

# A paramagnetic precursor for polymeric supramolecular assemblies based on multiply bonded dimetal units: $\mu$ -acetato-acetonitriletris- $(\mu$ - $N,N'$ -diphenylformamidinato)-diruthenium tetrafluoroborate dichloromethane hemisolvate

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Received 20 August 2004

Accepted 7 December 2004

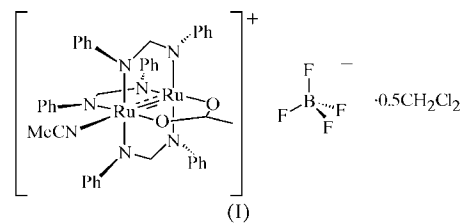
Online 15 January 2005

The title compound,  $[\text{Ru}_2(\text{C}_{13}\text{H}_{11}\text{N}_2)_3(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_2\text{H}_3\text{N})]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$  or  $[\text{Ru}_2(\mu\text{-DPhF})_3(\mu\text{-O}_2\text{CMe})(\text{MeCN})]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ , where DPhF is  $N,N'$ -diphenylformamidinate, crystallized as dark-blue block-shaped crystals. In the unit cell, the diruthenium cation lies on a general position, and the  $\text{BF}_4^-$  anions reside on two independent special positions with crystallographic twofold symmetry. Disorder was observed for one of the phenyl groups in the formamidinate ligand, the axial acetonitrile molecule and the interstitial dichloromethane molecule. The compound, which exhibits a long Ru–Ru bond of 2.4131 (5) Å, is the first  $\{\text{Ru}_2\}^{5+}$  formamidinate species that is both equatorially and axially functionalized so that it can be used as a precursor for polymeric paramagnetic supramolecular assemblies.

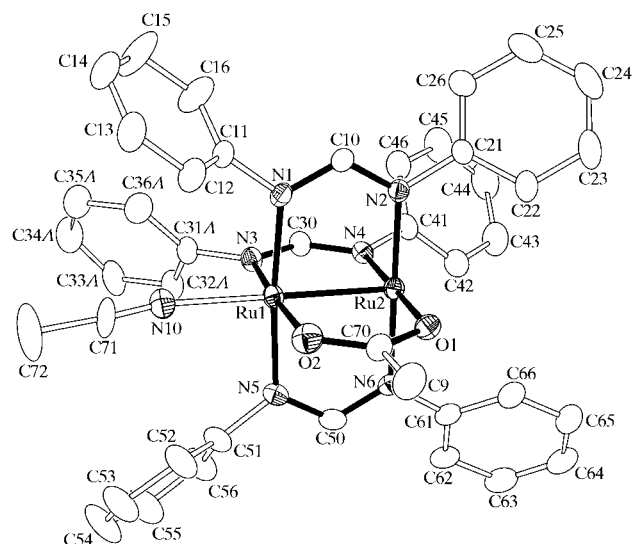
## Comment

In our efforts to synthesize paramagnetic diruthenium complexes with a mixed set of labile and non-labile bridging ligands that can be used as building block precursors for the construction of paramagnetic supramolecular assemblies, we have prepared complexes of the  $\{\text{Ru}_2\}^{5+}$  core of the general type  $\text{Ru}_2(\text{O}_2\text{CMe})_{4-n}(\text{DArF})_n\text{Cl}$  ( $n = 1, 2, 3$  and 4, and DArF is  $N,N'$ -diarylformamidinate), which are paramagnetic with three unpaired electrons. In these compounds, the equatorial formamidinate groups are non-labile, while the acetate groups are easily exchanged by various linkers. We have reported the syntheses and magnetic properties of the monoformamidinate complex  $\text{Ru}_2(\text{O}_2\text{CMe})_3(\text{D}^{2,6}\text{XylF})\text{Cl}$ , where  $\text{D}^{2,6}\text{XylF}$  is  $N,N'$ -

bis(2,6-xylyl)formamidinate (Angaridis, Cotton *et al.*, 2004), the bis-formamidinate complexes *trans*- $\text{Ru}_2(\text{O}_2\text{CMe})_2(\text{D}^{2,6}\text{XylF})_2\text{Cl}$  and *cis*- $\text{Ru}_2(\text{O}_2\text{CMe})_2(\text{DAniF})_2\text{Cl}$ , where DAniF is  $N,N'$ -di-*p*-anisylformamidinate (Angaridis *et al.*, 2003), and the tris-formamidinate complex  $\text{Ru}_2(\text{O}_2\text{CMe})(\text{DAniF})_3\text{Cl}$  (Angaridis, Cotton *et al.*, 2004). The last two complexes have been used for the construction of the first paramagnetic molecular squares and molecular pairs, respectively, by replacing the labile acetate groups with dicarboxylate linkers. The monoformamidinate and both *cis* and *trans* bisformamidinate  $\{\text{Ru}_2\}^{5+}$  complexes have been characterized, while all attempts to obtain suitable diffracting crystals of the tris-formamidinate complex have been unsuccessful.



In this report, we present the crystal structure of a new tris-formamidinate complex,  $[\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3(\text{MeCN})]\text{BF}_4$ , (I), in which the axial chloride anion is replaced by a very labile acetonitrile molecule. At first glance this compound appears similar to  $\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3\text{Cl}$  [DPhF is  $N,N'$ -diphenylformamidinate; Barral *et al.*, 2004] and  $\text{Ru}_2(\text{O}_2\text{CMe})(\text{DAni}^o\text{F})_2(\text{O-DAni}^o\text{F})$ , where  $\text{DAni}^o\text{F}$  is  $N,N'$ -bis(*o*-methoxyphenyl)formamidinate and  $\text{O-DAni}^o\text{F}$  is the *o*-methoxyphenyl(*o*-oxyphenyl)formamidinate dianion derived from the previous formamidinate monoanion by removal of a methyl group of one of the methoxy groups (Ren *et al.*, 1999). However, there is an important difference in that compound (I) is further functionalized as a precursor for supramolecular



**Figure 1**  
The molecular structure of the cation in (I), with displacement ellipsoids shown at the 35% probability level. Only one orientation for the disordered phenyl group and the axially coordinated acetonitrile molecule is shown. H atoms have been omitted for clarity.

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arrays, because the axial positions are readily available for coordination to suitable linkers, which could allow the construction of higher-order architectures.

As shown in Fig. 1, the  $\{\text{Ru}_2\}^{5+}$  unit of (I), which lies on a general position in the unit cell, is coordinated by three DPhF ligands and one acetate group, forming the well known paddlewheel structure with eclipsed geometry. The  $\text{BF}_4^-$  anions lie on two independent twofold axes. The Ru1–Ru2 bond length [2.4131 (5) Å; Table 1] is significantly longer than the Ru–Ru distances in the tris-formamidinate complexes  $\text{Ru}_2(\text{O}_2\text{CMe})(\text{DPhF})_3\text{Cl}_2$  [2.325 (2) Å; Barral *et al.*, 2004] and  $(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{CO}_2)[\text{Ru}_2(\text{DAniF})_3\text{Cl}]_2$ , in which the average Ru–Ru distance is 2.329 (2) Å (Angaridis, Berry *et al.*, 2004). It is also longer than the metal–metal distances in the  $\{\text{Ru}_2\}^{5+}$  tetrakis-formamidinate complexes with a chloride anion as axial ligand (2.34–2.40 Å; Cotton & Ren, 1995; Bear *et al.*, 1996). This difference can be attributed to the axially coordinated acetonitrile molecule in (I). It appears that the  $\sigma$ -bonding interaction with the dimetallic core increases the anti-bonding  $\sigma^*$  electron density between the two metals, resulting in the lengthening of the Ru–Ru bond because of the ability of the acetonitrile ligand to act as  $\sigma$  donor. A  $\pi$  back-bonding interaction is possibly present to a small degree, as evidenced by the short Ru1–N10 distance of 2.166 (4) Å. The Ru1–O2 and Ru2–O1 distances are longer than the Ru–O distances in the  $\{\text{Ru}_2\}^{5+}$  tetracarboxylate complexes (Bino *et al.*, 1979). This difference can be ascribed to the strong *trans* influence of the formamidinate ligands, which has been shown to affect metal–metal bonded systems (Cotton *et al.*, 2004). The Ru–N distances are slightly shorter than those in the  $\{\text{Ru}_2\}^{5+}$  tetraformamidinate complexes (1.997–2.057 Å). The equatorial N atoms coordinated to atom Ru1, which is axially coordinated to the acetonitrile molecule, have slightly longer distances than the N atoms coordinated to atom Ru2 [2.041 (4)–2.057 (4) *versus* 1.997 (3)–2.017 (4) Å]. This difference can be attributed to steric repulsion between the DPhF ligands and the acetonitrile molecule.

### Experimental

To a mixture of  $\text{Ru}_2(\text{O}_2\text{CMe})_4\text{Cl}$  (237 mg, 0.500 mmol), HDPHF (294 mg, 1.50 mmol),  $\text{Et}_3\text{N}$  (202 mg, 2.00 mmol) and  $\text{LiCl}$  (500 mg) was added  $\text{MeCN}$  (30 ml). The mixture was stirred and heated at 323 K for 18 h and  $\text{HBF}_4$  (54 wt%) solution in  $\text{Et}_2\text{O}$  was then added (0.09 ml). The resulting dark-blue solution was stirred at room temperature for 2 h. After the solution had been concentrated to half of its original volume,  $\text{CH}_2\text{Cl}_2$  (5 ml) was added and the resulting solution was layered with  $\text{Et}_2\text{O}$  (60 ml). Dark-blue crystals of (I) grew at about 270 K over a period of one week.

#### Crystal data

$[\text{Ru}_2(\text{C}_{13}\text{H}_{11}\text{N}_2)_3(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_2\text{H}_3\text{N})]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$   
 $M_r = 1017.23$   
 Orthorhombic,  $Pnna$   
 $a = 18.0977$  (12) Å  
 $b = 37.603$  (3) Å  
 $c = 12.9239$  (9) Å  
 $V = 8795.2$  (10) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.536$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 6767 reflections  
 $\theta = 2.4\text{--}27.5^\circ$   
 $\mu = 0.81$  mm<sup>-1</sup>  
 $T = 213$  (2) K  
 Block, dark blue  
 0.30 × 0.24 × 0.20 mm

#### Data collection

Bruker SMART 1000 CCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*SADABS*; Blessing, 1995; Bruker, 2003)  
 $T_{\text{min}} = 0.793$ ,  $T_{\text{max}} = 0.855$   
 54 752 measured reflections  
 10 087 independent reflections

8029 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.030$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -21 \rightarrow 23$   
 $k = -36 \rightarrow 48$   
 $l = -16 \rightarrow 15$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.056$   
 $wR(F^2) = 0.144$   
 $S = 1.81$   
 10 087 reflections  
 565 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 4P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.25$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ru1–Ru2	2.4131 (5)	Ru1–N10	2.166 (4)
Ru1–N3	2.041 (4)	Ru2–N4	1.997 (3)
Ru1–O2	2.052 (4)	Ru2–N2	2.000 (3)
Ru1–N1	2.057 (4)	Ru2–N6	2.017 (4)
Ru1–N5	2.057 (4)	Ru2–O1	2.041 (3)
N3–Ru1–O2	175.09 (14)	N1–Ru1–N10	91.38 (14)
N3–Ru1–N1	90.64 (14)	N5–Ru1–N10	93.70 (15)
O2–Ru1–N1	89.65 (14)	N4–Ru2–N2	89.33 (14)
N3–Ru1–N5	90.56 (15)	N4–Ru2–N6	93.00 (14)
O2–Ru1–N5	88.72 (14)	N2–Ru2–N6	177.63 (14)
N1–Ru1–N5	174.69 (14)	N4–Ru2–O1	178.33 (13)
N3–Ru1–N10	93.75 (15)	N2–Ru2–O1	89.33 (13)
O2–Ru1–N10	91.15 (15)	N6–Ru2–O1	88.33 (13)
N3–Ru1–Ru2–N4	0.53 (14)	O2–Ru1–Ru2–O1	–1.30 (13)
N1–Ru1–Ru2–N2	–0.84 (14)		

During refinement, all H atoms were treated as riding atoms, with phenyl C–H distances of 0.94 Å and methyl C–H distances of 0.97 Å, and with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$  for phenyl and formamidinate groups and  $1.5U_{\text{eq}}(\text{C})$  for methyl groups. One of the phenyl groups in the DPhF ligands and the axially coordinated acetonitrile molecule are both disordered over two positions. The dichloromethane molecule is disordered about a twofold axis. The disordered moieties were modeled with distance constraints. The largest difference-map peak is 0.85 Å from atom Ru1 and the largest negative peak is 0.68 Å from atom Cl1.

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*.

The authors would like to express their gratitude to the National Science Foundation and the Welch Foundation for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1512). Services for accessing these data are described at the back of the journal.

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