

## КРАТКИЕ СООБЩЕНИЯ

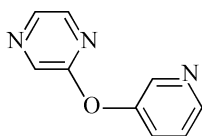
UDC 548.73;541.572

**CRYSTAL STRUCTURE OF A TWO-DIMENSIONAL Co(II) COORDINATION POLYMER:  
[Co( $\mu$ -PP)<sub>2</sub>(SCN)<sub>2</sub>]<sub>n</sub> [PP = 2-(PYRIDINE-3-YLOXY)PYRAZINE]**© 2009 **H. Li<sup>1</sup>, H.-Y. Zhao<sup>2</sup>, S.-G. Zhang<sup>1</sup>, J.-M. Shi<sup>2\*</sup>**<sup>1</sup>*Department of Chemistry and Chemical Engineering, Institute of Materials Chemistry, Binzhou University, Binzhou 256603, P.R. China*<sup>2</sup>*Department of Chemistry, Shandong Normal University, Jinan 250014, P.R. China**Received January, 28, 2008*

Solvothermal reaction (water/methanol) of cobalt perchlorate hexahydrate, sodium thiocyanate and 2-(pyridine-3-yloxy)pyrazine (PP) resulted in the formation of a two-dimensional coordination polymer [Co( $\mu$ -PP)<sub>2</sub>(SCN)<sub>2</sub>]<sub>n</sub>. The solid complex has been characterized by elemental analysis and IR spectroscopy; its crystal structure was determined by X-ray crystallography. The complex crystallizes in the monoclinic system, space group  $P2_1/n$ ,  $a = 7.4643(19)$ ,  $b = 9.237(2)$ ,  $c = 15.540(4)$  Å,  $\beta = 94.995(5)^\circ$ ,  $V = 1067.4(5)$  Å<sup>3</sup>,  $Z = 1$ . In the crystal structure each 2-(pyridine-3-yloxy)pyrazine molecule acts as a bidentate bridging ligand coordinating to two adjacent Co(II) ions with Co...Co separation of 9.5176(18) Å to yield a two-dimensional sheet structure in the plane (-1 0 1).

**Keywords:** crystal structure, cobalt(II) complex, 2D polymer, layered structure.

For a long time significant research efforts have been devoted to the coordination polymeric compounds because such coordination polymers may afford new materials with useful properties, such as catalytic activity, micro-porosity, electrical conductivity, non-linear optical activity, magnetic coupling behavior and so on [ 1, 2 ]. The 2-(pyridine-3-yloxy)pyrazine compound (Scheme 1) should be able to act as a bridging ligand due to its structural characteristics, but it only functions as a terminal ligand in the reported complexes [ 3, 4 ]. Being motivated to prepare new coordination polymers, we have synthesized the title coordination polymer and here we report its crystal structure.



*Scheme 1.* Structural formula of 2-(pyridine-3-yloxy)pyrazine (PP)

**Experimental. Preparations.** 2-(Pyridine-3-yloxy)pyrazine was prepared according to a literature method [ 5 ] by the reaction of 2-chloropyrazine and 3-hydroxypyridine. Other reagents were of analytical grade and used without further purification. C, H and N elemental analyses were carried out on a Perkin-Elmer 240 instrument. Infrared spectrum was recorded with a Bruker Tensor 27 infrared spectrometer in the 4000—500 cm<sup>-1</sup> range with KBr disc.

The complex was synthesized as follows. Methanol solution (10 ml) of 2-(pyridine-3-yloxy)pyrazine (0.0627 g, 0.36 mmol) was added into aqueous solution (20 ml) containing Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2650 g, 0.72 mmol) and NaSCN (0.1174 g, 1.45 mmol). The mixture was stirred for few minutes

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Table 1

## Crystal Data and Structure Refinement Summary

Empirical formula	C <sub>40</sub> H <sub>28</sub> Co <sub>2</sub> N <sub>16</sub> O <sub>4</sub> S <sub>4</sub>
<i>M</i>	1042.88
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell: <i>a</i> , <i>b</i> , <i>c</i> , Å	7.4643(19), 9.237(2), 15.540(4)
β, deg.	94.995(5)
<i>V</i> , Å <sup>3</sup>	1067.4(5)
<i>Z</i>	1
<i>D</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.622
μ, mm <sup>-1</sup>	1.037
Reflections collected / unique	5660 / 2106 [ <i>R</i> <sub>int</sub> = 0.052]
Data / restraints / parameters	2106 / 2 / 151
GOOF on <i>F</i> <sup>2</sup>	1.032
Final <i>R</i> indices [ <i>I</i> > 2( <i>σ</i> )]	<i>R</i> <sub>1</sub> = 0.0566, <i>wR</i> <sub>2</sub> = 0.1361
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0787, <i>wR</i> <sub>2</sub> = 0.1454
Residual peak and hole (e/Å <sup>3</sup> )	0.534 / -0.656
CCDC deposition No.	632293

and then placed in a Teflon-lined autoclave, heated for 80 hours at 160 °C at an autogenous pressure. After the contents of the autoclave were cooled to room temperature, red single crystals were recovered with the yield of 52 % based on 2-(pyridine-3-yloxy)pyrazine ligand. IR (cm<sup>-1</sup>): 2064 s, 1638 s, 1616 s, 1457 m, 1401 s, 1278 m. Anal. Found: C 46.27, H 2.98, N 21.83, Co 11.85 %. Calcd. for C<sub>40</sub>H<sub>28</sub>Co<sub>2</sub>N<sub>16</sub>O<sub>4</sub>S<sub>4</sub>: C 46.06, H 2.71, N 21.49, Co 11.30 %.

**Crystal Structure Determination.** A suitable single crystal with dimensions of 0.21×0.20×0.16 mm was selected and glued on the tip of a glass fiber. The crystal structure determination was carried out at 25 °C on an X-ray diffractometer, Bruker Smart-1000 CCD, using graphite-monochromatic MoK<sub>α</sub> radiation ( $\lambda = 0.71073$  Å) in the range of  $5.14 < 2\theta < 52.00^\circ$ . A total of 5660 reflections were collected, of which 2106 were independent (*R*<sub>int</sub> = 0.052) and 1571 observed reflections with *I* > 2 $\sigma$ (*I*) were used in the structure analysis. Corrections for *Lp* factors were applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in the calculated positions and refined as riding. The programs for structure solution and refinement were SHELXTL (Bruker, 2001). A summary of the crystallographic data is listed in Table 1; the atomic coordinates and isotropic thermal parameters are given in Table 2; selected interatomic dis-

Table 2

Atomic Coordinates ( $1 \times 10^5$ ) and Equivalent Thermal Parameters ( $\text{\AA}^2 \times 10^5$ )

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Co1	0	0	50000	2783(26)	C8	13898(58)	28888(51)	42412(28)	4034(108)
C1	23393(61)	44954(44)	72942(26)	3412(94)	C9	20863(65)	42779(54)	42411(30)	4657(121)
C2	7787(52)	38863(44)	73666(26)	3240(93)	C10	27330(52)	-14157(46)	37675(26)	3248(94)
C3	3962(63)	35722(57)	81573(32)	5107(125)	N1	11629(44)	21738(35)	49709(21)	3105(77)
C4	15362(57)	38721(49)	88798(29)	4018(107)	N2	31551(44)	44801(36)	88077(22)	3155(79)
C5	35445(56)	47860(41)	80089(27)	3109(93)	N3	18240(47)	-7680(41)	42044(23)	3949(89)
C6	22943(54)	42366(43)	57502(26)	3137(93)	N4	25460(60)	49901(47)	50118(29)	5759(117)
C7	16127(58)	28538(44)	57135(26)	3686(103)	O1	28602(45)	49427(31)	65134(19)	4351(79)
					S1	39905(17)	-23196(15)	31617(9)	5436(41)

Table 3

Selected Bond Lengths (Å) and Angles (deg.)

Bond lengths		Bond angles	
Co1—N1	2.190(3)	N3—Co1—N1	91.13(14)
Co1—N2C	2.262(3)	N3—Co1—N2C	88.18(13)
Co1—N3	2.044(4)	N1—Co1—N2C	90.15(12)

Symmetry code for N2C:  $x-1/2, -y+1/2, z-1/2$ .

Table 4

Hydrogen Bond Lengths (Å) and Angles (deg.)

D—H...A	D—H	H...A	D...A	$\angle D—H...A$
C4—H1...N3 <sup>i</sup>	0.93	2.55	3.137(6)	122
C5—H7...N3 <sup>ii</sup>	0.93	2.51	3.078(6)	120

Symmetry codes: (i)  $1/2-x, 1/2+y, 3/2-z$ , (ii)  $1/2+x,$ 

tances and bond angles for the complex are in Table 3. Full crystallographic information has been deposited with Cambridge Crystallographic Data Center and can be obtained free of charge at [www.ccdc.cam.ac.uk/data\\_request.cif](http://www.ccdc.cam.ac.uk/data_request.cif) (see the deposition number in Table 1).

**Results and Discussion.** Fig. 1 shows the coordination diagram with atomic numbering scheme. The central atom Co1 lies on an inversion center and is coordinated by six N atoms, N1, N1A, N2B, N2C, N3 and N3A, of which N3 and N3A atoms are from two isothiocyanate anions and the other four N atoms are from four 2-(pyridine-3-yloxy)pyrazine ligands. The data of Table 3 indicate that there are only minor differences among the coordination bond lengths and the associated angles implying that Co1 atom has a slightly distorted octahedral coordination geometry. Fig. 1 also reveals that each 2-(pyridine-3-yloxy)pyrazine molecule acts as a bidentate bridging ligand, with its pyridyl N atom and one of two pyrazinyl N atoms coordinated to two adjacent Co(II) ions with Co...Co separation of 9.5176(18) Å. This connection results in the formation of a 32-membered ring that consists of four Co(II) ions and four 2-(pyridine-3-yloxy)pyrazine molecules. Then a two-dimensional sheet structure in the plane  $(-1\ 0\ 1)$  is fabricated with the 32-membered ring as a construction unit, as shown in Fig. 2. In the crystal structure there is a weak  $\pi-\pi$ -stacking interaction between adjacent pyrazinyl rings and the relevant distances are  $Cg1...Cg1^i = 3.823(3)$  Å and  $Cg1...Cg1^i_{\text{perp}} = 3.541$  Å [symmetry code (i):  $-x, 1-y, 1-z$ ; Cg1 is the centroid of the N1,N4/C6—C9 pyrazinyl ring and  $Cg1...Cg1^i_{\text{perp}}$  is perpendicular distance from the Cg1 ring plane to the  $Cg1^i$  ring plane]. In addition to the  $\pi-\pi$ -stacking interaction, there are weak non-classic hydrogen bonds in the two-dimensional sheet as shown in Table 4 and Fig. 3. For 2-(pyridine-3-yloxy)pyrazine ligand, the dihedral angle between

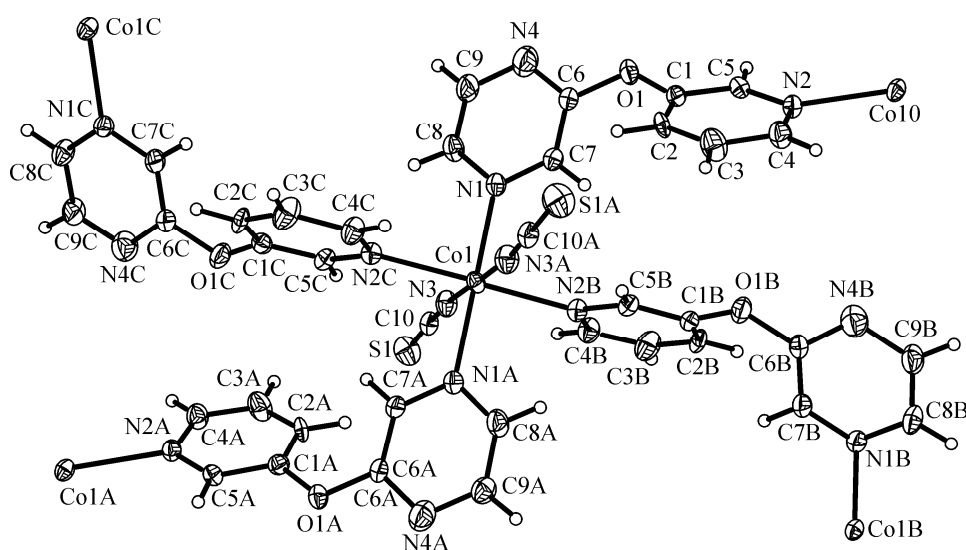


Fig. 1. Coordination diagram of the complex with the atom numbering scheme

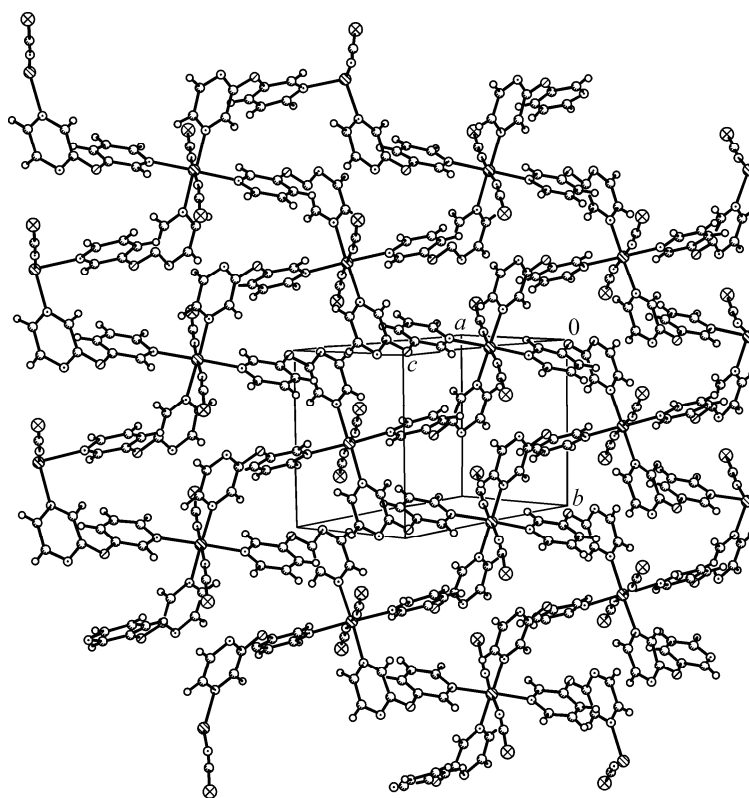


Fig. 2. Two-dimensional sheet structure of the compound studied

pyridyl ring and pyrazinyl ring of  $43.7(2)^\circ$  is smaller than that in a mono-nuclear Mn(II) complex ( $89.41(5)^\circ$ ) [ 3 ] and mono-nuclear Cu(II) complex ( $69.6(2)^\circ$ ) [ 4 ].

It is very interesting to compare the complex of this work with mono-nuclear Mn(II) complex [ 3 ] having the same ligands. For some ligands different ratios of reactants or different solvents may result in different coordination modes [ 6, 7 ]. The 2-(pyridine-3-yloxy)pyrazine ligand demonstrates different coordination modes, functioning either as a bidentate bridging ligand in the complex of this study or as a mono-dentate terminal ligand in the Mn(II) complex [ 3 ], even though the same ratio  $M(\text{ClO}_4) \cdot 6\text{H}_2\text{O} : \text{PP} : \text{NaSCN}$  and the same solvents were utilized. Obviously in the two complexes the

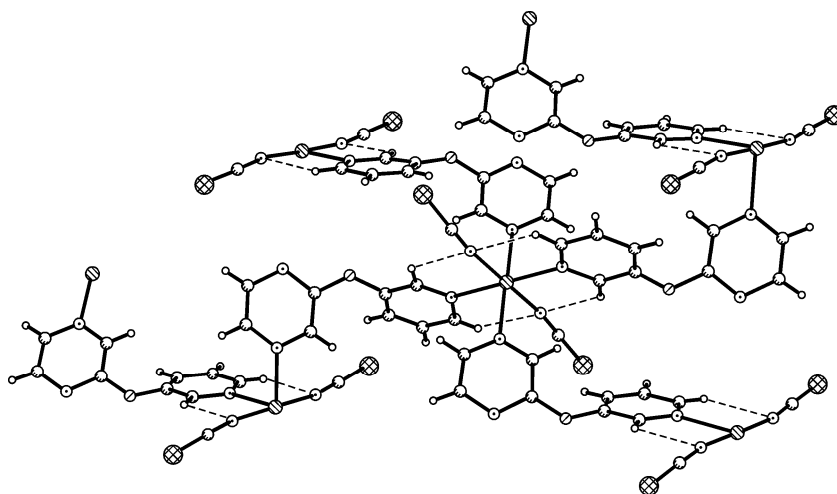


Fig. 3. Hydrogen bonds (lines of dashes) in the compound studied

metal ions play a key role for the coordination mode of 2-(pyridine-3-yloxy)pyrazine. In addition, as evident from the structure of 2-(pyridine-3-yloxy)pyrazine, there are three donor N atoms in the ligand, one from pyridyl group and other two from pyrazinyl group. It seems that 2-(pyridine-3-yloxy)pyrazine could act as a tridentate ligand, but it only acts as a bidentate ligand in the complex studied. The complexes with 2,6-bis(pyridine-3-yloxy)pyrazine as bridging ligand also exhibited a similar coordination mode [ 5 ], e.g. pyrazinyl only provided one of the two N atoms for coordination, which may result from various factors, such as metal salts, solvents and ratio of reactants.

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