ORIGINAL PAPER

Synthesis and Crystal Structures of Zn(II)/Co(II) Complexes with Condensed Heterocyclic Based 1,2,4-Triazole

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Abstract Three Zn(II)/Co(II) coordination compounds with condensed heterocyclic based 1,2,4-triazole 8*H*-4, 7-diphenyl-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazines (L^1), and 8*H*-4-phenyl-7-(pyridine-2-yl)-1,2,4-triazolo[3,4-b]-1,3, 4-thiadiazines (L^2), Co(L^1)₂Cl₂ (1), Zn(L^1)₂Cl₂ (2). and Co(L^2)₂Cl₂ (3) were synthesized and structurally characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction. Complexes 1, 2 and 3 have mononuclear structure, the mononuclear structures of 1 and 2 were further assembled by the C–H···Cl and C–H···N weak interactions into an infinite 2-D supramolecular sheet.

Keywords Zn(II)/Co(II) complex \cdot Synthesis \cdot Crystal structure

Introduction

The past decade has witnessed the explosive development of metal organic frameworks (MOFs), because of not only their intriguing varieties of molecular architectures and topologies [1] but also their potential applications in ferroelectrics, nonlinear optics, porous materials, and catalysis, etc. [2]. Recently remarkable progress has been made in this new field of chemistry and materials science, largely

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due to efficient design strategies [3-5], but it is still difficult to prepare metal organic frameworks with predictable topologies, and to predict the exact structures and composition of the coordination polymer, because the self-assembly progress is highly influenced by several factors such as the ligands' nature, solvents, templates, counteranions, metal to ligand ratio, etc. Therefore, systematic research on this topic is still important for understanding the role of these factors in the formation of metal coordination frameworks [6–8].

Great efforts have been focused on ligands based on azole heterocycle, which have both good coordination ability and diverse coordination modes [9]. As the simple small molecular ligands, triazole and its derivatives are potential multitopic ligands in constructions of coordination complexes [10]. 1,2,4-Triazole and its derivatives are very interesting ligands because they combine the coordination geometry of both pyrazoles and imidazoles with regard to the arrangement of their three heteroatoms [11]. A large number of mononuclear [12], dinuclear [13], and polynuclear [14] metal coordination compounds with 1,2,4triazole derivatives have been prepared and characterized because of their interesting luminescence properties and novel topologies [15]. However, there are still only rare reports of ligands based on condensed heterocyclic based 1,2,4-triazole as building blocks for the construction of coordination complexes.

In this work, two ligands of condensed heterocyclic based 1,2,4-triazole: (L^1) and (L^2) (Chart 1), have been designed and synthesized. The reactions of these ligands with the corresponding Zn(II)/Co(II) salts lead to the formation of three new metal organic complexes with 0-D structures. Those complexes were structurally characterized by elemental analyses, IR spectroscopy and single-crystal X-ray diffraction. This paper reports on the results

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Chart 1 The structure of ligands L^1 and L^2

of an X-ray structural investigation of complexes $Co(L^1)_2$ Cl₂ (1), Zn(L¹)₂Cl₂ (2) and Co(L²)₂Cl₂ (3).

Experimental Section

Materials and General Methods

Ethyl Benzoate, 85 % hydrazine hydrate, potassium hydroxide, 2-acetylpyridine, acetophenone reagents used for the syntheses were commercially available and employed without further purification. The intermediate of 3-phenyl-4-amino-5-sulfhydryl-1,2,4-triazole (**a**) was prepared according to reported procedures [16]. IR spectra were measured on a Bruker Equinox 55 FT-IR spectrometer with KBr Pellets in the range of 4,000–400 cm⁻¹. Elemental analyses of C, H and N were performed on a Thermo Flash EA 1112-NCHS-O analyzer. ¹H NMR data were collected using an INOVA-400 NMR spectrometer. Chemical shifts are reported in d relative to TMS.

Synthesis of Ligand L^1 and L^2

8*H*-4,7-Diphenyl-1,2,4-triazolo[3,4-b]-1,3,4-thiadiazines (L^{1})

The intermediate of 3-phenyl-4-amino-5-sulfhydryl-1,2,4-triazole (a) (5 mmol) and 2-bromo-1-phenylethanone (5 mmol) was added to absolute ethanol (30 mL), then was refluxed for 4 h. Removing the solvent under depress

pressure to give ligand L^1 , recrystallized from absolute ethanol to give ligand L^1 as white crystals (Chart 2). Yield: ~65 %. m.p. 210–212 °C. ¹H NMR (CDCl₃): δ : 7.50 ~ 8.15(m, 10H, benzene), δ : 4.05(s, 2H, thiadiazine); Anal. Calcd for C₁₆H₁₂N₄S: C, 65.73; H, 4.14; N, 19.16; Found: C, 65.75; H, 4.12; N, 19.17. IR (cm⁻¹, KBr pellets): 3376w, 3192w, 3104w, 3059m, 3031m, 2998s, 2904m, 2800w, 2449w, 1960w, 1905w, 1813w, 1761w, 1714w, 1595w, 1568w, 1503w, 1460s, 1370s, 1302s, 1284m, 1233w, 1176w, 1157w, 1113w, 1073w, 1023w, 998w, 966w, 919w, 870w, 832w, 769m, 739w, 690s, 638w, 591w, 551w, 510w.

8H-4-Phenyl-7-(pyridine-2-yl)-1,2,4-triazolo[3,4-b]-1,3, 4-thiadiazines (**L**²)

The intermediate of 3-phenyl-4-amino-5-sulfhydryl-1,2,4triazole (**a**) (5 mmol) and 2-bromo-1-(2-pyridyl)ethanone (5 mmol) was added to absolute ethanol (30 mL), then was refluxed for 4 h. Removing the the solvent under depress pressure to give ligand L^2 , recrystallized from absolute ethanol to give ligand L^2 as white crystals. Yield: ~60 %. m.p: 208–210 °C. ¹H NMR (CDCl₃): δ : 8.80 (dd, 1H, 6-pyridine), δ : 8.30 (dd, 1H, 4-pyridine), δ : 7.68–8.08 (m, 7H, 2,3-pyridine and benzene), δ : 4.76(s, 2H, thiadiazine); Anal. Calcd for C₁₅H₁₁N₅S: C, 61.43; H, 3.75; N, 23.89; Found: C, 61.45; H, 3.72; N, 23.90. IR (cm⁻¹, KBr pellets): 3308w, 3060w, 2997m, 2905m, 2793w, 2754w, 2660w, 2361s, 2008w, 1977w, 1725m, 1601m, 1569s, 1506s, 1486s, 1463s, 1437m, 1412s, 1391s, 1371m, 1328w, 1283w, 1253w, 1166w, 1092m, 1049w, 993w, 959w, 910w, 878m, 841w, 777s, 686s, 584s, 556w, 501w.

Synthesis of Complexes 1-3

$$Co(L^{I})_{2}Cl_{2}(1)$$

Complex 1 was prepared by dissolving $CoCl_2 \cdot 6H_2O$ (0.3 mmol) and L^1 (0.3 mmol) in ethanol solution (15 mL), then was refluxed for 3 h. After cooling and filtrated, Blue plate-shaped crystals were formed after several days with the evaporation of the filtrate (ca. 30 % yield



Chart 2 The route of synthesis of ligands L^1 and L^2

based on L¹). Yield: 30 %. Anal. Calcd for $C_{32}H_{24}Cl_2$ CoN₈S₂: C, 53.79; H, 3.39; N, 15.68. Found: C, 53.80; H, 3.41; N, 15.67. IR (cm⁻¹, KBr pellets): 3430w, 3058w, 2997w, 2917w, 2495w, 2262w, 1970w, 1896w, 1807w, 1763w, 1698w, 1593w, 1565w, 1530w, 1505s, 1479s, 1453s, 1437s, 1407m, 1384m, 1364m, 1315m, 1306m, 1276s, 1225m, 1182m, 1160w, 1124w, 1100w, 1073w, 993s, 915m, 833m, 806w, 786m, 768s, 758s, 742m, 689s, 641m, 597m, 557m, 510m, 475w, 432w.

$Zn(L^1)_2Cl_2(2)$

Complex **2** was prepared by dissolving ZnCl_2 (0.3 mmol) and \mathbf{L}^1 (0.3 mmol) in ethanol solution (15 mL). Colorless plate-shaped crystals were formed after several days with the evaporation of the solvent (ca. 30 % yield based on \mathbf{L}^5). Yield: 30 %. Anal. Calcd. for $C_{32}H_{24}Cl_2\text{ZnN}_8\text{S}_2$: C, 53.30; H, 3.35; N, 15.54. Found: C, 53.31; H, 3.33; N, 15.55. IR (cm⁻¹, KBr pellets): 3441*w*, 3059*w*, 2915*w*, 1971*w*, 1896*w*, 1810*w*, 1763*w*, 1689*w*, 1590*w*, 1529*w*, 1476*m*, 1455*s*, 1411*s*, 1363*m*, 1308*s*, 1222*w*, 1184*w*, 1156*w*, 1124*w*, 1073*w*, 1045*w*, 994*w*, 918*w*, 830*w*, 786*m*, 760*s*, 737*w*, 689*s*, 639*w*, 600*w*, 555*w*, 510*w*, 474*w*, 432*w*.

 $Co(L^2)_2Cl_2(3)$

Complex 3 was prepared by dissolving $CoCl_2 \cdot 6H_2O$ (0.3 mmol) and L^2 (0.3 mmol) in ethanol solution (15 mL), then was refluxed for 3 h. After cooling and filtrated, Blue plate-shaped crystals were formed after several

Table 1Crystal data andstructure refinement summaryfor complexes 1–3

days with the evaporation of the filtrate (ca. 30 % yield based on L^2). Yield: 25 %. Anal. Calcd for $C_{30}H_{22}Cl_2$ $N_{10}S_2Co: C, 50.29; H, 3.09; N, 19.55. Found: C, 50.35; H, 3.20; N, 19.67. IR (cm⁻¹, KBr pellets): 3058w, 2994m, 2913w, 2623w, 2248w, 2301w, 1994w, 1966w, 1891w, 1766w, 1700w, 1602m, 1565m, 1530w, 1453s, 1405m, 1365m, 1337s, 1312m, 1253m, 1225m, 1181m, 1155s, 1100m, 1072m, 1050m, 1020w, 923m, 840m, 801w, 770s, 751m, 694s, 652w, 622m, 599m, 565m, 512m, 472w, 442w.$

X-Ray Crystallography

X-ray single-crystal diffraction data for L and complex 1 were collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with Mo-K α radiation ($\lambda = 0.71073$ Å) by $\omega - \phi$ scan mode. The program SAINT [17] was used for integration of the diffraction profiles. Semi-empirical absorption corrections were applied using SADABS program. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [18]. Metal atoms in each complex were located from the E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . Hydrogen atoms of carbon were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The crystal data file in CIF format was deposited on CCDC and reference

	1	2	3
Formula	$C_{32}H_{24}Cl_2N_8S_2Co$	$C_{32}H_{24}Cl_2N_8S_2Zn$	C ₃₀ H ₂₂ Cl ₂ N ₁₀ S ₂ Co
Formula wt	714.54	696.96	716.53
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P21/n	P21/n	P21/n
<i>T</i> /K	293(2)	293(2)	293(2)
a/Å	10.904(2)	10.898(2)	10.454(2)
b/Å	17.993(4)	18.046(4)	17.949(4)
c/Å	16.278(3)	16.313(3)	16.849(3)
α/°	90.00	90.00	90.00
β/°	104.05(3)	103.90(3)	102.19(3)
γ/°	90.00	90.00	90.00
V/Å ³	3098.1(11)	3114.3(11)	3090.3(11)
Ζ	4	4	4
$D/g \text{ cm}^{-3}$	1.536	1.486	1.549
μ/mm^{-1}	0.900	1.130	0.909
<i>F</i> (000)	1460	1424	1460
Messured reflns	29844	29081	25832
Obsd reflns	7043	7067	6948
R^a/wR^b	0.0530/0.2161	0.0386/0.1195	0.0645/0.1938

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ^b $R_w = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$ numbers 857783–857785 (for complex **1–3**, respectively). This data can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam. ac.uk.

Results and Discussion

Syntheses and General Characterization

 L^1 and L^2 was prepared in higher yield as white crystalline solid by the reaction of 3-phenyl-4-amino-5-sulfhydryl-1,2,4-triazole (a) with 2-bromo-1-phenylethanone and 2-bromo-1-(2-pyridyl)ethanone, respectively. The structures of $L^1 \sim L^2$ were determined by ¹H NMR, IR, elemental analysis. The complexes 1–3 are air stable at room temperature. The infrared spectra of $1 \sim 3$ exhibits characteristic absorptions for corresponding ligands with a slight shift due to coordination. L^1 and L^2 and 1–3 all exhibited absorptions corresponding to the framework vibrations of aromatic rings at about 1,420–1,650 cm⁻¹.

Crystal Structures

$$Co(L^{I})_{2}Cl_{2}$$
 (1) and $Zn(L^{I})_{2}Cl_{2}$ (2)

Structural analyses were carried out and similar cell parameters of complexes 1 and 2 (Table 1). Compounds 1 and 2 have the general formula of $M(L^1)_2Cl_2$ [M = Co (1), M = Zn (2)]. In 1, the coordination environment of Co(II) ion is also the same as Zn(II) that of ion in 2. Therefore, we just describe structure of complex 1 later in this text in detail relatively.

Complex 1 crystallizes in P21/n space group and the selected bond distances and angles were listed in Table 2. The X-ray diffraction analysis shows that 1 has a mononuclear structure (see Fig. 1a). The Co(II) center features a distorted tetrahedral geometry, and linked to two distinct triazole N donors of two L¹ ligands and two chlorine atoms, the Co(1)–N(1) and Co(1)–N(5) bond distances are 2.035(3) and 2.027(3) Å, respectively, which are in the normal range [19]. Two L¹ ligands all adopt monodentate coordination mode.

It should be pointed out that the C–H…Cl weak interactions were observed between adjacent mononuclear structures. The distances of C(13)…Cl(1) and C(31)…Cl(2) are 3.765 and 3.504 Å, respectively. Therefore, mononuclear structures were further assembled by the C–H…Cl weak interactions into an infinite 1-D supramolecular chain (Fig. 1b). In addition, the C–H…N weak interactions were observed between 1-D supramolecular chains assembled by the C–H…Cl weak interactions. The

Table 2 Selected bond distances (Å) and angles (°) for complexes 1–3

Complex 1			
Co(1)–N(5)	2.027(3)	Co(1)–N(1)	2.035(3)
Co(1)–Cl(2)	2.2256(12)	Co(1)–Cl(1)	2.2313(12)
N(5)-Co(1)-N(1)	105.45(12)	N(5)-Co(1)-Cl(2)	116.20(10)
N(1)-Co(1)-Cl(2)	102.93 (8)	N(5)-Co(1)-Cl(1)	103.89(9)
N(1)-Co(1)-Cl(1)	115.14(9)	Cl(2)–Co(1)–Cl(1)	113.38(5)
Complex 2			
Zn(1)-N(5)	2.051(2)	Zn(1)–N(1)	2.048(2)
Zn(1)–Cl(2)	2.2363(8)	Zn(1)–Cl(1)	2.2315(9)
N(5)-Zn(1)-N(1)	104.79(9)	N(5)-Zn(1)-Cl(2)	113.92(7)
N(1)–Zn(1)–Cl(2)	104.76(7)	N(5)-Zn(1)-Cl(1)	103.24(6)
N(1)–Zn(1)–Cl(1)	114.47(7)	Cl(2)–Zn(1)–Cl(1)	115.44(4)
Complex 3			
Co(1)–N(6)	2.029(3)	Co(1)–N(1)	2.048(3)
Co(1)–Cl(1)	2.2583(13)	Co(1)–Cl(2)	2.2563(12)
N(6)-Co(1)-N(1)	106.24(13)	N(6)-Co(1)-Cl(1)	112.07(10)
N(1)-Co(1)-Cl(1)	102.55 (10)	N(6)-Co(1)-Cl(2)	103.54(10)
N(1)-Co(1)-Cl(2)	113.63(10)	Cl(1)-Co(1)-Cl(2)	118.44(5)

distance of C(24)…N(2) and C(8)…N(6) are 3.468 and 3.548 Å, respectively, the angles of C(24)–H(24A)…N(2) and C(8)–H(8b)…N(6) are 167.32 and 170.46°, respectively. So the mononuclear structures was further assembled by the C–H…Cl and C–H…N weak interactions into an infinite 2-D supramolecular sheet (Fig. 1c).

The mononuclear structure of complex **2** shows in Fig. 2. The C–H····Cl and C–H····N weak interactions were observed in **2**, The distances of C(4)····Cl(1) and C(22)····Cl(2) are 3.504 and 3.782 Å, respectively. The distance of C(30)····N(2) and C(14)····N(6) are 3.562 and 3.474 Å, respectively, the angles of C(14)–H(14A)····N(6) and C(30)–H(30A)····N(2) are 166.19 and 171.30°, respectively. The mononuclear structures were further assembled by the C–H····Cl and C–H···N weak interactions into an infinite 2-D supramolecular sheet.

$Co(L^2)_2Cl_2(3)$

Complex 3 crystallizes in the monoclinic symmetry space group P21/n. Crystallographic data and experimental details for structural analyses were summarized in Table 1, the selected bond distances and angles were listed in Table 2. The X-ray diffraction analysis shows 3 has a mononuclear structure (Fig. 3) with the center Co(II) ion four-coordinated by two N atoms from two distinct triazole N donors of two L² ligands and two chlorine atoms. Thus, Co(II) center lies in a distorted tetrahedral environment. L² ligand acts as a typical monodentate ligand coordinating to the Co(II) ion with the Co–N bond distances 2.029(3)– 2.048(3) Å, the N–Co–N angle being 106.24(13)°. In



Fig. 1 View of **a** the coordination environment of Co(II) ions in 1 **b** the 1-D chain by inter-plane C-H···Cl weak interactions of 1 **c** the 2-D sheet formed by the C-H···Cl and C-H···N weak interactions of 1 (H atoms omitted for clarity)



Fig. 2 View of the coordination environment of Zn(II) ions in 2 (H atoms omitted for clarity)

compared with ligand L^2 , we changed the one C atom of thiadiazine ring to N atom in due to add the site of coordination, but the N atom has not coordinated to the Co(II) ion.



Fig. 3 View of the coordination environment of Co(II) ions in 3(H atoms omitted for clarity)

In summary, three new complexes with (L^1) and (L^2) have been synthesized and structurally characterized. It is interesting that Complex 1 and 2 have the similar structure and general formula. The mononuclear structures of 1 and 2 were further assembled by the C-H···Cl and C-H···N weak interactions into an infinite 2-D supramolecular sheet. This result indicated that hydrogen-bonding interaction play an important role in the formation of supramolecular network structures.

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