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Synthesis, Crystal Structure, and Luminescence of Two Mono-Nuclear Zinc(II) Complex: $Zn^{II}(C_{10}H_8N_3Br)(SCN)_2$ and $Zn^{II}(C_5H_6N_2)_2(SCN)_2$[1]

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Abstract—Two mononuclear zinc(II) complexes, $Zn^{II}(C_{10}H_8N_3Br)(SCN)_2$ (**I**) ($C_{10}H_8N_3Br$ is 6-bromo-*N*-(pyridin-2-yl)pyridin-2-amine); $Zn^{II}(C_5H_6N_2)_2(SCN)_2$ (**II**) ($C_5H_6N_2$ is pyridin-2-amine), were synthesized by solvothermal reaction at 393 K. Both structures have been determined on the basis of X-ray diffraction data (CIF files CCDC nos. 1042001 (**I**) and 1042002 (**II**)). Complex **I** crystallized in monoclinic, space group $P2_1/c$, with $a = 7.4083(10)$, $b = 14.958(2)$, $c = 15.096(2)$ Å, $\beta = 103.861(2)°$, $Z = 4$, $\rho_{calcd} = 1.761$ mg/m^3, $V = 1624.1(4)$ Å^3. Complex **II** crystallized in monoclinic, space group $P2_1/c$, with $a = 15.870(6)$, $b = 13.571(5)$, $c = 7.822(3)$ Å, $\beta = 104.200(4)°$, $Z = 4$, $\rho_{calcd} = 1.504$ mg/m^3, $V = 1633.2(11)$ Å^3. Complex **I** shows strong emissions exposing to ultraviolet radiation.

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INTRODUCTION

For many years metal-organic complex has been a fast-growing chemical field, which drew much attention because of their structural diversity and potentially applying as material relating to gas storage, ion exchange, catalysis, luminescence, electric conductivity and so on [1, 2]. During our previous studies we have shown much interesting for synthesizing compounds displaying perfect luminescent properties [3–5], due to their promising prospects to perform as medical probes in some disease checking and luminescent material in preparing high quality displays of new generation and so on [6, 7]. To advance this study we recently selected pyridin-2-amine and its' derivative, 6-bromo-*N*-(pyridin-2-yl)pyridin-2-amine, to react with $Zn(SO_4)_2$ and KSCN respectively, and have prepared two new mononuclear zinc(II) complexes, $Zn^{II}(C_{10}H_8N_3Br)(SCN)_2$ (**I**) namely (6-bromo-*N*-(pyridin-2-yl)pyridin-2-amine)-bis(thiocyanate)-zinc(II) and $Zn^{II}(C_5H_6N_2)_2(SCN)_2$ (**II**) namely bis(pyridin-2-amine)-bis(thiocyanate)-zinc(II). In due course X-ray diffraction was employed in their structural characterization, and luminescent investigations have been carried out at room temperature. Against to the fact that the two compounds are similar in structure, they are different on luminescent properties. We report our work here.

EXPERIMENTAL

Materials and methods. All chemicals used were of reagent grade and used without additional purification. Luminescent data were recorded on luminescence spectrometer LS-55, X-ray diffraction tests were performed on a Bruker Apex-II area-detector diffractometer.

Synthesis of I and II. The title complexes were prepared in a similar way described bellow. 6-Bromo-*N*-(pyridin-2-yl)pyridin-2-amine (0.25 g, 1 mmol), KSCN (0.39 g, 4 mmol) and $Zn(SO_4)_2 \cdot 7H_2O$ (0.28 g, 1 mmol) for **I**; pyridin-2-amine (0.16 g, 1.70 mmol), KSCN (0.21 g, 2.16 mmol) and $Zn(SO_4)_2 \cdot 7H_2O$ (0.19 g, 0.66 mmol) for **II** were mixed with some solvent (10 mL water for **I** and 10 mL water with 5 mL methanol for **II**). Both mixtures were put into a steel bomb equipped with a teflon liner, respectively, and kept at 393 K for about five days, then filtration was followed, and both filtrates were set untouched in the air to let the solvent escape slowly, several days later, crystals of **I** and **II** were obtained. The yield was 0.0982 g, 22.8% (basing on $ZnSO_4 \cdot 7H_2O$) for **I** and 0.0533 g, 21.75% (basing on $ZnSO_4 \cdot 7H_2O$) for **II**.

X-ray structure determination. X-ray diffraction test were carried out at about 293(2) K. Intensity data were collected under a MoK_α radiation ($\lambda = 0.71073$ Å) using ϕ–ω scan method. A total of 11866 reflections were collected for **I** and 13594 for **II**, the unique reflections were 3660 ($R_{int} = 0.036$) for **I** and 3901 ($R_{int} = 0.052$) for **II**. The SAINT and SADABS programs in the Bruker AXS SMART APPEX(II)

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Table 1. Crystallographic gata and experimental details for compounds **I** and **II**

Parameters	Value	
Compounds	$Zn^{II}(C_{10}H_8N_3Br)(SCN)_2$ (**I**)	$Zn^{II}(C_5H_6N_2)_2(SCN)_2$ (**II**)
Formula weight	430.66	369.81
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	7.4083(10)	15.870(6)
b, Å	14.958(2)	13.571(5)
c, Å	15.096(2)	7.822(3)
β, deg	103.861(2)	104.200(4)
Volume, Å^3	1624.1(4)	1633.2(11)
Z	4	4
ρ_{calcd}, mg/m^3	1.761	1.504
Absorption coefficient, mm^{-1}	4.227	1.760
F(000)	844	752
θ Range for data collection, deg	2.0–28.2	2.0–28.4
Limiting indices	$-9 \le h \le 89, -19 \le k \le 19, -20 \le l \le 20$	$-20 \le h \le 21, -17 \le k \le 18, -10 \le l \le 10$
Reflections collected/unique (R_{int})	11866/3660 (0.036)	13594/3901 (0.052)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3660/0/201	3901/0/190
Goodness-of-fit on F^2	1.027	1.05
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0664$, $wR_2 = 0.1543$	$R_1 = 0.0547$, $wR_2 = 0.0785$
R indices (all data)	$R_1 = 0.1275$, $wR_2 = 0.1791$	$R_1 = 0.1095$, $wR_2 = 0.0998$
Largest diff. peak and hole, e Å^{-3}	0.67 and –0.69	0.37 and –0.41

software package were used for integration and absorption correction. Both structures were solved by direct methods using SHELXS-97 program and refined on F^2 with XSHELL6.2. H atoms of pyridine rings were all located at calculated positions and refined as riding on their parent atoms with C–H bond length fixed to 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$; H atoms of amino groups in **I** were all found in electron density map and refined with N–H bond length fixed to 0.90 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$, H atoms of amino groups in **II** were all located at calculated positions and refined as riding on their parent atoms with N–H bond length fixed to 0.86 Å and with $U_{iso}(H) = 1.2U_{eq}(N)$. The crystallographic data and analysis parameters for complexes **I** and **II** are given in Table 1, selected bond lengths and angles are listed in Table 2.

Supplementary materials have been deposited in the Cambridge Crystallographic Data Centre (CCDC nos. 1042001 for **I** and 1042002 for **II**; deposit@ccdc.cam.ac.uk or http://www.ccde.cam.ac.uk).

RESULTS AND DISCUSSION

Structural analysis basing on X-ray diffraction data shows the two title compounds are very similar in their structure, zinc(II) ions were both four coordinated and fell into a tetrahedron coordination geometry with four coordination N atoms setting at its' four apexes and zinc(II) ion enclosed inside it (Fig. 1). Bond lengths of N–Zn(II) are 1.910(8)–2.010(6) Å for **I** and 1.942(4)–2.037(3) Å for **II**. The dihedral angle between two pyridine rings in every coordination molecule are 2.1° for **I** and 84.2° for **II**, so the two pyridine rings in **I** via the amino N atom which shows sp^2 hybridization can extend their conjugation systems to each other. In **I** Br atoms are of disorder in two positions: Br(1*A*) and Br(1*B*), with the occupancy ratio being 0.62656 and 0.37344, respectively.

Luminescence test performed at room temperature in solid state found **I** displayed strong absorption for 412, 395, and 335 nm radiations. Exposing to ultraviolet radiations of 412, 395, and 335 nm, respectively, three similar emitting spectrums were obtained, strong emissions all appeared at about 445 nm, and the most effective exciting source was 412 nm radiation (Fig. 2). The same tests found **II** (Fig. 3) displayed strong absorption for 265 and 340 nm radiations, under 265 and 340 nm ultraviolet radiations, obvious emissions have been recorded only under 340 nm with the strong emission appearing at about 430 nm. Against to the fact that zinc(II) ions have similar coordination environment in the two compounds, **II** displays

Table 2. Selected bond lengths (Å) and bond angles (deg) for compounds **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
	I		
Zn(1)–N(1)	2.010(6)	Zn(1)–N(4)	1.914(6)
Zn(1)–N(3)	2.010(5)	Zn(1)–N(5)	1.910(8)
	II		
Zn(1)–N(1)	2.019(3)	Zn(1)–N(5)	1.942(4)
Zn(1)–N(3)	2.037(3)	Zn(1)–N(6)	1.944(4)
Angle	**ω, deg**	**Angle**	**ω, deg**
	I		
N(1)Zn(1)N(3)	94.7(2)	N(4)Zn(1)N(3)	108.9(3)
N(1)Zn(1)N(4)	114.1(3)	N(5)Zn(1)N(3)	113.4(5)
N(1)Zn(1)N(5)	110.4(3)	N(4)Zn(1)N(5)	113.8(3)
	II		
N(1)Zn(1)N(3)	108.95(12)	N(3)Zn(1)N(5)	105.08(15)
N(1)Zn(1)N(5)	112.29(14)	N(3)Zn(1)N(6)	108.99(14)
N(1)Zn(1)N(6)	104.76(14)	N(5)Zn(1)N(6)	116.63(16)

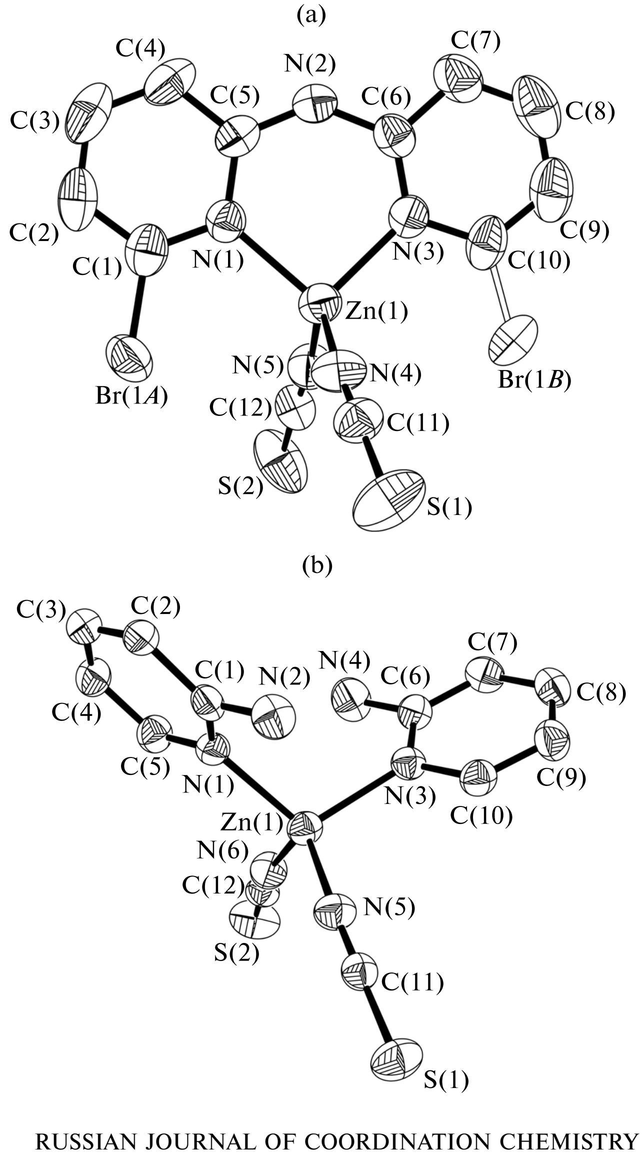

Fig. 1. Coordination environment of zinc(II) ions in **I** (a) and **II** (b), showing 30% probability displacement ellipsoids, all H atoms were omitted for clarity.

weaker absorption and therefore weaker emissions comparing to **I**, which may be attribute to the difference between their molecular inflexibility, and their organic ligand's conjugated scale. Comparing to **II**, the organic ligand in **I**, with close bind between the two pyridine rings, is more rigid, in addition to its' bigger conjugated scale, both are helpful in enhancing its' luminescence properties.

In conclusion, we have reported two new mononuclear zinc(II) complexes in this paper, luminescent tests revealed $\mathrm{Zn^{II}(C_{10}H_8N_3Br)(SCN)_2}$ displayed stronger emissions than $\mathrm{Zn^{II}(C_5H_6N_2)_2(SCN)_2}$ under proper ultraviolet radiations, which may be attributed

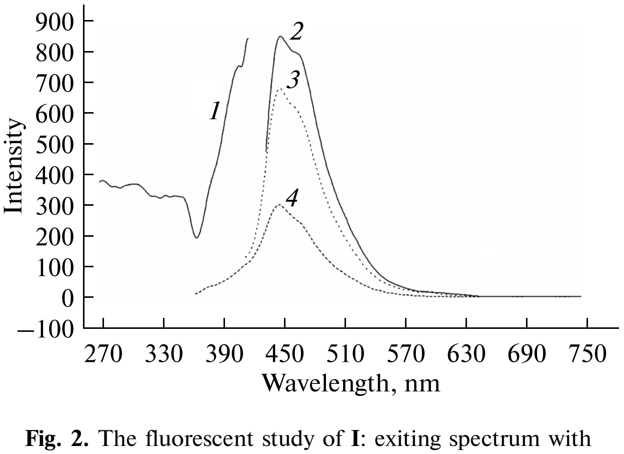

Fig. 2. The fluorescent study of **I**: exiting spectrum with emission fixed at 445 nm (*1*), emitting spectrum under ultraviolet radiation of 412 (*2*), 395 (*3*), 335 nm (*4*).

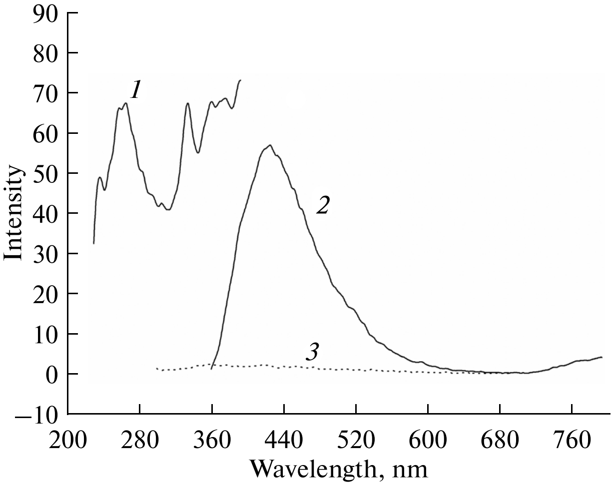

Fig. 3. The fluorescent study of **II**: exiting spectrum with emission fixed at 426 nm (*1*), emitting spectrum under ultraviolet radiation of 340 (*2*), 265 (*3*).

to the facts that it has more rigid molecular structure and bigger conjugated scales.

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