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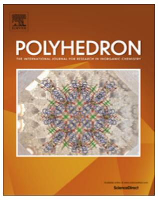

Synthesis and properties of three coordination compounds with a monodentate Schiff-base ligand

Zhao-Peng Qi [a,b,*], Jiao-Jiao Sun [a], Le-Le Zhu [a], Hui Zhang [a]

[a] School of Chemistry and Chemical Engineering, Huangshan University, Huangshan 245041, China
[b] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China

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ABSTRACT

Three new coordination compounds have been synthesized with new Schiff-base ligand (3-imidazole-1-yl-propyl)-(4-nitro-benzylidene)-amine (L), and their structures were characterized by X-ray crystallography. Interestingly, the coordination compounds have diverse structures from mononuclear $[Co(L)_4(SCN)_2]$ (**1**), dinuclear $[Cu_2(L)_4(SCN)_4]$ (**2**), to one-dimensional double chain polynuclear $[Cd(L)_2(SCN)_2]_n$ (**3**) with different coordination mode of thiocyanate anions. The results indicated that the metal ions have a remarkable impact on the frameworks of the coordination compounds. Also, the pH has moderate influence, and metal/ligand ratio, temperature have little influence on the formation of compounds **1**–**3**. Meanwhile, the magnetic susceptibility of coordination compound **2** and the photoluminescent property of coordination compound **3** are discussed.

1. Introduction

In the past decades, rational design and construction of one-(1D), two-(2D), and three-dimensional(3D) coordination polymers has been an active field due to its attractive topologies, as well as the potential applications in magnetism, gas adsorption, luminescence, biomimic functions, and so on [1–4]. In particular, the elaborate selection of organic ligands was found to be one of the most efficient ways to construct predefined architectures with well properties among the various influence factors like metal ions, anions, pH, temperature, solvents, etc. [2–4]. Recently, we focus our attention on novel imidazole-containing ligands and its derivates, for example, we once synthesized and investigated imidazolate-bridged dinuclear coordination compounds with imidazole-containing macrocyclic ligands, which acted as biomimics of copper(II)–zinc(II) superoxide dismutase (Cu_2Zn_2–SOD) [5]. In addition, Schiff-base and their coordination compounds were reported to exhibit unusual coordination, biological activities, fluorescence, magnetism properties [6,7]. Moreover, non-ligating substituents like nitro group have also aroused great interest and are used to construct functional materials lately [8]. Considering the above, and as an extension of our work, we designed a new Schiff-base ligand (3-imidazole-1-yl-propyl)-(4-nitro-benzylidene)-amine (L), and report herein three new coordination compounds $[Co(L)_4(SCN)_2]$ (**1**), $[Cu_2(L)_4(SCN)_4]$ (**2**), and $[Cd(L)_2(SCN)_2]_n$ (**3**) (Scheme 1). The synthesis conditions of coordination compounds are discussed. Meanwhile, the magnetic susceptibility of **2**, the photoluminescent property of ligand L and coordination compounds **1**–**3** are also investigated.

2. Experimental

2.1. Synthesis of the Schiff-base ligand L

1-(3-Aminopropyl)-imidazole (1.25 g, 0.01 mol) and 4-nitrobenzaldehyde (1.51 g, 0.01 mol) were stirred in 30 mL of methanol solution for 6 h, and then evaporated under reduced pressure. The residue was recrystallized from ethanol to get yellow powder (2.30 g, 89%). ^1H NMR: ($CDCl_3$, 500 MHz): $\delta = 8.36$ (s, 1H), 8.31 (s, 2H), 7.92 (s, 2H), 7.52 (s, 1H), 7.10 (s, 1H), 6.97 (s, 1H), 4.15 (t, 2H), 3.65 (t, 2H), 2.32 (t, 2H) ppm. UV–Vis, λ_{max} (nm) (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (DMF): 288 (15530).

2.2. Synthesis of the coordination compounds

2.2.1. Synthesis of $[Co(L)_4(SCN)_2]$ (1)

An ethanol solution (3 ml) of L (0.0125 g, 0.05 mmol) and KSCN (0.0097 g, 0.1 mmol) was added to an acetonitrile solution (3 ml) of $Co(ClO_4)_2{\cdot}6H_2O$ (0.0183 g, 0.05 mmol). The solution was filtered, and the filtrate was allowed to stand for several days, yellow crystals were obtained. Yield: (45%). Crystals **1** can also be obtained with pH

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* Corresponding author at: School of Chemistry and Chemical Engineering, Huangshan University, Huangshan 245041, China. Fax: +86 559 2546554.

E-mail address: zhaopengqi@hsu.edu.cn (Z.-P. Qi).

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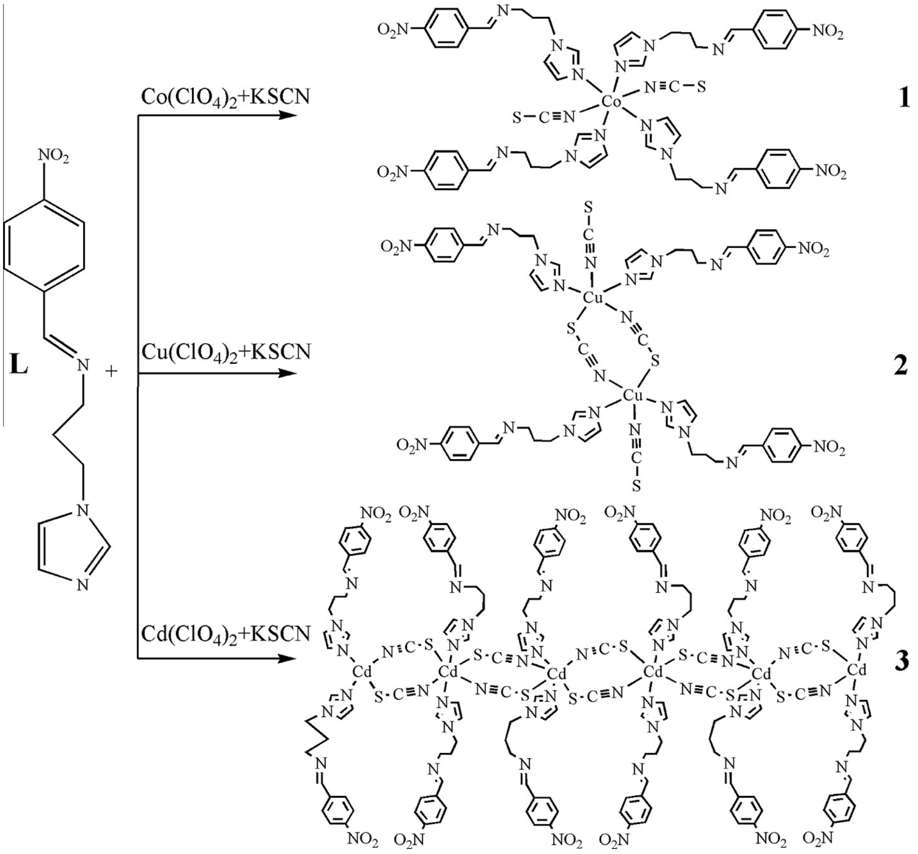

Scheme 1. Schematic drawing for formation of **1**–**3** with Schiff-base ligand L.

7–8 controlled by adding several drops of concentrated ammonia, or using NH_4SCN instead of KSCN, or $Co(NO_3)_2$ instead of $Co(ClO_4)_2$, or with metal/ligand ratio from 1:1:1 to 1:4:2. *Anal.* Calc. for $C_{54}H_{56}CoN_{18}O_8S_2$: C, 53.68; H, 4.67; N, 20.87. Found: C, 53.60; H, 4.78; N, 20.89%. IR: (KBr, cm^{-1}): 3414 (s), 3235(m), 2938 (w), 2842 (w), 2067(m), 1638 (s), 1617 (s), 1519 (m), 1457 (w), 1344 (m), 1106 (w), 832 (w), 747 (w), 622 (m). Solubility: Soluble in DMF, DMSO, and acetonitrile, insoluble in H_2O, methanol and ethanol. UV–Vis, λ_{max} (nm) (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (DMF): 288 (8716).

2.2.2. Synthesis of $[Cu_2(L)_4(SCN)_4]$ (**2**)

The single crystal of **2** was obtained by the same method used for **1** except that $Cu(ClO_4)_2{\cdot}6H_2O$ was used instead of $Co(ClO_4)_2{\cdot}6H_2O$. Green crystals were obtained after evaporation of the filtrate solution. Yield: (55%). Crystals **2** can also be obtained with pH 7–9 controlled by adding several drops of concentrated ammonia, or using NH_4SCN instead of KSCN, or $Cu(NO_3)_2$ instead of $Cu(ClO_4)_2$, or with metal/ligand ratio from 1:1:1 to 1:2:2. *Anal.* Calc. for $C_{56}H_{56}Cu_2N_{20}O_8S_4$: C, 48.30; H, 4.05; N, 20.12. Found: C, 48.18; H, 4.32; N, 20.26%. IR: (KBr, cm^{-1}): 3150 (w), 3126 (w), 2945 (w), 2845 (w), 2117(s), 2086 (vs), 1645 (m), 1602 (m), 1520 (s), 1455 (m), 1345 (s), 1233(m), 1099 (m), 851 (m), 829 (m), 749 (m). Solubility: Soluble in DMF, DMSO, slightly soluble in acetonitrile, insoluble in H_2O, methanol and ethanol. UV–Vis, λ_{max} (nm) (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (DMF): 272 (10503), 366 (1564).

2.2.3. Synthesis of $[Cd(L)_2(SCN)_2]_n$ (**3**)

The single crystal of **3** was obtained by the same method used for **1** except that $Cd(ClO_4)_2{\cdot}6H_2O$ was used instead of $Co(ClO_4)_2{\cdot}6H_2O$. Yellow crystals were obtained in 60% yield. Crystals **3** can also be obtained with pH 7–9 controlled by adding several drops of concentrated ammonia, or using NH_4SCN instead of KSCN, or $Cd(NO_3)_2$ instead of $Cd(ClO_4)_2$, or with metal/ligand ratio from 1:1:1 to 1:2:2. *Anal.* Calc. for $C_{28}H_{28}CdN_{10}O_4S_2$: C, 45.13; H, 3.79; N, 18.80. Found: C, 45.32; H, 3.72; N, 18.65%. IR: (KBr, cm^{-1}): 3115 (w), 2920 (w), 2851 (w), 2090 (vs), 1643 (w), 1600 (m), 1520 (s), 1447 (m), 1345 (s), 1229 (m), 1106 (w), 855 (m), 827 (m), 753 (m). Solubility: Soluble in DMF, DMSO, slightly soluble in acetonitrile, insoluble in H_2O, methanol and ethanol. UV–Vis, λ_{max} (nm) (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (DMF): 286 (12329).

Caution! Perchlorate salts of metal coordination compounds with organic ligands are potentially explosive. Only small amounts of materials should be prepared, and the samples should be handled with caution.

2.3. Physical measurements

All commercially available chemicals are of reagent grade and used as received without further purification. Elemental analyses for C, H and N were made on a Perkin-Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å), in which the X-ray tube was operated at 40 kV and 40 mA. Infrared (IR) spectra were recorded on a Nicolet 380 FT-IR spectrophotometer by using KBr pellets. Magnetic measurements were performed on a MPMS-SQUID magnetometer at a field of 2000G on crystalline samples in the range of 1.8–300 K. The luminescence spectra for the samples were measured at room temperature on a Hitachi F-4500 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 10 nm.