with arbitrary radii.

Experimental

For the preparation of compound (I), di-μ-benzoato-tetracarbonyldipyridinediruthenium(I), *viz.* $[Ru(PhCO_2)(CO)_2(py)]_2$, $[Ru(CO)_2Cl_2]_n$ (231 mg, 1.01 mmol) was reacted with NaO_2CPh (1.4 g, 9.7 mmol) and pyridine (0.1 ml, 1.29 mmol) in methanol (30 ml) according to the method for the preparation of $[Ru(PhCO_2)(CO)_2(py)]_2$ described by Kepert *et al.* (2000). Yellow crystals of a new polymorph of $[Ru(PhCO_2)(CO)_2(py)]_2$ were obtained (yield 8%, 30 mg). (It is not yet clear what is the determinant of the new, *cf.* the previous, phase.) Analysis found: C 47.3, H 2.6, N 3.9%; calculated for $C_{28}H_{20}N_2O_8Ru_2$: C 47.1, H 2.8, N 3.9%. For the preparation of compound (II), di-μ-trifluoroacetato-tetracarbonyldipyridinediruthenium(I), *viz.* $[Ru(CF_3CO_2)(CO)_2(py)]_2$, $[Ru(MeCO_2)(CO)_2(py)]_2$ (109 mg, 0.185 mmol) was added to degassed trifluoroacetic acid (20 ml) and refluxed for 3 h. The reaction mixture was then stored at 277 K overnight and filtered, and the filtrate was evaporated to give a yellow residue, which was recrystallized from methanol, yielding yellow crystals of (II) (yield 12%, 16 mg). Analysis found: C 32.0, H 1.5, N 3.9%; calculated for $C_{18}H_{10}F_6N_2O_8Ru_2$: C 31.0, H 1.5, N 4.0%. In another preparation, trifluoroacetic acid (0.5 ml) was added at room temperature to $[Ru(MeCO_2)(CO)_2(py)]_2$ (56 mg, 0.091 mmol) in methanol (5 ml), producing a yellow precipitate of the product in much higher yield (yield 80%, 51 mg). IR and NMR data for both compounds have been deposited with the supplementary material.

Compound (I)

Crystal data

$[Ru_2(C_7H_5O_2)_2(C_5H_5N)_2(CO)_4]$
$M_r = 714.61$
Monoclinic, $P2_1/c$
$a = 8.6623$ (3) Å
$b = 18.6501$ (7) Å
$c = 16.7546$ (6) Å
$\beta = 92.6800$ (10)°
$V = 2703.79$ (17) $Å^3$
$Z = 4$
$D_x = 1.755$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 7794 reflections
$\theta = 1.8$–28.2°
$\mu = 1.17$ mm^{-1}
$T = 150$ (2) K
Prism, pale yellow
0.35 × 0.15 × 0.12 mm

Table 1
Selected geometric parameters (Å, °) for (I).

Ru1—Ru2	2.6724 (2)	Ru2—C21	1.8391 (18)
Ru1—C11	1.8469 (18)	Ru2—C22	1.8396 (18)
Ru1—C12	1.8383 (19)	Ru2—O112	2.1433 (13)
Ru1—O111	2.1091 (13)	Ru2—O122	2.1166 (13)
Ru1—O121	2.1326 (13)	Ru2—N201	2.2332 (15)
Ru1—N101	2.2164 (15)		
Ru2—Ru1—C11	98.02 (6)	Ru1—Ru2—C21	92.11 (6)
Ru2—Ru1—C12	91.81 (6)	Ru1—Ru2—C22	95.82 (6)
Ru2—Ru1—O111	82.60 (4)	Ru1—Ru2—O112	84.33 (3)
Ru2—Ru1—O121	84.16 (4)	Ru1—Ru2—O122	82.71 (4)
Ru2—Ru1—N101	162.02 (4)	Ru1—Ru2—N201	162.92 (4)
C11—Ru1—C12	90.69 (8)	C21—Ru2—C22	89.13 (8)
C11—Ru1—O111	174.96 (7)	C21—Ru2—O112	174.77 (7)
C11—Ru1—O121	92.24 (7)	C21—Ru2—O122	93.23 (7)
C11—Ru1—N101	97.46 (7)	C21—Ru2—N201	96.42 (7)
C12—Ru1—O111	94.30 (7)	C22—Ru2—O112	95.03 (7)
C12—Ru1—O121	175.31 (7)	C22—Ru2—O122	177.26 (7)
C12—Ru1—N101	97.10 (7)	C22—Ru2—N201	99.07 (7)
O111—Ru1—O121	82.83 (5)	O112—Ru2—O122	82.54 (5)
O111—Ru1—N101	81.19 (5)	O112—Ru2—N201	86.07 (5)
O121—Ru1—N101	86.15 (5)	O122—Ru2—N201	82.05 (5)

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.64$, $T_{\rm max} = 0.79$
44 142 measured reflections
10 364 independent reflections
9057 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\rm max} = 33.8°$
$h = -13 \rightarrow 13$
$k = -29 \rightarrow 29$
$l = -25 \rightarrow 25$

Refinement

Refinement on F
$R = 0.026$
$wR = 0.039$
$S = 1.13$
9057 reflections
361 parameters
H-atom parameters not refined
$w = 1/(\sigma^2F + 0.02F + 0.0003F^2)$
$(\Delta/\sigma)_{\rm max} = 0.007$
$\Delta\rho_{\rm max} = 0.86$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.48$ e Å^{-3}

Compound (II)

Crystal data

$[Ru_2(C_2F_3O_2)_2(C_5H_5N)_2(CO)_4]$
$M_r = 698.41$
Triclinic, $P\overline{1}$
$a = 9.211$ (2) Å
$b = 9.292$ (2) Å
$c = 15.266$ (4) Å
$\alpha = 105.280$ (6)°
$\beta = 94.669$ (6)°
$\gamma = 111.726$ (6)°
$V = 1147.3$ (5) Å^3
$Z = 2$
$D_x = 2.022$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7874 reflections
$\theta = 2.9$–$28.3°$
$\mu = 1.41$ mm^{-1}
$T = 150$ (2) K
Prism, pale yellow
$0.30 \times 0.12 \times 0.10$ mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.66$, $T_{\rm max} = 0.79$
13 924 measured reflections
5738 independent reflections
5127 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 28.9°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -20 \rightarrow 20$

Refinement

Refinement on F
$R = 0.033$
$wR = 0.06$
$S = 1.07$
5127 reflections
325 parameters
H-atom parameters not refined
$w = 1/(\sigma^2F + 0.04F + 0.002F^2)$
$(\Delta/\sigma)_{\rm max} = 0.011$
$\Delta\rho_{\rm max} = 0.92$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.94$ e Å^{-3}

H atoms were located from difference Fourier maps and placed at idealized positions [C—H = 0.95 Å, with $U_{\rm iso}$(H) = 1.25$U_{\rm eq}$(C) for CH and CH_2 H atoms, and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for CH_3 H atoms].

Table 2
Selected geometric parameters (Å, °) for (II).

Ru1—Ru2	2.7122 (5)	Ru2—C21	1.842 (5)
Ru1—C11	1.839 (5)	Ru2—C22	1.830 (4)
Ru1—C12	1.834 (4)	Ru2—O112	2.147 (3)
Ru1—O111	2.137 (3)	Ru2—O122	2.138 (3)
Ru1—O121	2.153 (3)	Ru2—N201	2.202 (3)
Ru1—N101	2.215 (3)		

Ru2—Ru1—C11	95.65 (9)	Ru1—Ru2—C21	93.01 (10)
Ru2—Ru1—C12	90.94 (10)	Ru1—Ru2—C22	96.29 (10)
Ru2—Ru1—O111	83.75 (6)	Ru1—Ru2—O112	83.96 (6)
Ru2—Ru1—O121	84.32 (6)	Ru1—Ru2—O122	83.49 (6)
Ru2—Ru1—N101	163.39 (10)	Ru1—Ru2—N201	163.76 (10)
C11—Ru1—C12	86.2 (2)	C21—Ru2—C22	88.0 (2)
C11—Ru1—O111	177.95 (15)	C21—Ru2—O112	175.32 (14)
C11—Ru1—O121	95.85 (16)	C21—Ru2—O122	94.10 (16)
C11—Ru1—N101	97.46 (14)	C21—Ru2—N201	97.77 (14)
C12—Ru1—O111	95.73 (17)	C22—Ru2—O112	95.87 (18)
C12—Ru1—O121	174.99 (13)	C22—Ru2—O122	177.91 (18)
C12—Ru1—N101	100.04 (13)	C22—Ru2—N201	96.19 (14)
O111—Ru1—O121	82.15 (12)	O112—Ru2—O122	82.04 (12)
O111—Ru1—N101	82.79 (12)	O112—Ru2—N201	84.47 (12)
O121—Ru1—N101	84.23 (11)	O122—Ru2—N201	83.66 (11)

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1419). Services for accessing these data are described at the back of the journal.

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