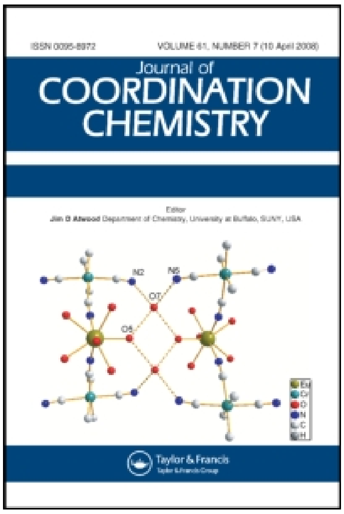

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Synthesis, Crystal Structure and Fluorescence of A 1-D Polymeric Zinc(Ii) Complex with Pyrazine-2-Carboxylate as a Bridging Ligand

Jin-Min Li[a]; Jing-Min Shi[b]; Chang-Ju Wu[b]; Wei Xu[b]
[a] Vocational College of Datong, Datong, P.R. China [b] Department of Chemistry, Shandong Normal University, Jinan, P.R. China

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SYNTHESIS, CRYSTAL STRUCTURE AND FLUORESCENCE OF A 1-D POLYMERIC ZINC(II) COMPLEX WITH PYRAZINE-2-CARBOXYLATE AS A BRIDGING LIGAND

JIN-MIN LI[a], JING-MIN SHI[b,*], CHANG-JU WU[b] and WEI XU[b]

[a]*Vocational College of Datong, Datong 037008, P.R. China;*
[b]*Department of Chemistry, Shandong Normal University, Jinan 250014, P.R. China*

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A one-dimensional chain complex $\{[Zn(pyz)(SCN)(H_2O)_2]\cdot H_2O\}_\infty$ (pyz = pyrazine-2-carboxylic anion) has been synthesized and its crystal structure determined by X-ray crystallography. The complex crystallizes in an orthorhombic system and the space group is $P2_12_12_1$ with $a = 6.873(3)$, $b = 9.847(4)$, $c = 16.466(7)$ Å. The Zn(II) ion is located in a distorted octahedral environment with two oxygen atoms O(3) and O(4) from terminal ligands of two water molecules, another oxygen atom O(1) from the carboxylate group of pyz, and three nitrogen atoms, N(1), and N(2A) from two different pyz and N(3) from a terminal thiocyanate anion, in which a chelated five-membered ring is formed by coordination of O(1) and N(1) to the Zn(1) atom. Therefore, an infinite zigzag chain consisting of Zn(II) ions and pyz anions is constructed and the chains are linked together with hydrogen bonding from coordinated and uncoordinated water molecules. The fluorescence spectra for the bridging ligand Na(pyz) and the complex were measured at room temperature in aqueous solution and in the solid state.

Keywords: Synthesis, Crystal structure, Cobalt(II) Complex, Fluorescence

INTRODUCTION

Interest has been focused on crystal engineering of coordination polymers because such new compounds may afford new materials with useful properties such as catalytic behavior, micro-porosity, electrical conductivity, non-linear optical activity and co-operative magnetic behavior [1–6]. In order to synthesize ideal coordination polymers the key is the design and selection of bridging ligands. Many complexes with pyrazine [7,8] and its derivatives, such as pyrazine-2-carboxylate [9–22], pyrazine-2,3-dicarboxylate [23–33], and so on [34–39] as ligands have been synthesized and some physical properties of these complexes investigated. Complexes with pyrazine-2-carboxylate (pyz) as a bridging ligand are very few [11,13] and fluorescent properties

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*Corresponding author. E-mail: Shijingmin@beelink.com

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for this kind of complex has not been reported. Here we report the synthesis, crystal structure and fluorescence emission of the title complex.

EXPERIMENTAL

Preparation

The one-dimensional complex $\{[Zn(pyz)(SCN)(H_2O)_2]\cdot H_2O\}_\infty$ was prepared as follows. Pyrazine-2-carboxylic acid (0.2102 g, 1.69 mmol) and $Zn(ClO_4)_2\cdot 6H_2O$ (0.6335 g, 1.70 mmol) were dissolved in 25 mL H_2O, then NaSCN (0.2860 g, 3.53 mmol) was added to the solution and the solution was stirred for about 1 h at room temperature. The colorless transparent single crystal was obtained after the solution was allowed to stand at room temperature for three weeks (yield: 0.3219 g, 63%). Anal, Calcd. for $C_6H_9N_3O_5SZn$: C, 23.97; H, 3.02; N, 13.98; Zn, 21.75%. Found: C, 24.34; H, 3.35; N, 14.25; Zn, 22.12%. Infrared and fluorescent spectra were recorded with a Shimadzu Corporation 408 IR spectrophotometer using KBr discs and a Perkin-Elmer LS-50 fluorescence spectrophotometer, respectively.

Crystal Structure Determination

A single crystal with dimensions $0.29 \times 0.23 \times 0.17\,\text{mm}^3$ was selected and the determination was carried out with graphite-monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart-1000 diffractometer using ω scan mode. A total of 6870 reflections were collected in the range of $2.41 \leq \theta \leq 27.10°$ at 298(2) K, of which 2453 reflections were independent ($R(\text{int}) = 0.0289$) and 1965 reflections with $I > 2\sigma(I)$ were observed and used in the succeeding refinement. Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier map and refined using the riding model with displacement parameters isotropically. The final refinement including hydrogen atoms converged to $R = 0.0248$ and $wR = 0.0476$. $w = 1/[\sigma^2(F_o)^2 + (0.0215P)^2 + 0.0000P]$ where $P = (F_o + 2F_o^2)/3$, $S = 0.836$, $(\Delta\rho)_{\max} = 0.230\,\text{e/Å}^3$, $(\Delta\rho)_{\min} = -0.448\,\text{e/Å}^3$, $(\Delta/\sigma)_{\max} = 0.001$. The programs for structure solution and refinement are SHELXS-97 and SHELXL-97, respectively.

RESULTS AND DISCUSSION

Crystal Structure

Crystal Data

$C_6H_9N_3O_5SZn$, $M = 300.59$, orthorhombic, space group $P2_12_12_1$, $a = 6.873(3)$, $b = 9.847(4)$, $c = 16.466(7)$ Å, $V = 1114.3(8)$ Å^3, $Z = 4$, $Dc = 1.792\,\text{g cm}^{-3}$, $F(000) = 608$, $\mu(\text{Mo K}_\alpha) = 2.401\,\text{mm}^{-1}$. Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Table I. Selected bond distances and angles are listed in Table II.

Figure 1 shows the coordination diagram of the complex with the atom numbering scheme. It indicates that Zn(1) is coordinated by O(1), O(3), O(4), N(1), N(3) and

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$). U(eq) defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x*	*y*	*z*	*U*(eq)
Zn(1)	2331(1)	6510(1)	6346(1)	27(1)
N(1)	3657(3)	4899(2)	7103(1)	23(1)
N(2)	5874(3)	2989(2)	7935(1)	26(1)
N(3)	−33(3)	6544(3)	7110(1)	38(1)
O(1)	4964(3)	5981(2)	5720(1)	28(1)
O(2)	7285(3)	4403(2)	5609(1)	34(1)
O(3)	1020(4)	5391(3)	5428(2)	43(1)
O(4)	1638(4)	8260(2)	5710(2)	55(1)
O(5)	3069(4)	3456(3)	4596(2)	67(1)
S(1)	−2311(1)	6406(1)	8513(1)	42(1)
C(1)	5917(4)	4960(3)	5966(2)	25(1)
C(2)	5299(4)	4405(3)	6785(2)	22(1)
C(3)	6394(4)	3439(3)	7198(2)	26(1)
C(4)	4247(4)	3504(4)	8246(2)	31(1)
C(5)	3139(4)	4455(3)	7834(2)	29(1)
C(6)	−975(4)	6479(3)	7691(2)	30(1)

TABLE II Selected bond lengths (Å) and bond angles (°)

Zn(1)–N(3)	2.055(2)	Zn(1)–O(4)	2.072(2)	Zn(1)–O(3)	2.076(2)
Zn(1)–O(1)	2.146(2)	Zn(1)–N(1)	2.214(2)	Zn(1)–N(2A)	2.246(2)

N(3)–Zn(1)–O(4)	96.57(11)	N(3)–Zn(1)–O(3)	96.40(11)
O(4)–Zn(1)–O(3)	88.49(11)	N(3)–Zn(1)–O(1)	164.63(9)
O(4)–Zn(1)–O(1)	98.80(10)	O(3)–Zn(1)–O(1)	83.56(9)
N(3)–Zn(1)–N(1)	89.55(9)	O(4)–Zn(1)–N(1)	167.20(9)
O(3)–Zn(1)–N(1)	102.03(10)	O(1)–Zn(1)–N(1)	75.48(8)
N(3)–Zn(1)–N(2A)	95.79(10)	O(4)–Zn(1)–N(2A)	81.56(9)
O(3)–Zn(1)–N(2A)	165.06(9)	O(1)–Zn(1)–N(2A)	86.96(8)
N(1)–Zn(1)–N(2A)	86.66(8)		

N(2A) atoms; O(3) and O(4) are from H_2O molecules and O(1), N(2A) and N(1) from bridging pyrazines, and N(3) from a thiocyanate anion, in which a five-membered chelate ring is formed through coordination of O(1) and N(1) to Zn(1). The bond lengths and associated angles indicate that Zn(1) is located in a distorted octahedral environment. The bond lengths for Zn(1) range from 2.055(2) to 2.246(2) Å; the bond lengths from the coordinated atoms of pyrazine rings (2.146(2), 2.214(2) and 2.246(2) Å) are longer than those from the terminal ligands H_2O and thiocyanate anion. The angle between Plane 1 [consisting of Zn(1), C(1), C(2), C(3), C(4), C(5), O(1), O(2), N(1), N(2); the plane equation being $3.829x + 6.914y + 7.299z = 10.0472$] and Plane 2 [consisting of Zn(1), C(1A), C(2A), C(3A), C(4A), C(5A), O(1A), O(2A), N(1A), N(2A); the plane equation being $-3.675x + 7.144y - 7.135z = -0.8385$] is 88.9°, indicating that the two planes are almost perpendicular. The one-dimensional zigzag chain is constructed through coordination of Zn(II) ion and bridging ligand pyz and the one-dimensional chain extends along the *b* axis. The chain structure is similar to that of complexes $[\text{CuCl(pyz)}(H_2O)]_\infty$ and $[\text{Cu}(N_3)(\text{pyz})(H_2O)]_\infty$ [13], but the chains of the latter two complexes appear as straight lines. The difference obviously comes from the distinct coordination numbers of the two metal ions. Hydrogen bonding exists in the inter-chains consisting of uncoordinated

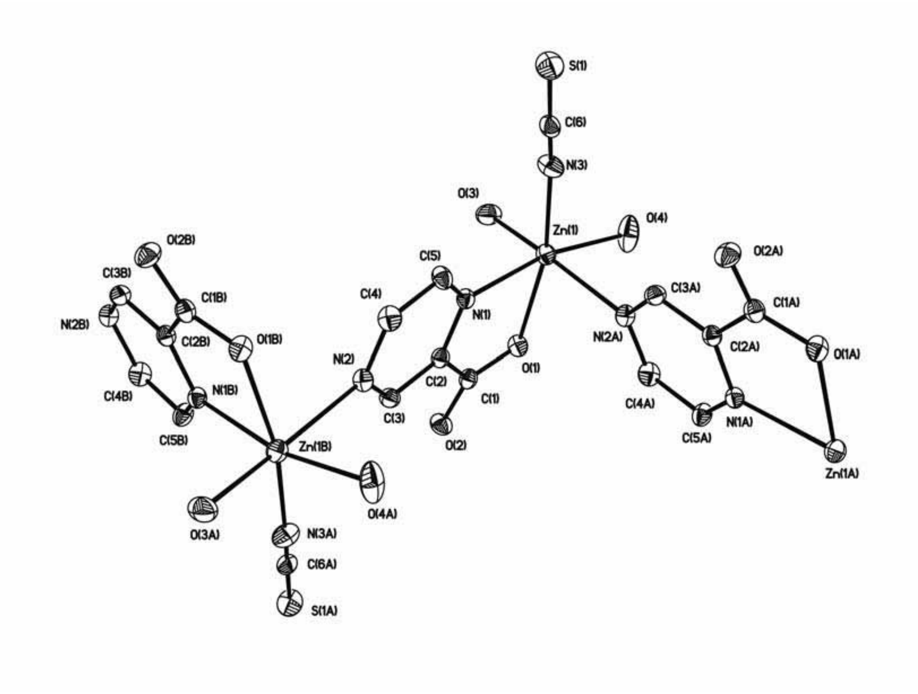

FIGURE 1 A perspective view of the title complex with atom numbering scheme.

H_2O molecules, coordinated H_2O molecules, the sulfur atom of the thiocyanate anion and oxygen atoms of carboxylic groups. Through the hydrogen bonding the two-dimensional sheet is formed in the *ab* plane and the sheets pile up along the *c* direction to construct the three-dimensional structure. The deposition number of the crystal at CCDC is 178984.

Infrared Spectrum

The IR absorption bands of free pyrazine-2-carboxylic acid exhibit the following bands: 1720 cm^{-1} (br, vs) and 1315 cm^{-1} (vs) for vibration of ν(C=O), 1272 cm^{-1} (m), 1152 cm^{-1} (vs), 1052 cm^{-1} (s), 1020 cm^{-1} (s), 890 cm^{-1} (m) and 820 cm^{-1} (m) for pyrazine ring vibration. In the complex these appeared at 1634 cm^{-1} (vs) and 1380 cm^{-1} (vs) for vibration of ν_{as}(C=O) and ν_s(C=O), respectively, and 1195 cm^{-1} (s), 1185 cm^{-1} (s), 1168 cm^{-1} (s), 1071 cm^{-1} (s), 1048 cm^{-1} (s) and 865 cm^{-1} (s) for pyrazine ring vibrations. The large separation between ν_{as}(C=O) and ν_s(C=O) suggests that the $-COO^-$ group coordinates as a monodentate ligand; this is identical with the X-ray analytical result. The IR spectrum of the complex also exhibits the strong and broad band of H_2O at ca. 3300 cm^{-1} and the strong sharp peak at 2050 cm^{-1} indicating that thiocyanate coordinates to Zn(II) as a terminal ligand [40].

Fluorescence Spectra

Fluorescence spectra for the bridging ligand Na(pyz) and the complex were measured at room temperature in aqueous solution and in the solid state. In the solid state the

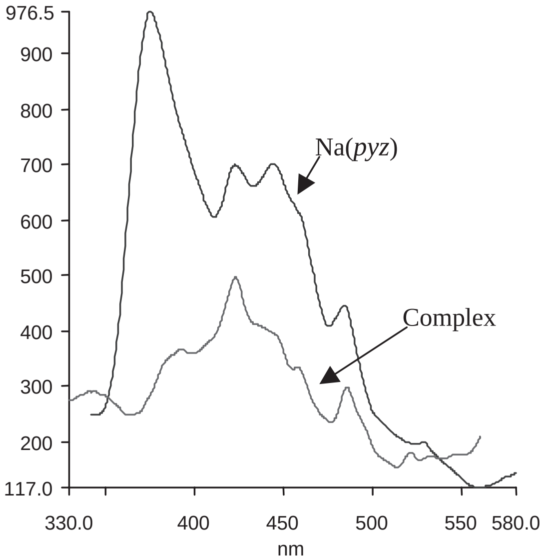

FIGURE 2 The fluorescence spectra for Na(pyz) and the title complex in the solid state.

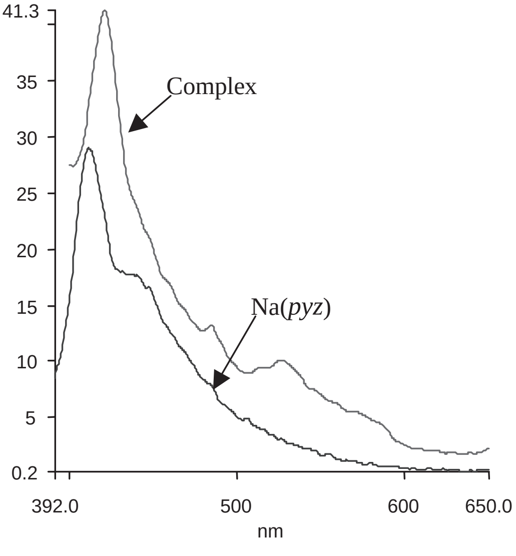

FIGURE 3 The fluorescence spectra of Na(pyz) and the title complex in aqueous solution.

maximum excited wavelengths are 375 nm for Na(pyz) and 297 nm for the complex, while the maximum emission bands are located at about 375 nm for Na(pyz) and 423 and 485 nm for the complex, as shown in Fig. 2. Figure 3 shows the fluorescence spectra in aqueous solution, in which the maximum excited wavelengths are 362 nm for Na(pyz) (3.50×10^{-3} M) and 370 nm for the complex (1.45×10^{3} M), while the maximum emission peaks are at 412 nm for Na(pyz) and 421 nm for the complex. In solution the peak shapes are very similar and the maximum emission bands are very close, which implies that the fluorescence emission of the complex arises from bridging ligand pyz. In the solid state a few emission peaks appear for both the complex and Na(pyz), but the peak shapes and peak positions are different, which may imply that the potential fields around the complex and bridging ligand pyz have an important influence on the fluorescence spectra. The appearance of a few emission peaks in the solid state obviously indicate that there are several stable excited states, which may arise from the orderly arrangement of the chains or pyz ligands in the solid state. This is the first report dealing with the fluorescent spectra of pyrazine derivatives and their complexes.

Acknowledgments

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Supplementary Material

The X-ray crystallographic file, in CIF format, is available from the Cambridge Crystallographic Data Center on quoting the deposition number CCDC 178984.

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