



Repositorio Institucional de la Universidad Autónoma de Madrid

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:
This is an **author produced version** of a paper published in:

Inorganica Chimica Acta 453 (2016): 574-582

DOI: <https://doi.org/10.1016/j.ica.2016.08.040>

Copyright: © 2017 American Chemical Society

El acceso a la versión del editor puede requerir la suscripción del recurso

Access to the published version may require subscription

Rhodium and Copper 6-Methylpicolinate complexes. Structural Diversity and Supramolecular Interaction Study

F. García[†], J. Perles[§], F. Zamora[†] and P. Amo-Ochoa^{†}*

[†]Departamento de Química Inorgánica. Universidad Autónoma de Madrid. 28049 Madrid, Spain. [§]Laboratorio de Difracción de Rayos X de Monocrystal, Servicio Interdepartamental de Investigación. Universidad Autónoma de Madrid, 28049, Spain.

KEYWORDS: Coordination compounds; coordination polymers; copper complexes; rhodium complexes; 6-methylpicolinic ligand; supramolecular networks.

Abstract

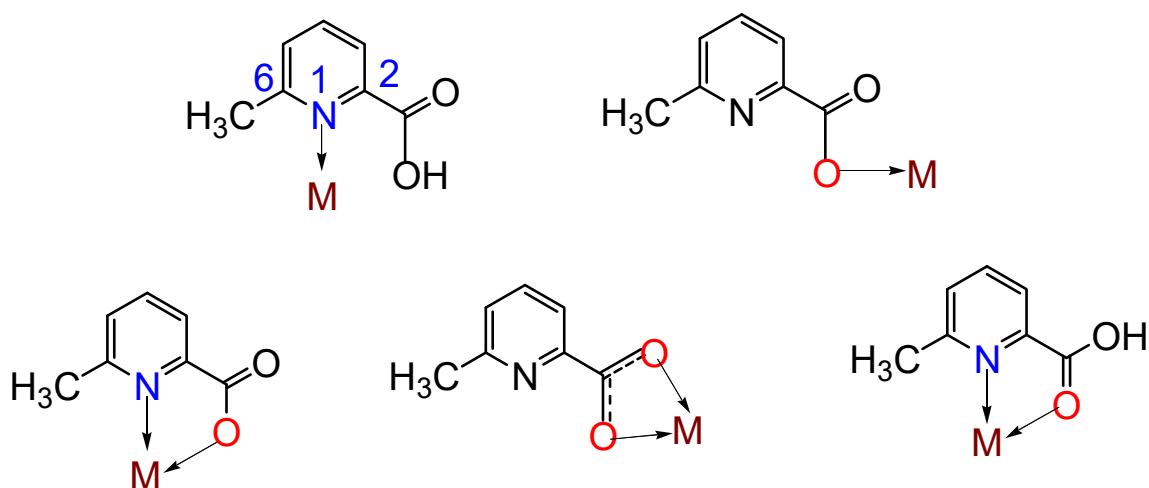
Seven new coordination compounds with 6-methylpicolinic acid (6-HMepic) and rhodium(III) or copper(II) of formula $[\text{Rh}(6\text{-Mepic})_3]$ (**1**), $[\text{Rh}(6\text{-Mepic})_2(\text{H}_2\text{O})\text{Cl}]$ (**2**), $[\text{Rh}(6\text{-HMepic})(6\text{-Mepic})\text{Cl}_2] \cdot 3.5(\text{H}_2\text{O})$ (**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.

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(picolate)oxovanadium(IV) complex, VO(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 VO(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 necessary 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].



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

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 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].

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 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 wolframium wires (25 μm 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 $\text{Mo K}\alpha$ 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 $\text{Cu K}\alpha$ 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).

Experimental

[Rh(6-Mepic)₃] (1). A mixture of RhCl₃·3H₂O (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 C₂₁H₁₈RhN₃O₆: C, 49.32 (48.03); H, 3.52 (3.45) N, 8.22 (7.76). IR selected data (KBr, cm⁻¹): 3440(bw), 3075(w), 3029(w), 3008(w), 1671(s), 1604(m), 1469(m), 1330(s), 1243(m), 777(m) 476(m).

[Rh(6-Mepic)₂(H₂O)Cl] (2) and **[Rh(6-Mepic)(6-HMepic)Cl₂]·3.5(H₂O) (3).** A mixture of RhCl₃·3H₂O (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 C₁₄H₁₄RhN₂O₅Cl: C, 39.37 (39.90); H, 3.28 (3.57); N, 6.56 (6.15). IR selected data (KBr, cm⁻¹): 3438(w), 1633(s), 1604(m), 1467(m), 1374(s), 1270(m).

Compound **3**: 39.5 % yield. Anal. Calcd (found) for C₁₄H₂₀RhN₂O_{7.5}Cl₂: C, 33.01 (33.40); H, 3.73 (3.57); N, 5.50 (5.19). IR selected data (KBr, cm⁻¹): 1634(s), 1605(m), 1469(m), 1374(s), 1263(m).

[Cu(6-Mepic)₂(H₂O)]·H₂O (4). A suspension of Cu(CH₃COOH)₂·H₂O (100 mg, 0.5 mmol) and 6-HMepic (65 mg, 0.5 mmol) in H₂O (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 C₁₄H₁₆CuN₂O₆: C, 45.18 (45.34); H, 4.30 (4.23); N, 7.53 (7.42). IR selected data (KBr, cm⁻¹): 3401(m), 1649(s), 1602(s), 1468(s), 1365(m), 1260(m).

[Cu(6-Mepic)₂]_n (5), [Cu(6-HMepic)(6-Mepic)I] (6) and [Cu(6-Mepic)(6-HMepic)Cl] (7).

To a mixture of CuI (50 mg, 0.3 mmol) and 6-HMepic (36 mg, 0.3 mmol) in 20 mL CH₃CN, a solution of KI (44 mg, 0.3 mmol) in 10 mL CH₃CN was added. The initial yellow solution turned to orange within few minutes. Then 3 mL of HCl 1M 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]**, (35% yield), green, corresponding to **[Cu(6-Mepic)₂]_n** (37 % yield), and dark green, corresponding to complex **[Cu(6-Mepic)(6-HMepic)Cl]**, (21 % yield) crystals suitable for single crystal X-ray diffraction were obtained. The crystals were manually separately, washed with ethanol and diethyl ether and dried on air.

Anal. Calcd (found) for C₁₄H₁₂CuN₂O₄: C, 50.07 (50.34); H, 3.58 (3.23); N, 8.34 (8.42). IR selected data (KBr, cm⁻¹): 3430 (bw), 3075(w), 3028(w), 1675(s), 1601 (m), 1469(m), 1320 (s), 1240 (m), 760(m) 466(m).

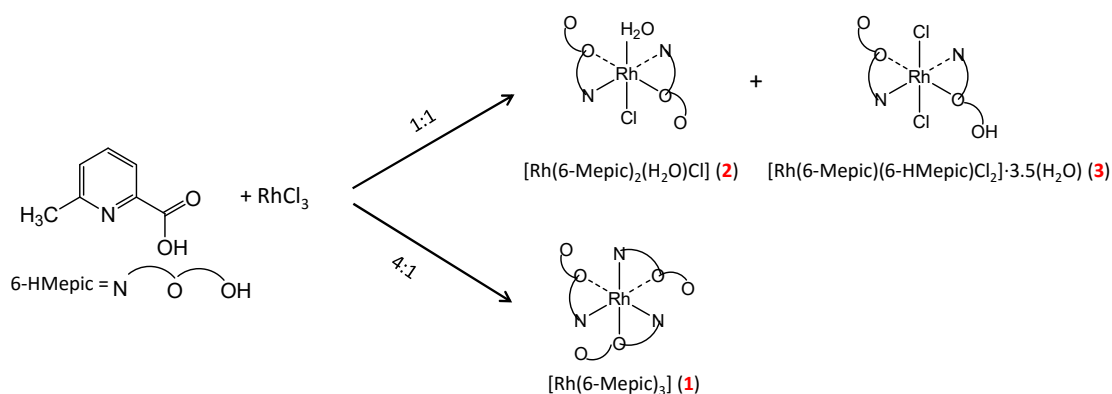
Anal. Calcd (found) for C₁₄H₁₃CuN₂O₄I: C, 36.15 (36.04); H, 2.79 (2.53); N, 6.02 (6.49). IR selected data (KBr, cm⁻¹): 3401 (m), 1650 (s), 1559 (s), 1475 (s), 1365 (m), 1260(m).

Anal. Calcd (found) for C₁₄H₁₃CuN₂O₄Cl: C, 45.13 (45.34); H, 3.49 (3.38); N, 7.52 (7.82). IR selected data (KBr, cm⁻¹): 3345(bw), 3064(w), 3010(w), 1661(s), 1602 (m), 1449(m), 1311(s), 1250(m), 751(m) 470(m).

[Cu(6-Mepic)₂(H₂O)]·H₂O (4) and [Cu(6-HMepic)(6-Mepic)I] (6). 50 mg (0.263 mmol) of CuI were mixed with 36 mg (0.263 mmol) of 6-HMepic in 30 mL CH₃CN. The yellow solution was stirred for 3 h at 25 °C. The orange solid was filtered off and the solution allowed to crystallize at 25 °C. After 4 days, red (corresponding to **[Cu(6-HMepic)(6-Mepic)I]**) and blue (corresponding to **[Cu(6-Mepic)₂(H₂O)]·H₂O**) crystals formed were manually separated, washed with ethanol and diethyl ether and dried on air (47 % and 18 % yield, respectively).

Results and Discussion

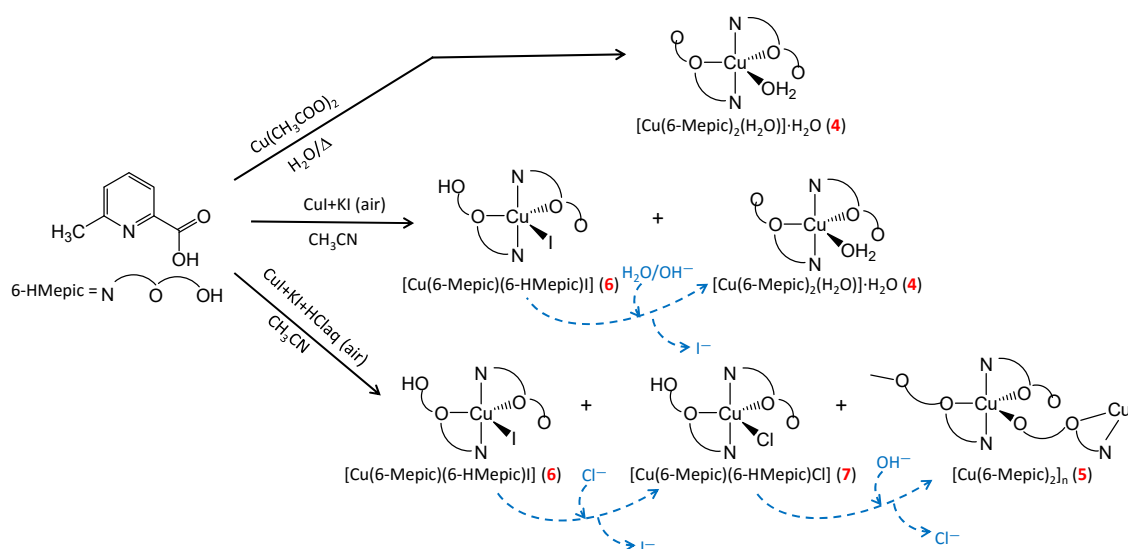
The reactions carried out between 6-HMepic and RhCl_3 in water-ethanol (3:1) at 120 °C at different molar ratios, 4:1 and 1:1, gave rise to several complexes $[\text{Rh}(\text{6-Mepic})_3]$ (**1**), $[\text{Rh}(\text{6-Mepic})_2(\text{H}_2\text{O})\text{Cl}]$ (**2**) and $[\text{Rh}(\text{6-HMepic})(\text{6-Mepic})\text{Cl}_2] \cdot 3.5\text{H}_2\text{O}$ (**3**) (Scheme 2). The stoichiometries are in agreement with the excess of ligand used.



Scheme 2. Representation of the reaction formation and schematic structures of the rhodium-6-methylpicolinate complexes.

However, the copper complexes have been obtained just using a 1:1 molar ratio, but under different experimental conditions. Scheme 3 represents a summary of the three reactions carried out under different experimental conditions. Thus, using $\text{Cu}(\text{CH}_3\text{COOH})_2 \cdot \text{H}_2\text{O}$, hydrothermal conditions and long reaction times, the only product isolated is $[\text{Cu}(\text{6-Mepic})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**4**). Therefore, we assume this is the most stable thermodynamic species in water. A different scenario is observed when the reaction is carried out using CuI/KI , under soft conditions (25 °C), in air and with CH_3CN as solvent. First, an almost immediate change in the color of the reaction solution, from yellow to orange, is observed due to the Cu(I) to Cu(II) oxidation, followed by the formation of crystals of $[\text{Cu}(\text{6-Mepic})(\text{6-HMepic})\text{I}]$ (**6**) and $[\text{Cu}(\text{6-Mepic})_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**4**). Then, we assume that the first complex obtained in this process is **6** that is just formed by the oxidation of copper

in air, and coordination of the 6-Mepic ligand in a hemiprotonated fashion; slow substitution of iodine by water and the fully deprotonation of the 6-HMepic to 6-Mepic ligand gives rise to the formation of **4**. Finally the analogous reaction carried out in presence of some amount of 1:1 HCl:water allowed the isolation of three different Cu(II)/6-Mepic containing crystals, including complexes **6** and [Cu(6-Mepic)(6-HMepic)Cl] (**7**), as well as the coordination polymer [Cu(6-Mepic)₂]_n (**5**). Compound **7** is generated in the medium because of the presence of the corresponding chloride, while the formation of **5** can only be rationalized based on the easier substitution of the chloride by the oxygen atom a neighboring 6-Mepic ligand of another copper complex. In this later reaction the 6-HMepic/6-Mepic mixture is fully deprotonated, despite the acidic medium, to produce **5**. The ligand substitution seems to be hampered for the case of iodine as we stated in the previous reaction.



Scheme 3. Representation of the reaction formation and schematic structures of the copper-6-methylpicolinate complexes.

Infrared spectroscopy data of **1-7** confirm the coordination of 6-Mepic ligand to the metal centers based on the presence of metal-ligand bands [25]. Additionally, the typical stretching $\nu(\text{C-N})$ vibrational mode of substituted pyridines that appears for the uncoordinated 6-Mepic ligand at 1612 cm^{-1} shows a significant shift of *ca.* $10\text{-}12\text{ cm}^{-1}$ to lower wave numbers in all the complexes.

Molecular structures of compounds **1-7** have been determined by single crystal X-ray diffraction and are depicted in Figures 1-8. Some selected interatomic bond distances and angles are listed in Tables 1-3, and hydrogen bond parameters are in Table 4.

Table 1. Coordination environment bond distances (Å) for compounds **1-7**

1			
Rh1-N1	2.078(2)	Rh1-O1	1.997(2)
Rh1-N2	2.058(2)	Rh1-O3	1.998(2)
Rh1-N3	2.069(2)	Rh1-O5	2.014(2)
2			
Rh1-N1	2.078(4)	Rh1-O1	2.010(4)
Rh1-N2	2.072(4)	Rh1-O3	2.025(4)
Rh1-Cl1	2.298(1)	Rh1-O5	2.096(3)
3			
Rh1-N1	2.062(10)	Rh1-O1	1.998(9)
Rh1-N1 ^a	2.062(10)	Rh1-O1 ^a	1.998(9)
Rh1-Cl1	2.326(3)	Rh1-Cl1 ^a	2.326(3)
a=-x+1, -y+1, -z			
4			
Cu1-N1	2.017(2)	Cu1-O1	1.963(2)
Cu1-N2	2.030(2)	Cu1-O3	1.964(2)
		Cu1-O5	2.156(2)
5			
Cu1-N1	1.995(2)	Cu1-O1	2.050(2)
Cu1-N2	1.994(2)	Cu1-O2	2.119(2)
		Cu1-O3	1.982(2)
6			
Cu1-N1	2.031(5)	Cu1-O1	1.997(4)
Cu1-N1 ^a	2.031(5)	Cu1-O1 ^a	1.997(4)
Cu1-I1	2.811(1)		
a = -x, y, -z+1/2			
7			
Cu1-N1	2.025(3)	Cu1-O1	2.126(2)
Cu1-N2	2.023(3)	Cu1-O3	2.039(2)

Cu1-Cl1	2.279(1)		
---------	----------	--	--

Table 2. Coordination environment bond angles (°) for compounds **1-3**.

1		2		3	
N1-Rh1-N2	165.76(8)	N1-Rh1-N2	179.39(15)	N1-Rh1-N1 ^a	180
N1-Rh1-N3	90.08(8)	N1-Rh1-O1	80.18(14)	N1-Rh1-O1	99.9(4)
N2-Rh1-N3	101.72(8)	N1-Rh1-O3	99.93(15)	N1-Rh1-O1 ^a	80.1(4)
N1-Rh1-O1	81.55(8)	N1-Rh1-O5	91.05(13)	N1-Rh1-Cl1	90.4(2)
N1-Rh1-O3	87.81(8)	N1-Rh1-Cl1	90.43(10)	N1-Rh1-Cl1 ^a	89.6(2)
N1-Rh1-O5	104.20(8)	N2-Rh1-O1	100.03(15)	N1 ^a -Rh1-O1	80.1(4)
N2-Rh1-O1	87.64(8)	N2-Rh1-O3	79.84(16)	N1 ^a -Rh1-O1 ^a	99.9(4)
N2-Rh1-O3	82.07(8)	N2-Rh1-O5	89.53(12)	N1 ^a -Rh1-Cl1	89.6(2)
N2-Rh1-O5	85.65(8)	N2-Rh1-Cl1	89.00(10)	N1 ^a -Rh1-Cl1 ^a	90.4(2)
N3-Rh1-O1	105.05(9)	O1-Rh1-O3	177.81(16)	O1-Rh1-O1 ^a	180
N3-Rh1-O3	168.92(8)	O1-Rh1-O5	89.52(13)	O1-Rh1-Cl1	89.2(3)
N3-Rh1-O5	81.25(8)	O3-Rh1-O5	92.66(12)	O1-Rh1-Cl1 ^a	90.8(3)
O1-Rh1-O3	85.40(8)	O1-Rh1-Cl1	88.90(11)	O1 ^a -Rh1-Cl1	90.8(3)
O1-Rh1-O5	171.63(8)	O3-Rh1-Cl1	88.91(10)	O1 ^a -Rh1-Cl1 ^a	89.2(3)
O3-Rh1-O5	88.73(8)	O5-Rh1-Cl1	177.63(9)	Cl1-Rh1-Cl1 ^a	180
				a= -x+1, -y+1, -z	

Table 3. Coordination environment bond angles (°) for compounds **4-7**.

Bond angles (°) for compounds 4-7							
4		5		6		7	
N1-Cu1-N2	173.43(7)	N1-Cu1-N2	171.92(9)	N1-Cu1-N1 ^a	160.1(3)	N1-Cu1-N2	165.9(1)
N1-Cu1-O1	82.42(7)	N1-Cu1-O1	81.32(9)	N1-Cu1-O1	81.9(2)	N1-Cu1-O1	79.5(1)
N1-Cu1-O3	94.61(7)	N1-Cu1-O2	95.61(8)	N1-Cu1-O1 ^a	92.0(2)	N1-Cu1-O3	90.2(1)
N1-Cu1-O5	88.26(7)	N1-Cu1-O3	94.81(8)	N1 ^a -Cu1-O1	92.0(2)	N2-Cu1-O1	93.79(9)
N2-Cu1-O1	96.76(7)	N2-Cu1-O1	93.79(9)	N1 ^a -Cu1-O1 ^a	81.9(2)	N2-Cu1-O3	81.57(9)
N2-Cu1-O3	81.91(7)	N2-Cu1-O2	92.24(8)	N1-Cu1-I1	99.96(15)	O1-Cu1-O3	116.4(1)

N2-Cu1-O5	98.27(7)	N2-Cu1-O3	82.77(8)	N1 ^a -Cu1-I1	99.96(15)	O1-Cu1-Cl1	111.40(8)
O1-Cu1-O3	141.13(8)	O1-Cu1-O2	113.63(9)	O1-Cu1-O1 ^a	144.3(3)	O3-Cu1-Cl1	131.93(7)
O1-Cu1-O5	102.73(8)	O1-Cu1-O3	125.66(9)	O1-Cu1-I1	107.87(14)	N1-Cu1-Cl1	93.30(7)
O3-Cu1-O5	115.95(8)	O2-Cu1-O3	120.68(9)	O1 ^a -Cu1-I1	107.87(14)	N2-Cu1-Cl1	100.77(7)
				a= -x, y, -z+1/2			

Table 4. Hydrogen bonds in compounds **3-7**.

	D-H	d(D-H)/ Å	d(H···A)/ Å	<DHA/°	d(D···A)/ Å	A
3	O2-H2O	0.820	1.784	156.46	2.557	O6 [-x+1, -y+1, -z+1]
	O6-H3W	0.887	1.887	169.99	2.765	O4
	O6-H4W	0.853	1.941	167.31	2.780	O4 [-x, -y+1, -z+1]
4	O5-H1W	0.867	1.905	173.40	2.768	O2 [-x+1, -y, -z]
	O5-H2W	0.869	1.846	165.37	2.696	O6 [-x+1, -y+1, -z+1]
6	O2-H2O	0.840	1.624	174.71	2.462	O2 [-x-1/2, -y+1/2, -z]
7	O4-H4O	0.820	1.673	161.47	2.465	O2 [-x-1/2, y-1/2, z]

Compound **1**, with formula [Rh(6-Mepic)₃], is a molecular compound that crystallizes in the monoclinic $P2_1/n$ space group with one molecule per asymmetric unit (Figure 1). The metal atom is surrounded by three oxygen atoms and three nitrogen ones from three different 6-methylpyridine-2-carboxylate molecules (acting as chelating κO , κN ligands). The environment of the Rh(III) atom (Tables 1 and 2) can be described as a distorted octahedron, due to the bite angle of the ligand, with the 6-methylpiconinate ligands in a *cis,trans,trans* disposition around the metal center (Figure 1). The bond lengths and angles around the metal center in **1** (Tables 2 and 3) are in accordance with the values reported for similar compounds [11]. An analogous structure was found in the literature [11], consisting of a [Rh(pic)₃] \cdot H₂O molecular complex where the rhodium atom is coordinated to three κO , κN picolinato ligands in a octahedral environment. This previously reported structure displays also one crystallization water molecule per [Rh(pic)₃] moiety, acting as a bridge between adjacent [Rh(pic)₃] molecules and forming a 1D spiral chain of hydrogen bonds. This results in poor solubility for the solvatomorph

[Rh(pic)₃]·H₂O, in contrast to the high solubility found in compound **1**, where the packing of the molecules is achieved only by weak van der Waals forces.

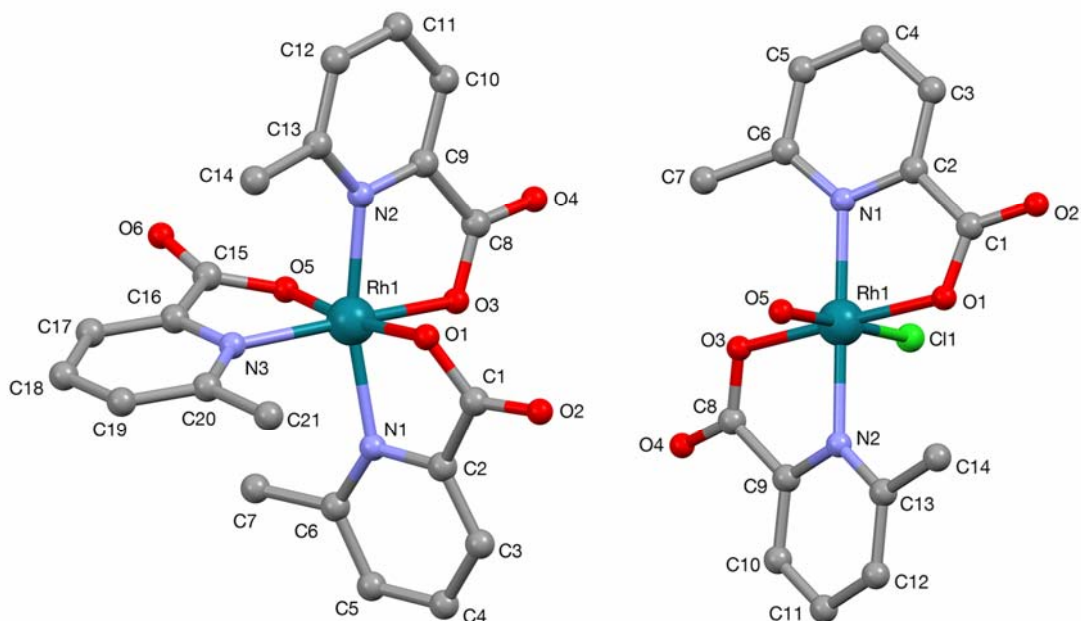


Fig. 1. View of the *cis,trans,trans*-[Rh(6-Mepic)₃] molecule in **1** (right) and the *trans*-[Rh(6-Mepic)₂(H₂O)Cl] molecule in **2** (left). Hydrogen atoms have been omitted for clarity.

Compound **2** (Fig. 1) is also a molecular compound, in this case with formula [Rh(6-Mepic)₂(H₂O)Cl], that crystallizes in the orthorhombic *Pna*2₁ group. The Rh(III) atom is surrounded by two chelating (κ O, κ N) 6-methylpyridine-2-carboxylate molecules in *trans* disposition, one chloride ligand, and one water molecule; showing a slightly distorted RhO₅N₂Cl octahedral environment. Some selected interatomic bond distances and angles are listed in Tables 1 and 2. In the structure of compound **2**, the bond lengths and angles in the coordination environment around Rh(III) fall within the range reported for other similar rhodium complexes with picolinic acid and the geometry is consistent with other derivatives of picolinic acid with transition metals, *i.e.* *trans*-diaquabis(picolinato-N,O)cobalt(II) [26]

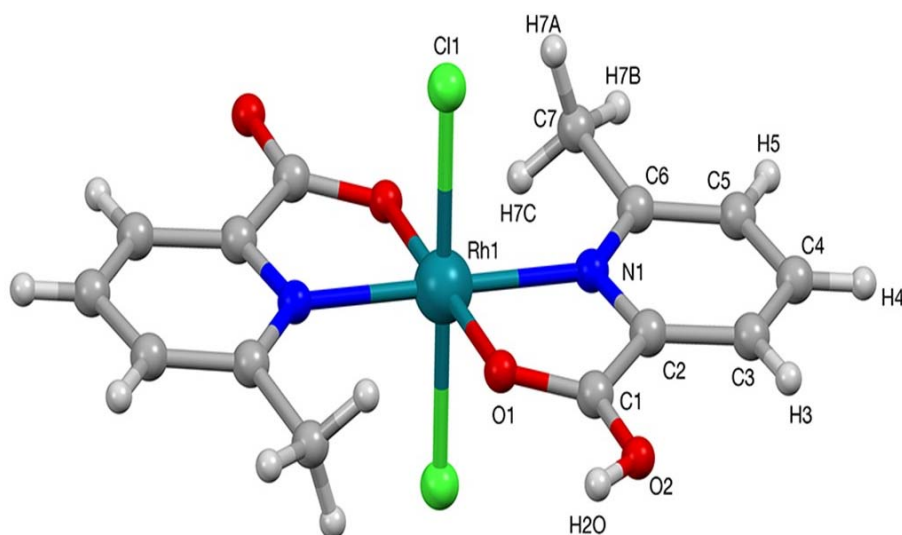


Fig. 2. View of the *trans*-[Rh(6-HMepic)(6-Mepic)Cl₂] molecule in **3** with atoms labelled in the asymmetric unit.

Compound **3** (Fig. 2), with formula [Rh(6-HMepic)(6-Mepic)Cl₂]·3.5(H₂O), crystallizes in the monoclinic *P*2₁/*c* space group with half a [Rh(6-HMepic)(6-Mepic)Cl₂]·molecule, plus three and a half disordered solvent water molecules per asymmetric unit. The Rh(III) atom is surrounded by one chelating (κO, κN) 6-methylpyridine-2-carboxylate, one (κO, κN) 6-methylpyridine-2-carboxylic acid, and two chloride ligands in a *trans* disposition, giving rise to a slightly distorted octahedral RhO₂N₂Cl₂ polyhedron (Tables 1 and 2). As there is only one organic ligand in the asymmetric unit, the occupation for the H atom attached to the carboxylic O2 atom is 50%, to yield the molecular formula [Rh(6-HMepic)(6-Mepic)Cl₂]. One of the oxygen sites for the disordered solvent water molecules also shows a 50% occupation. There are hydrogen bonds between carboxylic O2 and one of the oxygen atoms from interstitial water molecules (O6), as collected in table 4.

Compound **4**, with formula [Cu(6-Mepic)₂(H₂O)]·H₂O, crystallizes in the triclinic *P*-1 group, with one copper complex and one solvent water per asymmetric unit. The Cu(II) metal is located in a CuO₃N₂ distorted trigonal bipyramidal coordination geometry environment surrounded by two chelating (κO, κN) 6-methylpyridine-2-carboxylate ligands in a *trans* geometry, and a coordinated water molecule (Tables 1 and 3). Another solvatomorph [Cu(6-Mepic)₂(H₂O)], with a different structure and lacking co-crystallized

water molecules, had been synthesized from copper(II) sulphate in mildly alkaline aqueous solution [3]. The main difference between both complexes can be found in their supramolecular arrangement. In the case of $[\text{Cu}(6\text{-Mepic})_2(\text{H}_2\text{O})]$, the coordination compounds are linked by the intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds between oxygen atoms from carboxylic groups to yield a two-dimensional network (Fig. 5). In the solvatomorph here reported with interstitial water (compound **4**), the non-coordinated oxygen atom from the carboxylic group is involved in hydrogen bonds with the solvent water molecules (Fig. 4), but also with coordinated water molecules from other neighbor $[\text{Cu}(6\text{-Mepic})_2(\text{H}_2\text{O})]$ units, creating supramolecular two-dimensional layers parallel to the (01-1) plane (Figure 4). Both O atoms from coordinated and co-crystallized water molecules participate in three hydrogen bonds, as proton acceptors and double proton donors. Uncoordinated carboxylate O atoms also participate in hydrogen bonding as proton acceptors (Table 4). Thus, it seems clear that the reaction medium plays a key role on the supramolecular organization of the $[\text{Cu}(6\text{-Mepic})_2(\text{H}_2\text{O})]$ species.

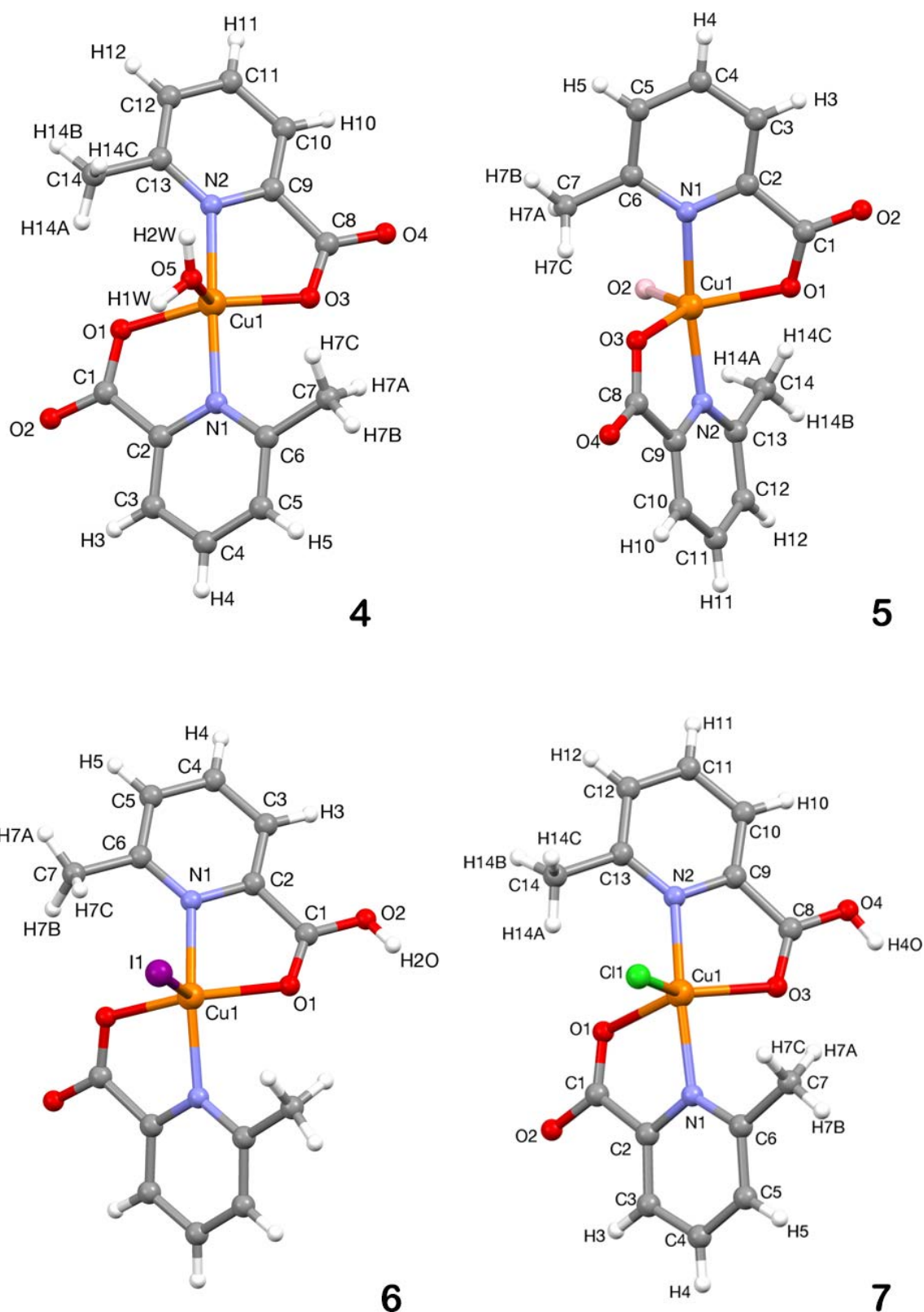


Fig. 3. Molecular view of the coordination compounds **4**, **5**, **6** and **7**. Only atoms in the asymmetric units have been labeled, except for the polymeric compound **5**, where an additional O2 atom from the neighbor unit (in pink) has been included and labeled in order to complete the coordination environment of the copper atom.

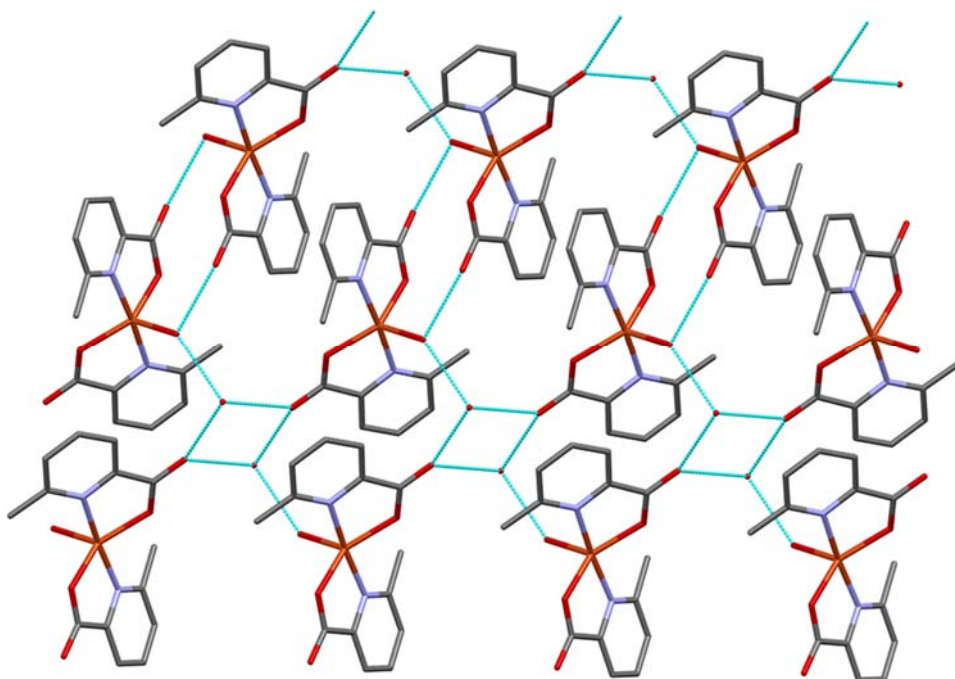


Fig. 4. View of the 2D network formed by hydrogen bonds (depicted in blue) between $[\text{Cu}(6\text{-Mepic})_2(\text{H}_2\text{O})]$ H_2O and crystallization water molecules in **4**.

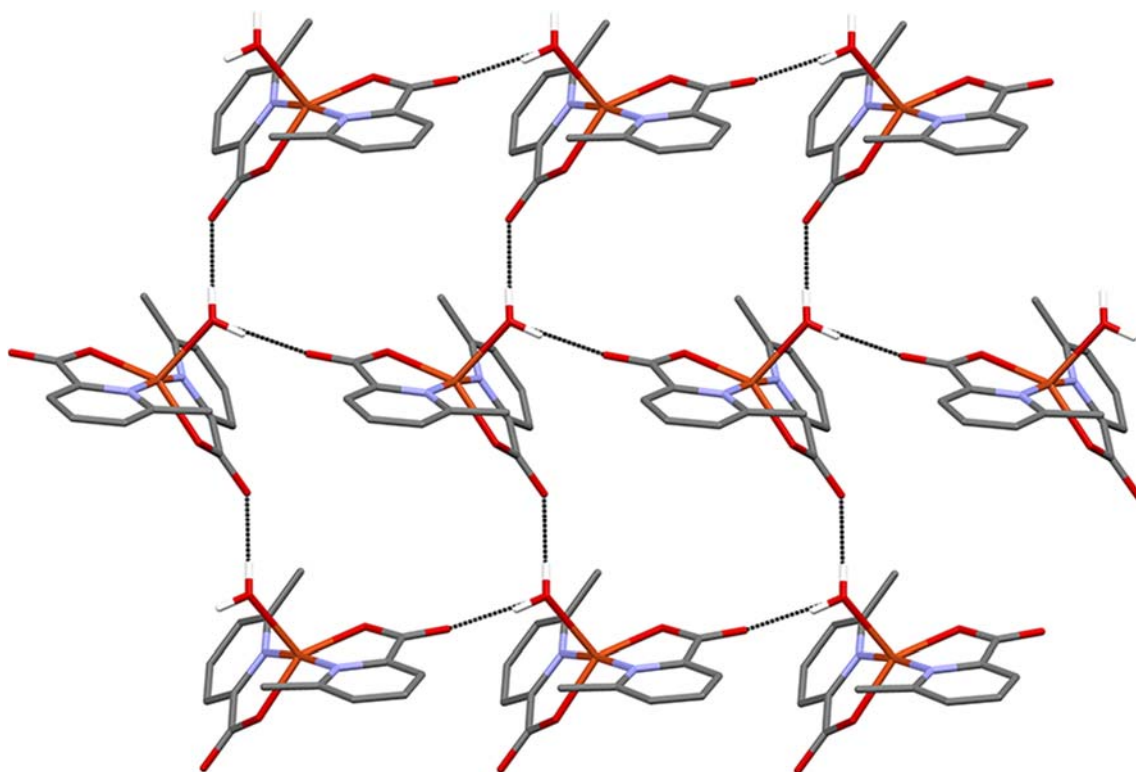


Fig. 5. View of the crystal packing of $[\text{Cu}(6\text{-Mepic})_2(\text{H}_2\text{O})]$ [**3**], showing the molecules linked into a two-dimensional layer by hydrogen bonds, represented by black dotted lines.

Compound **5** is a coordination polymer with formula $[\text{Cu}(\text{6-Mepic})_2]_n$ (Fig. 3). It crystallizes in the monoclinic $P2_1/c$ group, with a $[\text{Cu}(\text{6-Mepic})_2]$ monomer per asymmetric unit. The Cu(II) atom is located in a distorted CuO_3N_2 trigonal bipyramidal coordination geometry (Tables 1 and 3 for distances and angles), surrounded by one chelating ($1\kappa\text{O}, 2\kappa\text{N}$) and two bridging tridentate ($\mu_2-1\kappa\text{O}, 1\kappa\text{N} 2\kappa\text{O}'$), 6-methylpyridine-2-carboxylate ligands. This arrangement gives rise to $[\text{Cu}(\text{6-Mepic})_2]_n$ zigzag chains parallel to the crystallographic b direction (Fig. 6).

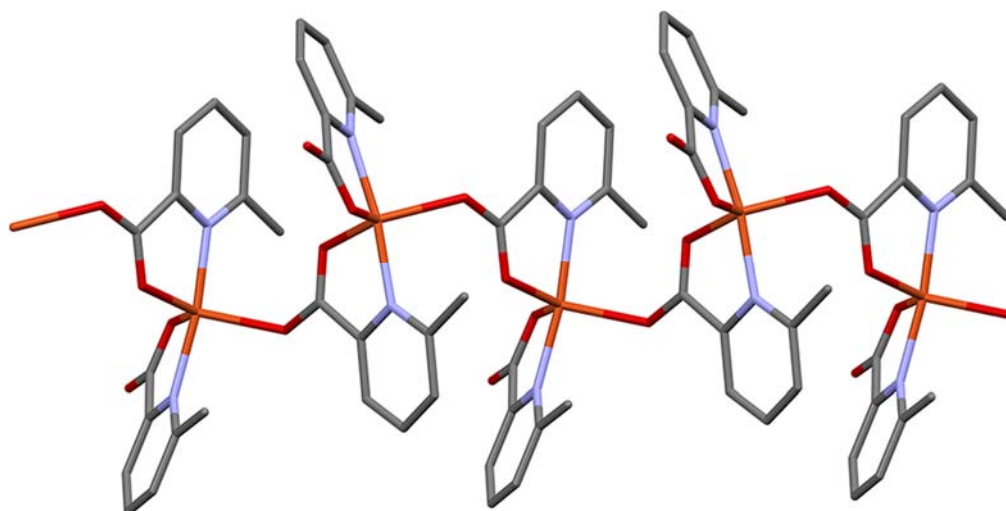


Fig. 6. View of the zigzag chain formed in the coordination polymer **5**. Hydrogen atoms have been omitted for clarity.

The electrical conductivity characterization of **5** shows a conductivity value of $1.5 \cdot 10^{-7} \text{ Scm}^{-1}$ measured in four different crystals, using the two contact method at 298 K. This value suggests a semiconducting behavior similar to that found in analogous 1D coordination polymers based on Cu(II) and carboxylate as bridged ligands. In these materials the electrical pathway is determined by the Cu-O-O-Cu bonds [16, 27] suggesting that the carboxylate bridge for copper chains is a moderate electrical connector.

Compound **6**, $[\text{Cu}(\text{6-HMepic})(\text{6-Mepic})\text{I}]$, crystallizes in the monoclinic $C2/c$ group. It displays half of the molecule per asymmetric unit. The Cu(I) atom is located in a $\text{CuO}_2\text{N}_2\text{I}$ distorted square pyramid environment surrounded by two chelating ($\kappa\text{O}, \kappa\text{N}$) 6-methylpyridine-2-carboxylic acid ligands in *trans* disposition and one iodine atom (Fig. 3). As happened in compound **3**, the two carboxylate groups from the coordinated organic

ligands share the H atom with a 50% probability each. The molecules are bonded through supramolecular hydrogen interactions between the non-coordinated oxygen atoms from the acid groups giving rise to molecular aggregates in a zigzag geometry, parallel to the crystallographic [101] direction (Fig. 7).

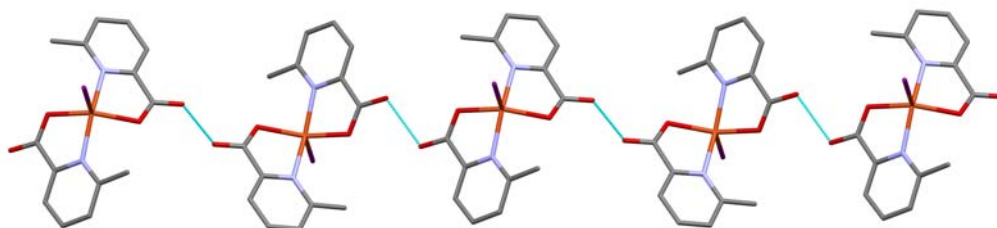


Fig. 7. View of the H-bond aggregate formed in compound **6**. Hydrogen atoms have been omitted for clarity.

Compound **7**, [Cu(6-HMepic)(6-Mepic)Cl] is very similar to compound **6** (Fig. 3). It crystallizes in the monoclinic $C2/c$ group but displays a whole molecule per asymmetric unit. The Cu(II) atom is located in a $\text{CuO}_2\text{N}_2\text{Cl}$ a distorted trigonal bipyramidal coordination geometry (Tables 1 and 3 for angles and distances), surrounded by one chelating (κO , κN) 6-methylpyridine-2-carboxylate, one chelating (κO , κN) 6-methylpyridine-2-carboxylic acid ligand in *trans* disposition and one chlorine atom (Fig. 8). The molecules are bonded through supramolecular hydrogen interactions between the non-coordinated oxygen atoms from the carboxylate and the acid group, giving rise to zigzag chains parallel to the crystallographic [010] direction (Fig. 8).

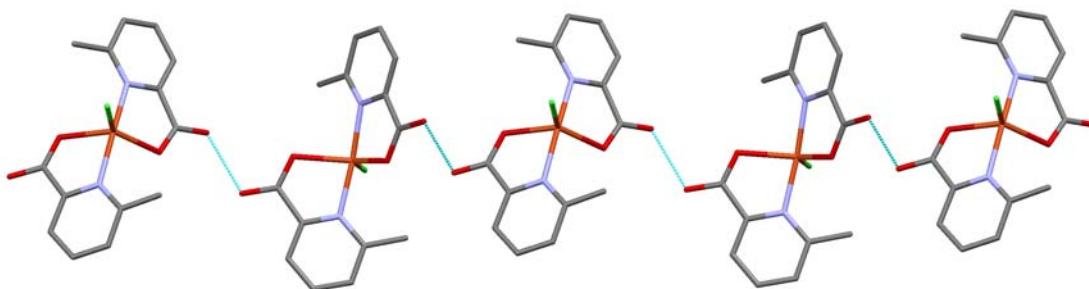


Fig. 8. View of the H-bond chain formed in compound **7**. Hydrogen atoms have been omitted for clarity.

Conclusions

Seven new coordination compounds of 6-methylpicolinic acid and either Rh(III) or Cu(II) have been synthesised and structurally characterised. All the complexes presented here show a N,O-chelation coordination mode of the 6-Mepicolinic acid or 6-Mepicolinate.

In the case of Rh(III) derivatives **1-3**, the 6-methylpicolinate complexes present a distorted octahedral environment in all the compounds. The modulation of the Rh(III) salt to 6-mepicolinic acid ratio in the reaction mixture allows the isolation of a series of compounds going from the $[\text{Rh}(\text{6-Mepic})_3]$ complex to $[\text{Rh}(\text{6-H}_{0.5}\text{Mepic})_2(\text{H}_2\text{O})_{0-1}(\text{Cl})_{1-2}]$ (compounds **2** and **3**, respectively) in which a competition between the solvent molecules and the chlorine is observed when the amount of 6-Mepicolinic acid is reduced. On the other hand, in the case of the copper derivatives, we have been able to obtain 6-methylpicolinate/6-methylpicolinic acid coordinated to copper in a distorted trigonal bipyramidal geometry. The compounds have been isolated under ambient conditions in CH_3CN and an acidic medium (diluted HCl) giving rise to an equilibrium between the neutral and the deprotonated species of the 6-methylpicolinic acid, acting both as ligands, and a variety of ligand substitution reactions that can be rationalized and modulated.

The free oxygen atoms of the carboxylic groups are implicated in the supramolecular interactions through hydrogen bonds formation in most of the compounds. Molecular aggregates, 1D and 2D networks can be obtained depending on the presence of solvent molecules in the crystal or the coordinated ligands (H_2O , I or Cl).

The combination of the chelating binding mode and the role of the carboxylic group of the 6-Mepic as a bridge between Cu(II) metal centers yields an unusual 1D coordination polymer of 6-methylpicolinate.

ACKNOWLEDGMENTS

We thank the financial support from the Spanish Ministerio de Economía y Competitividad (MAT2013-46502-C2-2P and MAT2013-46753-C2-1P). Also the scientific computing center (CCC) of the Autonomía University of Madrid for their time.

References

- [1] N. Yasumatsu, Y. Yoshikawa, Y. Adachi, H. Sakurai, *Bioorgan. Med. Chem.*, 15 (2007) 4917.

- [2] E. Lodyga-Chruscinska, G. Micera, E. Garribba, *Inorg. Chem.*, 50 (2011) 883.
- [3] B.-M. Kukovec, Z. Popović, B. Kozlevčar, Z. Jagličić, *Polyhedron*, 27 (2008) 3631.
- [4] R. March, W. Clegg, R.A. Coxall, L. Cucurull-Sánchez, L. Lezama, T. Rojo, P. González-Duarte, *Inorg. Chim. Acta*, 353 (2003) 129.
- [5] B.-M. Kukovec, Z. Popović, Š. Komorsky-Lovrić, V. Vojković, M. Vinković, *Inorg. Chim. Acta*, 362 (2009) 2704.
- [6] B.-M. Kukovec, P.D. Vaz, Z. Popović, M.J. Calhorda, K. Furić, G. Pavlović, M.R. Linarić, *Cryst. Growth Des.*, 8 (2008) 3465.
- [7] T. Takino, H. Yasui, A. Yoshitake, Y. Hamajima, R. Matsushita, J. Takada, H. Sakurai, *J. Biol. Inorg. Chem.*, 6 (2001) 133.
- [8] M. Regueiro-Figueroa, E. Ruscsák, L. Fra, G. Tircsó, I. Tóth, A. de Blas, T. Rodríguez-Blas, C. Platas-Iglesias, D. Esteban-Gómez, *Eur. J. Inorg. Chem.*, 2014 (2014) 6165.
- [9] L. Simon, J. Csillag, I. Szegvári, *Plant and Soil*, 254 (2003) 337.
- [10] S. Sarkar, S. Dey, T. Mukherjee, E. Zangrando, M.G.B. Drew, P. Chattopadhyay, *J. Mol. Struct.*, 980 (2010) 94.
- [11] S. Basu, S.-M. Peng, G.-H. Lee, S. Bhattacharya, *Polyhedron*, 24 (2005) 157.
- [12] M.A.S. Goher, Hafez, A. K., Abu-Youssef, M. A. M., Popitsch, A., Fritzer, H. P., Mautner, F. A., *Monats. Chem.*, 125 (1994) 833.
- [13] A.Y. Robin, K.M. Fromm, *Coord. Chem. Rev.*, 250 (2006) 2127.
- [14] J.J. Vittal, *Coord. Chem. Rev.*, 251 (2007) 1781.
- [15] R.S. Patil, H. Kumari, C.L. Barnes, J.L. Atwood, *Chem. Commun*, 51 (2015) 2304.
- [16] P. Amo-Ochoa, O. Castillo, C.J. Gómez-García, K. Hassanein, S. Verma, J. Kumar, F. Zamora, *Inorg. Chem.*, 52 (2013) 11428.
- [17] G. Beobide, O. Castillo, J. Cepeda, A. Luque, S. Pérez-Yáñez, P. Román, J. Thomas-Gipson, *Coord. Chem. Rev.*, 257 (2013) 2716.
- [18] D. Graham, G. Lamprecht, I. Potgieter, A. Roodt, J. Leipoldt, *Trans. Met. Chem.*, 16 (1991) 193.
- [19] J.G. Leipoldt, G.J. Lamprecht, D.E. Graham, *Inorg. Chim. Acta*, 101 (1985) 123.
- [20] M. Bhar, M. Chaudhury, E.R.T. Tiekink, *Acta Crystall. Sect., E*, 57 (2001) m305.
- [21] C.-J. Li, Z. Lin, L. Yun, Y.-L. Xie, J.-D. Leng, Y.-C. Ou, M.-L. Tong, *Crystengcomm*, 12 (2010) 425.
- [22] J. Liu, Y.-L. Qin, M. Qu, R. Clerac, X.-M. Zhang, *Dalton Trans.*, 42 (2013) 11571.
- [23] K.A. Siddiqui, *J. Coord. Chem.*, 65 (2012) 4168-4176.
- [24] J.-G. Lin, Y. Su, Z.-F. Tian, L. Qiu, L.-L. Wen, Z.-D. Lu, Y.-Z. Li, Q.-J. Meng, *Cryst. Growth Des.*, 7 (2007) 2526.
- [25] M.F.R. Moita, M. Duarte, R. Fausto, *J. Chem. Soc. Far. Trans.*, 90 (1994) 2953.
- [26] Zerrin Heren, Cem Cüneyt Ersanlr, Cem Keser, N.O. Ískeleli, *Acta Crystall. Sect. E*, 62 (2006) m796.
- [27] G. Givaja, P. Amo-Ochoa, C.J. Gomez-Garcia, F. Zamora, *Chem. Soc. Rev.*, 41 (2012) 115.

Graphical Abstract

