

INFLUENCE OF THE TYPE OF SYNTHESSES ON THE STRUCTURES OF MN(II) COMPLEXES WITH PYRIDINE-2,3-DICARBOXYLIC ACID

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The structural data on metal(II) complexes with pyridine-2,3-dicarboxylic acid (2,3pydcH₂) as a starting ligand have continuously received much attention. An examination of the literature data show that the coordination abilities of the pyridine-2,3-dicarboxylic acid towards metal ions depend on hydrothermal or non-hydrothermal methods of preparing complexes. This acid may function as a neutral N,O-donor ligand, or as the monodeprotonated-2-carboxylic acid. The hydrothermal method of synthesis usually give polymeric structures. Carboxylates as organic ligands readily interact with various metal ions through their negatively charged ends leading to metal-organic frameworks (MOFs materials). The molecular architectures comprising metal ion nodes bridged by organic ligands, which have attracted much interest recently due to their potential interest for gas storage, gas separation, as catalytic active phases, and as luminescent materials. In contrast, using non-hydrothermal synthesis we obtained as many as two types of compounds: monomeric and polymeric. For this reason, our aim is to gain information on influence of the type of preparation (hydrothermal and non-hydrothermal) on the product of the reaction. Additionally, we analyzed influence of manganese(II) salt applied to the synthesis on obtained by non-hydrothermal method compounds. Two manganese(II) complexes: [Mn(H₂O)₃(2,3pydc)]_n (1) (Fig. 1a) and [Mn(H₂O)₆][Mn(2,3pydcH)₃]₂ (2) (Fig. 1b) were successfully synthesized from the non-hydrothermal reaction system containing organic ligand and different Mn(II) salts [1]. Independently of the source of Mn²⁺ the same compounds were obtained. The results of the crystal study give some evidence that ligand exhibits various topological structures and interesting properties. Pyridine-2,3-dicarboxylic acid acts as monodicarboxylate N,O-chelating anion (complex (2)) or a doubly deprotonated three-dentate- N, O, O' dicarboxylate ion (complex (1)). In the [Mn(H₂O)₆][Mn(2,3pydcH)₃]₂ the coordination geometry around Mn(1) ion can be considered as being distorted octahedron {MnN₃O₃}. The Mn(2) cation which is placed at $\bar{3}$ possesses the same coordination polyhedron (octahedral). The crystal packing is stabilized by the moderate intermolecular hydrogen bonds of O–H...O type and π ... π interactions of pyridine rings. The manganese(II) cations (Mn(1)) with three coordinated pyridine-2,3-dicarboxylic ligands are packed in a pseudo-hexagonal 'propeller'-style pattern, with Mn(H₂O)₆ moiety in between. The coordination polyhedron of [Mn(H₂O)₃(2,3pydc)]_n can be described as a distorted {MnNO₅} octahedron and has a very interesting coordination network. The column of 2₁ symmetry is built up of translationally repeated mers, [(H₂O)₃-Mn-(2,3pydc)]_n, which rotate relative to each other by 180° forming a twisted zig-zag motif. Not only X-ray but also IR and Raman spectroscopy confirmed a bidentate fashion of coordination of the ligand to Mn(II) ions.

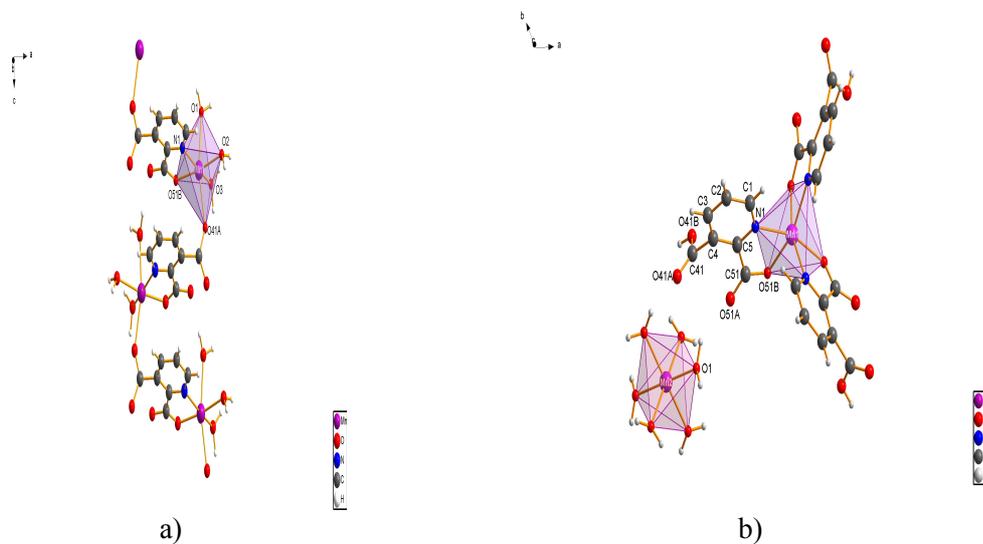


Figure 1. Molecular structures with the atom numbering scheme and coordination polyhedra of complex (1) (a) and complex (2) (b)

References

- [1] Jabłońska-Wawrzycka A., Zienkiewicz M., Hodorowicz M., Barszcz B., Rogala P., *J. Therm. Anal. Calorim.*, in press (2011).