Ultrasound-assisted synthesis of water-soluble monosubstituted diruthenium compounds

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The elusive monosubstituted diruthenium complexes [Ru3Cl(DAniF)(O2CMe)3] (1), [Ru3Cl(DPhF)(O2CMe)3] (2), [Ru3Cl(D-p-CNPhF)(O2CMe)3] (3), [Ru3Cl(D-o-TolF)(O2CMe)3] (4), [Ru3Cl(D-m-TolF)(O2CMe)3] (5), [Ru3Cl(D-p-TolF)(O2CMe)3] (6) and [RuCl(p-TolA)(O2CMe)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-toly)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 [Ru2Cl2(O2CR)4] (R = alkyl) compound and Cotton and col [2] the first crystal structure, a big number of Ru53-
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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 attainment of new diruthenium derivatives. 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 [Ru2Cl2(O2CR)4] by other bridging ligands. However, this method focuses mainly on obtaining fully substituted species, [Ru2Cl2(L-L)x] (L-L = O,O-donor, N,N-donor or N,O-donor bridging ligands), and it does not generally lead to the intermediate substitution species, [Ru2Cl2(L-L)4(O2CMe)4,x] (x = 1, 2, 3).

The properties of monosubstituted complexes, [Ru3Cl2(L-L)2(O2CMe)3], are quite unknown because they have been especially elusive with any synthetic procedure. With N,N-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-dimethylpyridinate compound [47] and several monoamidinopyridinatodiruthenium(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 heterometalic diruthenium(II,III) carbonate, Na/[Ni(H2O)4]Ru2(CO3)4-3H2O, 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 Ru25+ derivatives using ultrasound-assisted synthesis. To generalize this technique, six different formamidinates and one amidate ligands have been tested. Thus, the complexes [Ru2Cl(DAniF)(O2CMe)2] (1), [Ru2Cl(DPhF)(O2CMe)2] (2), [Ru2Cl(D-p-CNPhF)(O2CMe)2] (3), [Ru2Cl(D-o-TolF)(O2CMe)2] (4), [Ru2Cl(D-m-TolF)(O2CMe)2] (5), [Ru2Cl(D-p-TolF)(O2CMe)2] (6) and [Ru2Cl(p-TolA)(O2CMe)2] (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-toly)formamidinate; p-TolA = N4-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 [Ru2Cl(O2CMe)4] (0.4264 g, 0.9 mmol) and the corresponding N,N′-diarylformamidine (1–6) or amide (7) (0.9 mmol) was added Et3N (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 [Ru2Cl(O2CMe)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 MgSO4 was added. The solution was filtered off and concentrated to dryness. The solid was washed with a 1:6 mixture of hexane and acetone only in the case of compound 7 (10 mL). Then, the product was dried under vacuum.

[Ru2Cl(DAniF)(O2CMe)2] (1). Anal. Calcd for C24H26Cl2N2O8Ru2: H, 3.21; N, 2.71; ESI-MS (CH3Cl) m/z calcd for C24H26Cl2N2O8Ru2 [M+Cl]+ 636.0, found 635.9; Yield: 0.4066 g (65%).

[Ru2Cl(DPhF)(O2CMe)2] (2). Anal. Calcd for C24H26Cl2N2O8Ru2: H, 3.21; N, 2.71; ESI-MS (CH3Cl) m/z calcd for C24H26Cl2N2O8Ru2 [M+Cl]+ 575.0, found 574.9; Yield: 0.4563 g (86%).

[Ru2Cl(D-p-CNPhF)(O2CMe)2] (3). Anal. Calcd for C24H26Cl2N2O8Ru2: H, 3.21; N, 2.71; ESI-MS (CH3Cl) m/z calcd for C24H26Cl2N2O8Ru2 [M+Cl]+ 624.9, found 624.9; Yield: 0.4511 g (74%).

[Ru2Cl(D-o-TolF)(O2CMe)2] (4). Anal. Calcd for C24H26Cl2N2O8Ru2: H, 3.21; N, 2.71; ESI-MS (CH3Cl) m/z calcd for C24H26N2O8Ru2 [M+Cl]+ 603.9, found 603.9; Yield: 0.3951 g (63%).

[Ru2Cl(D-m-TolF)(O2CMe)2] (5). Anal. Calcd for C24H26Cl2N2O8Ru2: H, 3.21; N, 2.71; ESI-MS (CH3Cl) m/z calcd for C24H26N2O8Ru2 [M+Cl]+ 603.9, found 603.9; Yield: 0.4713 g (80%).

[Ru2Cl(D-p-TolF)(O2CMe)2] (6). Anal. Calcd for C24H26Cl2N2O8Ru2: H, 3.21; N, 2.71; ESI-MS (CH3Cl) m/z calcd for C24H26N2O8Ru2 [M+Cl]+ 603.9, found 603.9; Yield: 0.4976 g (84%).

[Ru2Cl(p-TolA)(O2CMe)2] (7). Anal. Calcd for C24H26Cl2N2O8Ru2: H, 3.21; N, 2.71; ESI-MS (CH3Cl) m/z calcd for C24H26N2O8Ru2 [M+Cl]+ 514.0, found 514.0; Yield: 0.3219 g (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 high. Table 1 summarizes the experimental conditions for the two monoformamidinato(diniruthenium(II,III)) compounds previously reported and the conditions used in the present work for complexes [Ru2Cl(DAniF)(O2CMe)3] (1), [Ru2Cl(DPhF)(O2CMe)3] (2), [Ru2Cl(D-p-CNPhF)(O2CMe)3] (3), [Ru2Cl(D-o-TolF)(O2CMe)3] (4) [Ru2Cl(D-m-TolF)(O2CMe)3] (5) [Ru2Cl(D-p-TolF)(O2CMe)3] (6) and [Ru2Cl(p-TolA)(O2CMe)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) Formamidinate 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. Formamidinates with electron donating group (R = OMe, Me) show higher reaction rates while the formamidinate 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 formamidinate 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 formamidinates [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 Ru2(μ-Cl) species under inert atmosphere (N2) 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, [Ru2Cl(L-L)(O2CMe)4] (L = 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.

Table 1

| Compound | Solvent | T (°C) | t (h) | Yield (%) | Ref |
|----------|---------|-------|------|-----------|-----|
| [Ru2Cl(DXylF)(O2CMe)4] | Toluene | ≈110 | 36 | 32 | [7,8] |
| [Ru2Cl(DphenF)(O2CMe)3] | 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 |

3.2. Structural characterization and properties

The isolated compounds 1–7 are stable in both solution (in water, dichloromethane, tetrahydrofuran, dimethyl sulfoxide, aceton, 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 (ν(C=C)α), ≈1490 cm−1 (ν(C-O-C)), ≈1350 cm−1 (ν(C–O)), ≈1070, 1020, 950 cm−1 (δ(CH–C=H–H)) and ≈690 cm−1 (δ(CH–C–Hα)). 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–O–CH3)) and 2217 cm−1 (ν(C=O–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+CH3OH]− 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 formamidinate 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

Table 2

| Solvent | Vapor pressure (kPa) | Viscosity (mPa·s) | Surface tension (kDyn/cm) | Uπ (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   |
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 formamidine 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 range were recorded in dichloromethane solution (Fig. S4, ESI). Compounds 1–6 display the typical profile of other high-spin (S = 3/2) partial substitution 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 formamidine ligand. In general, it can be observed a band around 370 nm that can be tentatively assigned to a π(π*) transition (a second band, which in some compounds appears with a shoulder) in the 450–650 nm region that can be attributed to π(RuO,N,Ru2) → π*(Ru2) transitions, and a less intense band in the 900–1050 nm region that can be attributed to a δ(Ru2) → δ*(Ru2) transition (Table S1, ESI).

Magnetization measurements at variable temperature were carried out for compounds 1–7. The χM/T values at room temperature of 1–7 are in the 2.23–1.84 cm² K mol⁻¹ range (Table 3). These values are close to the expected spin-only value, 1.87 cm² K mol⁻¹ (g = 2), for a quartet state arising from a σ⁵π⁴ electronic configuration [3,6,61]. On cooling, χM/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 χM and the χM/T data were fitted using the Cukierkni 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 monoformamidinodiruthenium(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 formamidine ligand (HDXy1825). 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-CH3Cl2 and 7-2CH3Cl2, crystallize with dichloromethane molecules in the monoclinic system, space group P21/c for compound 3 and P21/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 one acetate ligand 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 Ru2⁺ derivatives [6]. The chloride is aligned with the diruthenium core with a Ru2Ru1-Cl angle of 173.84° (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-C11 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 formamidine 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 interactions (H22A → δ(B15) and 176.61°). The presence of a different ligand (amidate or formamidinate) with an amidate ligand. For compound

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**Table 3**

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

| Compound | χM at 300 K (cm² K mol⁻¹) | g | D (cm⁻¹) | zJ (cm⁻¹) | TIP (cm³ mol⁻¹) | χ²
|----------|--------------------------|---|----------|-----------|---------------|---
| 1        | 2.19                     | 2.00* 68 | –0.28    | 1.14 × 10⁻⁵ | 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 × 10⁻⁴ | 3.62 × 10⁻⁴
| 5        | 2.09                     | 2.09 53  | –0.41    | 7.45 × 10⁻⁴ | 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.

** χ² = \( \sum (\chi_{M,\text{calcd}} - \chi_{M,\text{exp}})^2 / \sum (\chi_{M,\text{calcd}})^2 \)
The 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 than 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.

### Table 4

| Compound | $E_{1/2}$ | $\Delta E$ |
|----------|-----------|------------|
| 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       |

### 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 monosubstituted 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.
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.ultrasch.2021.105828.

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