

s13.m38.p11 Coordination Modes of Pyridinecarboxylates in Cu(II) Complexes with Ethylenediamine. Dusan Miklos^a, Peter Segla^a, Marian Koman^a, Jana Jasková^a, Tadeusz Glowiak^{†b} and Milan Melník^a, ^aFaculty of Chemical and Food Technology, Slovak Technical University, 812 37 Bratislava, Slovak Republic, ^bFaculty of Chemistry, University of Wrocław, 50 383 Wrocław, Poland. E-mail: dusan.miklos@stuba.sk

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As copper and pyridinecarboxylic acids and their derivatives play an important role in widely differing biological processes, elucidation of structure-property relations for this class of coordination compounds is aimed at. It is known that pyridinecarboxylate ligands can exhibit various modes of coordination to a central atom. This contribution presents a short overview of coordination modes of pyridinecarboxylates to Cu(II) in the presence of ethylenediamine for several such complexes studied with known crystal structures. The ionic complex $\{[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2][\text{Na}(\text{H}_2\text{O})_5][\text{Cu}(2,6\text{-pydca})_2]_2\}$, where en = ethylenediamine and 2,6-pydca = 2,6-pyridine-dicarboxylate, crystallizes with the space group P-1, $a = 8.1939(6)$, $b = 12.5229(10)$, $c = 13.8842(9)$ Å, $\alpha = 63.476(7)$, $\beta = 76.056(6)$, $\gamma = 76.915(7)^\circ$, $Z = 2$. All Cu(II) atoms are six-coordinated; Cu1 by two en and two H₂O ligands in a centrosymmetrical, tetragonal-bipyramidal arrangement with long axial Cu-O bonds of 2.59 Å; Cu2 (and Cu2') by two tridentate 2,6-pydca ligands through the N atom and one O atom of each of the two carboxyl groups in a highly distorted coordination octahedron, forming a crystallographically independent unit. Surprisingly, the Cu2-O distances of ~2.32 Å to carboxyl oxygen atoms of one 2,6-pydca are considerably longer than those (~2.08 Å) of the other 2,6-pydca, possibly being caused by a system of hydrogen bonds which hold the structure together. The charge balance is achieved with a sodium cation surrounded with five water molecules which cation, unlike in $[\text{Cu}(2,3\text{-pyridine-dicarboxylate})_2][\text{Na}_2(\text{H}_2\text{O})_6(\text{m-H}_2\text{O})_2]$ [1], does not fulfil any bridging function. The same $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]$ unit has been observed in $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](3\text{-pyridinepropionate})_2$, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](\text{isonicotinate})_2$ [2] and $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2](2,6\text{-dimethoxynicotinate})_2$, but in these cases neither 3-pyridine-propionate, nor isonicotinate and 2,6-dimethoxynicotinate are coordinated to Cu(II). In $[\text{Cu}(2,6\text{-dimethoxynicotinate})_2(\text{en})]$ (2,6-dimethoxynicotinic acid) the 2,6-dimethoxynicotinate is coordinated in an asymmetric chelating manner to the same Cu(II) atom as en, through both O atoms of the carboxyl group, while a neutral molecule of 2,6-dimethoxynicotinic acid is present in the structure. Similar coordination mode of carboxylates has been observed in $[\text{Cu}(2\text{-methyl-thionicotinate})_2(\text{en})]$ [3]. The above compounds have been characterized also by IR, electronic and EPR spectra and their biological properties studied.

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s13.m38.p12 One Channelled Nanoporous Polymers with Sorption and Chiral Recognition Properties. A. Monge, N. Snejko, E. Gutiérrez-Puebla, M. Medina, C. Cascales, C. Ruiz-Valero, M. Iglesias and B. Gómez-Lor. *Instituto de Ciencia de Materiales de Madrid. CSIC. Cantoblanco s/n. 28049 Madrid. Spain. E-mail: amonge@icmm.csic.es*

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The hydrothermal reaction of zinc(II) salt with 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) in water led to the formation of colorless single crystals and a microcrystalline material. Upon determining the crystal structure [1] the composition was found to be $[\text{Zn}(\text{C}_{17}\text{H}_8\text{F}_6\text{O}_4)] \cdot 0.5\text{H}_2\text{O}$. There are two crystallographically independent Zn atoms and two ligand molecules per asymmetric unit. Each metal centre is surrounded by four oxygen atoms of different ligands in a tetrahedral coordination. Carboxylate groups are bonding the Zn atoms related by the 3₁ axis to give two different helical chains of tetrahedra along the c direction. The anions link every two of these chains giving rise to a 3D channelled structure with two kinds of very different parallel tunnels with squared and hexagonal shapes. Walls of these latter channels are formed by one double helix of CF₃-groups, giving rise to a kind of fluoro-lined teflon[®]-like channels. The result is a structure with separated hydrophilic and hydrophobic channels and absorption properties. After heating several crystals to eliminate the water molecules located in the squared channels, they were treated with linear hydrocarbons and, in the case of heptane, its structure re-determined. An electron density found along the fluoro-lined hexagonal channels, with a certain positional disorder due to the 3₁ symmetry, was assigned to the heptane molecules in a ratio of 0.25 per formula weight $[\text{Zn}(\text{C}_{17}\text{H}_8\text{F}_6\text{O}_4)] \cdot 0.25(\text{C}_7\text{H}_{16})$. In order to clarify this point, the structure was also solved in the P2 space group of the monoclinic system. Although some positional disorder remained, a row of maxima of electron density at distances and angles assignable to sp³ atoms was also found in the difference map of Fourier. The other channels remained empty since the water located in them had been previously eliminated. The presence of the hydrocarbon inside the material was also confirmed by gas chromatography analysis. With the purpose of testing the purity of the samples before and after the treatment and following its evolution, simulation of the X-ray powder patterns with the coordinates obtained from single-crystal structures, without and with hydrocarbon in the channels, were calculated. The reversibility and reproducibility of the process of insertion-extraction of heptane in the hexagonal hydrophobic channels is clearly displayed and furthermore, it can be seen that the final product fully recovers the characteristic X-ray diffraction pattern of the initial framework. Its ability to show chiral recognition was studied on the acetalization of (R, S)-2-phenyl propionaldehyde as a test reaction, which proceeded with high conversion and moderate enantioselectivity.

- [1] Crystal data: crystal system: trigonal; space group: P3₁; $a = 21.232(8)$, $c = 7.708(1)$ Å; $n_{\text{ref}} = 6146$; $R1 = 0.040$.