

Coordination behavior of dimethyl pyridine-2,6-dicarboxylate towards mercury(II), cadmium(II) and chromium(III) in the solid- and gaseous state supported by CSD studies



Mohammad Hakimi^{a,*}, Zahra Mardani^b, Keyvan Moeini^a, Fabian Mohr^c

^a Chemistry Department, Payame Noor University, 19395-4697 Tehran, Islamic Republic of Iran

^b Chemistry Department, Urmia University, 57561-51818 Urmia, Islamic Republic of Iran

^c Fakultät für Mathematik und Naturwissenschaften, Anorganische Chemie, Bergische Universität Wuppertal, 42119 Wuppertal, Germany

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ABSTRACT

In this work, three complexes, [Hg(MPC)Cl₂] (**1**), [Cd(MPC)₃][CdBr₄] (**2**) and the coordination polymer, {K[Cr(PDC)₂]}_n (**3**) of dimethyl pyridine-2,6-dicarboxylate (MPC) and hydrolyzed MPC, pyridine-2,6-dicarboxylic acid (H₂PDC), were prepared and identified by elemental analysis, FT-IR, Raman, ¹H NMR spectroscopy and single-crystal X-ray diffraction. All coordination modes of dimethyl pyridine-2,6-dicarboxylate derivatives were studied by CSD to predict the behavior of MPC in reactions with metals. Subsequently, these coordination modes were optimized by DFT methods to determine of the most stable mode and charge distribution. In the crystal structure of **1**, the mercury atom has a HgNO₂Cl₂ environment and inclines to a trigonal bipyramidal geometry. The molecule of **2** has two cadmium atoms with different geometries. One Cd atom has coordination number four and ideal tetrahedral geometry which is determined by using a new formula proposed in this paper. The crystal structure of **3** revealed a rare 2D *s-d* mixed-metal coordination polymer containing dodecahedrally coordinated potassium(I) and octahedral chromium(III). Common coordination number for mercury(II), cadmium(II) and chromium(III) is determined by studying of all complexes of them in CSD.

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1. Introduction

Dialkyl pyridine-2,6-dicarboxylates are present in the structure of variety of compounds including cryptands [1], cyclic polyethers [2,3], pyridine diester spacers [4], triple-helical complexes [5] and macrocyclic ionophores [6,7]. These compounds are versatile ligands for erbium luminescence sensitization [8]. The fluxional behavior [9] and pseudopolymorphism [10] for some of them were investigated by dynamic NMR spectroscopy and density functional theory (DFT), respectively. Self-assembly of these compounds is due to π - π interactions between pyridine rings [11].

Recently, we have extended our studies to metal complexes of dialkylpyridine-2,6-dicarboxylates [12] and now focused on the coordination chemistry of dimethylpyridine-2,6-dicarboxylate (C₉H₉NO₄, MPC, Table 1) by structural and theoretical studies.

Dimethylpyridine-2,6-dicarboxylate is a potentially pentadentate ligand binding to a metal through one N atom of the pyridine ring and the four O atoms of the carboxylate groups. Due to geometrical restrictions however, the donor atoms cannot

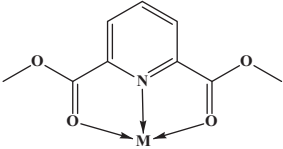
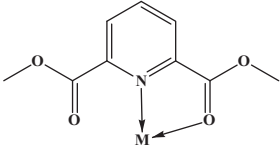
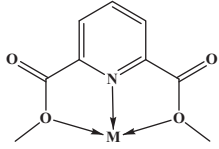
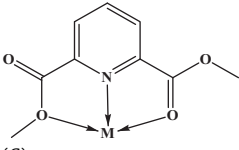
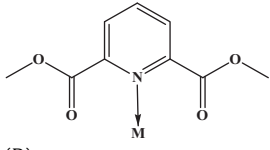
coordinate to a metal center simultaneously. Examination of the Cambridge structural database (CSD) [13] revealed, that the coordination chemistry of compounds containing a dimethylpyridine-2,6-dicarboxylate unit have not been investigated much. To introduce this type of ligands for coordination chemists, all reported structures containing a dimethylpyridine-2,6-dicarboxylate unit are collected in the “Supplementary material” and all coordination modes are summarized in Table 1. This ligand can acts as NO₂⁻, NOO⁻, NO₂⁻, NO⁻ and N-donor (O: oxygen atom of carbonyl group, O': oxygen atom of ester group). The data reveals that the nitrogen atom participates in all coordination modes. In addition, the coordination probability of carbonyl oxygen atoms is higher than that of the ether group. The energies of each coordination mode were calculated by DFT methods and compared in theoretical section (see below). In all CSD searches discussed here, structures containing errors or disorder have been omitted.

In this work, the preparation, characterization, crystal structures and theoretical studies of the complexes, [Hg(MPC)Cl₂] (**1**), [Cd(MPC)₃][CdBr₄] (**2**) and the coordination polymer, {K[Cr(PDC)₂]}_n (**3**), with dimethyl pyridine-2,6-dicarboxylate (MPC) and pyridine-2,6-dicarboxylic acid (H₂PDC) are described. H₂PDC was formed as hydrolysis product of MPC during the complexation

* Corresponding author. Tel.: +98 513 8691090; fax: +98 513 8683001.

E-mail address: mohakimi@yahoo.com (M. Hakimi).

Table 1
All coordination modes of dimethylpyridine-2,6-dicarboxylate unit in metal complexes found in the CSD database. The percentage of each mode and the corresponding metals are also listed.

Coordination modes				
Ions		(A) M: Co ²⁺ [50], Eu ³⁺ [5], Cd ²⁺ [12] 27.27%	(A') M: Re ⁺ [9], Cu ⁺ [51], Ag ⁺ [12] 27.27%	(B) M: K ⁺ [3], Ag ⁺ [49] 18.18%
Coordination modes				
Ions		(C) M: Cu ²⁺ [48,52] 18.18%		(D) M: Ag ⁺ [7] 9.09%

reactions [14]. We also present a new formula for the determination of geometry around a metal with coordination number four.

2. Experimental

2.1. Materials and instrumentation

All chemicals and solvents were reagent or analytical grade from commercial sources and used as received. The MPC ligand and K₃[Cr(O₂)₄] were prepared according to literature procedures [15,16]. Infrared spectra (as KBr pellets) in the range of 4000–400 cm⁻¹ were recorded with a FT-IR 8400-Shimadzu spectrometer. Raman spectra were performed using a Nicolet Model 910 Fourier-transform spectrometer. ¹H NMR spectra were recorded using a Bruker Avance 300 instrument; chemical shifts δ are given in parts per million, relative to TMS as an internal standard. The carbon, hydrogen and nitrogen contents were determined with a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The melting points were determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

2.1.1. Synthesis of [Hg(MPC)Cl₂] (1)

0.19 g (1.00 mmol) of MPC dissolved in EtOH (10 mL), was added with stirring to a solution of 0.27 g (1.00 mmol) of HgCl₂ in EtOH (20 mL). The reaction mixture was stirred at 60 °C for 5 h. Colorless crystals suitable for X-ray diffraction were obtained from the solution after standing for 5 days. Yield: 0.41 g, 88%; m. p. 158 °C. *Anal. Calc.* for C₉H₉Cl₂HgNO₄ (466.67): C, 23.16; H, 1.94; N, 3.00. *Found:* C, 24.32; H, 2.05; N, 3.85%. IR (KBr, cm⁻¹): 3078m (ν CH_{ar}), 2947m (ν CH), 1724 s (ν C=O), 1578m (ν C=N), 1435m (δ_{as} CH₃), 1312 s (δ_s CH₃), 1257 v (ν C–O), 748m and 694m (γ py). Raman (cm⁻¹): 3071 w (ν CH_{ar}), 2980 m (ν CH), 1634 m (ν C=N), 678m (γ py), 506 w (ν HgN), 385m (ν HgO), 239m (ν HgCl). ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ = 8.17–8.29 (m, 3 H, CH_{ar}), 3.91–3.92 (d, 6 H, CH).

2.1.2. Synthesis of [Cd(MPC)₃][CdBr₄] (2)

0.59 g (3.00 mmol) of MPC dissolved in MeOH (20 mL), was added with stirring to a solution of 0.68 g (2.00 mmol) of CdBr₂·4H₂O in MeOH (20 mL). The reaction mixture was stirred at 60 °C for 5 h. Colorless crystals suitable for X-ray diffraction were obtained from the solution after standing for 3 days. Yield: 0.44 g, 78%; m. p. 183 °C. *Anal. Calc.* for C₂₇H₂₇Br₄Cd₂N₃O₁₂

(1129.95): C, 28.70; H, 2.41; N, 3.72. *Found:* C, 30.03; H, 2.23; N, 4.27%. IR (KBr, cm⁻¹): 3086m (ν CH_{ar}), 2976m (ν CH), 1716 s (ν C=O), 1596 s (ν C=N), 1450m (δ_{as} CH₃), 1373m (δ_s CH₃), 1288m (ν C–O), 764 w and 687 w (γ py). Raman (cm⁻¹): 3040 w (ν CH_{ar}), 2946 w (ν CH), 1635m (ν C=N), 1374 w (δ_s CH₃), 1296m (ν C–O), 785 w and 684 w (γ py), 461 w (ν CdN), 338m (ν CdO), 131m (ν CdBr). ¹H NMR (300 MHz, DMSO-*d*₆, ppm): δ = 8.20–8.47 (m, 3 H, CH_{ar}), 3.92–3.96 (d, 6 H, CH).

2.1.3. Synthesis of [K[Cr(PDC)₂]]_n (3)

0.39 g (2.00 mmol) of MPC dissolved in EtOH (10 mL), was added with stirring to a solution of 0.30 g (1.00 mmol) of K₃[Cr(O₂)₄] in H₂O (10 mL). The reaction mixture was stirred at 60 °C for 5 h. Light brown crystals suitable for X-ray diffraction were obtained from the solution after standing for a week. Yield: 0.22 g, 53%; m. p. > 300 °C. *Anal. Calc.* for C₁₄H₆CrKN₂O₈ (421.31): C, 39.91; H, 1.44; N, 6.65. *Found:* C, 39.52; H, 1.68; N, 6.82%. IR (KBr, cm⁻¹): 3086m (ν CH_{ar}), 1715m (ν C=O), 1618m (ν C=N), 1452m (δ_{as} CH₃), 1379m (δ_s CH₃), 1281 v (ν C–O), 741m and 694m (γ py). Raman (cm⁻¹): 3024 w (ν CH_{ar}), 1696 s (ν C=O), 1541m (ν C=N), 1323m (ν C–O), 739m (γ py), 617m (ν CrN), 461m (ν CrO), 304m (ν KO).

2.2. Crystal structure determination and refinement

Suitable crystals of **1** and **2** were selected on a Xcalibur Eos Gemini Ultra and **3** on an Oxford Diffraction Gemini Ultra diffractometers. The crystals were kept at 150 K during data collection. Using OLEX-II [17], the structures were solved with the SHELXS [18] structure solution program using Direct Methods and refined with the SHELXL [18] refinement package using least squares minimisation. The molecular graphics were drawn with ORTEP-III [19,20], Mercury [21] and Diamond [22]. Crystallographic data and details of the data collection and structure refinement are listed in Table 2, selected bond lengths and angles in Table 3 and hydrogen bond geometries in Table 4.

2.3. Computational details

The ground state geometries of all coordination modes were optimized with the Gaussian 09 software [23] and calculated in the gas phase using DFT [24] at the B3LYP/DGTZVP level of theory for Cd(II), Zn(II) and Cr(III) and B3LYP/SDD for Hg(II).

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