

## Research paper

## Rhodium and copper 6-methylpicolinate complexes. Structural diversity and supramolecular interaction study

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## ABSTRACT

Seven new coordination compounds with 6-methylpicolinic acid (6-HMepic) and rhodium(III) or copper(II) of formula  $[\text{Rh}(6\text{-Mepic})_3]$  (**1**),  $[\text{Rh}(6\text{-Mepic})_2(\text{H}_2\text{O})\text{Cl}]$  (**2**),  $[\text{Rh}(6\text{-HMepic})(6\text{-Mepic})\text{Cl}_2] \cdot 3.5(\text{H}_2\text{O})$  (**3**),  $[\text{Cu}(6\text{-Mepic})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  (**4**),  $[\text{Cu}(6\text{-Mepic})_2]_n$  (**5**),  $[\text{Cu}(6\text{-Mepic})(6\text{-HMepic})\text{I}]$  (**6**) and  $[\text{Cu}(6\text{-Mepic})(6\text{-HMepic})\text{Cl}]$  (**7**) have been obtained. Their syntheses have been rationalized, and their structural and supramolecular characteristics have been studied and compared with other similar rhodium and copper picolinate complexes previously reported, in order to establish structural correlations and analogies. The electrical properties of coordination polymer  $[\text{Cu}(6\text{-Mepic})_2]_n$  (**5**) have been also analyzed and it has been found that it shows a moderated electrical transport along the chain.

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## 1. Introduction

Few reports regarding insulinomimetic activity of picolinate complexes bearing electron-donating substituents such as the methyl group [1,2] have been reported in the literature. As an example, 6-methyl-2-pyridinecarboxylic acid (methylpicolinic acid, 6-HMepic) and derivatives are widely explored as multidentate ligands [3–6], due to their great variety of physiological properties, especially as insulinomimetic models [5]. Diabetes Mellitus (DM) disease affects around 300 million adults which normally require daily insulin injections, constituting both a physical and mental burden. Furthermore, DM leads to serious life-threatening complications causing severe damage to several organs. This is one important reason to study new picolinate complexes, in order to replace painful insulin injections by more efficient therapy. Thanks to these studies, researchers found in 1995 an orally active bis(picolinate)oxovanadium(IV) complex,  $\text{VO}(\text{pa})_2$ , with high insulinomimetic activity [7]. Studies with copper(II) picolinate complexes also showed hypoglycemic effect *in vivo* [1], and seemed to be a better alternative than the  $\text{VO}(\text{pa})_2$  complex. Other metal complexes with Zn and Cr have also been tested with very interesting results [8,9].

In order to understand why these complexes present insulinomimetic activity and other physiological properties, it is neces-

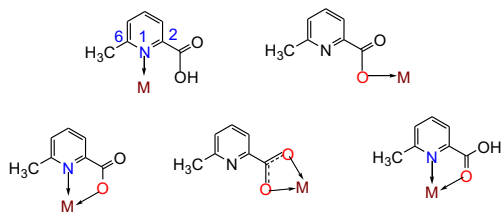
sary to get into their action mechanism and, even more importantly, to know about their structural details including potential supramolecular interactions. Although picolinic derivatives are known to bind to metal ions in different ways (Scheme 1), the most usual coordination mode is as bidentate N, O-donor (Scheme 1) forming a stable five-membered chelate ring. The donor sites are of significantly different nature. Thus, the pyridine nitrogen atom is a soft-donor site and a recognized stabilizer of transition metals in low oxidation states, whereas the carboxylate oxygen atom is a hard-donor site and is known to stabilize transition metals in high oxidation states [10,11]. This chelate binding mode, assisted with hydrogen bonding between the carboxylate group and water molecules is predominant, being much less common the coordination of the carboxylic group as bridging ligand between two different metal centers (Scheme 1) [12].

Other interesting structural aspects are the supramolecular interactions that the 6-Mepic complexes can establish, leading to the formation of extended frameworks [13,14]. In particular, hydrogen bonding has been exploited for molecular recognition associated with the biological activity and for the engineering of molecular solids [15]. The use of metal complexes as building blocks to assemble multi-dimensional frameworks *via* hydrogen bonds also attracted much recent attention due to the fact that these structures may lead to desirable flexible porous, optics, electronic or magnetic properties [16,17].

In the case of rhodium, the few examples found in the literature using picolinic derivatives have been focused on the obtention of

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**Scheme 1.** Schematic representation of most common mono- and bidentate coordination modes of the 6-methylpicolinate (6-Mepic) ligand.

organometallic compounds [18,19] with carbonyl and phosphine ligands to stabilize low oxidation states. There is just one coordination compound of formula  $[\text{Rh}(\text{pic})_3] \cdot \text{H}_2\text{O}$  (pic = picolinate) recently published, but this work focuses on electrochemical studies [11]. However, in the case of copper, hundreds of complexes based on picolinic acid derivatives have been prepared, giving rise to molecular complexes [20,21] and coordination polymers of different dimensionalities [21–23]. Interestingly, most of them have been obtained using picolinic acid as a ligand. A revision in the structures recorded in the CDS with 6-HMepic and copper shows just four examples, and none of them are coordination polymers [3,24].

Therefore, in this work we have focused on the preparation and structural characterization of novel metalpicolinate complexes by replacing the central oxovanadium(IV) moiety by other transition metals such as copper(II) and rhodium(III) and using 6-HMepic instead of the naked picolinate ligand with the aim to study the structural variations that this structural change can produce. Thus, we have obtained seven new coordination complexes with 6-Mepic and rhodium(III) or copper(II). We have compared the new structures of our 6-methylpicolinate complexes with those previously reported for similar compounds in order to establish correlations and analogies. Additionally, the structural comparison between  $[\text{Cu}(\text{6-Mepic})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$  (**4**) and the previously reported unsolvated polymorph  $[\text{Cu}(\text{6-Mepic})_2(\text{H}_2\text{O})]$  has also been carried out, since this is a topic of high current interest. Typically, solvent removal from the solvates gives rise to the most stable thermodynamic forms, but it might also result in the formation of further solvent-free modifications [6].

## 2. Materials and methods

6-methyl-2-pyridinecarboxylic acid (6-HMepic),  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$ , CuI and other chemicals were purchased from standard chemical suppliers and used as received. IR spectra were recorded on a PerkinElmer spectrum 100 spectrophotometer using a universal ATR sampling accessory and on a Bruker FT-IR Vector 22 model from 4000–400  $\text{cm}^{-1}$  in KBr pellets. Elemental analyses were carried out by the microanalytical service of the Universidad Autónoma de Madrid.

Two contact direct current (DC) electrical conductivity measurements were performed on different single crystals of compound **5** using carbon paint as electrodes. The contacts were made with tungsten wires (25  $\mu\text{m}$  diameter). The samples were measured at 300 K applying an electrical current with voltages from +10 to –10 V.

Single crystal X-ray diffraction data collection for structure determinations were collected at Bruker Kappa Apex II diffractometers with graphite-monochromated Mo  $K\alpha$  radiation for compounds **2**, **3**, **5**, **6** and **7** (Laboratorio de Difracción de Rayos X de Monocristal, Servicio Interdepartamental de Investigación, Universidad Autónoma de Madrid) and with graphite-monochromated Cu  $K\alpha$  radiation for compounds **1** and **4** (Servicio de Difracción

de Monocristal, Universidad de Salamanca). The structures were solved and refined using the Bruker SHELXTL Software Package. All non-hydrogen atoms were refined anisotropically. Crystal parameters and details of the final refinements of compounds **1–7** (CCDC 1484700–1484706) are collected in the [Supplementary Information](#) (Tables S1–S7).

## 3. Experimental

### 3.1. $[\text{Rh}(\text{6-Mepic})_3]$ (**1**)

A mixture of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (100 mg, 0.4 mmol) and 6-HMepic (260 mg, 1.9 mmol) in 50 mL water/ethanol (3:2) was stirred under reflux for 3 h, and then further stirred at 25 °C for 24 h. Finally, the yellow solution obtained was filtered off and allowed to crystallize at 25 °C. Yellow crystals suitable for single crystal X-ray diffraction were obtained after two–three weeks. The crystals were filtered off and washed with ethanol and diethyl ether and dried on air (35% yield). Anal. Calcd (found) for  $\text{C}_{21}\text{H}_{18}\text{RhN}_3\text{O}_6$ : C, 49.32 (48.03); H, 3.52 (3.45) N, 8.22 (7.76). IR selected data (KBr,  $\text{cm}^{-1}$ ): 3440(bw), 3075(w), 3029(w), 3008(w), 1671(s), 1604(m), 1469(m), 1330(s), 1243(m), 777(m) 476(m).

### 3.2. $[\text{Rh}(\text{6-Mepic})_2(\text{H}_2\text{O})\text{Cl}]$ (**2**) and $[\text{Rh}(\text{6-Mepic})(\text{6-HMepic})\text{Cl}] \cdot 3.5(\text{H}_2\text{O})$ (**3**)

A mixture of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (100 mg, 0.4 mmol) and 6-HMepic (65 mg, 0.4 mmol) in water/ethanol (3:2) 50 mL was stirred under reflux for 3 h, and then further stirred at 25 °C for 24 h. The yellow solution obtained was filtered off and allowed to crystallize at 25 °C for 2–3 weeks giving rise to yellow crystals of different morphologies, suitable for single crystal X-ray diffraction. The crystals were manually separated and washed with ethanol and diethyl ether and dried on air.

Compound **2**: 23% yield. Anal. Calcd (found) for  $\text{C}_{14}\text{H}_{14}\text{RhN}_2\text{O}_5\text{Cl}$ : C, 39.37 (39.90); H, 3.28 (3.57); N, 6.56 (6.15). IR selected data (KBr,  $\text{cm}^{-1}$ ): 3438(w), 1633(s), 1604(m), 1467(m), 1374(s), 1270(m).

Compound **3**: 39.5% yield. Anal. Calcd (found) for  $\text{C}_{14}\text{H}_{20}\text{RhN}_2\text{O}_7.5\text{Cl}_2$ : C, 33.01 (33.40); H, 3.73 (3.57); N, 5.50 (5.19). IR selected data (KBr,  $\text{cm}^{-1}$ ): 1634(s), 1605(m), 1469(m), 1374(s), 1263(m).

### 3.3. $[\text{Cu}(\text{6-Mepic})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**4**)

A suspension of  $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$  (100 mg, 0.5 mmol) and 6-HMepic (65 mg, 0.5 mmol) in  $\text{H}_2\text{O}$  (20 mL), was stirred for 5 min. at 25 °C. Then, the mixture was sealed in a 23 mL Teflon-lined steel autoclave and heated at 160 °C for 3 d and then cooled down to 30 °C at a rate of 4 °C/h. The resulting blue solution was allowed to crystallize at 25 °C. After ca. 15 days, blue crystals suitable for single crystal X-ray diffraction were formed, filtered off and washed with ethanol and diethyl ether and dried on air (48% yield). Anal. Calcd (found) for  $\text{C}_{14}\text{H}_{16}\text{CuN}_2\text{O}_6$ : C, 45.18 (45.34); H, 4.30 (4.23); N, 7.53 (7.42). IR selected data (KBr,  $\text{cm}^{-1}$ ): 3401(m), 1649(s), 1602(s), 1468(s), 1365(m), 1260(m).

### 3.4. $[\text{Cu}(\text{6-Mepic})_2]_n$ (**5**), $[\text{Cu}(\text{6-HMepic})(\text{6-Mepic})\text{I}]$ (**6**) and $[\text{Cu}(\text{6-Mepic})(\text{6-HMepic})\text{Cl}]$ (**7**)

To a mixture of CuI (50 mg, 0.3 mmol) and 6-HMepic (36 mg, 0.3 mmol) in 20 mL  $\text{CH}_3\text{CN}$ , a solution of KI (44 mg, 0.3 mmol) in 10 mL  $\text{CH}_3\text{CN}$  was added. The initial yellow solution turned to orange within few minutes. Then 3 mL of HCl 1 M were added and stirred at 25 °C for 3 h. Finally, the solution was filtered off and stored at 4 °C. After 4 days, red **[Cu(6-HMepic)(6-Mepic)I]**,

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