Short communication

Synthesis, Crystal Structure and Photoluminescence of a Novel Zinc-Isonicotinic Acid Complex

Wen-Tong Chen*

School of Chemistry and Chemical Engineering, Institute of Applied Chemistry, Jiangxi Province Key Laboratory of Coordination Chemistry, Jinggangshan University, 343009, Ji'an, Jiangxi, P.R. China

** Corresponding author: E-mail: wtchen_2000@yahoo.cn; Tel.: + 86(796)8100490; fax + 86(796)8100490*

Received: 12-05-2011

Abstract

A novel zinc-isonicotinic acid complex $[Zn(Hini)(Ini)Cl]_n$ (**1**) (Hini = isonicotinic acid; Ini = deprotoned isonicotinic acid) has been synthesized via a hydrothermal reaction and structurally characterized by a single-crystal X-ray diffraction. Complex **1** crystallizes in the space group $P2_1/c$ of the monoclinic system with four formula units in a cell: a = 7.654(4), b = 13.540(7), c = 14.213(3) Å, β = 122.21(1), V = 1246.2(10) Å^3, $C_{12}H_9ClN_2O_4Zn$, M_r = 346.05, D_c = 1.844 g/cm^3, S = 1.017, μ(Mo$K\alpha$) = 2.199 mm^{-1}, F(000) = 696, R = 0.0206 and wR = 0.0500. Complex **1** is characteristic of a novel one-dimensional (1-D) chain-like structure. Photoluminescence investigation reveals a strong emission, which may originate from $\pi \rightarrow \pi^*$ charge-transfer interaction of the isonicotinic acid ligand.

Keywords: Crystal, hydrothermal reaction, isonicotinic acid, photoluminescence, zinc.

1. Introduction

Transition metal compounds containing group 12 (IIB) elements are very attractive for some reasons, such as, the variety of coordination numbers and geometries offered by the d^{10} configuration of the IIB metal ions, photoluminescent and semiconductive properties, and the essential role of zinc played in biological systems.[1–5] I deem that IIB-containing compounds with aromatic carboxylic acids as ligands maybe possess novel structural topologies and properties, such as luminescence, semiconductivity, catalysis, thermochromism and so on. Isonicotinic acid, as a kind of aromatic carboxylic acids, has gained increasing attention due to its common character-delocalized π-electrons of the pyridyl rings which makes it a good candidate for the preparation of light emitting materials with potential applications in various technical fields. Moreover, isonicotinate anion is a quite interesting tecton in building extended structures because it is a divergent ligand with a nitrogen atom at one end and two oxygen atoms from the carboxylato group at the other one.[6–7] Therefore, isonicotinate anions can link two metal centers by binding to a metal center with the nitrogen atom and, to the other one, with one or two carboxylato oxygen atoms. Photoluminescent materials have been of intense interest for several decades because they display wide-range applications in many areas. Based on the above reasons, I recently became interested in the crystal engineering of IIB-containing compounds with isonicotinic acid as a ligand. In this paper, I report the synthesis, crystal structure and photoluminescence of $[Zn(Hini)(Ini)Cl]_n$ (**1**) (Hini = isonicotinic acid; Ini = deprotoned isonicotinic acid), which was prepared from a hydrothermal reaction.

2. Experimental

All reactants of A.R. grade were obtained commercially and used without further purification. The photoluminescent data were collected at room temperature on a computer-controlled JY FluoroMax-3 spectrometer.

2. 1. Synthesis of $[Zn(Hini)(Ini)Cl]_n$ (1)

The title complex was prepared by mixing $ZnCl_2$ (1 m mol, 136 mg), isonicotinic acid (2 mmol, 246 mg) and 5 mL distilled water in a 23 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 7 days. After being slowly cooled to room temperature at 6 °C/h, colorless crystals suitable for X-ray analysis were obtained. The yield was 56% (based on zinc).

2. 2. X-ray Structure Determination

X-ray diffraction data were collected on Rigaku Mercury CCD X-ray diffractometer with graphite monochromatic Mo-$K\alpha$ radiation (λ = 0.71073 Å) using a ω scan technique. CrystalClear software was used for data reduction and empirical absorption correction. The structure was solved by the direct methods using the Siemens SHELXTL™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The hydrogen atom positions were generated theoretically and allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but were not refined. The structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The summary of crystallographic data and structure analysis is given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

Table 1. Crystal data and structure refinement details for **1**.

Formula	$C_{12}H_9ClN_2O_4Zn$
Mr	346.05
color	colorless
Crystal size	0.25 mm × 0.23 mm × 0.20 mm
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	7.654(4)
b (Å)	13.540(7)
c (Å)	14.213(3)
β ()	122.21(1)
V (Å^3)	1246.2(10)
Z	4
$2\theta_{max}$ ()	50
Reflections collected	8003
Independent, observed reflections (R_{int})	2203, 2082 (0.0208)
$d_{calcd.}$ (g/cm^3)	1.844
μ (mm^1)	2.199
T (K)	123.15
F(000)	696
*R*1, *wR*2	0.0206, 0.0500
S	1.017
Largest and Mean Δ/σ	0.001, 0
$\Delta\rho$(max, min) (e/Å^3)	0.299, –0.264

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

Zn(1)-O(1)	1.942(1)
Zn(1)-O(3)	1.951(2)
Zn(1)-N(1)#1	2.059(2)
Zn(1)-Cl(1)	2.2292(8)
O(1)-C(1)	1.266(2)
O(2)-C(1)	1.224(2)
O(3)-C(7)	1.280(2)
O(4)-C(7)	1.227(2)
O(1)-Zn(1)-O(3)	125.24(6)
O(1)-Zn(1)-N(1)#1	94.51(7)
O(3)-Zn(1)-N(1)#1	95.33(7)
O(1)-Zn(1)-Cl(1)	115.29(5)
O(3)-Zn(1)-Cl(1)	110.92(5)
N(1)#1-Zn(1)-Cl(1)	110.66(5)

Symmetry transformations used to generate equivalent atoms: #1 x-1, -y + 0.5, z-0.5.

3. Results and Discussion

X-ray diffraction analysis reveals that the structure of the title complex consists of infinite and neutral $[Zn(Hini)(Ini)Cl]_n$ chains, as shown in Fig. 1. All of the

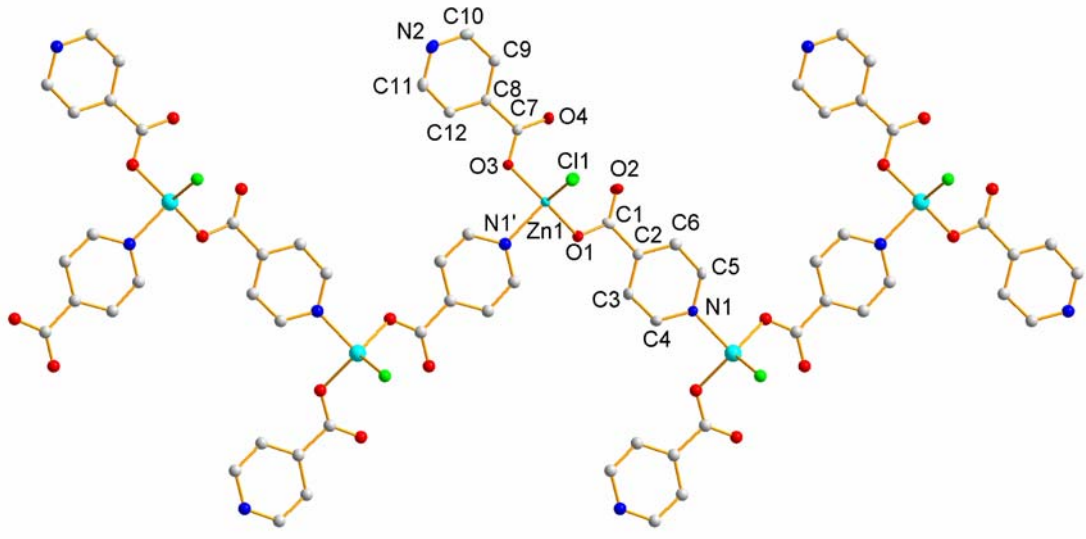

Fig. 1: ORTEP-drawing of **1** with 50% thermal ellipsoids. Symmetry code: `x-1, -y + 0.5, z-0.5.

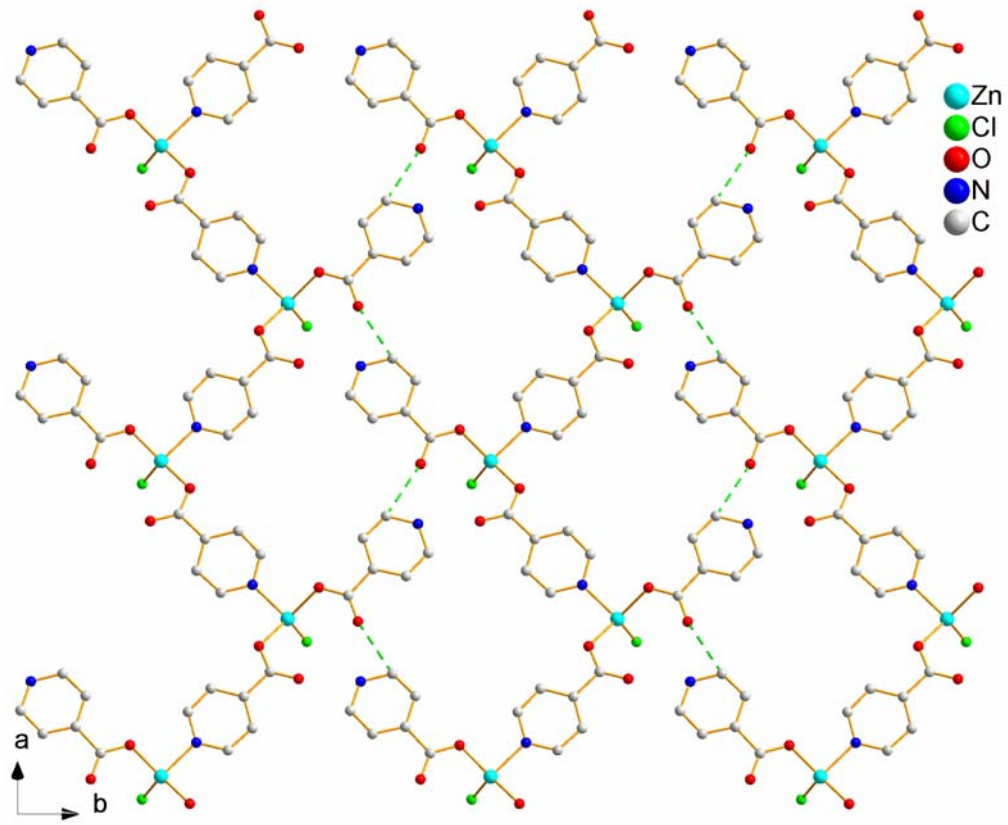

Fig. 2: The 2-D layer formed via the hydrogen bonds in dashed lines: C11-H···O4(-1 + x, 3/2-y, -1/2 + z) 2.938(3) Å, 116.1°.

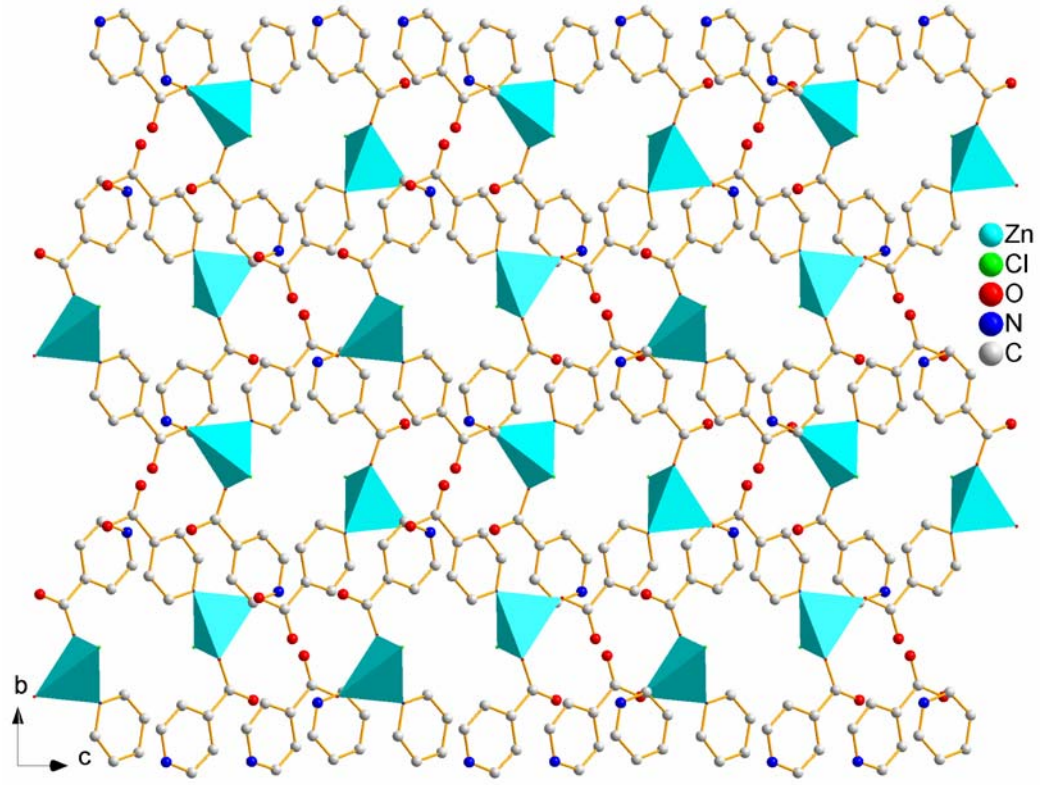

Fig. 3: Packing diagram of **1**.

crystallographically independent atoms are on general positions. The Zn1 atom is tetrahedrally coordinated by one terminal chlorine atom, one oxygen atom of a terminal isonicotinic acid, one oxygen atom and one nitrogen atom of two bridging isonicotinic acids, forming a ZnO_2NCl polyhedron. The bond length of Zn-Cl is 2.2292(8) Å that is normal and comparable with the values reported in the literatures.[8–11] The bond lengths of Zn-O are 1.942(1) and 1.951(2) Å, similar to those reported previously.[12–14] The bond length of Zn-N is 2.059(2) Å that is close to those documented. [15] In **1**, the isonicotinic acid ligands can be grouped into two kinds, namely, one acts as a monodentate ligand while the other acts as a bidentate bridging ligand. To keep charge balance of the complex, the hydrogen atom bonded to carboxyl group moves to the nitrogen atom, as the cases found in other references. [16–21] To our knowledge, several complexes containing both monodentate and bidentate isonicotinic acid ligands have been documented previously.[22] Two neighboring zinc atoms are bridged by one μ_2-isonicotinic acid ligand to construct a 1-D zigzag chain, as shown in Fig. 1. To our knowledge, several 1-D chain complexes containing isonicotinic acid have been recently reported.[23–26] In **1**, no π···π stacking interaction was established between the adjacent isonicotinic acid ligands, but there is some hydrogen bonding interactions (C11-H···O4(-1 + x, 3/2-y, -1/2 + z) 2.938(3) Å, 116.1°) existing among the zigzag chains to form a 2-D layer (Fig. 2). The layers stack along the c axis to yield a 3-D network (Fig. 3).

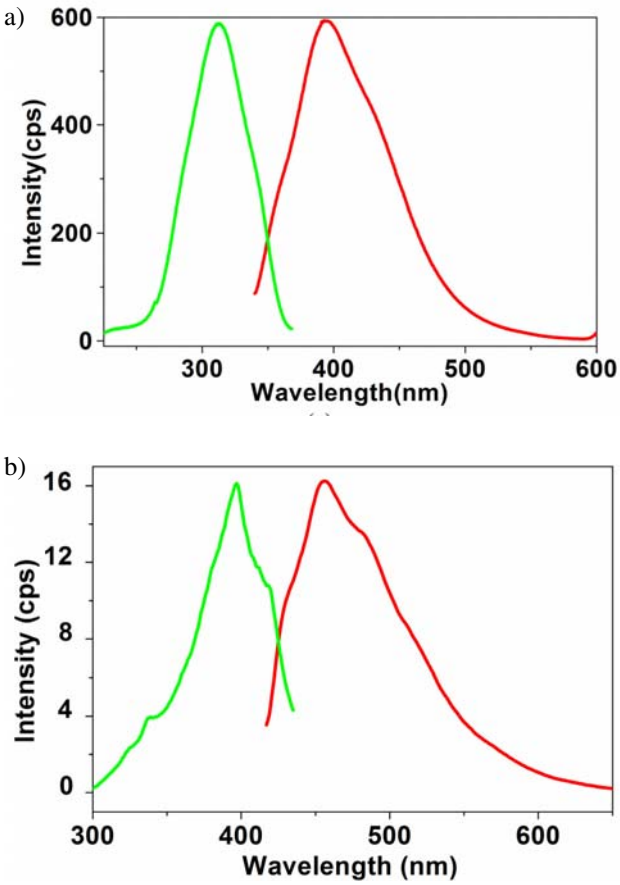

Fig. 4: The emission and excitation spectra at room temperature: (a) complex **1** and (b) isonicotinic acid. Red lines: emission spectra; green lines: excitation spectra.

The photoluminescence of **1** in distilled water was investigated under room temperature (Fig. 4a). The excitation spectra of the title complex exhibit that the effective energy absorption mainly takes place in the ultraviolet region of the range 250–350 nm. The excitation band of complex **1** shows one main peak at 313 nm. We further measured the corresponding emission spectrum and it displays one main and intense emission band with the maximum wavelength of 394 nm upon photo-excitation at 313 nm. In order to reveal the nature of the photoluminescence of **1**, the photoluminescent spectrum of pure isonicotinic acid was also conducted under same conditions. As for pure isonicotinic acid, the emission spectrum has one intense emission band with the maximum wavelength of 455 nm upon photo-excitation at 397 nm (Fig. 4b). The similarity of the photoluminescent spectra between **1** and pure isonicotinic acid indicates that the emission spectrum of **1** is probably ascribed to an intraligand $\pi \rightarrow \pi^*$ charge-transfer interaction of the isonicotinic acid ligand.

4. Conclusion

In summary, we have prepared a zinc-isonicotinic acid complex via a hydrothermal reaction. The X-ray structure analysis of the title complex revealed a 1-D zigzag chain-like structure. The title complex exhibits an intense photoluminescent emission band, which can be attributed to the $\pi \rightarrow \pi^*$ charge-transfer interaction of the isonicotinic acid ligand. Further investigations on finding IIB-containing complexes with good photoluminescent properties are in progress in my laboratory.

5. Acknowledgements

We gratefully acknowledge the financial support of the NSF of Jiangxi Province (200007GQH1685).

6. Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 813227. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

7. Reference

1. J. A. Drewry, P. T. Gunning, *Coord. Chem. Rev*. **2011**, *255*, 459–472.
2. W. Maret, Y. Li, *Chem. Rev.* **2009**, *109*, 4682–4707.
3. S. P. Gupta, *Chem. Rev.* **2007**, *107*, 3042–3087.
4. H. Kozlowski, A. Janicka-Klos, J. Brasun, E. Gaggelli, D. Valensin, G. Valensin, *Coord. Chem. Rev*. **2009**, *253*, 2665–2685.
5. Y.-I. Kim, R. Seshadri, *Inorg. Chem.* **2008**, *47*, 8437–8443.
6. J. Y. Lu, A. M. Babb, *Chem. Commun.* **2001**, 821–822.
7. M. E. Chapman, P. Ayyappan, B. M. Foxman, G. T. Yee, W. Lin, *Cryst. Growth Des.* **2001**, *1*, 159–163.
8. A. Bino, F. A. Cotton, Z. Dori, M. Shaia-Gottlieb, M. Kapon, *Inorg. Chem*. **1988**, *27*, 3592–3596.
9. A. J. Dickie, D. C. R. Hockless, A. C. Willis, J. A. McKeon, W. G. Jackson, *Inorg. Chem*. **2003**, *42*, 3822–3834.
10. Z. Tao, Q.-J. Zhu, S.-F. Xie, W. G. Jackson, Z.-Y. Zhou, X.-G. Zhou, *Polyhedron* **2003**, *22*, 1603–1606.
11. A. Dogan, B. Sarkar, A. Klein, F. Lissner, T. Schleid, J. Fiedler, S. Zalis, V. K. Jain, W. Kaim, *Inorg. Chem*. **2004**, *43*, 5973–5980.
12. G. A. Santillan, C. J. Carrano, *Inorg. Chem*. **2008**, *47*, 930–939.
13. Y.-T. Wang, H.-H. Fan, H.-Z. Wang, X.-M. Chen, *Inorg. Chem*. **2005**, *44*, 4148–4149.
14. S. Noro, H. Miyasaka, S. Kitagawa, T. Wada, T. Okubo, M. Yamashita, T. Mitani, *Inorg. Chem*. **2005**, *44*, 133–146.
15. W. Huang, S. Gou, D. Hu, S. Chantrapromma, H.-K. Fun, Q. Meng, *Inorg. Chem*. **2002**, *41*, 864–868.
16. W.-B. Yan, Z.-H. Zhou, H. Zhang, D.-Q. Yu, Z.-G. Xu, *Huaxue Xuebao (Acta Chim. Sinica) (Chin.)* **1996**, *54*, 167–173.
17. H. An, Y. Li, E. Wang, D. Xiao, C. Sun, L. Xu, *Inorg. Chem.* **2005**, *44*, 6062–6070.
18. X.-R. Zeng, R.-G. Xiong, X.-Z. You, *Wuji Huaxue Xuebao (Chinese J. Inorg. Chem.)* **2000**, *16*, 641–645.
19. W. Chen, Z. Yao, D. Liu, S. Ying, J. Liu, *J. Coord. Chem.* **2009**, *62*, 1553–1560.
20. C.-M. Wang, Y.-L. Chuang, S.-T. Chuang, K.-H. Lii, *J. Solid State Chem.* ***2004****, 177, 2305–2310.*
21. *D. Huang, W. Wang, X. Zhang, C. Chen, F. Chen, Q. Liu, D. Liao, L. Li, L. Sun, Eur. J. Inorg. Chem.* ***2004****, 1454–1464.*
22. F.-C. Liu, Y.-F. Zeng, J.-P. Zhao, B.-W. Hu, X. Hu, J. Ribas, X.-H. Bu, *Discuss. Faraday Soc*. **2009**, 2074–2076.
23. L.-Z. Chen, Y.-M. Gao, J. Zou, M.-N. Huang, *Chinese J. Struct. Chem*. **2011**, *30*, 284–288.
24. Y.-F. Deng, X.-W. Tan, C.-H. Zhang, D.-Z. Kuang, M.-S. Chen, *Chinese J. Inorg. Chem*. **2010**, *26*, 909–912.
25. L. Han, X. Sun, Y. Zhu, W. Zhou, Q. Chen, Y. Xu, *J. Chem. Crystallogr.* **2010**, *40*, 579–582.
26. L.-Z. Cai, G.-C. Guo, M.-L. Fu, M.-S. Wang, W.-T. Chen, J.-S. Huang, *Inorg. Chim. Acta*, **2006**, *359*, 4483–4492.

Povzetek

S hidrotermalno sintezo smo pripravili nov kompleks cinka z izonikotinsko kislino, [Zn(Hini)(Ini)Cl]*n* (**1**) (Hini = izonikotinska kislina; Ini = deprotonirana izonikotinska kislina) in z rentgensko strukturno analizo na monokristalu določili njegovo kristalno strukturo. Kompleks **1** kristalizira v prostorski skupini $P2_1/c$ v monoklinskem kristalnem sistemu s štirimi formulskimi enotami v osnovni celici: a = 7,654(4), b = 13,540(7), c = 14,213(3) Å, β = 122,21(1)°, V = 1246,2(10) Å^3, $C_{12}H_9ClN_2O_4Zn$, M_r = 346,05, D_c = 1,844 g/cm^3, S = 1,017, μ(Mo$K\alpha$) = 2,199 mm^{-1}, F(000) = 696, R = 0,0206 in wR = 0,0500. Kompleks **1** ima karakteristično eno-dimenzionalno (1-D) verižno strukturo. Fotoluminescencna študija je pokazala močno emisijo, ki je lahko posledica $\pi \rightarrow \pi^*$ prehoda s prenosom naboja v koordinirani izonikotinski kislini.