Tetra-μ-acetato-κ⁸O:O′-bis[(N¹,N²-di-p-anisylformamidine-κN²)ruthenium(II)]-(Ru—Ru): an example of an axial bis-adduct of {Ru₂}⁴⁺ tetracarboxylate with N-donor ligands

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The title compound, [Ru$_2$(C$_2$H$_3$O$_2$)$_4$(C$_{15}$H$_{16}$N$_2$O$_2$)$_2$], lies on a crystallographic inversion center and exhibits an Ru—Ru bond length of 2.2847 (8) Å. There are weak intramolecular hydrogen-bonding interactions between the N^1,N^2-di-p-anisyl-formamidine (HDAniF) ligands and the bridging acetate ligands. The molecule is one of the few examples of a crystallographically characterized axial bis-adduct of a {Ru$_2$}$^{4+}$ complex with two N-donor ligands.

Comment

Paddlewheel Ru$_2$ compounds with carboxylate bridges, [Ru$_2$(O$_2$CR)$_4$]$^{n+}$ (n = 1 or 0), were the first types of Ru$_2$ compounds to be discovered and still form the majority of Ru$_2$ complexes. The typical characteristic of this type of compound is their strong tendency to react with Lewis bases, which coordinate to the axial positions of the dimetal core, forming adducts or polymeric structures, depending on the type of base.

Although, in the case of the {Ru$_2$}$^{5+}$ tetracarboxylates, a variety of Lewis bases with O-, N-, P- and S-donor atoms have been used as axial ligands, for the {Ru$_2$}$^{4+}$ tetracarboxylates, the majority of the axially coordinated Lewis bases are O-donors (Cotton & Walton, 1993). There are only a few reports on {Ru$_2$}$^{4+}$ tetracarboxylates with axially coordinated N-donor ligands in the literature. These involve the one-dimensional polymeric chain structures formed from the reaction of Ru$_2$(O$_2$CR)$_4$ compounds with the bifunctional N-donors pyz (pyrazine), phz (phenazine) and DMDCNQI (2,5-dimethyl-N,N'-dicyanoquinone diimine) (Wesemann & Chisholm, 1997; Miyasaka et $al.$, 2001; Huckett et $al.$, 1991), a two-dimensional network formed by the reaction of Ru$_2$(O$_2$CCF$_3$)$_4$ with the

polyfunctional donor TCNQ (7,7,8,8-tetracyanoquinodimethane) (Miyasaka et $al.$, 2000), the bis-MeCN adducts Ru$_2$(O$_2$CMe)$_4$(MeCN)$_2$ (Lindsay et $al.$, 1985) and Ru$_2$-(O$_2$CC$_6$H$_4$-p-Me)$_4$(MeCN)$_2$ (Chisholm et $al.$, 1996), and the bis-NO adducts Ru$_2$(O$_2$CEt)$_4$(NO)$_2$ and Ru$_2$(O$_2$CCF$_3$)$_4$-(NO)$_2$ (Lindsay et $al.$, 1987). The reactions of {Ru$_2$}$^{4+}$ compounds with monofunctional N-donors are sometimes unexpectedly complicated. When excess pyridine (py) reacts with Ru$_2$(O$_2$CCR)$_4$ compounds (R = Me or CF$_3$), the cleavage products Ru(O$_2$CR)$_2$(py)$_4$ are obtained (Lindsay et $al.$, 1987). Similarly, Ru$_2$(O$_2$CCF$_3$)$_4$ reacts with MeCN causing cleavage of the metal–metal bond and giving [Ru(O$_2$CCF$_3$)(MeCN)$_5$]-(O$_2$CCF$_3$) (Lindsay et $al.$, 1987).

(I)
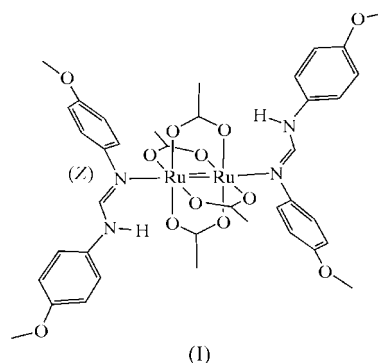
In this report, we present the crystal structure of a bis-adduct of an {Ru$_2$}$^{4+}$ tetracarboxylate with a different type of N-donor Lewis base than those that have been used to date, namely the title compound, Ru$_2$(O$_2$CMe)$_4$(HDAniF)$_2$, (I).

Complex (I) was synthesized from the reaction of Ru$_2$(O$_2$CMe)$_4$ with HDAniF in refluxing tetrahydrofuran. The
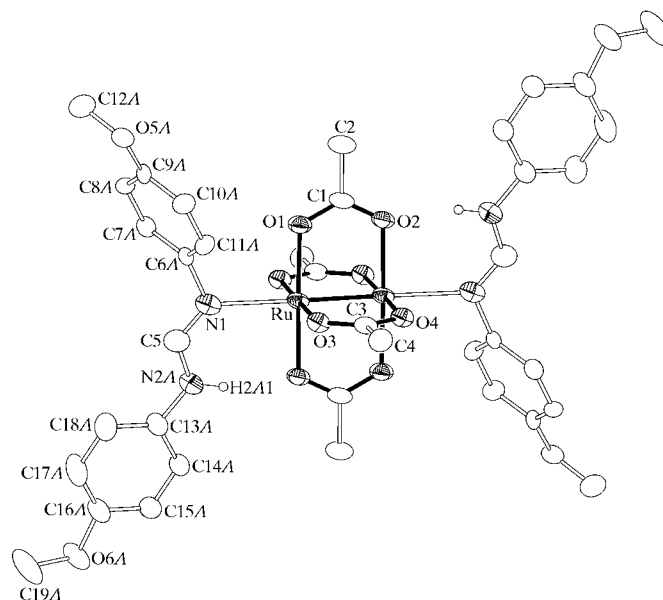

Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level. Only one of the disordered conformers is shown. H atoms have been omitted for clarity, except for those attached to the N atoms of the HDAniF ligands, which are shown as small spheres of arbitrary radii.

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analogous reaction of $Ru_2(O_2CMe)_4Cl$ with HDAniF under the same experimental conditions resulted in the replacement of two equatorially coordinated acetate groups of $Ru_2(O_2CMe)_4Cl$ and the formation of $Ru_2(O_2CMe)_2(DAniF)_2Cl$ (Angaridis *et al.*, 2003).

The molecule of (I) lies on a crystallographic inversion center, at the mid-point of the Ru1—Ru1^i bond [Fig. 1; symmetry code: (i) $1 - x$, $1 - y$, $1 - z$]. Selected bond distances and angles are listed in Table 1. The $\{Ru_2\}^{4+}$ unit is embraced by four acetate groups, forming the well known paddlewheel structure, with eclipsed geometry and two axially coordinated HDAniF ligands. The Ru1—Ru1^i distance falls in the middle of the range of the corresponding Ru=Ru double-bond distances found in $\{Ru_2\}^{4+}$ tetracarboxylates (2.252–2.311 Å; Cotton & Walton, 1993). The Ru—O distances have an average of 2.064 (7) Å.

The HDAniF ligands are *trans*-oriented with respect to the metal–metal bond, with Ru—N distances of 2.374 (4) Å. These are only slightly longer than the axial Ru—N distances of 2.276 (1) Å in the analogous bis-adduct $Ru_2(O_2CC_6H_4$-p-$Me)_4(MeCN)_2$ (Chisholm *et al.*, 1996). The Ru—Ru—N angles are almost linear, with values of 178.24 (9)°.

There are intramolecular hydrogen-bonding interactions between the H atoms attached to the N atoms of the axially coordinated HDAniF ligands and the O atoms of the bridging acetate groups (Table 2). Similar hydrogen-bonding interactions between axial and bridging ligands have been observed in the $\{Ru_2\}^{5+}$ axial bis-adduct $[Ru_2(O_2CMe)_4(quinoline)_2]$-$PF_6$, which was reported recently by Gilfoy *et al.* (2001).

Experimental

HDAniF (0.160 g, 0.62 mmol) was added to a solution of $Ru_2(O_2CMe)_4$ (0.110 g, 0.25 mmol) in tetrahydrofuran (15 ml). The reaction mixture was stirred and refluxed for 48 h, resulting in a dark red–brown solution. Removal of the solvent under low pressure resulted in a dark red–brown solid, which was washed with hexanes (2 × 25 ml) and dried under vacuum. The residue was extracted with toluene (15 ml). A red–brown solution was obtained, which was layered with hexanes (35 ml). Dark-brown crystals of (I) formed over a period of one week.

Crystal data

$[Ru_2(C_2H_3O_2)_4(C_{15}H_{16}N_2O_2)_2]$	$D_x = 1.626$ Mg m^{-3}
$M_r = 950.91$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5138
$a = 15.2123$ (14) Å	reflections
$b = 14.7393$ (13) Å	$\theta = 2.7$–27.5°
$c = 8.9550$ (8) Å	$\mu = 0.85$ mm^{-1}
$\beta = 104.649$ (2)°	$T = 213$ (2) K
$V = 1942.6$ (3) Å^3	Block, brown
$Z = 2$	0.38 × 0.35 × 0.26 mm

Data collection

Bruker SMART 1000 diffractometer	4460 independent reflections
ω scans	3289 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan [*SADABS*; Blessing (1995) and Bruker (2003)]	$R_{int} = 0.043$
	$\theta_{max} = 27.6°$
	$h = -19 \rightarrow 11$
	$k = -19 \rightarrow 19$
$T_{min} = 0.739$, $T_{max} = 0.810$	$l = -9 \rightarrow 11$
12 766 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$+ 2.231P]$
$wR(F^2) = 0.134$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
4460 reflections	$\Delta\rho_{max} = 1.48$ e Å^{-3}
342 parameters	$\Delta\rho_{min} = -0.85$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ru—Ru^i	2.2847 (8)	Ru—O3	2.072 (3)
Ru—O1	2.055 (3)	Ru—O4^i	2.062 (3)
Ru—O2^i	2.067 (3)	Ru—N1	2.374 (4)
O1—Ru—O2^i	178.04 (14)	O2^i—Ru—O3	91.07 (11)
O1—Ru—O4^i	90.42 (12)	O1—Ru—N1	90.26 (13)
O4^i—Ru—O2^i	88.93 (12)	O4^i—Ru—N1	88.73 (13)
O1—Ru—O3	89.54 (12)	O2^i—Ru—N1	91.57 (13)
O4^i—Ru—O3	178.61 (13)	O3—Ru—N1	92.66 (13)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2A—H21$A\cdots$O2^i	0.87	1.97	2.796 (5)	158
N2B—H21$B\cdots$O2^i	0.87	1.99	2.796 (5)	154

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

During refinement, all H atoms were treated as riding atoms, with phenyl C—H distances of 0.94 Å, methyl C—H distances of 0.97 Å and N—H distances of 0.87 Å, and with U_{iso}(H) values of $1.2U_{eq}$(C,N) for phenyl and formamidine groups, and $1.5U_{eq}$(C) for methyl groups. A p-anisyl group on one of the HDAniF ligands was found to be disordered over two positions, with site occupancies of 0.652 (7) and 0.348 (7), while a p-anisyl group on the other HDAniF ligand was disordered over three positions, with site occupancies of 0.323 (3), 0.350 (7) and 0.327 (7). The disordered p-anisyl groups were refined with distance constraints. The largest positive and negative peaks in the final difference map are 0.75 and 1.00 Å, respectively, from the Ru atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1513). Services for accessing these data are described at the back of the journal.

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