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Ultrasound-assisted synthesis of water-soluble monosubstituted diruthenium compounds

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Dedicated to the memory of Prof. Carlos A. Murillo.

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ABSTRACT

The elusive monosubstituted diruthenium complexes $[Ru_2Cl(DAniF)(O_2CMe)_3]$ (**1**), $[Ru_2Cl(DPhF)(O_2CMe)_3]$ (**2**), $[Ru_2Cl(D\text{-}p\text{-}CNPhF)(O_2CMe)_3]$ (**3**), $[Ru_2Cl(D\text{-}o\text{-}TolF)(O_2CMe)_3]$ (**4**), $[Ru_2Cl(D\text{-}m\text{-}TolF)(O_2CMe)_3]$ (**5**), $[Ru_2Cl(D\text{-}p\text{-}TolF)(O_2CMe)_3]$ (**6**) and $[Ru_2Cl(p\text{-}TolA)(O_2CMe)_3]$ (**7**) have been synthesized using for the first time ultrasound-assisted synthesis to carry out a substitution reaction in metal–metal bonded dinuclear compounds ($DAniF^- = N,N'$-bis(4-anisyl)formamidinate; $DPhF^- = N,N'$-diphenylformamidinate; D-*p*-$CNPhF^- = N,N'$-bis(4-cyanophenyl)formamidinate; D-*o*/*m*/*p*-$TolF^- = N,N'$-bis(2/3/4-tolyl)formamidinate; *p*-$TolA^- = N$-4-tolylamidate). This is a simpler and greener method than the tedious procedures described in the literature, and it has permitted to obtain water-soluble complexes with good yields in a short period of time. A synthetic study has been implemented to find the best experimental conditions to prepare compounds **1**–**7**. Two different types of ligands, formamidinate and amidate, have been used to check the generality of the method for the preparation of monosubstituted complexes. Five new compounds (**2**–**6**) have been obtained using a formamidinate ligand, the synthesis of the previously described compound **1** has been improved, and an unprecedented monoamidate complex has been achieved (**7**). The crystal structures of compounds **3** and **7** have been solved by single crystal X-ray diffraction. These compounds show the typical paddlewheel structure with three acetate ligands and one formamidinate (**3**) or amidate (**7**) bridging ligand at the equatorial positions. The axial positions are occupied by the chloride ligand giving rise to one-dimensional polymer structures that were previously unknown for monosubstituted compounds.

1. Introduction

Since mid-1960's when Stephenson and Wilkinson [1] described the synthesis of the first mixed-valent $[Ru_2Cl(O_2CR)_4]$ (R = alkyl) compound and Cotton and col [2] the first crystal structure, a big number of Ru_2^{5+} paddlewheel diruthenium complexes with Ru-Ru bond order of 2.5 have been synthesized and characterized [3–8]. These compounds have attracted interest for their practical applications in catalysts [9–16], biomedicine [17–20], biotechnology [21–26] or by their potential in material science due to their unique magnetic [27–36] and redox properties [37].

The precise control of synthetic procedures is essential for the obtention of new diruthenium derivates. The most common synthetic routes are conventional methods, like the direct reaction in refluxing solvents or in melted ligand precursors. In the last decade, our research group has investigated the application of microwave-assisted synthesis (MWS) as a greener molecular activation method to prepare diruthenium compounds [38–45]. The MWS has demonstrated to be very useful to substitute the four acetate ligands in $[Ru_2Cl(O_2CMe)_4]$ by other bridging ligands. However, this method focuses mainly on obtaining fully substituted species, $[Ru_2Cl(L\text{-}L)_4]$ (L-L = *O*,*O*-donor, *N*,*Ń*-donor or *N*,*O*-donor bridging ligands), and it does not generally lead to the intermediate substitution species, $[Ru_2Cl(L\text{-}L)_x(O_2CMe)_{4\text{-}x}]$ (x = 1, 2, 3).

The properties of monosubstituted complexes, $[Ru_2Cl(L\text{-}L)(O_2CMe)_3]$, are quite unknown because they have been especially elusive with any synthetic procedure. With *N*,*Ń*-donor ligands there are two examples of monoformamidinatodiruthenium(II,III) complexes [7,8], one 2-amino-4,6-dimethylpyridinate derivative [46], one 2-amino-4,6-dimethylpyrimidinate compound [47] and several monoanilinopyridinatodiruthenium(II,III) complexes [48,49]. Their obtention, based on a conventional synthesis method, is facilitated using a steric hindrance ligand or requires chromatographic column

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purification. To date, no synthetic procedures have been described to carry out monosubstitution processes using *O,O*- or *N,O*-donor bridging ligands and only a few cases of bisubstituted species using carboxylate ligands with high steric hindrance have been published [50,51]. In most cases, only the tetrasubstituted species were described.

In the search of a more direct and greener synthetic method for the preparation of monosubstituted compounds, sonochemistry arises as a promising alternative [52]. In fact, ultrasound-assisted synthesis (USS) is becoming one of the most popular techniques for the preparation of organic [53] or inorganic materials [54]. In addition, USS is associated with faster reaction rates, better yields and higher purity of products, better selectivity, lower energy consumption and less use of hazardous materials participating in the chemical processes [55]. This technique has been recently applied to carry out a self-assembly reaction of a heterometallic diruthenium(II,III) carbonate, $Na[Ni(H_2O)_4Ru_2(CO_3)_4]\cdot 3H_2O$, improving their synthesis conditions and magnetic properties [56].

Inspired by this approach, we now report a novel and general route for the preparation of monosubstituted Ru_2^{5+} derivatives using ultrasound-assisted synthesis. To generalize this technique, six different formamidinates and one amidate ligands have been tested. Thus, the complexes $[Ru_2Cl(DAniF)(O_2CMe)_3]$ (**1**), $[Ru_2Cl(DPhF)(O_2CMe)_3]$ (**2**), $[Ru_2Cl(D\text{-}p\text{-}CNPhF)(O_2CMe)_3]$ (**3**), $[Ru_2Cl(D\text{-}o\text{-}TolF)(O_2CMe)_3]$ (**4**), $[Ru_2Cl(D\text{-}m\text{-}TolF)(O_2CMe)_3]$ (**5**), $[Ru_2Cl(D\text{-}p\text{-}TolF)(O_2CMe)_3]$ (**6**) and $[Ru_2Cl(p\text{-}TolA)(O_2CMe)_3]$ (**7**) have been synthesized ($DAniF^- = N,N'$-bis(4-anisyl)formamidinate; $DPhF^- = N,N'$-diphenylformamidinate; D-p-$CNPhF^- = N,N'$-bis(4-cyanophenyl)formamidinate; D-$o/m/p$-$TolF^- = N,N'$-bis(2/3/4-tolyl)formamidinate; $p\text{-}TolA^- = N$-4-tolylamidate). The complexes have been characterized by elemental analyses, IR and UV–Vis spectroscopy, ESI-MS, cyclic voltammetry, and magnetization measurements. Single-crystal X-ray diffraction studies for compounds **3** and **7** have also been carried out.

2. Experimental

The Scheme 1 is a summary of the chemistry displayed in the present work.

Compounds **1**–**7** have been prepared according to the following procedure: To a round-bottomed flask containing $[Ru_2Cl(O_2CMe)_4]$ (0.4264 g, 0.9 mmol) and the corresponding N,N'-diarylformamidine (**1**–**6**) or amide (**7**) (0.9 mmol) was added Et_3N (300 μL) and ethanol (50 mL). The mixture was sonicated during 150 min (for **1**, **5** and **6**), 180 min (for **2** and **3**), 210 min (for **4**), and 300 min (for **7**) at 80 kHz, room temperature and atmospheric pressure. The mixture was filtered through Celite® in order to remove the unreacted $[Ru_2Cl(O_2CMe)_4]$ and the solvent was evaporated under vacuum. The solid was washed with ethyl ether (50 mL) for compounds **1**, **3**–**7** or toluene (10 mL) for compound **2**, solved in distilled water (150 mL), and the solution was filtered through Celite®. The aqueous solution was placed in a separatory funnel, treated with brine (5 mL) and extracted with dichloromethane (2 × 50 mL). To the organic solution $MgSO_4$ was added. The solution was filtered off and concentrated to dryness. The solid was washed with a 10:6 mixture of hexane and acetone only in the case of compound **7** (10 mL). Then, the product was dried under vacuum.

$[Ru_2Cl(DAniF)(O_2CMe)_3]$ (**1**). **Anal**. Calcd for $C_{21}H_{24}ClN_2O_8Ru_2\cdot H_2O$ (688.03 g/mol), C, 36.66; H, 3.81; N, 4.07; found C, 36.96; H, 4.10; N, 4.06; **ESI-MS** (CH_2Cl_2) m/z calcd for $C_{21}H_{24}N_2O_8Ru_2$ $[M-Cl]^+$ 636.0, found 635.9; **Yield**: 0.4066 g (65%).

$[Ru_2Cl(DPhF)(O_2CMe)_3]$ (**2**). **Anal**. Calcd for $C_{19}H_{20}ClN_2O_6Ru_2\cdot H_2O$ (627.99 g/mol), C, 36.34; H, 3.53; N, 4.46; found C, 36.61; H, 3.82; N, 4.60; **ESI-MS** (CH_2Cl_2) m/z calcd for $C_{19}H_{20}N_2O_6Ru_2$ $[M-Cl]^+$ 575.0, found 574.9; **Yield**: 0.4863 g (86%).

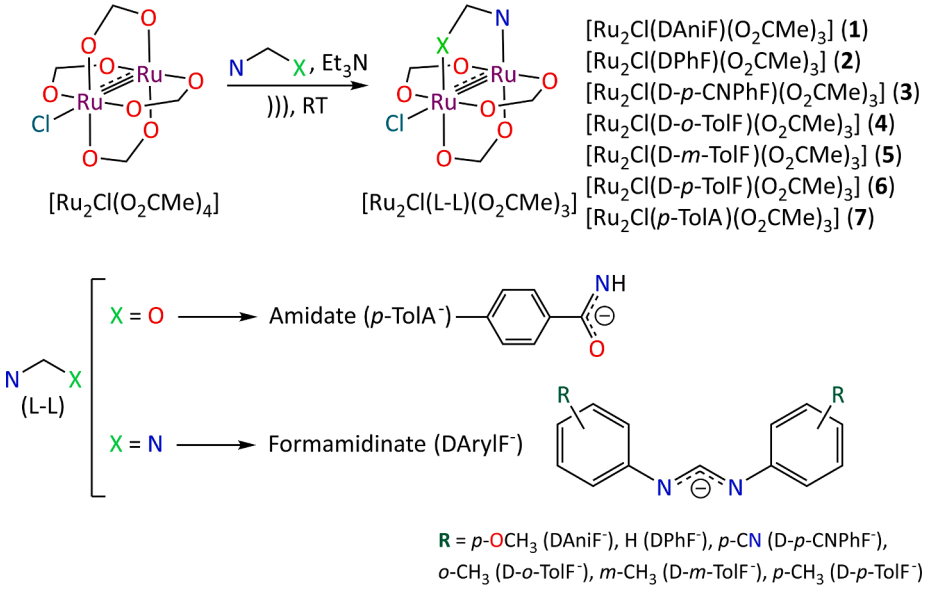
$[Ru_2Cl(D\text{-}p\text{-}CNPhF)(O_2CMe)_3]$ (**3**). **Anal**. Calcd for $C_{21}H_{18}ClN_4O_6Ru_2\cdot H_2O$ (678.00 g/mol), C, 37.20; H, 2.97; N, 8.26; found C, 37.45; H, 3.23; N, 8.12; **ESI-MS** (CH_2Cl_2) m/z calcd for $C_{21}H_{18}N_4O_6Ru_2$ $[M-Cl]^+$ 624.9, found 624.9; **Yield**: 0.4511 g (74%).

$[Ru_2Cl(D\text{-}o\text{-}TolF)(O_2CMe)_3]$ (**4**). **Anal**. Calcd for $C_{21}H_{24}ClN_2O_6Ru_2\cdot H_2O\cdot 0.5CH_2Cl_2$ (698.51 g/mol), C, 36.97; H, 3.90; N, 4.01; found C, 36.99; H, 4.16; N, 4.03; **ESI-MS** (CH_2Cl_2) m/z calcd for $C_{21}H_{24}N_2O_6Ru_2$ $[M-Cl]^+$ 603.9, found 603.9; **Yield**: 0.3951 g (63%).

$[Ru_2Cl(D\text{-}m\text{-}TolF)(O_2CMe)_3]$ (**5**). **Anal**. Calcd for $C_{21}H_{24}ClN_2O_6Ru_2$ (638.02 g/mol), C, 39.53; H, 3.79; N, 4.39; found C, 39.70; H, 4.14; N, 4.48; **ESI-MS** (CH_2Cl_2) m/z calcd for $C_{21}H_{24}N_2O_6Ru_2$ $[M-Cl]^+$ 603.9, found 603.9; **Yield**: 0.4713 g (80%).

$[Ru_2Cl(D\text{-}p\text{-}TolF)(O_2CMe)_3]$ (**6**). **Anal**. Calcd for $C_{21}H_{24}ClN_2O_6Ru_2\cdot H_2O$ (656.04 g/mol), C, 38.45; H, 3.99; N, 4.27; found C, 38.41; H, 4.03; N, 4.27; **ESI-MS** (CH_2Cl_2) m/z calcd for $C_{21}H_{24}N_2O_6Ru_2$ $[M-Cl]^+$ 603.9, found 603.9; **Yield**: 0.4976 g (84%).

$[Ru_2Cl(p\text{-}TolA)(O_2CMe)_3]$ (**7**). **Anal**. Calcd for $C_{14}H_{17}ClNO_7Ru_2$ (548.88 g/mol), C, 30.64; H, 3.12; N, 2.55; found C, 30.75; H, 3.40; N, 2.76; **ESI-MS** (CH_2Cl_2) m/z calcd for $C_{14}H_{17}NO_7Ru_2$ $[M-Cl]^+$ 514.0, found 514.0; **Yield**: 0.3219 (65%).



Scheme 1. Synthesis of monosubstituted diruthenium compounds.

3. Results and discussion

3.1. Synthetic method

According to the literature, all the methods described to obtain intermediate substitution species, using formamidinate ligands, have been carried out through conventional synthesis where the activation energy was heat. Table 1 summarizes the experimental conditions for the two monoformamidinatodiruthenium(II,III) compounds previously reported and the conditions used in the present work for complexes $[Ru_2Cl(DAniF)(O_2CMe)_3]$ (**1**), $[Ru_2Cl(DPhF)(O_2CMe)_3]$ (**2**), $[Ru_2Cl(D\text{-}p\text{-}CNPhF)(O_2CMe)_3]$ (**3**), $[Ru_2Cl(D\text{-}o\text{-}TolF)(O_2CMe)_3]$ (**4**) $[Ru_2Cl(D\text{-}m\text{-}TolF)(O_2CMe)_3]$ (**5**) $[Ru_2Cl(D\text{-}p\text{-}TolF)(O_2CMe)_3]$ (**6**) and $[Ru_2Cl(p\text{-}TolA)(O_2CMe)_3]$ (**7**).

To optimize the synthesis conditions of compounds **1**–**7**, a study of the most crucial variables involved in the process has been carried out:

a) Formamidine nature. Compounds **1**–**6** differ in the nature (donor/acceptor properties) of the R substituent on the phenyl ring of the formamidinates. Depending on the substituent nature the reaction rate varies. Formamidines with electron donating group (R = OMe, Me) show higher reaction rates while the formamidine with an electron withdrawing substituent (R = CN) requires longer reaction times. An exceptional case occurs in the synthesis of compound **4** (R = Me). Although the methyl group should make the formamidine more reactive, its position at *ortho* causes a great steric hindrance and a longer reaction time is needed for the substitution process. The amidine, as expected, is less reactive than the formamidines [39,40]. Therefore, compound **7** needs more time.
b) Atmosphere. In general, the compounds with metal–metal bonds are quite air-sensitive. Several authors have described different synthetic pathways for Ru_2^{5+} species under inert atmosphere (N_2 or Ar) [3,7,57] in order to protect the metal–metal bond, which adds difficulty to the procedure. In this work, all reactions were carried out in air and without dry solvents, maintaining the stability and properties of the binuclear core as demonstrated the physicochemical analyses. This had already been demonstrated by our research group through different articles involving conventional synthesis [30,58] and microwave-assisted synthesis [25,38–45], and it is also applicable to ultrasound-assisted synthesis.
c) Reagents. Although the use of LiCl is necessary for the synthesis of some intermediate species, $[Ru_2Cl(L\text{-}L)_x(O_2CMe)_{4\text{-}x}]$ (x = 2 and 3) [7,59], to improve the yield, in this case the synthesis with or without LiCl, gives the same results, so it has been omitted.
d) Solvent. The best solvent to carry out the sonochemical substitution of Ru_2^{5+} derivatives is ethanol in which the yield of the reaction is high. With other common organic solvents such as tetrahydrofuran (THF), dichloromethane (DCM), acetone, or toluene the substitution reaction does not occur. This inefficient sonochemical process can be explained by the physical properties of these organic solvents (Table 2) which produce low ultrasonic power (Up). Different attempts were also made to execute the synthesis in aqueous medium where the starting reagent $[Ru_2Cl(O_2CMe)_4]$ is soluble. However, the low solubility of the formamidines avoided the substitution reaction.
e) Time and temperature. The reaction times described in this work are the minimum to consume the most $[Ru_2Cl(O_2CMe)_4]$ starting material and the corresponding formamidine. Long sonication times generate an increase of solvent temperature (T > 45 °C) which may lead to increase the formation of by-products.

Table 1
Comparison of the experimental conditions to obtain monosubstituted complexes between conventional methods and sonochemical assisted synthesis.

Compound	Solvent	*T* (°C)	*t* (h)	Yield (%)	Ref
$[Ru_2Cl(DXyl^{2,6}F)(O_2CMe)_3]$	Toluene	≈110	36	32	[7,8]
$[Ru_2Cl(DAniF)(O_2CMe)_3]$ (1)	THF	≈45	12	28	[8]
1–6	Ethanol	RT	2.5–3.5	63–86	This work
7	Ethanol	RT	5 h	65	This work

Table 2
Ultrasonic power (Up) and physical properties of tested solvents [60].

Solvent	Vapor pressure (kPa)	Viscosity (mPa·s)	Surface tension (Dyn/cm)	U_p (W)
Acetone	24.53	0.33	23.3	1.98
Toluene	2.9	0.59	28.5	2.87
THF	17.3	0.55	28	2.14
DCM	46.99	0.44	28.1	1.38
Ethanol	5.9	1.08	22.3	3.47

The synthesis of $[Ru_2Cl(DAniF)(O_2CMe)_3]$ (**1**) complex had been described in the literature and involves inert atmosphere (N_2), THF as solvent, a 1:1.5 M ratio $[Ru_2Cl(O_2CMe)_4]$:HDAniF, temperature lower than 45 °C and 12 h of reaction time. A purification process of the final product through filtration and chromatographic column is also necessary. The application of USS has significatively enhanced the obtention of compound **1**, with a reduction of temperature and reaction time, without the need of inert atmosphere or chromatographic column during purification and achieving more than double yield. With the application of USS to the obtention of monosubstituted compounds, it becomes possible to reach some of the twelve principles of green chemistry, such as atom economy, the avoid of high temperatures and pressures or the design of energy-efficient processes.

This work describes for the first time that USS can be applied to carry out ligand substitution reactions in metal–metal bonded binuclear compounds.

3.2. Structural characterization and properties

The isolated compounds **1**–**7** are stable in both solution (in water, dichloromethane, tetrahydrofuran, dimethyl sulfoxide, acetone, methanol, and ethanol) and in the solid state under ambient conditions.

FTIR spectra of the compounds confirmed the presence of representative functional groups due to the coordination of formamidinate or amidate ligands to the diruthenium core (Fig. S1, ESI). Compounds **1**–**7** spectra contain the aromatic and non-aromatic C–H stretches around 3040 cm^{-1} and 2930 cm^{-1}, respectively, and sharp peaks at ≈1640 and 1600 cm^{-1} ($\nu(C{=}C)_{Ar}$), ≈1490 cm^{-1} (ν_a(O-C-O)), ≈1350 cm^{-1} (ν_s (O-C-O)), ≈1070, 1020, 950 cm^{-1} ($\delta_{ip}(C{=}C{-}H)_{Ar}$) and ≈690 cm^{-1} ($\delta_{oop}(C{=}C{-}H)_{Ar}$). The spectrum of compound **7** containing an amidate group shows a band at ≈3340 cm^{-1} due to N–H stretching vibration and a strong band in the 1430–1400 cm^{-1} region associated with a combination of the ν(C=O), ν(C-N) and ν(C–C) vibration. For compounds with formamidinate ligands (**1**–**6**), strong bands at ≈1435, 1310 and 1225 cm^{-1} related to ν(C-N) are observed. The spectra of derivatives **1** and **3** show representative peaks corresponding to the *para* substituent at 1025 cm^{-1} (ν(C-OCH_3)), and 2217 cm^{-1} (ν C≡N), respectively.

The compounds show the typical pattern of diruthenium isotopic distribution in ESI-MS. The maximum *m/z* peaks in all mass spectra are ascribed to the $[M{-}Cl]^+$ and $[M{+}CH_3CO]^+$ fragments that agree with the simulated MS patterns (Fig. S2, ESI). When ionization is performed by MALDI-MS, only the fragment $[M{-}Cl]^+$ appears in the spectrum, suggesting the absence of by-products. These results corroborate the integrity of paddlewheel structure maintaining three acetates and one formamidine or amidate bridging ligand bonded to the diruthenium core. This technique has also allowed us to monitor the substitution reaction for compounds **1**–**7**. It was recorded a spectrum of crude

reaction at 1.5 h for all the complexes (Fig. S3, ESI). There are two peaks for compounds **1**–**3**, **5** and **6** that can be assigned to the corresponding mono- and bis-substituted species losing the axial chloride ligand. The main peak corresponds to the monosubstituted species, $[M-Cl]^+$, being the other one almost residual. After purification, this by-product is eliminated. For compound **4**, the bisubstituted species does not appear probably because its formation is hindered by the steric effect of the methyl group at *ortho* position of the aromatic ring in the formamidinate ligand. For compound **7** there is also no species with a higher substitution degree, but this can be associated with the lower reactivity of the amides with respect to the formamidines. This lower reactivity has already been observed in the tetrasubstitution reactions carried out by microwave-assisted solvothermal synthesis. The reactions with formamidines require around 1–2 h [39], while 16 h are necessary when amides are used instead [40,43,44].

Complexes **1**–**7** show intense colors both in the solid state and in solution. The electronic absorption spectra in the vis-NIR region were recorded in dichloromethane solution (Fig. S4, ESI). Compounds **1**–**6** display the typical profile of other high-spin ($S = 3/2$) partial substituted diruthenium complexes reported in the literature [6]. In compound **7**, with an amidate ligand, the absorption spectrum is very similar to the monosubstituted compounds with a formamidinate ligand. In general, it can be observed a band around 370 nm that can be tentatively assigned to a $\pi(Cl) \rightarrow \pi^*(Ru_2)$ transition, a second band (which in some compounds appears with a shoulder) in the 450–650 nm region that can be attributed to $\pi(RuO/N,Ru_2) \rightarrow \pi^*(Ru_2)$ transitions, and a less intense band in the 900–1050 nm region that can be attributed to a $\delta(Ru_2) \rightarrow \delta^*(Ru_2)$ transition (Table S1, ESI).

Magnetization measurements at variable temperature were carried out for compounds **1**–**7**. The $\chi_M T$ values at room temperature of **1**–**7** are in the 2.23–1.84 $cm^3 \cdot K \cdot mol^{-1}$ range (Table 3). These values are close to the expected spin-only value, 1.87 $cm^3 \cdot K \cdot mol^{-1}$ ($g = 2$), for a quartet state arising from a $\sigma^2\delta^2\pi^4(\delta^*\pi^*)^3$ electronic configuration [3,6,61]. On cooling, $\chi_M T$ value decreases continuously (Figs. S5–S11, ESI), which is typically observed in this type of complexes and ascribed to a strong zero-field splitting (D) and a weak intermolecular antiferromagnetic coupling [3,6]. For this reason, the χ_M and the $\chi_M T$ data were fitted using the Cukiernik model [62–64] taking into account a weak intermolecular antiferromagnetic coupling (zJ) and a temperature-independent paramagnetism (TIP) term in addition to the D and g parameters (see equations S1-S5, ESI). The values obtained from the fits are shown in Table 3 and are similar to those previously reported for another monoformamidinatodiruthenium(II,III) complex [8].

According to the Cambridge Structural Database [65] (CSD 2020), no crystal structure of monosubstituted diruthenium compounds with amidate ligands has been reported and there are only two crystal structures with a formamidinate ligand ($HDXyl^{2,6}F$) [8]. In the present work, the crystal structures of compounds **3** and **7** have been solved by single crystal X-ray diffraction (see Tables S2 and S3, ESI). Both compounds, **3**·$\mathbf{CH_2Cl_2}$ and **7**·$\mathbf{2CH_2Cl_2}$, crystallize with dichloromethane molecules in the monoclinic system, space group $P2_1/n$ for compound **3** and $P2_1/c$ for compound **7**.

These compounds show the typical paddlewheel structure (Fig. 1). The coordination environment for both ruthenium atoms is octahedral. Each diruthenium unit has retained three acetate ligands along with one formamidinate (**3**) or amidate (**7**) bridging ligand at the equatorial positions, while the axial positions are occupied by bridging chloride ligands. The Ru-Ru bond distances of 2.306 Å (**3**) and 2.280 Å (**7**) are in the range described for related Ru_2^{5+} derivatives [6]. The chloride is aligned with the diruthenium core with a Ru2-Ru1-Cl1 angle of 175.38° (**3**) and 176.61° (**7**). The presence of a different ligand (amidate or formamidinate) in the structure results in two types of acetates, being the Ru-O bond distance of the acetate *trans* to the formamidinate (**3**) or amidate (**7**) longer than the acetates *trans* to each other, as it has been also observed for other mono-substituted compounds described in the literature [8,46–48]. This fact can be attributed to the better donor character of the *N*-donor ligand relative to the corresponding carboxylate ligand.

In both compounds the chloride ligand bridges two diruthenium units, giving rise to a polymeric structure. For complex **3**, the Ru1-Cl1-Ru2 angle is 174.02° giving an almost linear polymeric chain whereas for compound **7** this angle is 124.25°, giving rise to a clear zigzag chain (Fig. 2). In both compounds, the Ru1-Cl1 and Cl1-Ru2 distances are similar (2.625 and 2.637 Å for **3**; 2.534 and 2.548 Å for **7**), indicating the formation of an almost symmetrical bridge between the diruthenium units. These bond distances are longer for compound **3** than those usually observed for analogous compounds [8], suggesting weaker interactions.

In compound **3** (Fig. 2a), the steric hindrance of the formamidinate substituents imposes a rotation of 140° between the formamidinate ligands of consecutive dimeric units, resulting in a staggered conformation along the chains. The dichloromethane solvent molecule allows weak interchain (H22A···N3) and intrachain (H22A···O2 and H22B···O3) interactions that keep the different chains in contact. For compound **7** (Fig. 2b), the adjacent diruthenium units are rotated 180° along the zig-zag chains. The only observed interchain interaction is a weak π-π overlap between the aromatic rings of neighboring amidate units with an average interplanar distance of 3.38 Å. As in the previous compound, the dichloromethane solvent molecules participate in weak intrachain interactions (H15A···Cl1, H15B···O3, H16B···Cl1 and H16B···O5).

The redox properties of compounds **1**–**7** were analyzed using cyclic voltammetry (CV). The results are plotted in Fig. S12 and the electrochemical data are summarized in Table 4.

All the complexes show only one-electron redox couple within the cathodic limit of water. This is assigned to the Ru_2^{5+}/Ru_2^{4+} redox couple according to other diruthenium complexes with similar ligands in aqueous and nonaqueous solvents [48,49,58,66–72]. The redox properties of these compounds vary depending on the nature of the ligand. The substitution of one acetate bridging ligand (O,O-donor) for one formamidinate (N,N-donor) or amidate (N,O-donor) bridging ligand increases the electron density on the diruthenium core which results in more negative redox potentials relative to the starting $[Ru_2Cl(O_2CMe)_4]$ ($E_{1/2}$ = 0.04 V [48]). For complexes **1**–**6**, the presence of electron donating substituents in the aromatic ring (compounds **1**, **4**–**6**) generates more negative potentials, while the presence of an electron-

Table 3
Magnetic parameters obtained from the magnetic data of **1**–**7**.

Compound	$\chi_M T$ *at 300 K* ($cm^3 \cdot K \cdot mol^{-1}$)	g	D (cm^{-1})	zJ (cm^{-1})	TIP ($cm^3 \cdot mol^{-1}$)	σ^{2**}
1	2.19	2.00*	68	−0.28	1.14×10^{-3}	2.41×10^{-4}
2	2.10	2.00*	68	−0.32	8.75×10^{-4}	2.69×10^{-4}
3	2.23	2.19	67	−0.85	1.33×10^{-4}	3.58×10^{-4}
4	1.84	2.00*	75	−0.25	1.83×10^{-12}	3.62×10^{-4}
5	2.09	2.09	53	−0.41	7.45×10^{-14}	2.95×10^{-4}
6	2.00	2.00	63	−0.58	6.43×10^{-4}	3.04×10^{-4}
7	2.18	2.11	76	−1.28	6.28×10^{-4}	4.37×10^{-4}

*A g value of 2 was fixed in these fittings. Otherwise, values of 1.97, 1.98 and 1.95 were obtained for **1**, **2** and **4**, respectively.

** $\sigma^2 = \sum (\chi_M \cdot T_{calcd} - \chi_M \cdot T_{exp})^2 / \sum (\chi_M \cdot T_{exp})^2$.

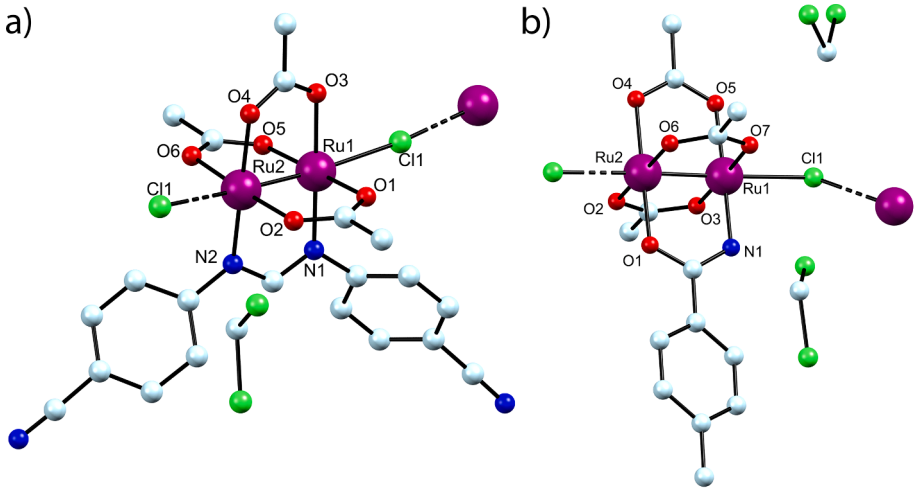


Fig. 1. Asymmetric unit representation of compound **3**·CH_2Cl_2 (a) and compound **7**·$2CH_2Cl_2$ (b). Hydrogen atoms have been omitted for clarity.

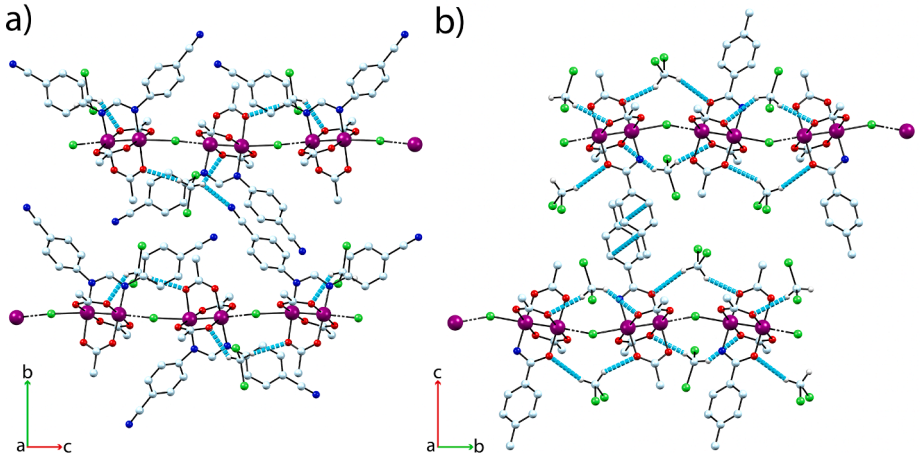


Fig. 2. Crystal packing of compound **3**·CH_2Cl_2 (a) and compound **7**·$2CH_2Cl_2$ (d) with the representative interactions marked in blue. Some hydrogen atoms have been omitted for clarity.

Table 4
Electrochemical data (V, vs. Ag/AgCl) from CV of complexes **1**–**7**.

Compound	$E_{1/2}$	ΔE
1	−0.35	0.15
2	−0.33	0.12
3	−0.18	0.15
4	−0.37	0.12
5	−0.32	0.19
6	−0.35	0.10
7	−0.16	0.16

withdrawing substituent (compound **3**) causes a positive cathodic shift. The substituent position on the aromatic ring (*ortho*, *meta* or *para*) seems to be more relevant that the electron donating character of functional group (i.e., $E_{1/2}$ = -0.35 V for compound **1** (*p*-OMe) and **6** (*p*-Me)). Moreover, it seems that the influence of substituent in *ortho* position is greater than in *para* position (i.e., $E_{1/2}$ = -0.37 V for compound **4** (*o*-Me), and being almost negligible when the electron donating substituent is located in *meta* position ($E_{1/2}$ = -0.32 V for compound **5**) compared to the unsubstituted formamidinate derivative ($E_{1/2}$ = -0.33 for compound **2**). The amidate ligand presents a lower donating character than the formamidinate, a fact reflected in the low negative reduction potential observed for the corresponding derivative, **7**.

4. Conclusions

This work presents an alternative method for the synthesis of metal–metal bonded compounds based on the sonochemical activation (compounds **1**–**7**). This procedure permits an effective replacement of only one acetate group. It works not only with different types of formamidines but also with amides which suggests that this is a general method of preparation for monosustituted complexes with *N*,*N*- or *N*,*O*-donor ligands.

Additionally, this method of synthesis considerably reduces reaction times, uses a greener solvent (ethanol) and saves energy with respect to other methods described for dimetallic compounds. The aqueous media solubility of these complexes may be very important for their potential in fields such as biomedicine or biotechnology.

Author contributions

A.T. carried out the experiments and wrote the original draft. M.C. described the magnetic behavior. A.G. solved the crystal structures. A.E. S.-P., S.H. and R.J.-A., realized the supervision of the work and the writing-review. S.H. was also in charge of the project administration.

CRediT authorship contribution statement

Aarón Terán: Methodology, Investigation, Writing – original draft, Visualization. **Miguel Cortijo:** Formal analysis. **Ángel Gutiérrez:** Formal analysis. **Ana E. Sánchez-Peláez:** Supervision, Writing – review & editing. **Santiago Herrero:** Supervision, Writing – review & editing, Conceptualization, Project administration, Funding acquisition. **Reyes Jiménez-Aparicio:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2021.105828.

References

[1] T.A. Stephenson, G. Wilkinson, New ruthenium carboxylate complexes, J. Inorg. Nucl. Chem. 28 (10) (1966) 2285–2291, https://doi.org/10.1016/0022-1902(66)80118-5.
[2] M.J. Bennett, K.G. Caulton, F.A. Cotton, Structure of tetra-n-butyratodiruthenium chloride, a compound with a strong metal-metal bond, Inorg. Chem. 8 (1) (1969) 1–6, https://doi.org/10.1021/ic50071a001.
[3] F.A. Cotton, C.A. Murillo, R.A. Walton, Multiple Bonds Between Metal Atoms, Springer, New York, Third Edition, 2005.
[4] S.T. Liddle, Molecular Metal-Metal Bonds: Compounds, Synthesis, Properties, Wiley-VCH Verlag GmbH & Co., Weinheim, Germany, 2015.
[5] M.A.S. Aquino, Recent developments in the synthesis and properties of diruthenium tetracarboxylates, Coord. Chem. Rev. 248 (11-12) (2004) 1025–1045.
[6] M. Cortijo, R. González-Prieto, S. Herrero, J.L. Priego, R. Jiménez-Aparicio, The use of amidinate ligands in paddlewheel diruthenium chemistry, Coord. Chem. Rev. 400 (2019) 213040, https://doi.org/10.1016/j.ccr.2019.213040.
[7] P.A. Angaridis, F.A. Cotton, C.A. Murillo, A.S. Filato, M.A. Petrukhina, Diruthenium Formamidinato Complexes, in: Inorganic Syntheses, John Wiley & Sons, Inc., 2014: pp. 114–121.
[8] P. Angaridis, F.A. Cotton, C.A. Murillo, D. Villagrán, X. Wang, Paramagnetic precursors for supramolecular assemblies: selective syntheses, crystal structures, and electrochemical and magnetic properties of $Ru_2(O_2CMe)_{4-n}(formamidinate)_nCl$ complexes, n = 1–4, Inorg. Chem. 43 (2004) 8290–8300, https://doi.org/10.1021/ic049108w.
[9] C.N. Kato, M. Ono, T. Hino, T. Ohmura, W. Mori, Room temperature oxidation of alcohols with 1atm dioxygen and air catalyzed by a novel three-dimensional microporous ruthenium(II, III) 4,4′,4″,4‴-(21H,23H-porphine-5,10,15,20-tetrayl) tetrakisbenzoate tetrafluoroborate, Catal. Commun. 7 (9) (2006) 673–677, https://doi.org/10.1016/j.catcom.2006.02.011.
[10] J.E. Barker, T. Ren, Diruthenium(II, III) Bis(tetramethyl-1,3-benzenedipropionate) as a novel catalyst for tert-butyl hydroperoxide oxygenation, Inorg. Chem. 47 (7) (2008) 2264–2266, https://doi.org/10.1021/ic800035w.
[11] M.E. Harvey, D.G. Musaev, J. Du Bois, A diruthenium catalyst for selective, intramolecular allylic C-H amination: reaction development and mechanistic insight gained through experiment and theory, J. Am. Chem. Soc. 133 (43) (2011) 17207–17216, https://doi.org/10.1021/ja203576p.
[12] T. Nakae, T. Yasunaga, M. Kamiya, Y. Fukumoto, N. Chatani, Skeletal reorganization of enynes catalyzed by a Ru(II)–Ru(III) mixed-valence complex under an atmosphere of O_2 or CO, Chem. Lett. 42 (12) (2013) 1565–1567, https://doi.org/10.1246/cl.130785.
[13] C.-H. Lee, C.-L. Wu, S.-A. Hua, Y.-H. Liu, S.-M. Peng, S.-T. Liu, Complexation of Tetrakis(acetato)chloridodiruthenium with Naphthyridine-2,7-dicarboxylate – Characterization and Catalytic Activity, Eur. J. Inorg. Chem. 2015 (8) (2015) 1417–1423, https://doi.org/10.1002/ejic.201403156.
[14] J.F. Berry, Metal–metal multiple bonded intermediates in catalysis, J. Chem. Sci. 127 (2) (2015) 209–214, https://doi.org/10.1007/s12039-015-0773-6.
[15] F. Lupi, T. Marzo, G. D'Adamio, S. Cretella, F. Cardona, L. Messori, A. Goti, Diruthenium diacetate catalysed aerobic oxidation of hydroxylamines and improved chemoselectivity by immobilisation to lysozyme, ChemCatChem 9 (22) (2017) 4225–4230, https://doi.org/10.1002/cctc.201701083.
[16] T. Miyazawa, T. Suzuki, Y. Kumagai, K. Takizawa, T. Kikuchi, S. Kato, A. Onoda, T. Hayashi, Y. Kamei, F. Kamiyama, M. Anada, M. Kojima, T. Yoshino, S. Matsunaga, Chiral paddle-wheel diruthenium complexes for asymmetric catalysis, Nat. Catal. 3 (10) (2020) 851–858, https://doi.org/10.1038/s41929-020-00513-w.
[17] D. de Oliveira Silva, Ruthenium Compounds Targeting Cancer Therapy, in: Frontiers in Anti-Cancer Drug Discovery, Bentham Science Publishers, 2014: pp. 88–156.
[18] Hanif-Ur-Rehman, T.E. Freitas, R.N. Gomes, A. Colquhoun, D. de Oliveira Silva, Axially-modified paddlewheel diruthenium(II, III)-ibuprofenato metallodrugs and the influence of the structural modification on U87MG and A172 human glioma cell proliferation, apoptosis, mitosis and migration, J. Inorg. Biochem. 165 (2016) 181–191, https://doi.org/10.1016/j.jinorgbio.2016.10.003.
[19] S.R. Alves Rico, A.Z. Abbasi, G. Ribeiro, T. Ahmed, X.Y. Wu, D. de Oliveira Silva, Diruthenium(II, III), metallodrugs of ibuprofen and naproxen encapsulated in intravenously injectable polymer–lipid nanoparticles exhibit enhanced activity against breast and prostate cancer cells, Nanoscale 9 (2017) 10701–10714, https://doi.org/10.1039/C7NR01582H.
[20] E. Barresi, I. Tolbatov, A. Pratesi, V. Notarstefano, E. Baglini, S. Daniele, S. Taliani, N. Re, E. Giorgini, C. Martini, F. Da Settimo, T. Marzo, D. La Mendola, A mixed-valence diruthenium(II, III) complex endowed with high stability: from experimental evidence to theoretical interpretation, Dalton Trans. 49 (2020) 14520–14527, https://doi.org/10.1039/D0DT02527E.
[21] R.L.S.R. Santos, R. van Eldik, D. de Oliveira Silva, Kinetic and mechanistic studies on reactions of diruthenium(II, III) with biologically relevant reducing agents, Dalton Trans. 42 (2013) 16796–16805, https://doi.org/10.1039/C3DT51763B.
[22] L. Messori, T. Marzo, R.N.F. Sanches, Hanif-Ur-Rehman, D. de Oliveira Silva, A. Merlino, Unusual structural features in the lysozyme derivative of the Tetrakis (acetato)chloridodiruthenium(II, III) Complex, Angew. Chem. Int. Ed. 53 (2014) 6172–6175, https://doi.org/10.1002/anie.201403337.
[23] G. Lozano, R. Jimenez-Aparicio, S. Herrero, E. Martinez-Salas, Fingerprinting the junctions of RNA structure by an open-paddlewheel diruthenium compound, RNA 22 (3) (2016) 330–338, https://doi.org/10.1261/rna.054353.115.
[24] L. Messori, A. Merlino, Protein metalation by metal-based drugs: X-ray crystallography and mass spectrometry studies, Chem. Commun. 53 (85) (2017) 11622–11633, https://doi.org/10.1039/C7CC06442J.
[25] Á. Valentín-Pérez, J. Perles, S. Herrero, R. Jiménez-Aparicio, Coordination capacity of cytosine, adenine and derivatives towards open-paddlewheel diruthenium compounds, J. Inorg. Biochem. 187 (2018) 109–115, https://doi.org/10.1016/j.jinorgbio.2018.06.010.
[26] I. Coloma, M. Cortijo, I. Fernández-Sánchez, J. Perles, J.L. Priego, C. Gutiérrez, R. Jiménez-Aparicio, B. Desvoyes, S. Herrero, pH- and time-dependent release of phytohormones from diruthenium complexes, Inorg. Chem. 59 (11) (2020) 7779–7788, https://doi.org/10.1021/acs.inorgchem.0c00844.
[27] P. Angaridis, F.A. Cotton, C.A. Murillo, D. Villagrán, X. Wang, Structural and magnetic evidence concerning spin crossover in formamidinate compounds with Ru_2^{5+} cores, J. Am. Chem. Soc. 127 (14) (2005) 5008–5009, https://doi.org/10.1021/ja050828r.
[28] M.C. Barral, S. Herrero, R. Jiménez-Aparicio, M.R. Torres, F.A. Urbanos, A spin-admixed ruthenium complex, Angew. Chem. Int. Ed. 44 (2) (2005) 305–307, https://doi.org/10.1002/anie.200461463.
[29] F.A. Cotton, S. Herrero, R. Jiménez-Aparicio, C.A. Murillo, F.A. Urbanos, D. Villagrán, X. Wang, How small variations in crystal interactions affect macroscopic properties, J. Am. Chem. Soc. 129 (42) (2007) 12666–12667, https://doi.org/10.1021/ja075808z.
[30] M.C. Barral, D. Casanova, S. Herrero, R. Jiménez-Aparicio, M.R. Torres, F. Urbanos, Tuning the magnetic moment of $[Ru_2(DPhF)_3(O_2CMe)L]^+$ Complexes (DPhF=N, N′-Diphenylformamidinate): a theoretical explanation of the axial ligand influence, Chem. Eur. J. 16 (21) (2010) 6203–6211, https://doi.org/10.1002/chem.200903404.
[31] A. Raghavan, F. Yuan, T. Ren, Drastic tuning of the electronic structures of diruthenium Aryl complexes by isoelectronic axial ligands, Inorg. Chem. 59 (13) (2020) 8663–8666, https://doi.org/10.1021/acs.inorgchem.0c01755.
[32] J. Zhang, W. Kosaka, Y. Kitagawa, H. Miyasaka, A metal–organic framework that exhibits CO_2-induced transitions between paramagnetism and ferrimagnetism, Nat. Chem. 13 (2) (2021) 191–199, https://doi.org/10.1038/s41557-020-00577-y.
[33] G. Estiú, F.D. Cukiernik, P. Maldivi, O. Poizat, Electronic, magnetic, and spectroscopic properties of binuclear diruthenium tetracarboxylates: a theoretical and experimental study, Inorg. Chem. 38 (1999) 3030–3039, https://doi.org/10.1021/ic981098.
[34] R. Jiménez-Aparicio, F.A. Urbanos, J.M. Arrieta, Magnetic properties of diruthenium(II, III) carboxylate compounds with large zero-field splitting and strong antiferromagnetic coupling, Inorg. Chem. 40 (4) (2001) 613–619, https://doi.org/10.1021/ic0001154.
[35] M. Mikuriya, D. Yoshioka, M. Handa, Magnetic interactions in one-, two-, and three-dimensional assemblies of dinuclear ruthenium carboxylates, Coord. Chem. Rev. 250 (17-18) (2006) 2194–2211, https://doi.org/10.1016/j.ccr.2006.01.011.
[36] G.M. Chiarella, F.A. Cotton, C.A. Murillo, K. Ventura, D. Villagrán, X. Wang, Manipulating magnetism: Ru_2^{5+} paddlewheels devoid of axial interactions, J. Am. Chem. Soc. 136 (27) (2014) 9580–9589, https://doi.org/10.1021/ja5020647.

[37] E. Van Caemelbecke, T. Phan, W.R. Osterloh, K.M. Kadish, Electrochemistry of metal-metal bonded diruthenium complexes, Coord. Chem. Rev. 434 (2021) 213706, https://doi.org/10.1016/j.ccr.2020.213706.

[38] S. Herrero, R. Jiménez-Aparicio, J. Perles, J.L. Priego, F.A. Urbanos, First microwave synthesis of multiple metal-metal bond paddlewheel compounds, Green Chem. 12 (2010) 965–967, https://doi.org/10.1039/C003411H.

[39] S. Herrero, R. Jiménez-Aparicio, J. Perles, J.L. Priego, S. Saguar, F.A. Urbanos, Microwave methods for the synthesis of paddlewheel diruthenium compounds with N, N-donor ligands, Green Chem. 13 (2011) 1885–1890, https://doi.org/10.1039/C0GC00800A.

[40] P. Delgado, R. González-Prieto, R. Jiménez-Aparicio, J. Perles, J.L. Priego, R. M. Torres, Comparative study of different methods for the preparation of tetraamidato- and tetracarboxylatodiruthenium compounds, Structural and magnetic characterization, Dalton Trans. 41 (2012) 11866–11874, https://doi.org/10.1039/C2DT30939D.

[41] M. Cortijo, P. Delgado-Martínez, R. González-Prieto, S. Herrero, R. Jiménez-Aparicio, J. Perles, J.L. Priego, M.R. Torres, Microwave and solvothermal methods for the synthesis of nickel and ruthenium complexes with 9-anthracene carboxylate ligand, Inorg. Chim. Acta. 424 (2015) 176–185, https://doi.org/10.1016/j.ica.2014.07.063.

[42] R. González-Prieto, S. Herrero, R. Jiménez-Aparicio, E. Morán, J. Prado-Gonjal, J. L. Priego, R. Schmidt, Microwave-assisted solvothermal synthesis of inorganic compounds (molecular and non molecular). Microwave Chemistry, De Gruyter, Berlin, Germany, 2017.

[43] P. Delgado-Martínez, C. Freire, R. González-Prieto, R. Jiménez-Aparicio, J. L. Priego, M.R. Torres, Synthesis crystal structure, and magnetic properties of amidate and carboxylate dimers of ruthenium, Crystals 7 (2017) 192, https://doi.org/10.3390/cryst7070192.

[44] P. Delgado-Martínez, R. González-Prieto, C.J. Gómez-García, R. Jiménez-Aparicio, J.L. Priego, M.R. Torres, Structural, magnetic and electrical properties of one-dimensional tetraamidatodiruthenium compounds, Dalton Trans. 43 (8) (2014) 3227–3237, https://doi.org/10.1039/C3DT52727A.

[45] P. Delgado-Martínez, A. Elvira-Bravo, R. González-Prieto, J.L. Priego, R. Jimenez-Aparicio, M.R. Torres, Synthesis of $Ru_2Br(\mu\text{-}O_2CC_6H_4\text{–}R)_4$ (R = *o*-Me, *m*-Me, *p*-Me) using microwave activation: structural and magnetic properties, Inorganics 2 (2014) 524–536, https://doi.org/10.3390/inorganics2030524.

[46] F.A. Cotton, A. Yokochi, Synthesis and characterization of the series of compounds $Ru_2(O_2CMe)_x(admp)_{4\text{-}x}Cl$ (Hadmp = 2-Amino-4,6-dimethylpyridine, x = 3, 2, 1, 0), Inorg. Chem. 37 (11) (1998) 2723–2728, https://doi.org/10.1021/ic971428a.

[47] C. Kachi-Terajima, H. Miyasaka, T. Ishii, K.-ichi. Sugiura, M. Yamashita, Structure and electrochemistry of the bridging-ligand mono-substituted diruthenium compound, $[Ru_2(II, III)(_O2CC_H3)_3(admpym)(Cl)(MeOH)]$ (Hadmpym=2-amino-4,6-dimethylpyrimidine), Inorg. Chim. Acta. 332 (1) (2002) 210–215, https://doi.org/10.1016/S0020-1693(02)00712-0.

[48] W.R. Osterloh, G. Galindo, M.J. Yates, E. Van Caemelbecke, K.M. Kadish, Synthesis, structural and physicochemical properties of water-soluble mixed-ligand diruthenium complexes containing anilinopyridinate bridging ligands, Inorg. Chem. 59 (1) (2020) 584–594, https://doi.org/10.1021/acs.inorgchem.9b02838.

[49] K.M. Kadish, R. Garcia, T. Phan, J. Wellhoff, E. Van Caemelbecke, J.L. Bear, Electrochemical and spectroscopic characterization of a series of mixed-ligand diruthenium compounds, Inorg. Chem. 47 (23) (2008) 11423–11428, https://doi.org/10.1021/ic8017369.

[50] R. Gracia, N.J. Patmore, Synthesis and characterisation of diruthenium paddlewheel compounds bearing 2,6-Di(p-tolyl)benzoate ligands, J. Clust. Sci. 21 (3) (2010) 339–350, https://doi.org/10.1007/s10876-010-0310-1.

[51] Y. Sekine, W. Kosaka, H. Kano, C. Dou, T. Yokoyama, H. Miyasaka, trans-Heteroleptic carboxylate-bridged paddlewheel diruthenium(II, II) complexes with 2,6-bis(trifluoromethyl)benzoate ligands, Dalton Trans. 45 (2016) 7427–7434, https://doi.org/10.1039/C6DT00569A.

[52] G. Chatel, R.S. Varma, Ultrasound and microwave irradiation: contributions of alternative physicochemical activation methods to Green Chemistry, Green Chem. 21 (22) (2019) 6043–6050, https://doi.org/10.1039/C9GC02534K.

[53] B. Banerjee, Recent developments on ultrasound-assisted one-pot multicomponent synthesis of biologically relevant heterocycles, Ultrason. Sonochem. 35 (2017) 15–35, https://doi.org/10.1016/j.ultsonch.2016.10.010.

[54] Z. Li, T. Zhuang, J. Dong, L. Wang, J. Xia, H. Wang, X. Cui, Z. Wang, Sonochemical fabrication of inorganic nanoparticles for applications in catalysis, Ultrason. Sonochem. 71 (2021) 105384, https://doi.org/10.1016/j.ultsonch.2020.105384.

[55] Y. Yao, Y. Pan, S. Liu, Power ultrasound and its applications: a state-of-the-art review, Ultrason. Sonochem. 62 (2020) 104722, https://doi.org/10.1016/j.ultsonch.2019.104722.

[56] J.-Y. Li, Y.-C. Tian, L.-N. Feng, Z.-Q. Zhou, L.-L. Wang, J.-H. Yang, B. Liu, Enhancing magnetic hardness by sonication assisted synthesis of heterometallic carbonato spin-glass $Na[Ni(H_2O)_4Ru_2(CO_3)_4]\cdot 3H_2O$, Chem. Commun. 56 (9) (2020) 1369–1372, https://doi.org/10.1039/C9CC07876B.

[57] W.-Z. Chen, T. Ren, Selective ligand modification on the periphery of diruthenium compounds: toward new metal-alkynyl scaffolds, Organometallics 24 (2005) 2660–2669, https://doi.org/10.1021/om050068t.

[58] M.C. Barral, T. Gallo, S. Herrero, R. Jiménez-Aparicio, M.R. Torres, F.A. Urbanos, Equatorially connected diruthenium(II,III) units toward paramagnetic supramolecular structures with singular magnetic properties, Inorg. Chem. 45 (9) (2006) 3639–3647, https://doi.org/10.1021/ic052174t.

[59] M.C. Barral, S. Herrero, R. Jiménez-Aparicio, M.R. Torres, F.A. Urbanos, Preparation, characterization, and crystal structure of $[Ru_2Cl(\mu\text{-}O_2CMe)(\mu\text{-}PhNCHNPh)_3]$: a way to tris(formamidinato)diruthenium(II, III) complexes, Inorg. Chem. Commun. 7 (1) (2004) 42–46, https://doi.org/10.1016/j.inoche.2003.09.016.

[60] C.P. Frizzo, C. Bacim, D.N. Moreira, L.V. Rodrigues, G.C. Zimmer, H.G. Bonacorso, N. Zanatta, M.A.P. Martins, Sonochemical heating profile for solvents and ionic liquid doped solvents, and their application in the N-alkylation of pyrazoles, Ultrason. Sonochem. 32 (2016) 432–439, https://doi.org/10.1016/j.ultsonch.2016.03.014.

[61] J.G. Norman, G.E. Renzoni, D.A. Case, Electronic structure of $Ru_2(O_2CR)_4^+$ and $Rh_2(O_2CR)_4^+$ complexes, J. Am. Chem. Soc. 101 (18) (1979) 5256–5267, https://doi.org/10.1021/ja00512a025.

[62] F.D. Cukiernik, D. Luneau, J.-C. Marchon, P. Maldivi, Mixed-valent diruthenium long-chain carboxylates. 2. magnetic properties, Inorg. Chem. 37 (15) (1998) 3698–3704, https://doi.org/10.1021/ic971366o.

[63] J. Telser, R.S. Drago, Reinvestigation of the electronic and magnetic properties of ruthenium butyrate chloride, Inorg. Chem. 23 (20) (1984) 3114–3120, https://doi.org/10.1021/ic00188a019.

[64] J. Telser R.S. Drago Correction: Reinvestigation of the electronic and magnetic properties of ruthenium butyrate chloride Inorg. Chem. 24 1985 4765 4765.

[65] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, The cambridge structural database, Acta Crystallogr. B. 72 (2) (2016) 171–179.

[66] A.R. Chakravarty, F.A. Cotton, D.A. Tocher, Syntheses, molecular structures, and properties of two polar diruthenium(II, III) complexes of 2-hydroxypyridine and 2-anilinopyridine, Inorg. Chem. 24 (2) (1985) 172–177, https://doi.org/10.1021/ic00196a011.

[67] J.L. Bear, Y. Li, B. Han, E. Van Caemelbecke, K.M. Kadish, Isomer effect on the structure and chemical reactivity of diruthenium complexes. synthesis and characterization of the (4,0), (3,1), and (2,2) trans isomers of $Ru_2(F_5ap)_4Cl$ and $Ru_2(F_5ap)_4(C{:}CC_6H_5)_2$ where F_5ap is the 2-(2,3,4,5,6-pentafluoroanilino) pyridinate anion, Inorg. Chem. 36 (24) (1997) 5449–5456, https://doi.org/10.1021/ic9602658.

[68] K.M. Kadish, L.-L. Wang, A. Thuriere, E. Van Caemelbecke, J.L. Bear, Factors affecting the electrochemical and spectroelectrochemical properties of diruthenium(III,II) complexes containing four identical unsymmetrical bridging ligands, Inorg. Chem. 42 (3) (2003) 834–843, https://doi.org/10.1021/ic020590x.

[69] K.M. Kadish, L.-L. Wang, A. Thuriere, L. Giribabu, R. Garcia, E. Van Caemelbecke, J.L. Bear, Solvent effects on the electrochemistry and spectroelectrochemistry of diruthenium complexes. Studies of $Ru_2(L)_4Cl$ where L = 2-CH_3ap, 2-Fap, and 2,4,6-F_3ap, and ap is the 2-anilinopyridinate anion, Inorg. Chem. 42 (2003) 8309–8319, https://doi.org/10.1021/ic034722d.

[70] K.M. Kadish, M. Nguyen, E. Van Caemelbecke, J.L. Bear, Synthesis, characterization, and electrochemistry of diruthenium(III,II) and monoruthenium (III) complexes containing pyridyl-substituted 2-anilinopyridinate ligands, Inorg. Chem. 45 (15) (2006) 5996–6003, https://doi.org/10.1021/ic060267k.

[71] S.P. Cummings, Z. Cao, C.W. Liskey, A.R. Geanes, P.E. Fanwick, K.M. Hassell, T. Ren, Diruthenium phenylacetylide complexes bearing para-/meta-amino phenyl substituents, Organometallics 29 (12) (2010) 2783–2788, https://doi.org/10.1021/om100263c.

[72] M. Manowong, B. Han, T.R. McAloon, J. Shao, I.A. Guzei, S. Ngubane, E. Van Caemelbecke, J.L. Bear, K.M. Kadish, Effect of axial ligands on the spectroscopic and electrochemical properties of diruthenium compounds, Inorg. Chem. 53 (14) (2014) 7416–7428, https://doi.org/10.1021/ic5007605.