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Synthesis and structural characterization of zinc(II) and cobalt(II) complexes based on multidentate hydrazone ligands

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ABSTRACT

Two multidentate Schiff base ligands containing a hydrazone unit have been synthesized and investigated for zinc(II) and cobalt(II) coordination chemistry. The reactions of the 4-pyridyl derived hydrazone ligand HL1 with zinc(II) or cobalt(II) salts gave three mononuclear complexes that were structurally characterized by X-ray diffraction analysis. The results revealed that the ligand could adopt different coordination modes when various counter anions were employed. While in the case that zinc dichloride was used as a metal salt a neutral mononuclear mono-ligand complex was formed, the deprotonation of hydrazone occurred when zinc(II) or cobalt(II) nitrate were present and two new isostructural mononuclear bis-ligand complexes were isolated. Modification of the hydrazone ligand with oxygen donors was found to have a significant impact on the ligand reactivity, and a similar reaction of H_2L2 with cobalt(II) nitrate gave a protonated product of H_2L2 without the incorporation of cobalt(II), which features a one-dimensional hydrogen-bonded network in the solid state.

1. Introduction

Schiff base-type ligands remain continuingly an important class of organic compartments for metal complexation, owing to their ready availability and facile structural modification [1,2]. In recent years, transition metal complexes of Schiff base ligands have attracted increasing attention from chemists for their widespread applications in molecular recognition, catalysis, and luminescence and magnetic materials [3–10]. Aroyl hydrazones constitute of a versatile type of Schiff base compounds that contain strong electron-donating N,O-chelating site for metal ions. Interests in coordination chemistry of such ligands have been focused on the introduction of additional coordination sites by using both aldehyde and hydrazide precursors, which brings possible expansion of structures from simple coordination complexes to complex supramolecules or polymeric networks that have been applied in functional materials, catalysis and as potential biological agents [11–17]. Aroyl hydrazones containing both a tridentate chelating site and an extra N-donating site such as ligands HL1 and H_2L2 (Scheme 1) can be readily approached through the effective condensation of isonicotinoyl hydrazide and pyridine-2-carbaldehyde or salicylaldehyde derivatives. This type of organic compounds have been extensively explored for their promising applications as effective antimicrobial agents [18–21]. In addition, they have been employed in metal-mediated self-assembly because of the strong ability of the hydrozone moiety in chelating metal ions [22]. Particular attention has also been paid to the utilization of such ligands as metalloligands in constructing extended multidimensional metal-organic frameworks, as the possible deprotonation of the hydrazone unit under proper pH conditions allows the formation of stable mononuclear metal complexes containing extra binding sites for further metal coordination [23]. Although transition metals such as Cu^{II}, Co^{II}, Cd^{II}, Ni^{II} and Mn^{II} were often chosen to study on the coordination chemistry of these ligands as well as their biological activity, coordination chemistry of the ligands with Zn^{II} remains little investigated [24–30].

In this work, we report on the synthesis and structural characterization of new zinc(II) and cobalt(II) complexes based on HL1 and the crystal structure of a nitric acid adduct of H_2L2 which was formed unexpectedly from the reaction of H_2L2 with cobalt(II)

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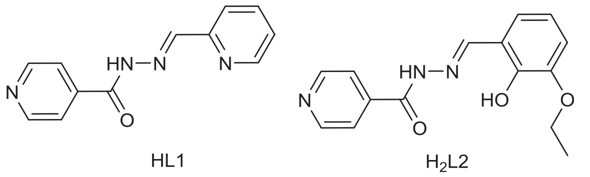

Scheme 1. The molecular structures of hydrazone ligands studied in this work.

nitrate.

2. Experimental

2.1. General

Solvents and reagents were purchased from Fisher Scientific or Sigma–Aldrich in the US. All reactions were performed under ambient conditions (no inert atmosphere). FT-IR spectra were measured on a Shimadzu 8400S instrument with solid samples using a Golden Gate ATR accessory. ^1H and ^{13}C NMR spectra were obtained at room temperature on a Bruker III 500 MHz spectrometer with TMS as an internal standard. High resolution mass spectra were recorded on an Agilent 6550 iFunnel ESI-QTOF-LC/MS instrument. Elemental Analyses were performed by Midwest Microlab LLC in Indianapolis. Ligand HL1 and H_2L2 were prepared according to published procedures in the literature [22,31].

2.2. Synthesis of complex **1**

HL1 (22.6 mg, 0.100 mmol) was dissolved in CH_2Cl_2–MeOH (10 mL, 1:1, v/v) in a 25 mL vial, to which a methanol solution of $ZnCl_2$ (40.2 mg, 0.300 mmol) was added upon stirring at room temperature. The resulting solution was allowed to stir for 30 min and then filtered. Slow evaporation of the filtrate over 5 days gave light yellow crystals, which were suitable for X-ray diffraction analysis. The product was collected by filtration, washed with CH_3OH and dried in air. Yield: 27.4 mg (76% based on HL1). FT-IR (solid, cm^{-1}): 3156 w, 1647 s, 1597 w, 1535 s, 1470 m, 1442 w, 1413 m, 1351 s, 1294 s, 1213 m, 1163 m, 1093 w, 1016 m, 936 m, 843 m, 778 s, 706 s, 694 s, 640 w. ^1H NMR (500 MHz, DMSO-d_6) δ 12.28 (s, 1H), 8.81 (d, $J = 6.0$ Hz, 2H), 8.65 (d, $J = 5.0$ Hz, 1H), 8.49 (s, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 7.92 (t, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 5.5$ Hz, 2H), 7.46 (t, $J = 5.5$ Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.86, 152.89, 150.37, 149.60, 149.15, 140.22, 137.00, 124.69, 121.56, 120.06 ppm. Anal. Calcd. for $C_{12}H_{10}Cl_2N_4OZn$: C 39.76, H 2.78, N 15.46%. Found C 39.75, H 2.75, N 15.43%.

2.3. Synthesis of complex **2**

The procedure is similar to that for **1**, except for the replacement of $ZnCl_2$ with $Zn(NO_3)_2 \cdot 6H_2O$ (29.6 mg, 0.100 mmol). After one week, yellow blocks of **2** were collected by filtration, washed with CH_3OH and dried in air. Yield: 20.5 mg (64% based on HL1). FT-IR (solid, cm^{-1}): 1614 s, 1564 m, 1481 s, 1422 w, 1359 s, 1315 w, 1283 s, 1154 s, 1071 m, 1015 s, 919 w, 858 m, 790 m, 766 s, 718 s. ^1H NMR (500 MHz, DMSO-d_6) δ 12.28 (s, 2H), 8.83 (s, 4H), 8.64 (s, 2H), 8.48 (s, 2H), 8.00 (d, $J = 7.5$ Hz, 2H), 7.94 (d, $J = 7.0$ Hz, 2H), 7.86 (s, 4H), 7.45 (s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 150.38, 149.58, 149.16, 136.99, 129.62, 124.70, 124.69, 123.10, 121.56, 120.07 ppm. Anal. Calcd. for $C_{24}H_{22}N_{10}O_8Zn$: C 44.77, H 3.44, N 21.75%. Found C 44.38, H 3.35, N 21.66%.

2.4. Synthesis of complex **3**

The procedure is similar to that for **1**, except for the replacement of $ZnCl_2$ with $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.100 mmol). After one week, purple crystals of **3** were collected by filtration, washed with CH_3OH and dried in air. Yield: 21.6 mg (68% based on HL1). FT-IR (solid, cm^{-1}): 3074br, 1637 m, 1534 m, 1484 m, 1449 s, 1379 s, 1338 s, 1290 s, 1214 m, 1150 m, 1074 m, 1034 w, 929 w, 839 w, 779 m, 752 m, 717 m, 601 m. Anal. Calcd. for $C_{24}H_{22}CoN_{10}O_8 \cdot 2CH_3OH$: C 44.52, H 4.31, N 19.97%. Found C 44.01, H 4.25, N 19.63%.

2.5. Synthesis of **4**

H_2L2 (28.5 mg, 0.100 mmol) was dissolved in CH_2Cl_2–MeOH (10 mL, 1:1, v/v) in a 25 mL vial, to which a methanol solution of $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.100 mmol) was added upon stirring at room temperature. The resulting solution was allowed to stir for 30 min and then the brown precipitate was filtered out. Slow evaporation of the resulting filtrate for one week gave light-orange crystals. The product was collected by filtration, washed with CH_3OH and dried in air. Yield: 13.5 mg. A 1: 1 adduct of ligand L2 and nitric acid without the involvement of metal ions was determined by X-ray structural analysis. In a separate synthesis, **4** can also be obtained in a quantitative yield by slow evaporation of a CH_2Cl_2–MeOH solution of H_2L2 and aqueous nitric acid (2.0 equiv.). FT-IR (solid, cm^{-1}): 3100br, 1677 s, 1604 s, 1552 w, 1503 w, 1458 m, 1404 m, 1354 m, 1283 m, 1251 s, 1118 w, 1005 w, 960 w, 882 m, 840 s, 788 s, 749 s, 683 s. ^1H NMR (500 MHz, CD_3OD) δ 7.92 (d, $J = 5.5$ Hz, 2H), 7.66 (s, 1H), 7.25 (d, $J = 6.0$ Hz, 2H), 6.23 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.19 (d, $J = 7.5$ Hz, 1H), 6.14 (d, $J = 7.5$ Hz, 1H), 6.10 (t, $J = 7.5$ Hz, 1H), 6.04 (d, $J = 8.0$ Hz, 1H), 5.88 (t, $J = 8.0$ Hz, 1H), 3.12 (q, $J = 7.0$ Hz, 2H), 0.43 (t, $J = 7.0$ Hz, 3H) ppm. ^{13}C NMR (125 MHz, CD_3OD) δ 159.66, 149.66, 144.64, 127.23, 126.53, 123.61, 122.53, 119.77, 117.92, 117.19, 114.16, 63.21, 12.41 ppm. HR-MS: m/z 286.1208 $[M + H]^+$ (calc. 286.1192). Anal. Calcd. for $C_{15}H_{16}N_4O_6$: C 51.72, H 4.63, N 16.09%. Found C 51.65, H 4.61, N 15.88%.

2.6. X-ray structural determinations

Suitable crystals of **1**–**4** were mounted on Cryoloops with Paratone-N oil. Data were collected with a Bruker APEX II CCD using Mo–Kα radiation and corrected for absorption with SADABS and structures solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2. Hydrogen atoms were found from Fourier difference maps and refined isotropically, otherwise they were placed in calculated positions with appropriate riding parameters. The structural refinement data is summarized in Table 1. Crystal structures and packing figures were drawn with the program Mercury v. 2.4.

3. Results and discussion

3.1. Synthesis and crystal structure of **1**

Ligand HL1 was prepared by the Schiff base condensation of isonicotinoyl hydrazide and pyridine-2-carbaldehyde in high yield, and its spectroscopic data and structure have been previously reported (Fig. 1c) [22–26]. The reaction of HL1 with one equivalent of zinc dichloride in a CH_2Cl_2–MeOH solution afforded colourless crystals of **1** suitable for X-ray diffraction analysis after slow evaporation. Elemental analysis data reveals an empirical formula of $Zn(HL1)Cl_2$, suggesting a 1:1 metal–ligand complex. **1** is poorly soluble in common solvents, yet soluble in dimethyl sulfoxide (DMSO). The ^1H NMR spectrum of **1** in DMSO-d_6 reveals a single set of signals corresponding to the protons in HL1. X-ray structural