



Synthesis and characterization of two 1D polymeric zinc(II) azido complexes derived from pyridine-*N*-oxide co-ligands



Franz A. Mautner^{a,*}, Christian Berger^a, Salah S. Massoud^b

^a Institut für Physikalische und Theoretische Chemie, Technische Universität Graz, Stremayrgasse 9, A-8010 Graz, Austria

^b Department of Chemistry, University of Louisiana at Lafayette, P.O. Box 43700, Lafayette, LA 70504, USA

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ABSTRACT

The synthesis and structural characterization of two new polymeric zinc(II) azido complexes with pyridine-*N*-oxide derivative co-ligands, namely *catena*-[Zn(4-methylpyridine-*N*-oxide)($\mu_{1,1}$ -N₃)₂] (**1**) and *catena*-{[Zn₂(μ_2 -isonicotinato-*N*-oxide)₂($\mu_{1,1}$ -N₃)₂(H₂O)₃](H₂O)} (**2**) are reported. Single crystal structure determination revealed the penta-coordinated geometry of the Zn(II) centers in the polymeric chains of **1** with di-EO azido bridging mode, whereas five and six coordination modes around Zn(II) centers are observed in complex **2**, and the 1D system is formed via alternating single EO-azide and μ (O,O')-bridging carboxylate group of the isonicotinato-*N*-oxide molecules. The solid state luminescence properties of **1** were examined.

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1. Introduction

The polymeric transition metal azido complexes with pyridine-*N*-oxide derivatives as co-ligands have been less studied compared to the large number of investigations on the analogous 3d azido complexes with the parent pyridine derivative co-ligands [1–4]. In general, these azido polynuclear and polymeric coordination compounds enriched our knowledge in the field of molecular magnetic materials where paramagnetic metal centers are bridged via the azido groups. This was attributed to the versatile coordination modes of the azido ligand and hence to the different mechanisms by which the magnetic exchange interaction between the azido-bridged metal ions is transmitted. In most cases predominantly anti-ferromagnetic (AF) interactions via its end-to-end (EE, $\mu_{1,3}$) bridging mode and ferromagnetic (F) interactions via its end-on (EO, $\mu_{1,1}$) bridging mode were observed. Although, there have been a few studies dealing with the corresponding pyridine-*N*-oxide polymeric metal azido complexes, where the pyridine-*N*-oxides have further coordination site(s) such as tetrazolate [5,6], benzoate [7,8], carboxylate [9–16] or bis-pyridyl-*N*-oxide bridges [17–19], more work has to be directed to this class of compounds in order to explore their coordination, magnetic and luminescent properties with 3d metal ions. Aside from the magnetic properties

of 3d^{1–9} azido complexes of pyridine-*N*-oxides, 1D azido-bridging systems with d¹⁰ metal centers such as Zn(II) and Cd(II) have been shown to exhibit luminescent properties [20–22] and these were demonstrated in our recent work [23–27], where these complexes have the ability to affect the emission wavelength and strength of the coordinated organic materials.

In progress of our previous investigations on luminescent materials [23–27] we now report the synthesis and structural characterization of two new Zn(II) azido 1D systems with the pyridine-*N*-oxide derivatives as co-ligands namely *catena*-[Zn(4-methylpyridine-*N*-oxide)($\mu_{1,1}$ -N₃)₂] (**1**) and *catena*-{[Zn₂(μ_2 -isonicotinato-*N*-oxide)₂($\mu_{1,1}$ -N₃)₂(H₂O)₃](H₂O)} (**2**), and the luminescence properties of the former complex.

2. Experimental

2.1. Materials and physical measurements

The pyridine-*N*-oxide ligands were purchased from TCI and all other chemicals were of analytical grade quality. Infrared spectra of solid complexes were recorded on a Bruker Alpha P (platinum-ATR-cap) and UV-VIS-NIR spectra were performed with a LS950 Perkin–Elmer Lambda-spectrometer in the range 4000–45000 cm^{–1} (pulsed D₂O lamp). Emission Spectra were recorded with a Perkin–Elmer LS55 spectrofluorometer. Elemental microanalyses were carried out with an Elementar Vario EN3 analyser.

Caution: Salts of azides and their metal complexes are potentially

* Corresponding author.

E-mail address: mautner@tugraz.at (F.A. Mautner).

explosive and should be handled with great care and in small quantities.

2.2. Synthesis of the complexes

2.2.1. Synthesis of catena-[Zn(4-methylpyridine-*N*-oxide)($\mu_{1,1}$ -N₃)₂] (**1**)

A mixture of ZnSO₄·7H₂O (0.58 g, 2.00 mmol), 4-methylpyridine-*N*-oxide (0.28 g, 2.00 mmol) and NaN₃ (0.26 g, 4.00 mmol) were dissolved in 20 mL distilled water at 40 °C. The resulting solution was then allowed to crystallize at room temperature. The colorless crystals of **1** which were separated within two days were collected by filtration (yield: 0.39 g, 66%). Anal. Calc. for C₉H₇N₇OZn (294.61 g/mol): C 36.7; H, 2.4; N, 33.3. Found: C, 36.0; H, 2.3; N, 32.7%. Selected IR bands (ν , cm⁻¹): 2086 (vs), 2062 (vs), 1647 (w), 1581 (m), 1516 (m), 1455 (w), 1393 (m), 1350 (w), 1292 (m), 1267 (m), 1214 (m), 1178 (w), 1139 (m), 1088 (s), 1052 (m), 879 (m), 799 (s), 770 (s), 724 (m), 665 (m), 625 (w), 583 (m), 566 (s), 500 (m), 478 (w), 435 (w).

2.2.2. Synthesis of catena-[[Zn₂(μ_2 -isonicotinato-*N*-oxide)₂($\mu_{1,1}$ -N₃)₂(H₂O)₃](H₂O)] (**2**)

Isonicotinic acid *N*-oxide (0.30 g, 2 mmol), ZnSO₄·7H₂O (0.58 g, 2 mmol), and NaN₃ (0.26 g, 4.00 mmol) were dissolved in 90 mL of MeOH/H₂O (1:1) at 55 °C and this was followed by slow cooling to room temperature. The resulting clear solution was allowed to concentrate by slow evaporation of solvent in an open beaker. After three weeks, the colorless prism shaped crystals of **2** were collected by filtration (yield: 0.29 g, 52%). Anal. Calc. for C₁₂H₁₆N₈O₁₀Zn₂ (563.11 g/mol): C 25.8; H, 2.6; N, 20.2. Found: C, 25.6; H, 2.9; N, 19.9%. Selected IR bands (ν , cm⁻¹): 3360 (m,br), 2077 (vs), 1604 (s), 1551 (vs), 1485 (w), 1393 (vs), 1303 (s), ν_s 1209 (vs), 1142 (s), 10377 (w), 955 (w), 863 (s), 807 (ms), 783 (s), 686 (m), 641 (vs), 567 (w), 458 (wm), 415 (w).

2.3. X-ray crystal structure analysis

The X-ray single-crystal data of both compounds were collected on a Bruker-AXS SMART CCD diffractometer at 100(2) K. The crystallographic data conditions retained for the intensity data

Table 1
Crystallographic data and processing parameters for complexes **1** and **2**.

Compound	1	2
Empirical formula	C ₉ H ₇ N ₇ OZn	C ₁₂ H ₁₆ N ₈ O ₁₀ Zn ₂
Formula mass	258.58	563.11
System	Monoclinic	Monoclinic
Space group	P2 ₁ /c	C2/c
a (Å)	12.2116(14)	20.475(4)
b (Å)	13.0588(16)	7.3747(15)
c (Å)	6.1961(9)	14.597(3)
α (°)	90	90
β (°)	100.469(18)	112.68(3)
γ (°)	90	90
V (Å ³)	971.6(2)	2033.6(7)
Z	4	4
T (K)	100(2)	100(2)
M (mm ⁻¹)	2.512	2.429
D _{calc} (Mg/m ³)	1.768	1.839
Crystal size (mm)	0.42 × 0.24 × 0.15	0.40 × 0.20 × 0.10
Θ max (°)	26.31	25.49
Data collected	6504	6798
Unique refl./R _{int}	1972/0.0253	1880/0.0610
Parameters/Restraints	137/0	167/5
Goodness-of-Fit on F ²	1.053	1.134
R1/wR2 (all data)	0.0209/0.0556	0.0644/0.1629
Residual extrema (e/Å ³)	0.27/-0.47	0.87/-0.91

collection and some features of the structure refinements are listed in Table 1. The intensities were collected with Mo-K α radiation ($\lambda = 0.71073$ Å). Data processing, Lorentz-polarization and absorption corrections were performed using SMART, SAINT and the SADABS computer programs [28]. The structures were solved by direct methods and refined by full-matrix least-squares methods on F², using the SHELXTL [29] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from different Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. Molecular plots were performed with the Mercury program [30].

3. Results and discussion

3.1. IR spectra of the complexes

The IR spectra of the complexes under investigation are dominated by the very strong absorption bands of the asymmetric stretching azide vibration, $\nu_{as}(\text{N}_3^-)$ at 2086 and 2062 cm⁻¹ for **1**, and at 2077 cm⁻¹ for **2**, respectively. For complex **2** the absence of the strong band around 1700 cm⁻¹, which was observed in the free isonicotinic acid *N*-oxide confirms the coordination of the isonicotinate-*N*-oxide through its carboxylato group. This band was replaced by two very strong bands at 1604 and 1551 cm⁻¹ for $\nu_{as}(-\text{COO}^-)$ and 1393 cm⁻¹ for $\nu_s(-\text{COO}^-)$. The aqua ligands and water of crystallization in **2** were demonstrated by the appearance of the very broad medium intensity band centered at 3360 cm⁻¹ [31].

3.2. Description of the crystal structures

3.2.1. catena-[Zn(4-methylpyridine-*N*-oxide)($\mu_{1,1}$ -N₃)₂] (**1**)

A section of the crystal structure of catena-[Zn(4-methylpyridine-*N*-oxide)($\mu_{1,1}$ -N₃)₂] (**1**) is shown in Fig. 1a, and selected bond parameters are listed in Table 2. Zn(1) is penta-coordinated by four $\mu(1,1)$ bridging azido groups and a terminal 4-methylpyridine-*N*-oxide molecule. The ZnN₄O polyhedron has a distorted square planar geometry (SP), $\tau = 0.27$ [32], with O(1) in the apical position [Zn(1)–O(1) = 1.9800(12) Å] and N(11), N(21), N(11') and N(21') in the basal sites [Zn–N from 2.0182(12) to 2.1884(13) Å]. Zn(1) deviates by 0.505 Å from the basal N₄ plane. Along the *c*-axis of the monoclinic unit cell the Zn(II) centers are connected by asymmetric di-EO azido bridges [EO = end-on, $\mu(1,1)$] to zig-zag polymeric chains (Zn...Zn...Zn = 143.9°). The four-membered Zn₂N₂ rings formed by the di-EO azido bridges are planar. The $\mu(1,1)$ azido bridges have the following bond parameters: Zn(1)–N(11)–Zn(1') = 100.79 (5)°, Zn(1)–N(21)–Zn(1'') = 102.16(5)°; N(11)–Zn(1)–N(21) = 78.52(5)°, N(11)–Zn(1)–N(21') = 78.47(5)°. The “out-of plane” angles (δ) N(11)···N(21)–N(22) and N(21)···N(11)–N(12) are 167.0 and 156.0°, respectively. The intra-chain Zn(1)···Zn(1') distance is 3.2583(5) Å, the shortest Zn···Zn inter-chain separation is 6.1961(9) Å. The terminal 4-methylpyridine-*N*-oxide molecule have a Zn(1)–O(1)–N(1) bond angle of 115.49(8)°; and the Zn–O(1)–N(1)–C(1) torsion angle is 88.8°. Similar [Zn(L)(N₃)₂]_n 1D systems have been reported for L = 2-methylpyridine-*N*-oxide [33] and for other substituted pyridines [34–36].

3.2.2. catena-[[Zn₂(μ_2 -isonicotinato-*N*-oxide)₂($\mu_{1,1}$ -N₃)₂(H₂O)₃](H₂O)] (**2**)

The title complex **2** (Fig. 2a) crystallizes in the monoclinic system (space group C2/c, no. 15). Selected bond parameters are listed in Table 3. From Fig. 2a it is apparent that there exists two differently coordinated Zn(II) centers. Zn(2) has a hexa-coordinate with

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