Scientific paper

Two Concomitant Polymorphs of Monomeric Nickel Acetate with 2-Pyridineethanol

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Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70th birthday

Abstract

A new mononuclear nickel(II) acetate with 2-pyridineethanol, $Ni(ac)_2(2\text{-}PyEtOH)_2$ has been prepared. The reaction product is a mixture of two polymorphic forms that crystallize concomitantly: triclinic ($P\bar{1}$) and monoclinic ($P2_1/c$). Their structures have been determined at 150 K. The molecular structure of the mononuclear complex shows similar geometry in both polymorphic structures but they differ notably in the arrangement of mononuclear entities in space. The crystal densities are significantly different, nevertheless they behave as concomitant polymorphs.

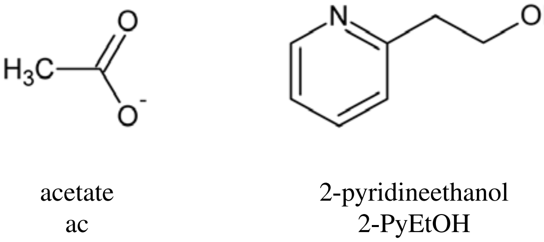
Keywords: Nickel(II) acetate, pyridine alcohols, concomitant polymorphs

1. Introduction

The synthesis of metal-organic hybrid materials remains one of the major trends in coordination chemistry. The most interesting among organic ligands are compounds with more functional groups being able to coordinate to metal centers. Such ligands offer the possibility of aggregation of small coordination units to form larger architectures, i.e. coordination polymers.[1–4]

In this light we have been interested for some time in the use of simple pyridine alcohol ligands for the construction of Cu(II) polynuclear compounds. These simple ligands contain two functional groups: i) pyridine nitrogen atom and ii) hydroxo group of a pyridine side chain. Both can participate in coordination to metal centers either in chelating or bridging manner. Additionally, the hydroxo group may be deprotonated to give the alkoxo group, known as a good bridging species.

We have previously reported on the chemistry and magnetic properties of Cu(II) complexes with the above mentioned ligands.[5,6] Recently, we have extended our research to the preparation of new complexes with other transition metal ions. Herein, we report the synthesis and structural investigation of a mononuclear nickel acetate with 2-pyridineethanol ligand (2-PyEtOH) which concomitantly crystallizes in two polymorphic forms.



Scheme 1. Ligands discussed in this work.

2. Experimental

2. 1. General Considerations

Chemicals were purchased from Aldrich or Fluka and were used without further purification. Elemental analyses were performed on a Perkin-Elmer 240 C, H, N analyzer by Organic Chemistry Department at the University of Ljubljana.

2. 2. Preparation of $Ni(ac)_2(2\text{-}pyEtOH)_2$

The compound was prepared by the reaction of nickel(II) acetate hydrate with 2-pyridineethanol (2-PyEtOH) in an acetonitrile solution. 2-PyEtOH (0.4 mL) was added to 10.0 mL of acetonitrile, stirred and heated to the boiling point. $Ni(CH_3COO)_2 \cdot 4H_2O$ (500 mg) was added gradually with intense stirring. The resulting green solution was filtered while still hot. The solution was allowed to cool slowly to room temperature. After standing a few days at ambient conditions light blue crystals precipitated which turned out to be a mixture oftwo polymorphic forms of Ni(Ac)$_2$(2-PyEtOH)$_2$ denoted as **1** and **2** throughout the text.

2. 3. X-ray Crystallography

Single crystals of **1** and **2** were mounted on a tip of glass fibers with small amount of silicon grease. Data were collected on a Nonius Kappa CCD diffractometer using the graphite monochromated Mo $K\alpha$ radiation at 150 K. Data reduction and integration were performed with the DENZO-SMN software package.[7] The structures were solved by direct methods implemented in SIR.[8] The positions of the remaining non-hydrogen atoms were found in Difference Fourier maps during the subsequent least-squares refinement using the program SHELX.[9] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in Difference Fourier maps but were included in the final refinement cycles on their calculated positions and refined as riding on their parent atoms. Figures depicting the structures were prepared by ORTEP-III[10], Platon[11] and CrystalMaker.[12] A summary of the crystallographic data and structure refinements is given in Table 1. The relevant bond distances and angles are listed in Table 2.

Table 1. Crystallographic data for polymorphs **1** and **2**.

	1	**2**
Formula	$C_{18}H_{24}N_2NiO_6$	$C_{18}H_{24}N_2NiO_6$
Formula weight (g/mol)	423.10	423.10
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.0784(2)	8.4777(2)
b (Å)	9.8113(2)	7.9182(2)
c (Å)	12.3803(2)	15.1985(3)
α (°)	100.8972(12)	90
β (°)	104.9007(11)	104.983(2)
γ (°)	107.3424(12)	90
V (Å^3)	974.09(3)	985.56(4)
Z' (Z)	2 (2)	2 (4)
μ(Mo $K\alpha$) (mm^{-1})	1.032	1.020
T (K)	150	150
ρ_{calc} (g cm^{-3})	1.443	1.426
Independent reflections	4412	2245
Observed reflections [I>2σ(I)]	3938	1786
Goodness-of-fit	1.037	1.033
R_1 (all data)	0.031	0.044
R_1[I>2σ(I)]	0.026	0.030
wR_2 (all data)	0.068	0.079
wR_2[I>2σ(I)]	0.065	0.073

X-ray powder diffraction data were collected using a PANalytical X'Pert PRO MPD diffractometer with θ–2θ reflection geometry, primary side Johansson type monochromator and Cu $K\alpha_1$ (λ = 1.54059 Å) radiation. The ambient temperature XRD spectrum of a sample was acquired from 2θ angles of 10° to 70° in steps of 0.034°.

3. Results and Discussion

Pyridine alcohol ligands are simple and commercially available compounds and it is surprising that they have not been employed widely as ligands in coordination chemistry. For example, the literature reports on only six Ni(II) complexes in which 2-pyridineethanol is coordinated to nickel center. In five of the reported structures 2-PyEtOH exists as a neutral ligand with its preserved alcohol function.[13–17] In these compounds it is coordinated in a chelating manner, all five species are mononuclear. Only one structure contains 2-PyEtOH in its anionic form acting as a bridging ligand between nickel atoms in a dinuclear unit.[18]

Reaction of nickel acetate with 2-pyridineethanol in acetonitrile afforded a light blue chemically pure product precipitated as single crystals, later identified as a mixture of crystals of two different polymorphic forms of mononuclear Ni(ac)$_2$(2-PyEtOH)$_2$. The polymorphic forms are not easily identified by their crystal habits. Their existence was unexpectedly found by testing the quality of the crystals before a routine X-ray data collection. The reaction was repeated several times to give a light blue product which was subsequently characterized by X-ray powder diffraction. Simulated powder diffraction patterns of the two polymorphs are significantly different; the measured diffractogram of the reaction product is a clear evidence that the blue crystals are a mixture of both polymorphic forms (Figure 1).

The triclinic polymorph, **1**, crystallizes with two neutral Ni(ac)$_2$(2-PyEtOH)$_2$ molecules in the unit cell. Each of the two molecules possesses an inversion center. Thus, the asymmetric unit consists of two halves of the molecule, each belonging to two independent molecules. The ORTEP view of the two monomeric units of **1** is depicted in Figure 2. Nickel atoms are sited on inversion centers. Each Ni atom is coordinated by two symmetry related acetate anions and two 2-PyEtOH molecules. Acetates are coordinated in a monodentate manner involving only one of the carboxylate oxygen atoms in the coordination. 2-PyEtOH ligands exist as neutral molecules and are coordinated in bidentate chelating mode involving both functional groups (pyridine nitrogen atom and hydroxyl group) in the coordination to the nickel atom. Thus, almost perfect octahedral NiO_4N_2 geometry is achieved in both monomeric entities. Details of the coordination bond

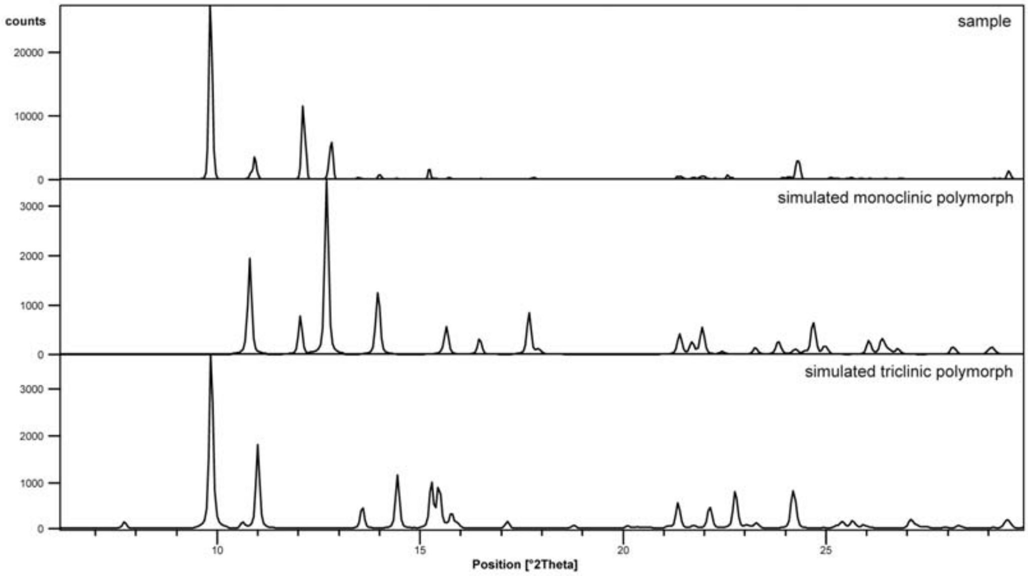


Figure 1. Comparison of the measured powder pattern of the reaction product and simulated powder patterns of the two polymorphic forms.

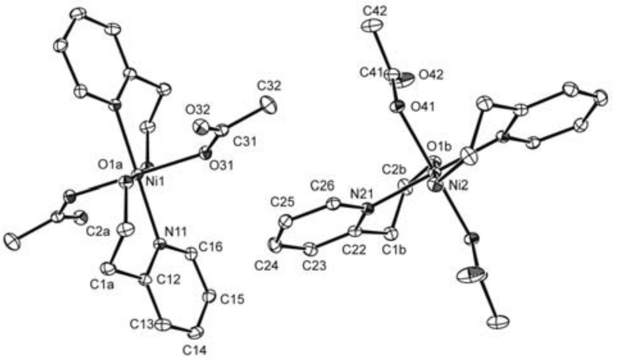


Figure 2. An ORTEP view of the two distinct Ni(ac)$_2$(2-PyEtOH)$_2$ molecules in **1**. Ellipsoids are drawn at the 30% probability level. Only the atoms of an asymmetric unit are labeled. Hydrogen atoms are omitted for clarity.

lengths and angles are given in Table 2. If the coordination geometry is essentially the same, where are then the differences between the two monomeric units? As it can be clearly seen in Figure 3, there is almost no offset of the 2-PyEtOH ligands, but the disposition of the acetate ligands is apparent. The difference in the positions of the acetate ligands is reflected also in hydrogen bonding geometry. The only observed hydrogen bonds in the structure are of intramolecular type and involve the hydroxyl groups of the 2-PyEtOH ligands as donor and the acetato oxygen atoms as acceptors. The strongest intramolecular H-bond contact involves the hydroxyl group and the non-coordinated acetate oxygen atom in both molecules. However, the attractive interaction exists also between the OH group and the coordinated oxygen atom of the acetate ligand, bringing the two oxygen atoms as close as 2.93 Å. The acceptor-donor distances are comparable for the two crystallographically distinct molecules, while there is a difference in the values of H-bond angles. The details are listed in Table 3.

The second polymorphic form crystallizes in the monoclinic space group $P2_1/c$ with the unit cell volume being 11.5 Å^3 larger as that of the triclinic form. There are two symmetry-related molecules in the unit cell, the ORTEP view of a molecule of **2** is depicted in Figure 4. The nickel atom occupies the inversion center and is coordinated by two monodentate acetates and two chelating 2-PyEtOH ligands. The coordination environment and the overall geometry of the molecule are similar to the two independent molecules of **1** (for comparison see Table 2). As in its polymorphic analogue, the only observed H-bond contact is of intramolecular type and involves the OH group of 2-PyEtOH ligand and both, coordinated and non-coordinated oxygen atoms of the acetate anion.

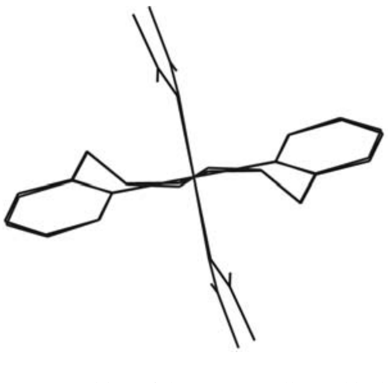


Figure 3. A superposition of the two crystallographically different molecules in **1.**

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

1			
Ni1-N11	2.0955(11)	O31-Ni1-N11	90.27(4)
Ni1-O1a	2.0850(9)	O31-Ni1-O1a	90.03(4)
Ni1-O31	2.0644(10)	O1a-Ni1-N11	89.93(4)
Ni2-N21	2.0833(11)	O41-Ni2-N21	89.24(4)
Ni2-O1b	2.0828(10)	O41-Ni2-O1b	89.71(4)
Ni2-O41	2.0798(10)	O1b-Ni2-N21	89.68(4)
2			
Ni1-N11	2.0905(14)	O31-Ni1-N11	88.09(5)
Ni1-O1a	2.1038(12)	O31-Ni1-O1a	90.90(5)
Ni1-O31	2.0643(12)	O1a-Ni1-N11	88.93(5)

Table 3. Hydrogen bonds distances (Å) and angles (°) in **1** and **2**.

D-H···A	O-H	H···O	O···O	O-H···O
1				
O1a-H1a···O32	0.82	1.74	2.5480(15)	167.5
O1a-H1a···O31	0.82	2.56	2.9349(14)	109.6
O1b-H1b···O42	0.82	1.71	2.5246(15)	171.6
O1b-H1b···O41	0.82	2.56	2.9359(14)	113.1
2				
O1a-H1a···O32	0.82	1.71	2.524(2)	170.3
O1a-H1a···O31	0.82	2.56	2.9705(18)	112.4

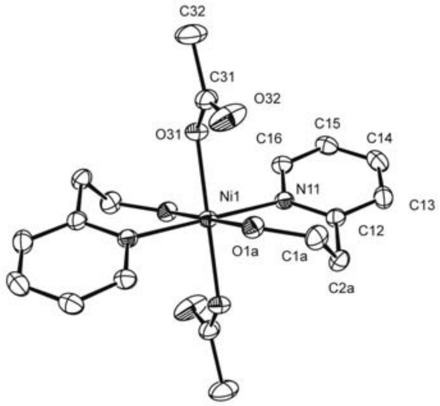


Figure 4. An ORTEP view of a Ni(ac)$_2$(2-PyEtOH)$_2$ molecule in **2**. Ellipsoids are drawn at the 30% probability level. Only the atoms of an asymmetric unit are labeled. Hydrogen atoms are omitted for clarity.

The two polymorphs differ primarily in their packing arrangements. While there is nothing remarkable about the packing in the monoclinic polymorph (Figure 6), the monomeric units in the triclinic polymorph are arranged in layers parallel to (001) as shown in Figure 5. There are two types of layers arranged along the *c*-axis, each layer contains only one set of molecules that are related only by translation. Within the layers the molecules are arranged in different ways. Their orientation in the layer (a) is such to bring the molecules closer through the interactions of pyridine rings, while in the second layer (b) the molecules are oriented to each other with the CH$_3$ group of the acetato ligand (Figure 5). The interactions between adjacent molecules in the triclinic polymorph are reflected in greater density (1.443 *vs.* 1.426 g/cm^3). Crystal densities are often used to indicate which polymorph is more stable ("the density rule").[19–22] The differences in the values of crystal densities for the reported polymorphs are not in agreement with their concomitant behaviour.

4. Conclusions

Our research originally oriented to the preparation of new coordination compounds with simple pyridine alcohol ligands yielded two new polymorphs of nickel acetate with 2-pyridineethanol. The structures of the two con-

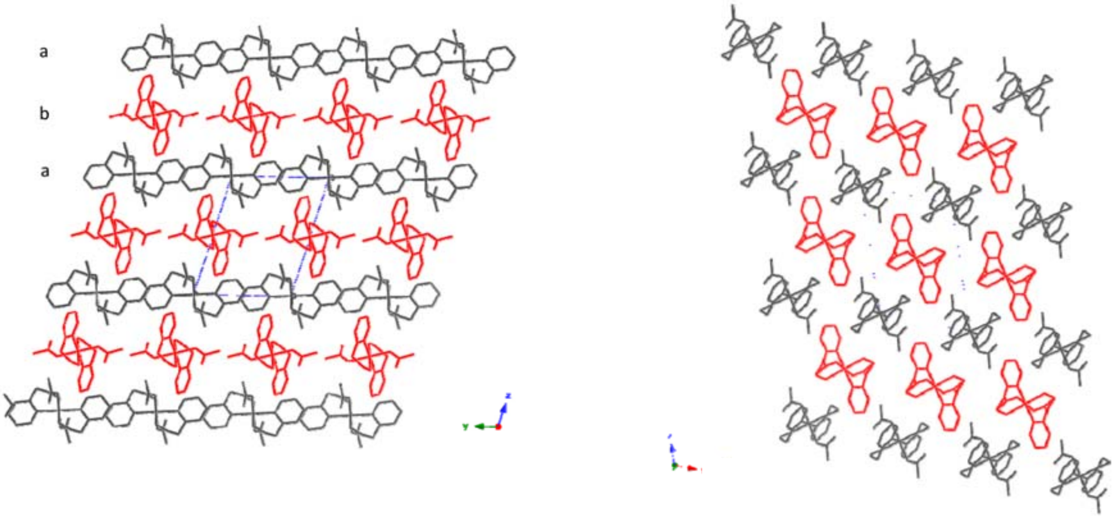


Figure 5. Packing diagram of **1** viewed along *a* axis (left) and *b* axis (right) illustrating different relative arrangement of two types of Ni(ac)$_2$(2-Py-EtOH)$_2$ molecules.

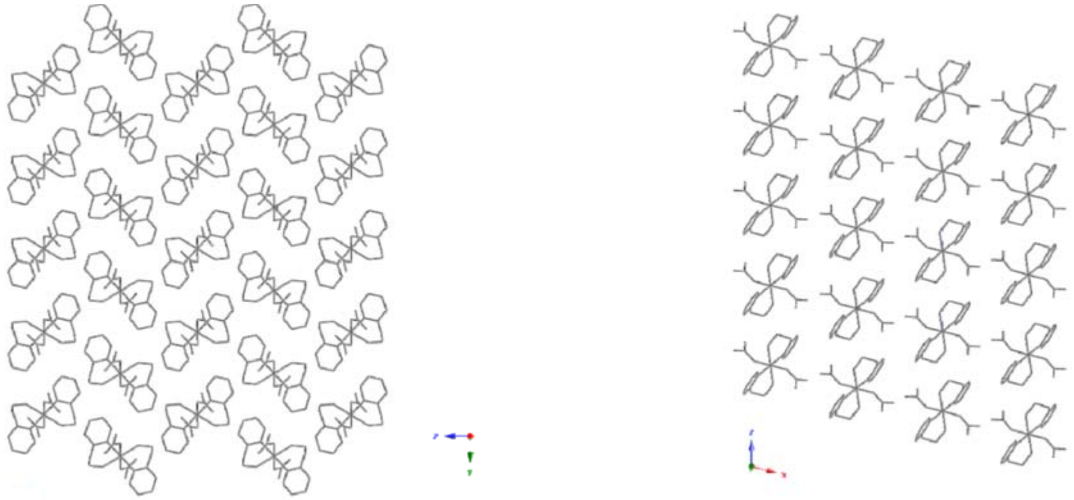


Figure 6. Two perspectives of the packing diagram of **2**. View down *a* axis (left) and down *b* axis (right).

comitant polymorphs are compared revealing their significantly different packing of molecules.

5. Supplementary Material

CCDC-862506 (**1**) and CCDC-862505 (**2**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6. Acknowledgement

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7. References

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Povzetek

Pripravili smo nov monomeren nikljev acetat z enostavnim piridinskim alkoholom (2-piridinetanol, 2-PyEtOH) kot kelatnim ligandom. Reakcija nikljevega acetata in 2-PyEtOH v acetonitrilu vodi do kemijsko čistega produkta stehiometrije $Ni(ac)_2(2\text{-}PyEtOH)_2$, ki kristalizira vsakokrat v dveh polimorfnih oblikah: monoklinski in triklinski. Določili smo kristalni strukturi obeh polimorfnih oblik in jih med seboj primerjali. Strukturi se razlikujeta v razporeditvi monomernih enot $Ni(ac)_2(2\text{-}PyEtOH)_2$ v prostoru. Posledično imata kristalni obliki različno gostoto. Kljub različni gostoti ne moremo govoriti o večji termodinamski stabilnosti ene od oblik; polimorfni obliki vedno kristalizirata hkrati.