

Synthesis and characterization of polymeric azido Zn(II) and Ni(II) complexes based on 3-hydroxypyridine



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ABSTRACT

The synthesis and structural characterization of two new complexes *catena*-[Ni(3-O-py)(3-HO-py)₂(μ_{1,3}-N₃)(H₂O)] (**1**) and *catena*-[Zn(μ-3-O-py)(μ_{1,1}-N₃)] (**2**), where 3-HO-py = 3-hydroxypyridine, are reported. The complexes were characterized by the elemental microanalyses, IR, and X-ray crystallography and by UV–Vis spectroscopy for complex **1**. Single crystal X-ray crystallography revealed the polymeric nature of the complexes: **1** as 1D with a single EE azide bridging, and **2** as 2D with μ(O,O',N) bridging of the deprotonated 3-O-py anions and di-EO azide groups, respectively. In **1** the neutral and deprotonated 3-hydroxypyridine molecules act only as N-terminal ligands. The emission spectral properties of the Zn(II) complex were investigated.

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1. Introduction

Small molecular ion such as azide, N₃⁻ and its metal complexes is considered to be as one of the most investigated ligand not only because of its ability to assemble metal ions to produce low-dimensional polynuclear and polymeric coordination compounds but also due to its ability to effectively transmit the magnetic coupling between the bridged paramagnetic metal ions [1–20]. Some of these compounds showed unique and unexpected topological structures as well as interesting magnetic properties [1,2,11–13]. In general, the azido ligand has two common bridging modes: the end-to-end (EE or μ_{1,3}-N₃) and the end-on (EO or μ_{1,1}-N₃) [3–10]. The EE bonding mode usually leads to antiferromagnetic interaction, whereas the EO mode leads to ferromagnetic interaction [3–10]. Alternate bridges of μ_{1,3}-N₃ and μ_{1,1}-N₃ were also reported in some compounds [1,13–16]. In addition to the above mentioned two bridging modes, the bridging azido ligand exhibits a wide range of coordination modes that include triple-bridges μ_{1,1,3}-N₃ and μ_{1,1,1}-N₃ [16], quarterly-bridges μ_{1,1,1,1}-N₃ and

μ_{1,1,2,2}-N₃ [17,18] as well as hexa-bridges μ_{1,1,1,3,3,3}-N₃ [19]. These modes have been occasionally summarized [1,2,12,20].

3-hydroxypyridine is also a versatile ligand, which may exist as neutral molecule, or in its O-deprotonated anionic and N-protonated cationic form. It can act as N-terminal ligand [21], as μ(O,N) bridging ligand in the neutral form [22,23], or acts as μ(O,O) bridge [24]. Furthermore the μ(O,O',N) bridging mode was also observed [22(d),25].

Herein we report the synthesis and characterization of two new coordination polymers which are bridged by azido ligands and derived from 3-hydroxypyridine. The complexes display different topologies depending on the nature of the central metal ions and the coordinated co-ligands.

2. Experimental

2.1. Materials and physical measurements

3-Hydroxypyridine was purchased from TCI and the other chemicals were of analytical grade quality. Infrared spectra of solid complexes were recorded on a Bruker Alpha P (platinum-ATR-cap) spectrometer (4000–400 cm⁻¹). The refractive spectrum (UV-VIS-

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NIR spectra) of the solid nickel(II) complex, **1** was recorded with a LS950 Perkin-Elmer Lambda-spectrometer (200–2500 nm). Emission Spectra were recorded with a Perkin-Elmer LS55 spectrofluorometer. Powder X-ray diffraction measurements were done with a Bruker AXS D8 Advance diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$). Elemental microanalyses were carried out with an Elementar Vario EN3 analyser.

Caution: Salts of azides and their complexes are potentially explosive and should be handled with great care and in small quantities.

2.2. Synthesis of the complexes

2.2.1. Synthesis of *catena*-[Ni(3-O-py)(3-HO-py) $_2(\mu_{1,3}$ -N $_3$)(H $_2$ O)] (**1**)

NiSO $_4 \cdot 6\text{H}_2\text{O}$ (0.26 g, 1 mmol), 3-hydroxypyridine (0.10 g, 1 mmol) and NaN $_3$ (0.26 g, 4 mmol) were dissolved in 15 mL distilled water and the resulting solution was allowed to stand at room temperature. After two days, the green crystals which separated were collected by filtration and dried in air (yield: 0.23 g, 57%). Anal. Calcd. for C $_{15}$ H $_{16}$ N $_6$ NiO $_4$ (403.03 g/mol): C, 44.7; H, 4.0; N, 20.9. Found: C, 45.0; H, 4.0; N, 20.7%. Selected IR bands (ATR-IR, cm $^{-1}$): 3213 (s,br), 2088 (vs), 2055 (vs), 1619 (w), 1581 (w), 1496 (m), 1454 (m), 1427 (w), 1384 (w), 1355 (m), 1294 (s), 1202 (s), 1102 (m), 1029 (m), 990 (m), 926 (w), 834 (s), 784 (s), 718 (w), 668 (m), 600 (m), 573 (w), 532 (s). Solid UV-VIS-NIR spectrum: three maxima at 1610, 880 and 520 nm with some shoulders around 1850, 1395 and 904 nm.

2.2.2. Synthesis of *catena*-[Zn(3-O-py)($\mu_{1,1}$ -N $_3$)] (**2**)

ZnSO $_4 \cdot 7\text{H}_2\text{O}$ (0.29 g, 1 mmol), NaN $_3$ (0.26 g 4 mmol) and 3-hydroxypyridine (0.38 g, 4 mmol) were dissolved in 20 mL distilled water and the resulting solution was allowed to stand at room temperature. After four days, the resulting yellow crystals were collected by filtration and dried in air (yield: 0.16 g 77%). Anal. Calcd. for C $_5$ H $_4$ N $_4$ OZn (205.51 g/mol): C, 29.8; H, 2.0; N, 27.8. Found: C, 29.5; H, 2.0; N, 27.9%. Selected IR bands (ATR-IR, cm $^{-1}$): 2105 (s), 1618 (w), 1581 (m), 1492 (m), 1387 (w), 1186 (s), 1102 (m), 1033 (w), 993 (w), 938 (w), 912 (w), 824 (s), 786 (s), 680 (m), 567 (w), 541 (w), 520 (m), 493 (w), 465 (m).

2.3. X-ray crystal structure analysis

The X-ray single-crystal data of the two compounds were collected on a Bruker-AXS APEX CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. The intensities were collected with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data processing, Lorentz-polarization and absorption corrections were performed using APEX, and the SADABS computer programs [26]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F 2 , using the SHELXTL [27] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. For **1** refinement of racemic twinning (i.e. Flack parameter = 0.50) was applied. Molecular plots were performed with the Mercury program [28].

3. Results and discussion

3.1. Synthesis and spectra of the complexes

At room temperature, the reactions of aqueous solutions

Table 1
Crystallographic data and processing parameters.

Compound	1	2
Empirical formula	C $_{15}$ H $_{16}$ N $_6$ NiO $_4$	C $_5$ H $_4$ N $_4$ OZn
Formula mass	403.03	201.51
System	Monoclinic	Monoclinic
Space group	Cc	$P2_1/n$
a (Å)	18.7446(18)	10.9558(12)
b (Å)	12.1281(13)	5.9412(7)
c (Å)	7.1260(9)	11.2590(14)
α (°)	90	90
β (°)	101.069(18)	107.295(14)
γ (°)	90	90
V (Å 3)	1589.9(3)	699.72(15)
Z	4	4
T (K)	100(2)	100(2)
μ (mm $^{-1}$)	1.258	3.448
D $_{\text{calc}}$ (Mg/m 3)	1.684	1.913
Crystal size (mm)	0.37 \times 0.25 \times 0.18	0.42 \times 0.22 \times 0.16
θ max (°)	26.35	26.30
Data collected	6210	5191
Unique refl./R $_{\text{int}}$	3142/0.0217	1419/0.0263
Parameters/Restraints	248/5	100/0
Goodness-of-Fit on F 2	1.096	1.125
R1/wR2 (all data)	0.0405/0.1023	0.0249/0.0721
Residual extrema (e/Å 3)	0.58/−0.35	1.06/−0.58

containing MSO $_4$ (M = Zn or Ni) and 3-hydroxypyridine, in the presence of NaN $_3$ afforded the crystalline coordination polymers *catena*-[Ni(3-O-py)(3-HO-py) $_2(\mu_{1,3}$ -N $_3$)(H $_2$ O)] (**1**) and *catena*-[Zn(3-O-py)($\mu_{1,1}$ -N $_3$)] (**2**) in moderate yields. These complexes were characterized by the elemental microanalyses, IR and by X-ray single crystal crystallography. In addition, the UV-VIS-NIR spectrum of nickel(II) complex, **1** was measured in the solid state.

The IR spectra of the complexes under investigation display general characteristic features as expected for the azido compounds: strong absorption band(s) in the 2110–2050 cm $^{-1}$ region due to the asymmetric stretching frequencies, $\nu_{\text{as}}(\text{N}_3)$ of the coordinated azido ligands. The azido complexes **1** displayed two bands, whereas **2** showed a single band at 2105 cm $^{-1}$. Probably, we should indicate that the number of stretching frequency bands $\nu_{\text{as}}(\text{N}_3)$ cannot be considered as a criterion to differentiate between the azido-bridging bonding modes complexes [1]. The complexes exhibit medium-strong intensity bands in the 1295–1190 cm $^{-1}$ region which can be assigned to the symmetrical stretching vibration, $\nu_{\text{s}}(\text{N}_3)$. The complex **1** exhibits a broad frequency band at 3213 cm $^{-1}$ due to $\nu(\text{O-H})$ of the coordinated aqua ligand and/or the hydroxyl group in 3-hydroxypyridine of complex **1**. This band

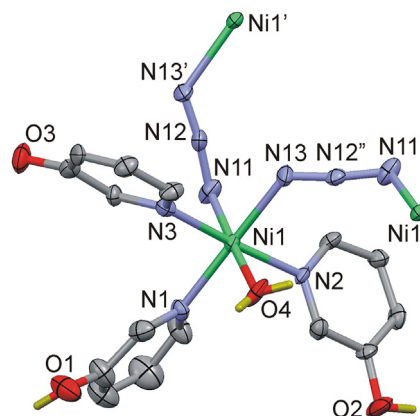


Fig. 1. Perspective view with partial atom numbering scheme of **1**. Symmetry code: (') $x, 2-y, -1/2+z$; (") $x, 2-y, 1/2+z$.

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