

# Synthesis and characterization of $\text{Ru}_2(\eta^2\text{-DmAniF})_2(\mu\text{-DmAniF})_2(\mu\text{-OAc})(\mu\text{-O})$



Stacey R. Opperwall<sup>a</sup>, Bin Liu<sup>b,\*</sup>, Alice L. Pilo<sup>a</sup>, Zhi Cao<sup>a</sup>, Phillip E. Fanwick<sup>a</sup>, Tong Ren<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

<sup>b</sup> Department of Chemistry, Northwest University, Xi'an City 710069, PR China

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Dedicated to Professor Malcolm Chisholm, a dear friend and pioneer in M–M bond chemistry, on the occasion of his 70th birthday.

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## ABSTRACT

A new diruthenium compound,  $\text{Ru}_2(\eta^2\text{-DmAniF})_2(\mu\text{-DmAniF})_2(\text{OAc})(\text{O})$  (**1**), where *DmAniF* is *N,N'*-di(*m*-methoxyphenyl)formamidinate, was isolated as a secondary product from the reaction between  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$  and  $\text{K}_2\text{CO}_3$ , and its formulation was established using both single crystal X-ray diffraction and high resolution mass-spectrometry techniques. Compound **1** has an  $S = 3/2$  ground state, and exhibits an unusually large zero-field splitting ( $D = 308 \text{ cm}^{-1}$ ) as revealed by the measurement of temperature dependent magnetism.

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## 1. Introduction

Metal–metal bonded diruthenium compounds have been shown to exhibit a wide range of interesting properties including redox flexibility, rich spin states and ability to catalyze oxidative transformation [1]. A number of conjugated diruthenium alkynyl compounds have been investigated as the prototype of molecular wires by our laboratory [2–8] and others [9,10], and incorporated into nano-devices [11–13]. Incorporation of diruthenium units into ordered 1D [14–16] and 3D structures [17] through axial ligation has led to materials of interesting magnetic properties [18–21]. Diruthenium(II,III) tetracarboxylates and derivatives are excellent catalysts for organic sulfide oxygenation [22–26] and C=C bond cleavage reactions [27].

Along with the laboratories of Cotton [28–30] and Jiménez-Aparicio and co-workers [31–33], our laboratory has developed robust synthetic methods to prepare the  $\text{Ru}_2(\text{DArF})_{4-x}(\text{OAc})_x$  type compounds, where DArF is diarylformamidinate and  $x = 1–3$  [34–36]. The labile nature of acetate ligands in  $\text{Ru}_2(\text{DArF})_{4-x}(\text{OAc})_x$  allows for their substitution by bridging *N,N'*-bidentate ligands, which enables the ensuing peripheral modification through cross

coupling reactions [37–41]. Currently we are interested in the preparation of the  $\text{Ru}_2(\text{DArF})_3(\mu\text{-CO}_3)$  type compounds, and possible on-complex reduction of the coordinated carbonate. During the course of preparing  $\text{K}[\text{Ru}_2(\text{DmAniF})_3(\mu\text{-CO}_3)\text{Cl}]$  (*DmAniF* = *N,N'*-di(*m*-methoxyphenyl)-formamidinate), the title compound  $\text{Ru}_2(\eta^2\text{-DmAniF})_2(\mu\text{-DmAniF})_2(\text{OAc})(\text{O})$  (**1**) was isolated as a byproduct and characterized. Described herein are the molecular structure, electrochemical and magnetic properties of this unusual  $\text{Ru}_2(\text{III,IV})$  species.

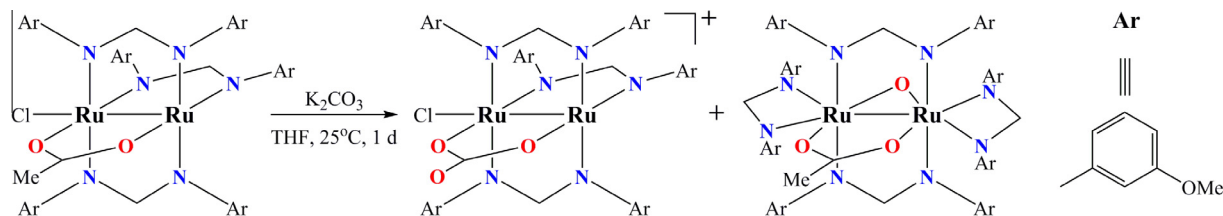
## 2. Results and discussion

### 2.1. Synthesis

Aiming at the preparation of a  $\text{Ru}_2(\text{DmAniF})_3(\text{CO}_3)$  type compound,  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$  was reacted with 4 equiv of  $\text{K}_2\text{CO}_3$  in THF in the ambient conditions for 24 h (Scheme 1). In addition to the expected  $\text{K}[\text{Ru}_2(\text{DmAniF})_3(\mu\text{-O},\text{O}'\text{-CO}_3)\text{Cl}]$  as the major product ( $R_f = 0.68$ , MeOH-acetone (v/v, 1:5), to be reported elsewhere [42]), there is a minor and less polar product ( $R_f = 0.80$ , EtOAc-hexanes (v/v, 1:1)). Further column purification provided the title compound **1** in a yield about 12%. The chemical composition of **1** was established through the combination of X-ray structure determination and high resolution mass spectrometry as described in

\* Corresponding authors.

E-mail addresses: [liubin@nwu.edu.cn](mailto:liubin@nwu.edu.cn) (B. Liu), [tren@purdue.edu](mailto:tren@purdue.edu) (T. Ren).



Scheme 1. Synthesis of compound 1.

Section 2.2. It is worth noting that compound **1** is a persistent by-product as well from the reaction between  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$  and phosphate or formate [42]. The formation of **1** is peculiar as it contains four *DmAniF* ligands, one of which must come from a ligand disproportionation reaction of the starting compound  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$ . Furthermore, the  $\text{Ru}_2$  core in **1** is two electrons less than that in  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$ , hinting at possible aerobic oxidation with concurrent incorporation of the bridging oxo ligand. While the high spin ( $S = 3/2$ , see below) nature prevents unambiguous NMR study, compound **1** has been characterized by elemental analysis, HR-MS, UV-vis and FT-IR techniques.

## 2.2. Molecular and electronic structure

Single crystals of X-ray quality were obtained through slow diffusion of hexanes into an ethyl acetate solution of **1**. The molecular structure of **1** is shown in Fig. 1 and the selected bond lengths and angles are listed in Table 1. While there is a pair of *trans-DmAniF* ligands remaining bridging bidentate, each Ru center is also coordinated with a  $\eta^2$ -chelating *DmAniF* ligand. The coordination sphere of diruthenium core is completed with the bridging oxo and acetate ligands, which are *trans*- to each other. Such a ligand arrangement, a hybrid between the classic paddlewheel and common edge-sharing bioctahedral (ESBO) motifs [43], is very rare for diruthenium compounds [1]. Prior examples of diruthenium(III, III) ESBO compounds include  $\text{Ru}_2(\text{C}_5\text{NH}_4\text{NH})_6(\text{PMe}_2\text{Ph})_2$  [44],  $\text{Ru}_2\text{Cl}_6(\text{dmpm})_2$  [45],  $[\text{Ru}_2(\text{OMe})(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-OMe})_3(1\text{-MeIm})_4]^{2+}$  [46],  $\text{Ru}_2(\text{F}_5\text{ap})_4(\mu\text{-CN})_2$  [47] and  $[\text{Ru}_2(3,5\text{-Cl}_2\text{cat})_4(\text{OMe})_2]^{2-}$  [48], and the Ru–Ru distances therein ( $2.55 \pm 0.06 \text{ \AA}$ ) are consistent with the existence of a Ru–Ru single bond. There is also an example of diruthenium(IV,III) ESBO species, namely  $[\text{Ru}_2(3,5\text{-Cl}_2\text{cat})_4(\text{OMe})_2]^{1-}$  [48], which has a Ru–Ru distance of  $2.53 \text{ \AA}$  and a bond order of 1.5. The Ru1–Ru2 distance in **1** is  $2.646 \text{ \AA}$ , which is indicative of bonding interaction between two Ru centers. Based

Table 1

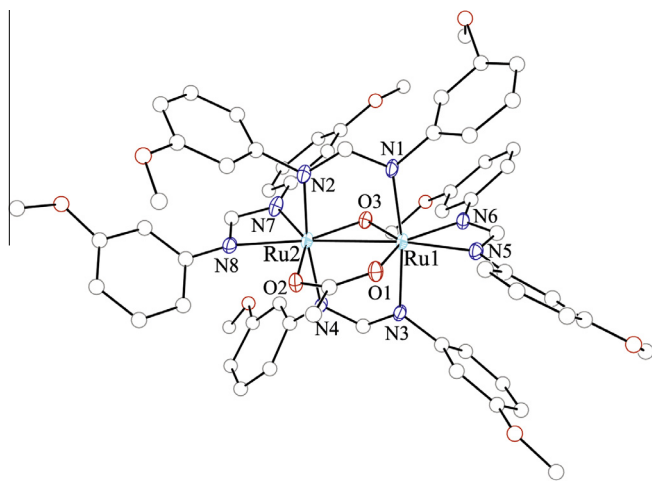
Selected bond lengths (Å) and angles (°) for compound **1**.

Ru1–Ru2	2.6464(7)	Ru1–N6	2.111(6)
Ru1–O3	1.862(4)	Ru2–O2	2.057(5)
Ru2–O3	1.863(5)	Ru2–N2	2.087(7)
Ru1–O1	2.053(5)	Ru2–N4	2.109(6)
Ru1–N1	2.083(7)	Ru2–N7	2.101(6)
Ru1–N3	2.118(6)	Ru2–N8	2.121(6)
Ru1–N5	2.123(5)		
Ru1–O3–Ru2	90.5(2)	Ru2–Ru1–N1	87.39(16)
Ru1–Ru2–O3	44.73(14)	Ru2–Ru1–N3	83.65(15)
Ru2–Ru1–O3	44.75(15)	Ru2–Ru1–O1	83.45(13)
N5–Ru1–N6	62.5(2)	O1–Ru1–N5	84.6(2)
N7–Ru2–N8	62.1(2)	O2–Ru2–N8	85.2(2)
Ru2–Ru1–N5	167.89(18)	N1–Ru1–N3	171.0(2)
Ru2–Ru1–N6	129.50(16)	N2–Ru2–N4	171.2(2)
Ru1–Ru2–N7	129.06(18)	N1–Ru1–O1	88.7(2)
Ru1–Ru2–N8	168.55(19)	N2–Ru2–O2	89.3(2)
O3–Ru1–N1	85.7(2)	N3–Ru1–O1	90.0(2)
O3–Ru1–N3	88.1(2)	N4–Ru2–O2	89.1(2)
O3–Ru1–N6	84.9(2)	N1–Ru1–N5	94.1(2)
O3–Ru1–O1	128.05(19)	N1–Ru1–N6	93.3(2)
O3–Ru2–N2	89.5(2)	N3–Ru1–N5	94.6(2)
O3–Ru2–N4	84.6(2)	N3–Ru1–N6	92.7(2)
O3–Ru2–N7	84.7(2)	N2–Ru2–N7	91.4(2)
O3–Ru2–O2	128.00(19)	N2–Ru2–N8	94.0(2)
Ru1–Ru2–N2	83.65(16)	N4–Ru2–N7	94.6(2)
Ru1–Ru2–N4	87.56(16)	N4–Ru2–N8	94.5(2)
Ru1–Ru2–O2	83.53(12)		

on the comparison with the aforementioned ESBO compounds, it is likely that the Ru–Ru bond order in **1** is one half. Further telling evidence of bonding interaction is the Ru1–O3–Ru2 angle ( $90.3^\circ$ ), which is much smaller than the M–( $\mu$ -X)–M angles observed for ESBO species without M–M bonds [43].

Also worth commenting on is the pseudo-octahedral Ru coordination geometry in **1**, especially the presence of an  $\eta^2$ -chelating *DmAniF*, which is rare among  $\text{M}_2$  compounds supported by diarylformamidinate and bicyclic guanidinate ligands. Literature precedents include  $\text{M} = \text{Mo}$  [49],  $\text{Cr}$  [50],  $\text{Nb}$  [51], and several examples with  $\text{M} = \text{W}$  [52–55], where the  $\eta^2$ -chelating *N,N'*-bidentate ligand is a recurring structural feature. The averaged Ru–N bond length for the bridging *DmAniF* in **1** is about  $2.100(7) \text{ \AA}$ , which is longer than that in the parent compound  $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$  ( $2.064(5) \text{ \AA}$ ) and slightly shorter than the averaged value for the  $\eta^2$ -*DmAniF* in **1** ( $2.114(6) \text{ \AA}$ ). The averaged Ru–O distance ( $1.863(5) \text{ \AA}$ ) is similar to those found for other ESBO diruthenium compounds containing oxo-bridge [56–58].

As elegantly outlined in a review by Cotton [43], the metal–metal bonding configuration in an ESBO bimetallic species depends significantly on the valence electron count of the metal center. ESBO bimetallic species of  $d^4$ – $d^4$  and  $d^5$ – $d^5$  valence electron counts were predicted to have the  $\sigma^2\pi^2(\delta\delta^*)^4$  and  $\sigma^2\pi^2(\delta\delta^*)^4\pi^2$  configurations, respectively. Hence, a  $\sigma^2\pi^2(\delta\delta^*)^4\pi^*$  configuration (and a M–M bond order of  $3/2$ ) would be expected for a  $d^4$ – $d^5$  bimetallic species of an idealized ESBO geometry. Though compound **1** does not belong to the ESBO structural class, its electronic configuration may be derived from the abovementioned one by

Fig. 1. Structural plot of **1** with hydrogen atoms eliminated for clarity.

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