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 H₂L2 with cobalt(II) nitrate gave a protonated product of H₂L2 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 H₂L2 (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 H₂L2 which was formed unexpectedly from the reaction of H₂L2 with cobalt(II) nitrate.

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

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 ¹³C 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 H₂L2 were prepared according to published procedures in the literature [22, 31].

2.2. Synthesis of complex *I*

HL1 (22.6 mg, 0.100 mmol) was dissolved in CH₂Cl₂-MeOH (10 mL, 1:1, v/v) in a 25 mL vial, to which a methanol solution of ZnCl₂ (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 CH₃OH and dried in air. Yield: 27.4 mg (76% based on HL1). FT-IR (solid, cm⁻¹): 3156w, 1647s,

1597w, 1535s, 1470m, 1442w, 1413m, 1351s, 1294s, 1213m, 1163m, 1093w, 1016m, 936m, 843m, 778s, 706s, 694s, 640w. ^1H NMR (500 MHz, DMSO- d_6) δ 12.28 (s, 1 H), 8.81 (d, J = 6.0 Hz, 2 H), 8.65 (d, J = 5.0 Hz, 1 H), 8.49 (s, 1 H), 8.01 (d, J = 8.0 Hz, 1 H), 7.92 (t, J = 7.5 Hz, 1 H), 7.85 (d, J = 5.5 Hz, 2 H), 7.46 (t, J = 5.5 Hz, 1 H) 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 $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_4\text{OZn}$: 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 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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}): 1614s, 1564m, 1481s, 1422w, 1359s, 1315w, 1283s, 1154s, 1071m, 1015s, 919w, 858m, 790m, 766s, 718s. ^1H NMR (500 MHz, DMSO- d_6) δ 12.28 (s, 2 H), 8.83 (s, 4 H), 8.64 (s, 2 H), 8.48 (s, 2 H), 8.00 (d, J = 7.5 Hz, 2 H), 7.94 (d, J = 7.0 Hz, 2 H), 7.86 (s, 4 H), 7.45 (s, 2 H) 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 $\text{C}_{24}\text{H}_{22}\text{N}_{10}\text{O}_8\text{Zn}$: 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 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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, 1637m, 1534m, 1484m, 1449s, 1379s, 1338s, 1290s, 1214m, 1150m, 1074m, 1034w, 929w, 839w, 779m, 752m, 717m, 601m. Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{CoN}_{10}\text{O}_8 \cdot 2\text{CH}_3\text{OH}$: C 44.52, H 4.31, N 19.97%. Found C 44.01, H 4.25, N 19.63%.

2.5. Synthesis of **4**

$\text{H}_2\text{L2}$ (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 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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 CH₃OH 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 CH₂Cl₂-MeOH solution of H₂L2 and aqueous nitric acid (2.0 equiv.). FT-IR (solid, cm⁻¹): 3100br, 1677s, 1604s, 1552w, 1503w, 1458m, 1404m, 1354m, 1283m, 1251s, 1118w, 1005w, 960w, 882m, 840s, 788s, 749s, 683s. ¹H NMR (500 MHz, CD₃OD) δ 7.92 (d, *J* = 5.5 Hz, 2 H), 7.66 (s, 1 H), 7.25 (d, *J* = 6.0 Hz, 2 H), 6.23 (dd, *J* = 7.5, 1.5 Hz, 1 H), 6.19 (d, *J* = 7.5 Hz, 1 H), 6.14 (d, *J* = 7.5 Hz, 1 H), 6.10 (t, *J* = 7.5 Hz, 1 H), 6.04 (d, *J* = 8.0 Hz, 1 H), 5.88 (t, *J* = 8.0 Hz, 1 H), 3.12 (q, *J* = 7.0 Hz, 2 H), 0.43 (t, *J* = 7.0 Hz, 3 H) ppm. ¹³C NMR (125 MHz, CD₃OD) 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 C₁₅H₁₆N₄O₆: C 51.72, H 4.63, N 16.09%. Found C 51.65, H 4.61, N 15.88%.

Table 1. Structural Refinement Data for Compounds **1-4**.

Compound	1	2	3	4
Formula	C ₁₂ H ₁₀ Cl ₂ N ₄ OZn	C _{25.50} H ₂₆ N ₁₀ O _{9.5} Zn	C ₂₆ H ₂₈ CoN ₁₀ O ₁₀	C ₁₅ H ₁₆ N ₄ O ₆
Formula Weight	362.51	689.93	699.51	348.32
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	7.4641(12)	10.2802(5)	10.6163(15)	6.7534(6)
<i>b</i> /Å	18.185(3)	11.8499(6)	10.8622(14)	6.9666(5)
<i>c</i> /Å	10.1607(15)	14.1794(6)	14.010(2)	16.5537(16)
<i>α</i> /°	90	102.048(2)	104.227(4)	81.186(5)
<i>β</i> /°	102.613(3)	107.0650(10)	103.937(5)	81.253(5)
<i>γ</i> /°	90	110.5430(10)	104.384(4)	81.675(4)
<i>U</i> /Å ³	1345.9(4)	1449.50(12)	1436.3(3)	754.77(11)
<i>D_c</i> /Mg m ⁻³	1.789	1.581	1.617	1.533
<i>Z</i>	4	2	2	2
<i>μ</i> /mm ⁻¹	2.220	0.921	0.675	0.121
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)
Reflections/Unique	11996/2755	5584/4414	5884/4446	11847/3095
Parameters	184	394	394	236
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0313, 0.0738	0.0410, 0.1012	0.0504, 0.1190	0.0371, 0.0880
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0392, 0.0769	0.0562, 0.1061	0.0719, 0.1291	0.0536, 0.0973
GOF	1.027	1.061	1.045	1.034

^a*R*₁ = (*F*_o − *F*_c)/*F*_o. ^b*wR*₂ = [*w*(*F*_o² − *F*_c²)²/*w*(*F*_o)²]^{1/2}

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-K α 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. 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 CH₂Cl₂-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)Cl₂, 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 analysis confirmed the formation of a mononuclear mono-ligand complex and the structure is drawn in Fig. 1a. **1** crystallizes in the monoclinic space group *P*2(1)/*c* and in the asymmetric unit there contains only one independent molecule of **1**. Relevant bond parameters that are unexceptional are listed in the caption of Fig. 1. The zinc(II) center is bound within the chelating site of the ligand as expected, and thus zinc(II) ion resides in a pentacoordinate environment with two chloride anions and the NNO donor set including 2-pyridyl N, imine N and amide O atoms. It was noticed that the outer 4-pyridyl N remains uncoordinated, even though an excess amount of ZnCl₂ was used. Previously, while extended polymeric networks involving additional 4-pyridyl-N coordination were often observed when the same ligand was reacted with ZnSO₄ or various cadmium salts [24, 26], mononuclear zinc(II) complex with this ligand was unknown, indicating the coordination versatility of this type of ligand. It was also found that in **1** the amide N3 atom is not deprotonated, remaining the N3-C7 bond ca. 0.08 Å longer than N2-C6 imine bond, although the deprotonation of this

nitrogen atom frequently occurred upon metal complexation with HL1 [24–30]. Molecules of **1** pack along the crystallographic *a* axis through both significant intermolecular N–H...Cl hydrogen bonds and π -stacking interactions. The molecules arrange in an alternate head-to-tail fashion to form a columnar packing as shown in Fig. 1b. Specifically, each amide NH acts as a hydrogen bonding donor to form bifurcated hydrogen bonds with two adjacent Cl acceptors that are bonded to the zinc(II) centers, and the Cl...N...Cl angle for the bifurcated H-bonds is 69.14° and the N–H...Cl distances are 3.277(2) and 3.264(2) Å, respectively. Meanwhile, effective π -stacking also occurs between the adjacent molecules of **1** owing to the conjugation and co-planarity of hydrazone ligands. The closest interatomic distance for the π -stacking is approximately 3.339 Å.

Fig. 1. (a) The crystal structure of **1**. Selected bond parameters: Zn1–N1 = 2.2524(7), Zn1–N2 = 2.142(2), Zn1–Cl1 = 2.2453(7), Zn1–Cl2 = 2.2240(7), Zn1–O1 = 2.2660(18), N2–C6 = 1.285(3), N2–N3 = 1.363(3), N2–C6 = 1.285(3), N3–C7 = 1.362(3), C7–O1 = 1.233(3) Å; Cl2–Zn1–Cl1 = 116.42(3), N1–

Zn1-O1 = 144.88(7), Cl1-Zn1-N1 = 105.16(6), O1-Zn1-Cl1 = 94.77(5)°. (b) The ball-stick representation of the molecular packing in **1** along crystallographic *a* axis showing intermolecular C-H...Cl hydrogen bonding.

3.2. Syntheses and Crystal Structures of **2** and **3**

The mononuclear mono-ligand structure observed in **1** that is different from the zinc(II) coordination polymer previously reported can be attributed to the effect of counter anions. We, therefore, studied the reaction of zinc(II) nitrate with HL1. Thus, the reaction similar to that for **1** was conducted by replacing zinc dichloride with zinc nitrate in a CH₂Cl₂-MeOH solution and yellow crystals of **2** were isolated after solvent evaporation over one week. Elemental analysis of dried bulky sample suggested a metal-to-ligand ratio of 1 : 2 in **2**, distinct with that of **1**. Furthermore, X-ray structural analysis also confirmed the formation of a mononuclear bis-ligand complex. **2** crystallizes in the triclinic space group *P*-1 and one independent complex molecule is found in the unsymmetric unit. Zinc(II) is hexacoordinate with two NNO chelating sites from two distinct ligand molecules, being in an octahedral coordination environment (Fig. 2a). In contrast to **1**, in **2** the amide N atoms of both ligands are deprotonated. In general, the Zn-N and Zn-O bond lengths are in the range of 2.036-2.195 Å, slightly shorter than those found in **1**, yet the Zn-N1_{pyridyl} bond (~2.322 Å) is significantly longer than others. It was interesting to note that although the outer 4-pyridyl N atoms remain uncoordinated again, they are protonated by two protons presumably coming from those generated by deprotonation of the amide units. Similar protonation has been observed in the structure of Co^{III}(L1)(HL1)(NO₃)₂ reported by Bernhardt and coworkers, in which, however, only one of two coordinated HL1 molecules was protonated [26]. Both protonated N atoms are hydrogen bonded to two nitrate counterions (N4...O4 = 2.732(3) Å, <N4-H...O4 = 176(3)°; N8...O6 = 2.647(3) Å, <N8-H...O6 = 171(3)°). Further inspection of intermolecular packing interactions discloses effective π -stacking between conjugated ligands from adjacent complexes that are illustrated in Fig. 2b as yellow and grey colours, respectively. The closest interatomic distance responsible for the π -stacking is 3.397 Å.

Given the different structures observed in complexes **1** and **2**, resulting from the use of zinc salts with distinct counter ions, we were interested to explore the influence of other transition metals such as cobalt, while remaining the same nitrate anions as used for the synthesis of **2**. Thus, the reaction of HL1 with cobalt(II) nitrate under conditions identical to

that for **2** gave purple crystals of **3** that are suitable for X-ray diffraction studies. **3** has a formula of $\text{Co}(\text{HL1})_2(\text{NO}_3)_2$ and was found to be isomorphic to **2** except the replacement of zinc(II) center with cobalt(II) (Fig. 2c). Interestingly, although cobalt complexes including either Co^{II} or Co^{III} centers built on the same ligand were previously reported [26], the structure of **3** is essentially different. This is not unusual as it is found that the conditions for the reactions between HL1 and $\text{Co}(\text{NO}_3)_2$ can be determining factors for the formation of different cobalt products. The only known cobalt(II) complex $\text{Co}(\text{L1})_2$ in the literature was prepared in the presence of excess amount of triethylamine, a base to promote deprotonation of both ligand molecules, leading to a neutral product. In contrast, all cobalt(III) complexes with this ligand were made through the self-oxidation of Co^{II} precursor by heating in the air [26].

(a)

(b)

Fig. 2. (a) The ORTEP structure of **2** with ellipsoids plotted at the 50% probability level. Selected bond parameters: Zn1-N2 = 2.036(2), Zn1-N6 = 2.098(2), Zn1-O1 = 2.1105(17), Zn1-N5 = 2.147(2), Zn1-O2 = 2.1951(18), Zn1-N1 = 2.322(2), O1-C7 = 1.273(3), O2-C19 = 1.245(3), N2-C6 = 1.270(3), N2-N3 = 1.388(3), N3-C7 = 1.326(3), N6-N7 = 1.373(3), N6-C18 = 1.267(3), N7-C19 = 1.352(3) Å; N2-Zn1-N6 = 161.67(8), N1-Zn1-N5 = 97.24(8), N2-Zn1-N5 = 108.79(8), O1-Zn1-O2 = 95.74(7), N2-Zn1-O1 = 76.46(7)°. (b) Part of molecular packing in **2** showing intermolecular π -stacking interactions. (c) The X-ray crystal structure of complex **3** showing it is isostructural to **2**. Selected bond angle (Å): Co1-N2 = 1.854(2), Co1-N6 = 1.857(2), Co1-O1 = 1.923(2), Co1-N5 = 1.934(3), Co1-O2 = 1.918(2), Co1-N1 = 1.929(2).

3.3. Synthesis and Crystal Structure of **4**

The structural diversity of complexes based on HL1 discussed above urged us to further investigate the reactions of another hydrazone derivative, H₂L2 (Scheme 1) [31]. A preliminary attempt was made to synthesize a cobalt complex by reacting H₂L2 with cobalt(II) nitrate hexahydrate under the same conditions used for the preparation of complexes **1-3**. However, the crystalline product obtained from this experiment was determined to be a simple adduct H₂L2·HNO₃ (**4**), in addition to some unidentified precipitate from the reaction. The crystal structure of **4** has been analyzed by single-crystal X-ray diffraction. In a separate experiment, **4** was also isolated in high yield directly by mixing H₂L2 with aqueous HNO₃ (2.0 equiv.). X-ray structural analysis reveals that **4** crystallizes in the triclinic space group *P*-1. The ORTEP representation of adduct **4** is shown in Fig. 3a and the unsymmetric unit contains one independent pyridyl-N protonated H₃L2 cation and a nitrate counterion. Both intra-

and inter-molecular hydrogen bonding interactions were observed in the crystals, which served to generate a one-dimensional hydrogen bonded network, as shown in Fig. 3b and relevant hydrogen bonding parameters are listed in the caption of Fig. 3. Specifically, the intramolecular hydrogen bond occurs between the phenol donor and the imine N3 acceptor, and intermolecular hydrogen bonds contain those between nitrate oxygen donors and the amide NH donor of ligand or protonated pyridyl NH. Thus, the protonated ligand molecules arrange along the crystallographic *b* axis mediated by nitrate groups to form an infinite sheet-like structure (Fig. 3b).

Although ligand H₂L2 has been previously prepared and structurally characterized [31], its nitric acid adduct **4** was unknown. In the present work, we were unable to isolate and structurally characterize any cobalt complexes by using this ligand, yet it is likely that some unidentified cobalt complexes had formed during the reaction. Further investigation will be desired to understand the coordination chemistry of this ligand with transition metals. In addition, an initial ligand deprotonation might be required for it to subsequently coordinate with metal ions.

(a)

Fig. 3. (a) The ORTEP representation of **4** with ellipsoids plotted at the 50% probability level. Selected bond length (Å): O1-C6 = 1.2177(18), O2-C9= 1.3551(18), N2-C6 = 1.357(2), N2-N3 = 1.3763(17), N3-C7 = 1.283(2). (b) A one-dimensional hydrogen-bonded network found in the crystals of **4**. H-bond parameters: O2-H...N3 = 2.5874(16) Å, $\angle$ O2-H...N3 = 150.8(16)°; N1-H...O4ⁱ = 2.8157(17) Å, $\angle$ N1-H...O4ⁱ = 159.0(18)°; N2-H...O5 = 2.9815(17) Å, $\angle$ N2-H...O5 = 165.6(17)°. Symmetry code: *i* = - *x*, - *y*, - *z*.

4. Conclusions

In summary, we have studied the coordination chemistry of two hydrazone ligands with zinc(II) and cobalt(II) ions. It was revealed that the use of different counter anions (Cl⁻ or NO₃⁻) of zinc(II) salts have influenced the structures of the resulting coordination complexes, although both feature simple mononuclear complexes. While the presence of coordinating anion Cl⁻ tends to saturate the coordination sphere of zinc(II) center by affording neutral complex, the use of weakly coordinating anion NO₃⁻ was responsible for the hydrazone deprotonation as well as pyridyl-N protonation of ligand HL1 observed in the bis-ligand ionic complex. In addition, structural modification on the hydrazone moiety was found to drastically affect their reactivity towards metal ions, and the coordination chemistry of such ligand derivatives deserves further exploration.

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