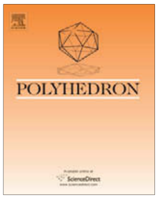
Polyhedron 29 (2010) 1191–1200

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Comparative study on Cd(II) and Ca(II) model complexes with pyridine-2,3-dicarboxylic acid: Synthesis, crystal structure and spectroscopic investigation

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ARTICLE INFO

Article history:
Received 18 August 2009
Accepted 10 December 2009
Available online 11 January 2010

Keywords:
Pyridinedicarboxylate
Calcium complex
Cadmium complexes
X-ray data
Spectroscopic data

ABSTRACT

Two novel cadmium and one calcium complex, in which pyridine-2,3-dicarboxylic acid (2,3pydcH$_2$) acts as a monodicarboxylate anion (2,3pydcH) with one acid hydrogen on the hetero-nitrogen or a doubly deprotonated dicarboxylate anion (2,3pydc), have been synthesized and characterized using single crystal X-ray diffraction, elemental analysis and IR, Raman, ^{1}H and ^{13}C NMR spectroscopies: [Cd(2,3pydcH)$_3$][Cd(H$_2$O)$_6$]$_{0.5}$ (**1**), [Cd(2,3pydc)(H$_2$O)$_3$]$_n$ (**2**), [Ca(2,3pydcH)$_2$(H$_2$O)$_3$]$_n$ (**3**). Complex **1** crystallizes in the trigonal system space group $P\bar{3}$. The cadmium anion Cd(1) {CdN$_3$O$_3$} and cation Cd(2) (coordinated by 6 water molecules) possess the same coordination polyhedra (octahedral). Packing analysis reveals that complex **2** (space group $Pca2_1$) has a very interesting coordination network. The column of 2_1 symmetry is built up of translationally repeated mer units, [–O–Cd(3H$_2$O)C$_7$NO$_3$–O–]$_n$, arranged into two dimers rotated relative to each other by 180° (a twisted zigzag screen). Polymeric complex **3** crystallizes in the monoclinic system (space group $P2_1/c$). Two molecules of ligand and three molecules of water are bounded directly to the metal ion to give a {CaNO$_7$} chromophore, which results in coordination polyhedron described as a pseudo-dodecahedron. It is worth noticing that two types of coordination modes of the 2,3pydcH ligand exist in the structure: one of them acts as chelating (N,O) bidentate ligand in which the carboxyl groups are bound to each other by a very short strong hydrogen bond (O(9)···O(12)); the other acts as tridentate (O, O, O′) coordinating anion with one acid hydrogen attached to the nitrogen atom.

1. Introduction

Calcium, as one of the most important elements, plays a versatile role within cells in all living creatures, predominantly as a second messenger transmitting signals between the plasma membrane and intracellular machinery [1,2]. Additionally, more than 99% of the calcium in the human body is in bones and teeth, in which calcium provides not only structural strength but also serves as a reservoir of extracellular calcium concentration. Calcium homeostasis is maintained within a narrow range, 2.10–2.60 mmol/l, by balancing between calcium absorption, calcium exertion, calcification and decalcification of bone [3,4]. This fairly narrow range of extracellular fluid calcium concentration can be easily disturbed by toxic metals such as cadmium [5,6], especially as both ions (Cd^{2+} and Ca^{2+}) have similar radii. Therefore, a comparison of the coordination chemistry of calcium and cadmium model complexes ought to provide a solid based example of how toxic metal ion substitution may perturb the structure of a calcium compound with the same ligand. For this reason, we report the syntheses and structural characterization of Ca(II) and Cd(II) complexes with pyridine-2,3-dicarboxylic acid, as elucidated by spectroscopic (IR, Raman, NMR) and X-ray crystallographic methods. Bearing in mind on one hand that pyridine-2,3-dicarboxylic acid is a tryptophan metabolite of the kynurenic pathway [7,8] and exerts neurotoxic effects by activation of N-methyl-D-aspartate receptor and calcium channels opening [9–11], and on the other hand cadmium enters the cell by receptor or voltage operated calcium channels [12,13], we have used this N,O-donor biologically relevant ligand to assess the similarities and differences in the coordination behavior of Ca(II) and Cd(II) ions. An examination of the literature data [14–18] shows that the coordination ability of pyridine-2,3-dicarboxylic acid towards metal ions depends on the hydrothermal or non-hydrothermal methods used to prepare the complexes. This acid may function as a neutral N,O-donor ligand, as found in the structure of [Cu(C$_7$H$_5$NO$_4$)$_2$] [14], or as

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doi:10.1016/j.poly.2009.12.031

monoprotonated-2-carboxylic acid as in [Cu(2,3pydcH)$_2$] [15]. The first crystal was obtained using this ligand, $CuCl_2$, $NH_4Cl \cdot H_2O$ and 1-propanol/water as the solvent (pH 7.0). The second one was prepared using this ligand and $Cu(CH_3COO)_2 \cdot H_2O$ in water solution at room temperature. The same bidendate mode of coordination was found in the structure of *trans*-[Co(2,3pydcH)$_2$(H_2O)$_2$] [16] and for a complex with the Ru(II) ion [17]. Recently, catenated polymeric structures have been reported for two novel Ca(II) complexes [18] in which molecules of the ligand act as chelating N,O or bridging OO′ or O-forms. One of the forms of the ligand has a proton attached to the hetero-nitrogen atom. This phenomenon is connected with the structurally known fact [19,20] that the molecule of pyridine-2,3-dicarboxylic acid is zwitterionic in the solid state with one acid hydrogen on nitrogen, and with an O–H···O hydrogen bond between two carboxylate groups. Preparation of metal complexes of 2,3-pydcH$_2$ by hydrothermal reaction with $Cd(NO_3)_2 \cdot 4H_2O$ [21] or $Mn(NO_3)_2 \cdot 6H_2O$ [22] under basic conditions (NaOH) led to coordination polymers in which the doubly deprotonated dicarboxylate anions acts as tetra-donating and penta-donating ligands. In our work we describe non-hydrothermal methods for the synthesis of different Cd(II) (**1** and **2**) and Ca(II) (**3**) complexes in which pyridine-2,3-dicarboxylic acid (2,3pydcH$_2$) acts as a monodicarboxylate anion (2,3pydcH) (**1** and **3**), monodicarboxylate anion with one acid hydrogen on the hetero-nitrogen (**3**) or doubly deprotonated dicarboxylate anion (2,3pydc) (**2**). These results indicate the importance of the choice of reaction conditions in preparing coordination compounds.

2. Experimental

2.1. Physical measurements and instrumentation

Elemental analyses were run on a Model 240 Perkin–Elmer CHN Analyzer. Infrared spectra (Perkin–Elmer 180 spectrophotometer; 4000–400 cm^{-1}) were recorded in KBr and FTIR spectra of the complexes in Nujol on a polyethylene window. Raman spectra were performed at room temperature with a Bio-Rad spectrometer, resolution 4 cm^{-1}. The incident radiation (λ = 1064 nm) was provided by a Neodymium laser YAG (Spectra-Physics).

^1H and ^{13}C NMR spectra were run on a Mercury-400BB spectrometer. ^1H NMR spectra were recorded at 400.09 MHz. Chemical

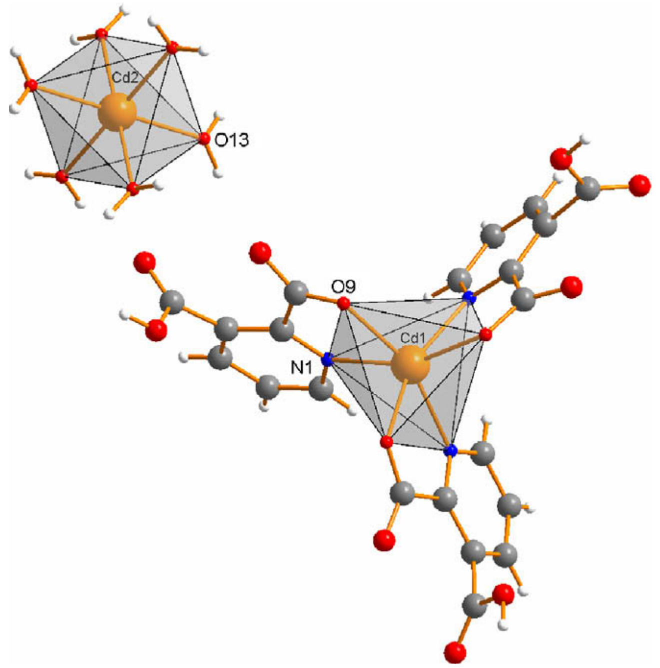

Fig. 1. Coordination environment of the cationic and anionic forms of complex **1** [27b].

Table 1
Crystal data and structure refinement for **1**, **2** and **3**.

Complex	1	2	3
Empirical formula	$Cd_{1.50}C_{21}H_{18}N_3O_{15}$	$CdC_7H_9NO_7$	$CaC_{14}H_{14}N_2O_{11}$
Formula weight	720.98	331.49	426.35
Temperature (K)	293(2)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, Space group	trigonal, $P\bar{3}$	orthorhombic, $Pca2_1$	Monoclinic, $P2_1/c$
Unit cell dimensions			
a (Å)	14.8260(3)	16.8540(4)	6.6135(3)
b (Å)	14.8260(3)	6.8430(2)	30.1060(10)
c (Å)	6.3582(2)	8.7023(2)	8.2270(3)
α (°)	90	90	90
β (°)	90	90	90.386(2)
γ (°)	120	90	90
Volume (Å^3)	1210.35(5)	1003.65(4)	1638.01(11)
Z, D_{calc} (Mg/m^3)	2, 1.978	4, 2.194	4, 1.729
Absorption coefficient (mm^{-1})	1.416	2.197	0.453
$F(0\,0\,0)$	714	648	880
Crystal size (mm)	0.30 × 0.25 × 0.15	0.30 × 0.03 × 0.02	0.18 × 0.07 × 0.01
θ (°)	3.17–34.95	3.98–27.48	2.48–27.50
Index ranges	$-23 \leqslant h \leqslant 23$, $-20 \leqslant k \leqslant 20$, $-9 \leqslant l \leqslant 10$	$-21 \leqslant h \leqslant 21$, $-8 \leqslant k \leqslant 8$, $-11 \leqslant l \leqslant 11$	$0 \leqslant h \leqslant 8$, $-38 \leqslant k \leqslant 38$, $-10 \leqslant l \leqslant 10$
Reflections collected/unique/observed [$I > 2\sigma(I)$]	6836/3538 [R_{int} = 0.0189]	7394/2269 [R_{int} = 0.0476]	6764/3737 [R_{int} = 0.1059]
Completeness to 2θ (%)	2θ = 34.95°, 99.9	2θ = 27.48°, 99.5	2θ = 27.50°, 99.2
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Maximum and minimum transmission	0.8157 and 0.6760	0.9574 and 0.5586	0.9955 and 0.9228
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	3538/3/133	2274/9/169	3737/8/278
Goodness-of-fit (GOF) on F^2	1.110	1.043	1.006
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0352, wR_2 = 0.1024	R_1 = 0.0276, wR_2 = 0.0534	R_1 = 0.0727, wR_2 = 0.1448
Final R indices (all data)	R_1 = 0.0495, wR_2 = 0.1093	R_1 = 0.0386, wR_2 = 0.0567	R_1 = 0.1692, wR_2 = 0.1712
Largest differences in peak and hole (e Å^{-3})	1.788 and −1.393	0.772 and −0.401	0.409 and −0.400