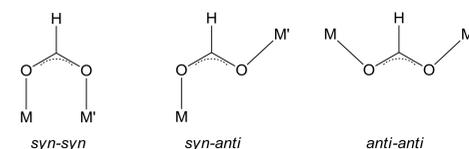


Introduction

The most simple carboxylate is the formate and a series of 3D frameworks have been investigated within the formate anion as bridging ligand between transition metals (M-O-CH-O-M). Between two transition metals the formate ion can adopt three different coordination modes: *syn-syn*, *syn-anti* or *anti-anti* (Scheme 1). [1, 2]

The interest in bridging carboxylates originates in its ability to mediate magnetic exchange interactions over short distances. [3]

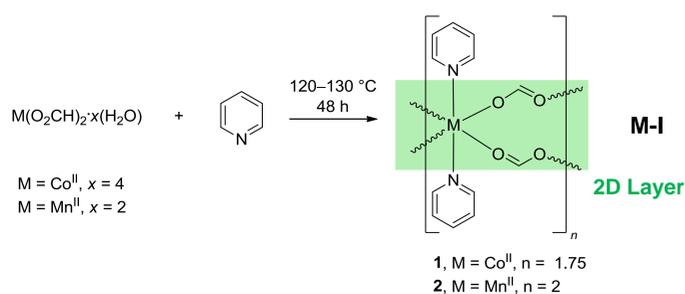
A large number of polymeric structures having μ^2 -formate anions as structural building block have been published already [1]. Of particular concern are pillared-layered structures: 2D metal-organic layers that are connected with each other by another kind of ligand. These structures show magnetic interactions within these layers, as well as between the layers if the connecting ligand is short enough to mediate magnetic interactions. Magnetic properties of these kind of polymers can be influenced by selection of bridging ligands, temperature and magnetic field strength [4]. The here presented compounds have been obtained by the reaction of metal(II) formates with pyridine. Within these reaction polymeric as well as monomeric structures could be obtained.



Scheme 1. Coordination modes of the formate anion as μ^2 -bridging ligand.

Results

Synthesis of the Polymeric Structures $[M(O_2CH)_2(py)_n]_\infty$



Complexes **1** and **2** were obtained by the reaction of metal(II) formates in pyridine at 120 – 130 °C for 48 hours (Reaction **M-I**). After cooling **1** to ambient temperature and **2** to 5 °C they precipitate as crystalline solids. Under anaerobic conditions crystals of **1** and **2** can be isolated and washed by ethanol and diethyl ether. **1** was obtained as violet crystalline pads, while **2** forms colorless small block shaped crystals with Mn(II) formate impurities (Figure 1).

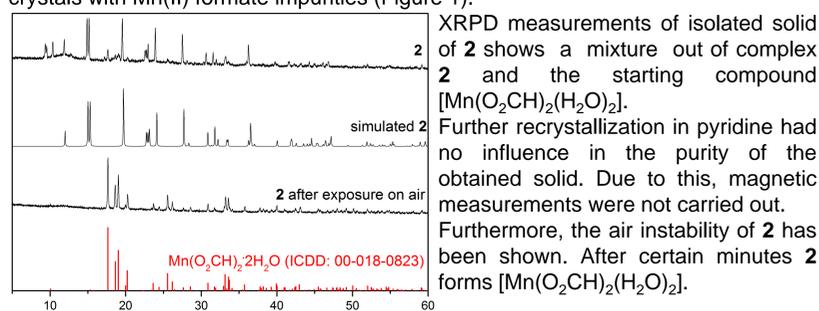


Figure 1. Experimental and simulated powder diffraction patterns showing the impurity within **2** and its conversion to $[Mn(O_2CH)_2(H_2O)_2]$.

Complexes **1** and **2** form polymeric networks consisting of 2D layers of $[M(O_2CH)_2]_n$ that are connected with each other by π - π interactions of the pyridine ligands. The pyridine ligands of two stacked layers interact for **1** by π - π ($D_{\pi\pi} = 3.6 - 3.7 \text{ \AA}$) and T-shaped interactions to each other forming a three dimensional network.[5] However, for **2** non of these interactions could be found.

The metal(II) ion is octahedral coordinated by two pyridine ligands in the axial and four formate ligands in the equatorial positions. Thereby each formate ion bridges two M^{II} ions in an *anti-anti* binding mode generating the 2-dimensional layer.

The 2D layers in **1** have a distance between 7.35 – 7.60 Å while the distances for **2** are around 7.37 Å.

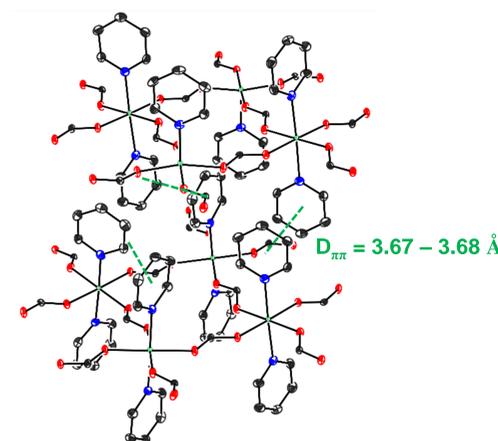


Figure 3. 3D framework formed by π - π interactions between pyridines of **1**.

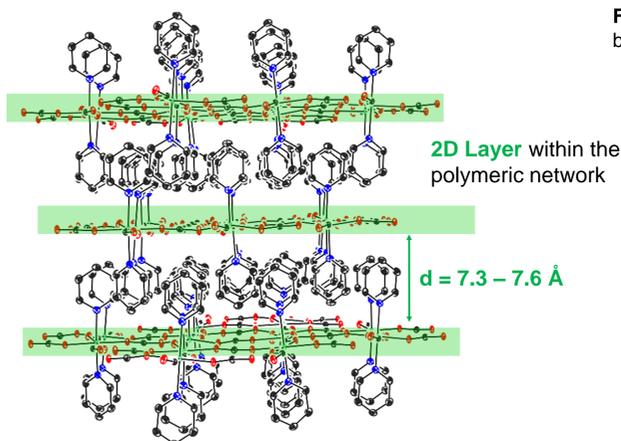
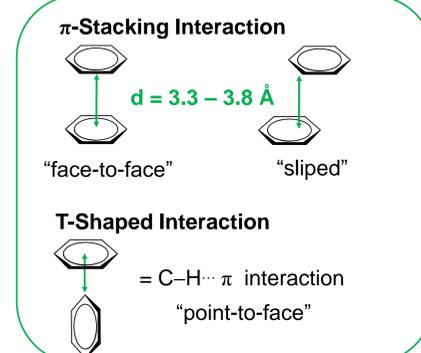
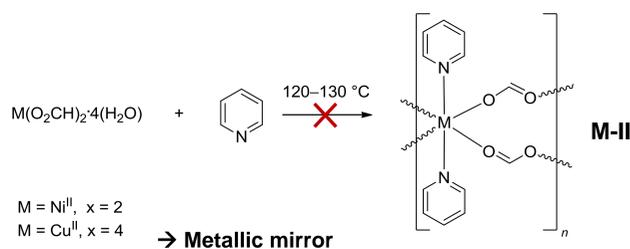


Figure 2. Structure of $[Co(O_2CH)_2(py)_2]_n$ (**1**) in the solid state. Green highlighted areas show the 2D Layer of $[Co(O_2CH)_2]_n$.



Scheme 2. Schematic representation of π - π interactions between aromatic ligands. [5]

Reaction of Ni^{II} and Cu^{II} formates



Treatment of the analogue Cu(II) and Ni(II) formates with pyridine at 120 – 130 °C no analogue polymeric structures according to **1** and **2** could be obtained (Reaction **M-II**). For both reactions a metallic mirror and in the case of Ni(II) also a magnetic solid were formed. XRPD measurements of the black residue (**Ni-II**) shows the formation of metallic nickel (Figure 4).

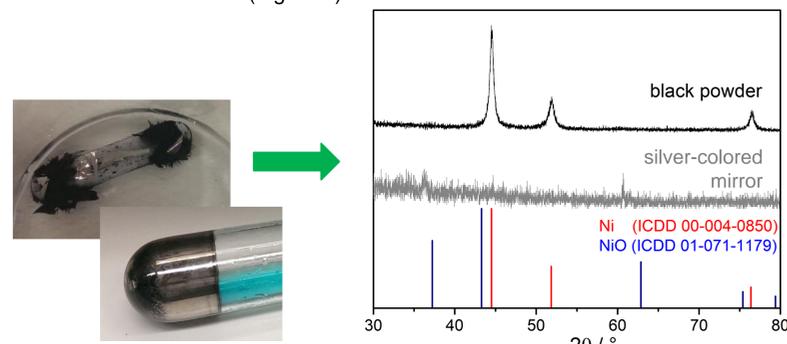


Figure 4. Formation of metallic mirror and black solid (left) within the reaction **Ni-II** and XRPD-measurements (right) of the obtained residues.

Monomer Structures: $[M(O_2CH)_2(py)_4]$

Complexes **3** and **4** were obtained after crystallization out of a solution of the metal(II) formates in pyridine at room temperature (**M-III**). [6] To obtain **4**, the reaction has to be heated up initially to 100 °C for 0.5 h. The air sensitive crystals could be isolated by removing the solvent with a cannula. The solids were washed with *n*-pentane and carefully dried under vacuum.

Especially complex **3** seems to be very instable. After few hours the crystals become brittle when stored in a Schlenk tube even under argon at room temperature.

Complexes **3** and **4** are monomeric structures. Four pyridine ligands are coordinated in equatorial and two formate ligands in axial positions to the metal(II) ion. Both complexes have a nearly perfect octahedral shape in the solid state (Figure 6).

By elemental analysis the loss of pyridine ligands can be proven.

Reaction of metal(II) formates in pyridine at ambient temperature

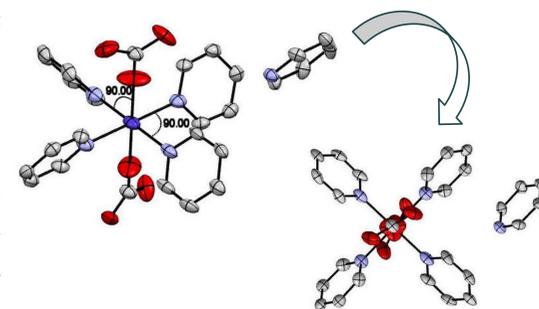
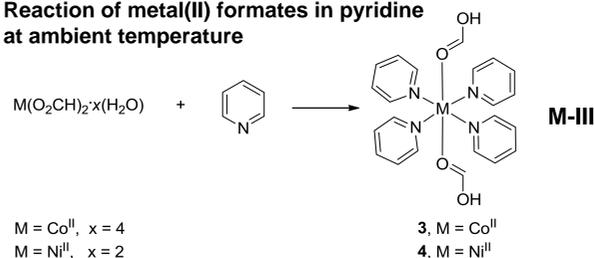


Figure 5. Structure of **3** in the solid state showing the nearly perfect octahedral coordination around the metal(II) ion.

Table 1. Selected crystallographic data of **3** and **4**.

$[Co(py)_4(O_2CH)_2]_2 \cdot 2py$ 3	$[Ni(py)_4(O_2CH)_2]_2 \cdot 2py$ 4
$C_{32}H_{32}N_6O_4Co$	$C_{32}H_{32}N_6O_4Ni$
623.56 g/mol	623.34 g/mol
orthorhombic	orthorhombic
Ccca	Ccca
<i>a/b/c</i> : 11.5907(2)/ 14.8835(3)/ 17.2340(3)	<i>a/b/c</i> : 11.93(2)/ 15.10(2)/ 17.14(1)

References & Acknowledgement

We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for financial support.

- [1] a) P. Samarasekera, X. Wang, A.J. Jacobson, J. Tapp, A. Moller, *Inorg. Chem.* **2014**, *53*, 244–256. b) K.V. Domasevitch, J. Sieler, E.B. Rusanov, A.N. Chernega, *Z. Anorg. Allg. Chem.* **2002**, *628*, 51–56. c) S.V. Kotilov, A.V. Shvets, V.N. Solomakha, *Theor. Exp. Chem.* **2006**, *42*, 43–47. d) Z.-X. Li, J.-P. Zhao, E.C. Sañudo, H. Ma, Z.-D. Pan, Y.-F. Zeng, X.-H. Bu, *Inorg. Chem.* **2009**, *48*, 11601-11607. [2] X.-Y. Wang, H.-Y. Wei, Z.-M. Wang, Z.-D. Chen, S. Gao, *Inorg. Chem.* **2005**, *44*, 572–583. [3] Z. Wang, B. Zhang, Y. Zhang, M. Kurmoo, T. Liu, S. Gao, H. Kobayashi, *Polyhedron*, **2007**, *26*, 2207–2215. [4] S. Rettig, R.C. Thompson, J. Trotter, S. Xia, *Inorg. Chem.* **1999**, *38*, 1360–1363. [5] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896. [6] D.V. Soldatov, J. Lipkowski, *Zh. Strukt. Khim. (Russ.) (J. Struct. Chem.)* **1995**, *36*, 979–982.