

## Mechanochemical syntheses of Ru(II) complexes with isothiazole-type of ligand

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**Abstract** : Mechanochemistry is concerned with chemical transformations induced by mechanical means such as pressure, shear or friction. The main advantage of mechanochemistry is its focus on green chemistry, which is based on the pharmaceutical and chemical industry's need for cleaner, safer and more efficient transformations. The hallmark of mechanochemistry is the performance of chemical transformations by grinding or milling, without the need for large amounts of environmentally harmful solvents. In this paper, the mechanochemical synthesis and characterization of the [Ru-( $\eta^6$ -*p*-cymene)Cl<sub>2</sub>L] complex with the ligand 5-(methylamino)-3-morpholine-4-ylisothiazole-4-carbonitrile are presented. The complex was obtained in good yield as an orange-coloured powder and was characterized by FTIR. Mechanochemistry is a broad field that is applicable to subjects from triboemission to the direct manipulation of individual molecules, mechanical alloying, and organic synthesis. It has a fascinating history and promises interesting new results and a variety of applications in the future.

**Keywords:** mechanochemistry, syntheses, Ru(II) complexes

### 1. Introduction

Mechanochemistry is concerned with chemical transformations induced by mechanical means such as pressure, shear or friction [1]. While the beginnings of “inadvertent mechanochemistry” fade into prehistory, the first systematic studies of mechanochemical reactions were carried out only at the end of the 19th century and significant progress was delayed until the 1960s [2]. The main inspiration for the rediscovery of mechanochemistry is green chemistry, particularly the need of the pharmaceutical and chemical industries for cleaner, safer and more efficient transformations. The hallmark of mechanochemistry is the performance of chemical transformations by grinding or crushing without the need to dissolve reactants in the bulk.

However, mechanochemistry could in future become a more mainstream technique for two reasons [3]. Firstly, it is becoming increasingly clear that it is effective and even advantageous for more and more types of synthesis. Secondly, our current reliance on solvents appears increasingly unsustainable and very environmentally problematic, dangerous and energy consuming in terms of solvent production, purification and recycling.

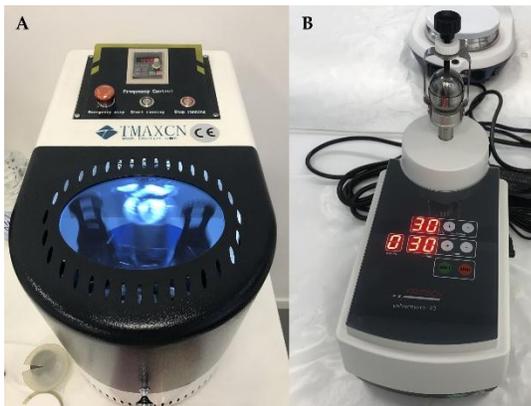
For these reasons, we have applied mechanochemical syntheses as a method to obtain complexes of the palladium group metals in a green, solvent-free manner. In this work, the mechanochemical syntheses and the characterisation of Ru-*p*-cymene complexes with isothiazole type of ligand are presented with the aim of demonstrating a more environmentally friendly method for the synthesis of complex compounds.

## 2. Experimental

[Ru-( $\eta^6$ -*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> was purchased from Sigma-Aldrich, used as received. The ligand 5-(methylamino)-3-morpholine-4-ylisothiazole-4-carbonitrile was prepared by the previously reported procedure [4]. IR spectra in the 400–4000 cm<sup>-1</sup> range were recorded with a PerkinElmer FT-IR Spectrum Two spectrophotometer.

Mills used to perform the mechanochemical experiments:

1. Planetary Ball Mill: Tmax ball mill (Figure 1A) was equipped with two 12 mL stainless steel jars, each one containing 2 stainless steel balls of diameter  $\varnothing = 10$  mm
2. Vibration mill: Pulverisette 23 (Figure 1B), it was equipped with one 10 mL stainless steel jar, containing 2 stainless steel balls of diameter  $\varnothing = 5$  mm and 1 stainless steel balls of diameter  $\varnothing = 10$  mm



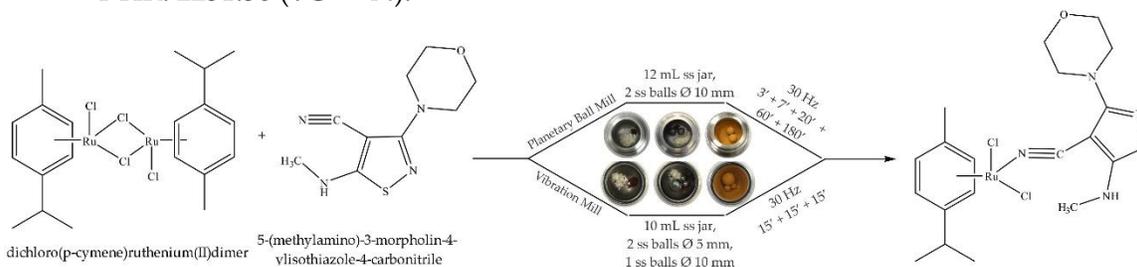
**Figure 1.** Planetary Ball Mill (1A) and vibration mill (1B) using for mechanochemical syntheses

Mechanochemical synthesis methods:

1. [Ru-( $\eta^6$ -*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (0.0306 g, 0.05 mmol, 1.0 equiv.) and 5-(methylamino)-3-morpholine-4-ylisothiazole-4-carbonitrile (0.0336 g, 0.15 mmol, 3.0 equiv.) were introduced in a 12 mL stainless steel jar with two ss ball (10 mm diameter). The jar was closed, sealed with parafilm, placed in the planetary ball mill and ground

for the first 3', then 7', then 20', then 60' and 120' summary 180' at 30 Hz. Yield: 68%. FTIR:  $\nu$  (cm<sup>-1</sup>) 3432 ( $\nu$  = CH), 2969, 2923 ( $\nu$ CH), 2232.73.

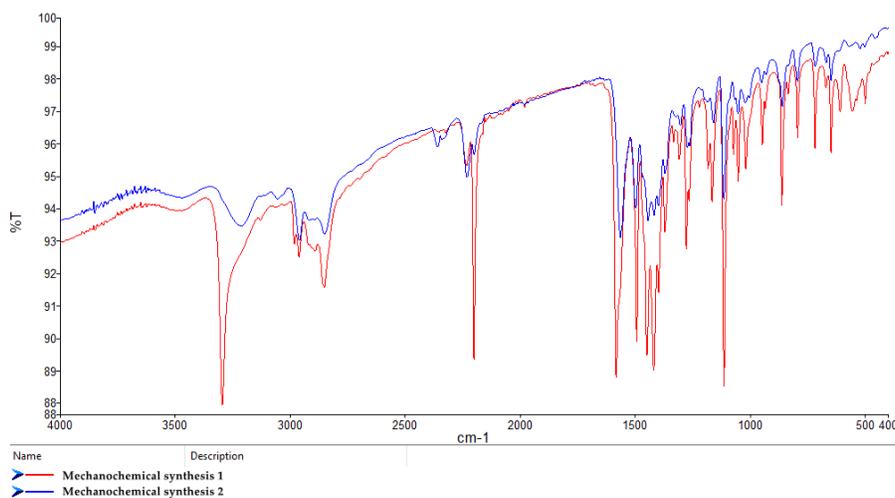
- [Ru-( $\eta^6$ -*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (0.0306 g, 0.05 mmol, 1.0 equiv.) and 5-(methylamino)-3-morpholine-4-ylisothiazole-4-carbonitrile (0.0224 g, 0.1 mmol, 2.0 equiv.) were introduced in a 10 mL stainless steel jar with three ss ball (two 5 mm diameter and one 10 mm diameter). The jar was closed, placed in the vibration mill and ground for the first 30', then 15' summary 45' at 30 Hz (Figure 2.). Yield: 77%. FTIR: 2231.56 ( $\nu$ C  $\equiv$  N).



**Figure 2.** Scheme of different type of mechanochemical synthesis of Ru(II) complex

### 3. Results and discussion

FT-IR was used to characterise the synthesised complexes (Figure 3). The IR spectra of the complexes showed a strong band in the range of 2200–2239 cm<sup>-1</sup>, which is characteristic of the functional group -C  $\equiv$  N. This band is at a higher frequency than the same band in the spectra of the uncoordinated ligand, indicating coordination to Ru(II) ion via the -C  $\equiv$  N group. The molecular structure of the [Ru( $\eta^6$ -*p*-cymene)Cl<sub>2</sub>L] complex is already known from its previous synthesis and full characterisation from solution [5]. The FTIR spectrum of the mechanochemically synthesised complex is identical to that of the solution-prepared analogue, confirming that both synthetic routes yield the complex of same molecular structure.



**Figure 3.** FTIR spectrum of the mechanochemically synthesised Ru(II) complex

#### 4. Conclusions

In this work, we have synthesised  $[\text{Ru}-(\eta^6\text{-}p\text{-cymene})\text{Cl}_2\text{L}]$  complex by a solvent-free mechanochemical method and characterized it by FTIR spectroscopy. The complex was obtained in good yield as an orange-coloured powder. FTIR analysis confirmed that the product is identical to the previously characterised complex obtained from solution, demonstrating that mechanochemistry can deliver the same molecular structure under greener, more sustainable conditions.

Starting from a few groundbreaking experiments some 120 years ago, mechanochemistry grew into a well-established research area with increasing research activity and some actual and many more potential applications. These results highlight the potential of mechanochemical approaches for the synthesis of organometallic complexes, combining structural integrity with reduced environmental impact. The use of mechanochemical methods in organic and organometallic synthesis is relatively new, but it is a very active and promising research area. The development of greener, more selective processes and new compounds attracts increasing attention. The possibilities are substantial in the preparation of drug precursors and other fine chemicals. It has a fascinating history and promises interesting new results and a variety of applications in the future.

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