# Synthesis and Structural Properties of Thiapyridinophane and Its Complex with Ni(II) and Ag(I)<sup>1</sup>

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Abstract—The 2,11-dithia[3.3](3,5)pyrdinophane (L<sup>1</sup>) has been synthesized by a new method and characterized by <sup>1</sup>H NMR, which is used to form coordination complexes  $C_{14}H_{14}N_4O_6S_2Ni$  (I) by addition of Ni<sup>2+</sup> cation and  $C_{14}H_{14}N_3O_3S_2Ag$  (II) by addition of Ag<sup>+</sup> cation. 2,11,20-Trithia[3.3.3](3,5)pyridinophane (L<sup>2</sup>) and 2,11,20,29-tetrathia[3.3.3](3,5)pyridinophane (L<sup>3</sup>) have also been synthesized as by-products. Single-crystal X-ray analysis reveals that the conformation of the L<sup>1</sup> is *syn*(boat-chair), complexes I and II also adopt *syn*(boat-chair) (CIF files CCDC nos. 1400332 (I) and 700724 (II)). While in I, Ni(II) is coordinated with L<sup>1</sup> with two nitrogen and four oxygen atoms, in II, Ag(I) is coordinated with L<sup>1</sup> by two nitrogen and two sulfur atoms came from four ligands. In complexes I and II, the formation of three-dimensional structure depends on  $\pi$ ··· $\pi$  stacking and hydrogen bonds.

idinophane.

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### **INTRODUCTION**

Since the definition was given by Cram [1], cyclophanes, which are organic compounds comprising of aromatic elements as structural units, have been studied [2–4]. Cyclophanes known as bridged aromatic compounds have been intensively studied from various points of view for the last few decades [5, 6]. Among them large-sized cyclophanes capable of forming an inner cavity have been playing a central role as synthetic receptors in molecular recognition [7-10]. On the contrary, small-sized cyclophanes can be characterized by their aromatic components fixed in a forced proximity and their particular orientation. Considering their unique three-dimensional structure and conformational mobility, the small-sized cyclophanes possibly provide the fascinating supramolecular selfassembly upon coordination.

In recent years, many review articles and books on cyclophanes have been published [11-16]. The aromatic units can be interlinked by hydrocarbon units, heteroatom containing units, or mixed substituents. Our group is interested in thiapyridinophane [17] and its complexes. 2,11-Dithia[3.3](3,5)pyrdinophane (L<sup>1</sup>), 2,11,20-trithia[3.3.3](3,5)pyridinophane (L<sup>2</sup>) and 2,11,20,29-tetrathia[3.3.3](3,5)pyridinophane (L<sup>3</sup>) have been synthesized in our lab using Ramberg-Bäcklund reaction. Ligand L<sup>1</sup> contains sulfur and

by TLC with glass-backed silica gel HF<sub>254</sub> plates and visualized under  $\lambda = 254$  nm or by iodine adsorption as appropriate. Flash column chromatography was performed using silica gel neutral alumina (100–200 mesh). <sup>1</sup>H NMR spectra were obtained with a Varian Mercury 300 spectrometer. Chemical shift were reported as  $\delta$  values (ppm) relative to internal tetramethylsilane (TMS) in DMSO unless otherwise

Synthesis of compound  $L^1$ ,  $L^2$ , and  $L^3$ . To a solution of Na<sub>2</sub>S · 9H<sub>2</sub>O (3.68 g, 15.3 mmol) in 95% EtOH (100 mL) was added dropwise a solution of freshly prepared 3,5-bis(chloromethyl)pyridine (0.98 g, 2.86 mmol) in EtOH (50 mL) at room temperature

noted. Reagents were used without further purifica-

tion from commercial sources unless otherwise stated.

nitrogen atoms, respectively, and its molecular skeletons are located towards different directions, thus,  $L^1$ 

has unique coordination properties. In this paper, we

report the Ni(II) and Ag(I) complexes with  $L^1$  which

show interesting structure. These studies enrich the

knowledge of structure and physical properties of pyr-

idinophane as well as its complexes. To the best of our

knowledge, the formation of dual-core coordination

in complex I is new coordination examples of thiapyr-

**EXPERIMENTAL** 

Materials and methods. Reactions were monitored

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over a period of 5 h, and then the mixture was heated to reflux for 24 h. After cooling, the solvent was evaporated under reduced pressure. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were dried with MgSO<sub>4</sub> and filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by PTLC on silica gel with EtOH to give white power L<sup>1</sup> (0.400 g, 26%,  $R_f$ = 0.57); <sup>1</sup>H NMR (300 MHz; DMSO; 25°C;  $\delta$ , ppm): 7.94 (s. 4H, 2,6-PyH, 7.62 (s., 2H, 4-PyH), 3.89 (s., 8H, -CH<sub>2</sub>SCH<sub>2</sub>-) and L<sup>2</sup> (0.350 g, 15%,  $R_f = 0.41$ ); <sup>1</sup>H NMR (300 MHz; DMSO; 25°C;  $\delta$ , ppm): 8.45 (s., 6H, 2,6-PyH), 7.46 (s., 3H, 4-PyH), 3.65 (s., 12H,  $-CH_2SCH_2-$ ); MS (LCQ) m/z: 412.1 [M<sup>+</sup>]. Anal. calcd. for  $C_{21}H_{21}N_3S_3$  (412.4). L<sup>3</sup> (0.09 g, 3%,  $R_f = 0.21$ );  $\delta$  8.28 (s., 6H, 2,6-PyH), 7.45 (s., 3H, 4-PyH), 3.68 (s., 12H,  $-CH_2SCH_2-$ ); MS (LCQ) m/z: 549.12 [M<sup>+</sup>]. Anal. calcd. for  $C_{28}H_{28}N_4S_4$  (549.4).

Synthesis of 2,11-dithia[3.3](3,5)pyrdinophane  $L^1$ ,  $L^2$ ,  $L^3$  are given in Scheme:



Synthese of complex I. The solution of  $CHCl_3$ (5 mL) containing compound L<sup>1</sup> (19.7 mg, 0.07 mmol) was poured into a 6 mm diameter bottomsealed glass tube and then layered with  $CH_3CN$  solution (5 mL) of Ni(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (49.4 mg, 0.17 mmol). The glass tube was sealed. Green block crystals of complex I, suitable for X-ray diffraction analysis, was obtained after 10 days. Complex II was obtained by the similar method.

**X-ray crystallography.** Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart Apex CCD diffractometer at room temperature (293(2) K). The data collections were performed with Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). Unit cell dimensions were obtained with least squares refinements, and all structures were solved by direct method. The non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for nonhydrogen atoms on  $F^2$  [18]. Hydrogen atoms were added theoretically and were riding on their parent atoms. Crystallographic data are summarized in table.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1400332 (I) and 700724 (II); deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

## **RESULTS AND DISCUSSION**

Although preparation of compound L<sup>1</sup> reported by H.A. Staab et al. via the coupling reaction, we used another method to obtain L<sup>1</sup> and L<sup>2</sup>. Comparing to the previous method, the yield of compound L<sup>1</sup> declined, but the yield of compound L<sup>2</sup> increased. We produced 3,5-bis(chloromethyl)pyridine by direct chlorination of 3,5-lutidine with N-chlorosuccinimide. The freshly prepared 3,5-bis(chloromethyl)pyridine was reacted with Na<sub>2</sub>S · 9H<sub>2</sub>O in EtOH under high dilution conditions to give L<sup>1</sup> (26.0%) and L<sup>2</sup> (15.0%).

In the crystal structure of I, Ni(II) was coordinated by the four oxygen atoms of  $NO_3$ — and two nitrogen atoms which come from different ligands, two ligands and two Ni(II) formed dual-core complex. Every Ni(II) adopted a distorted octahedron coordination geometry. The coordination environment of Ni(1) and Ni(1A) was same, as well as in crystallography. The distance between Ni(1) and Ni(1A) was 3.417 Å, which was smaller than the van der Waals radius but larger than the metallic radius of Ni…Ni, it indicated that in

## SYNTHESIS AND STRUCTURAL PROPERTIES

#### Crystallographic data and structure refinement summary for compounds I and II

Parameter	Value	
	Ι	II
Empirical formula	$C_{14}H_{14}N_4O_6S_2Ni$	$C_{14}H_{14}N_3O_3S_2Ag$
Formula weight	457.12	444.27
Crystal system; space group	Monoclinic; $P2_1/n$	Monoclinic; $P2_1/n$
Unit cell dimensions:		
a, Å	9.374(2)	15.319(3)
b, Å	18.472(5)	15.456(2)
<i>c</i> , Å	10.341(2)	16.237(3)
β, deg	94.236(19)	90
Volume, Å <sup>3</sup>	1785.7(7)	3844.3(12)
Ζ	4	8
$\rho_{calcd}, mg/m^3$	1.700	1.535
$\mu$ , mm <sup>-1</sup>	1.361	1.280
<i>F</i> (000)	936	1776
Crystal size, mm	$0.46 \times 0.34 \times 0.31$	$0.37 \times 0.32 \times 0.27$
$\theta$ Range for data collection, deg	2.21 to 26.02	1.87 to 29.19
Limiting indices	$-11 \leqslant h \leqslant 1, -1 \leqslant k \leqslant 22, -12 \leqslant l \leqslant 12$	$-21 \leqslant h \leqslant 1, -19 \leqslant k \leqslant 1, -1 \leqslant l \leqslant 20$
Reflections collected/ unique $(R_{int})$	4450/3514 (0.0289)	2804/2452 (0.0545)
Completeness to $\theta = 27.51, \%$	99.9	85.3
Max and min transmission	0.6761 and 0.5757	0.7254 and 0.6495
Data/restraints/ parameters	3514/0/244	2452/1/208
Goodness-of-fit on $F^2$	1.029	1.179
Final <i>R</i> indices $(I \ge 2\sigma(I))$	$R_1 = 0.0395, wR_2 = 0.1023$	$R_1 = 0.0508, wR_2 = 0.1589$
R indices (all data)	$R_1 = 0.0539, wR_2 = 0.1110$	$R_1 = 0.0822, wR_2 = 0.1821$
Largest diff. peak and hole, $e \text{ Å}^{-3}$	0.754 and -0.304	1.375 and -0.857

complex Ni(1) and Ni(1*A*) have some strong interaction, which can be called dual-core complex. The conformation of the ligand in complex I is syn(boatchair), which is the same as the ligand (syn(boatchair)). But the distance of two nitrogens in every pyridinophane was 3.518, which was smaller than the ligand. The dihedral angle of pyrazine ring in complex I is 8.88°, which is smaller than the dihedral angle of ligand by 1.41° as shown in Fig. 1a. The intermolecular pyridine rings also have  $\pi$ ... $\pi$  stacking (distance between two pyridine rings was 3.419 Å) as shown in Fig. 2, the distance of N...H was 2.624 Å which was smaller than the van der Waals radius of N...H (2.750 Å). The distance of O...H was 2.355 and

2016

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 42 No. 7



(b)



Fig. 1. Coordination environment of the nickel and silver atoms in complexes I (a) and II (b).



Fig. 2. Fragment of the chain in complex I.



Fig. 3. Perspective view of the 3D structures of I along the *x* axis (a) and II along the *z* axis (b).

RUSSIAN JOURNAL OF COORDINATION CHEMISTRY Vol. 42 No. 7 2016

2.688 Å which were smaller than the van der Waals radius of O···H (2.720 Å). We think the N···H, O···H have some weak interaction. In addition, the distance between S and O was 3.027 Å which was smaller than the van der Waals radius of O···S (3.320 Å). Due to all of above, complexes between molecules formed in layered structure as shown in Fig. 3a.

In the crystal structure of II, Ag(I) was coordinated with two nitrogen and two sulfur atoms came from four ligands, respectively, as shown in Fig. 1b, and form a near square cyclic structure by Ag(I) which further extend in one dimension. The size of cavity was  $8.133 \times 7.953$  Å as shown in Fig. 3b. The conformation of the ligand in complex II is also *syn*(boat-chair). But the dihedral angle of pyrazine ring in complex is 11.3°, which was warped as the coordination between Ag(I) and nitrogen in the pyrazine ring.

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