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Four polynuclear complexes based on a versatile salicylamide salen-like ligand: Synthesis, structural variations and magnetic properties

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ABSTRACT

Four new polynuclear complexes based on a versatile asymmetric ligand, $[Cu_2(H_2L)_2Cl_2]$ (**1**), $[Cu_4(H_2L)_2(L)_2]\cdot 4CH_3OH$ (**2**), $[MnL]_n$ (**3**), $[Er_2(HL)_2(NO_3)_4]\cdot 4CH_3CN$ (**4**), H_3L = 2-hydroxy-N-(2-((2-hydroxybenzylidene)amino)ethyl)benzamide], were prepared and structurally characterized. The coordination behavior as well as deprotonation of the H_3L in the four complexes reveal considerable variations depending on the metal ions as well as counter anion. The hydroxyl-bridged dinuclear complex **1** with a Cu–O–Cu–O four-membered ring was obtained when copper chloride was used as metal source. The tetranuclear complex **2** with two Cu–O–Cu–O four-membered rings which bridged both through hydroxy and amide group was obtained using copper acetate instead. Reacting the ligand with manganese acetate yielded complex **3** which exhibits 1-D zig–zag chains only bridged through amide group. While complex **4** which holds a dinuclear one by aid of hydroxyl-bridge without nitrogen atom participating in coordination when erbium nitrate was introduced. The experimental magnetic susceptibilities indicate **1**, **2** and **4** exhibit antiferromagnetic interactions through hydroxy bridge, while **3** exhibits dominant antiferromagnetic interactions with spin canting through the amido bridge.

1. Introduction

Polynuclear metal complexes exhibit a fascinating variety of unusual symmetries and structural patterns [1]. The potentially important functions in magnetic behavior [2], optical materials [3], catalytic [4] and biological activities [5] add to their interest and significance. The possibility of obtaining multifunctional materials comes from the structure and flexibility for structural design of these compounds. However, the rational construction of desirable architectures remains a long-term challenge due to the wide range of factors which may influence structures of coordination compounds, including organic ligand, metal ion, solvent system, pH value of the solution, the metal-to-ligand ratio, counter anions, etc [6]. Among these, the organic ligand is an important factor undoubtedly. On the other hand, metal ions, especially their radii and coordination geometry, determine the extending directions important for the structure of the complexes. Therefore, much more work is required to establish proper synthetic strategies that can lead to the desired species with predictable structures and properties.

Multidentate organic ligands based on N- and O-donors have been witnessed to be excellent structural constructors due to their various coordination modes related to metal ions. Up to now, a number of polynuclear compounds with chelating-bridging organic ligands based on N- and O-donors have received considerable attention because they can incorporate virtues of different functional groups and it is easier to get architecture controlled by delicate modification [7–10]. In addition, salicylamide salen-like ligands are alterative excellent ligands because of their interesting features as follows: (a) they have multiple O- and N-coordination sites together with hydrogen-bond acceptors as well as hydrogen bond donors, which are good candidates for the assembly of novel 3d, 4f or 3d–4f architectures; (b) they have abstractable protons that allow various acidity dependant coordination modes, and as a result different structures can be constructed via changing only the pH values while using the same reagents; (c) This kind of ligands can be good choices to construct coordination compounds because the flexible nature of spacers between the amide and imine groups allow the ligands to bend and rotate to adapt somewhat to the changing size of the host metal ions. However, there are few reports on compounds base on salicylamide salen-like ligands. To date, some Mn(III) CPs with ligands incorporating salicylamide derivatives have been isolated [11,8a], and the previously results showed that substituted groups

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of this kind of ligands can impact the coordination structures as well as the magnetic properties effectively. This observation prompted us to extend the synthesis of this kind of ligands together with their complexes.

In the present work, two transition metal elements, Mn^{II} and Cu^{II}, and one lanthanide element, Er^{III}, are selected to investigate metal ion effects on the coordination ability of the ligand. As a result, four new complexes which were determined by single-crystal X-ray diffraction analyses and further characterized by elemental analysis, infrared spectra (IR), thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) were obtained: $[Cu_2(H_2L)_2Cl_2]$ (**1**), $[Cu_4(H_2L)_2(L)_2]\cdot 4CH_3OH$ (**2**), $[MnL]_n$ (**3**), $[Er_2(HL)_2(NO_3)_4]\cdot 4CH_3OH$ (**4**). Their magnetic properties were investigated and the results indicate **1**, **2** and **4** exhibit antiferromagnetic interactions through hydroxy bridge, while **3** exhibits dominant antiferromagnetic interactions with spin canting through the amido bridge.

2. Experimental

2.1. Materials and instrumentation

All chemicals and solvents were obtained from commercial sources and used as received. N-(2-aminoethyl)-2-hydroxybenzamide was prepared according to the literature [12].

Carbon, nitrogen, and hydrogen analyses were performed using an EL elemental analyzer. Melting points were determined on a Kofler apparatus. Powder X-ray diffraction patterns (PXRD) were determined with Rigaku-D/Max-II X-ray diffractometer with graphite-monochromatized Cu Kα radiation. Thermogravimetric analyses were carried out on a SDT Q600 thermogravimetric analyzer from room temperature to 800 °C under N_2 atmosphere. A platinum pan was used for heating the sample with a heating rate of 10 °C/min. Infrared spectra (4000–400 cm^{-1}) were obtained with KBr discs on a Nicolet FT-170SX instrument in the wavenumber range of 4000∼400 cm^{-1} with an average of 128 scans and 4 cm^{-1} of spectral resolution. ^1H NMR spectra were recorded in $CDCl_3$ solution at room temperature on a Bruker 400 instrument operating at a frequency of 400 MHz and referenced to tetramethylsilane (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet and m = multiplet. The magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS SQUID magnetometer.

2.2. Synthesis of the ligand

The synthetic route for 2-hydroxy-N-(2-((2-hydroxybenzylidene)amino)ethyl)benzamide (H_3L) is shown in Scheme 1. 10 mmol (1.22 g) salicylaldehyde in 10 mL anhydrous ethanol was added dropwise in 10 min to a 10 mL ethanol solution of 10 mmol (1.80 g) N-(2-aminoethyl)-2-hydroxybenzamide. The resulted mixture was stirred and heated at reflux for 4 h. Then the mixture was allowed to stand overnight at room temperature. The crude product was separated by filtration and further recrystallized with ethanol to give a yellow solid which was washed with diethyl ether and dried in air. H_3L: 2.16 g, Yield 76.0%. m.p. 135–136 °C. *Anal.* Calc. for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.81, H, 5.65, N, 9.87%; IR (KBr, υ, cm^{-1}): 3381 (w), 1633 (s), 1594 (s), 1553 (s), 1490 (m), 1449 (m), 1360 (m), 1276 (m), 1230(m), 823 (m), 781 (m), 753 (s). ^1H NMR ($CDCl_3$, 400 MHz): δ: 3.80 (m, 2H, CH_2), 3.85 (m, 2H, CH_2), 6.71 (s, 1H, ArH), 6.80 (m, 1H, ArH), 6.88 (m, 1H, ArH), 6.97 (m, 1H, ArH), 7.23(m, 1H, ArH), 7.35 (m, 3H, CH=N), 8.41 (t, 1H, NH, J = 4 Hz), 12.21(s, 2H, OH).

2.3. Synthesis of the complexes

To the acetonitrile solution of 0.1 mmol (0.028 g) H_3L, 0.1 mmol metal salt was added and the solution was stirred for another 4 h to obtain a suspension. To this turbid solution 5 mL methanol was add to obtain a clear solution. The mixture was filtered into a sealed 10–20 mL glass vial for crystallization at room temperature. After about two weeks single crystals suitable for crystal analysis were obtained.

$[Cu_2(H_2L)_2Cl_2]$ (**1**) The empirical formula and the molecular weight is $C_{32}H_{30}Cl_2Cu_2N_4O_6$ and 764.60 respectively. Yield: 22 mg, 58% based on $CuCl_2\cdot 2H_2O$). *Anal.* Calc. for C, 50.27; H, 3.95; N, 7.33. Found: C, 50.48; H, 3.96; N, 7.30%; IR (KBr, ν, cm^{-1}): 3360(m), 1608 (s), 1533 (s), 1477(s), 1288 (s), 1209 (m), 1157 (m), 816 (w), 755 (s).

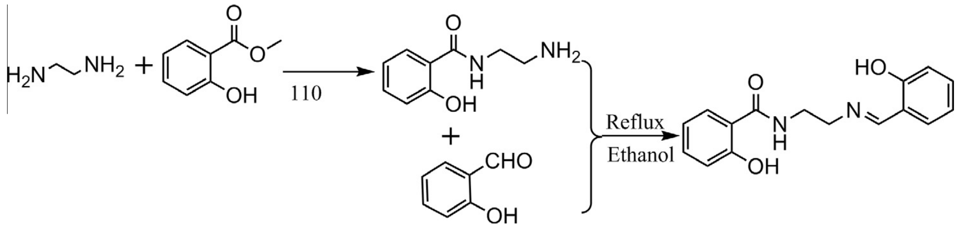
$[Cu_4(H_2L)_2L_2]\cdot 4CH_3OH$ (**2**) The empirical formula and the molecular weight is $C_{68}H_{72}Cu_4N_8O_{16}$ and 1511.50 respectively. Yield: 26 mg, 68% based on $Cu(OAc)_2\cdot H_2O$). *Anal.* Calc. for C, 54.03; H, 4.80; N, 7.41. Found: C, 54.24; H, 4.78; N, 7.46; IR (KBr, ν, cm^{-1}): 3455 (w), 2932(w), 2854 (w), 1635(s), 1600(s), 1525 (s), 1485 (s), 1449(s), 1387(m), 1293(s), 1262(m) 1127(m) 1052 (m), 847 (w), 757 (s).

$[MnL]_n$ (**3**) The empirical formula and the molecular weight is $C_{16}H_{12}MnN_2O_3$ and 335.22 respectively. Yield: 24.8 mg, 74% based on Mn(OAc) $2\cdot 2H_2O$). *Anal.* Calc. for C, 57.33 H, 3.61; N, 8.36. Found: C, 57.40; H, 3.60; N, 8.38%; IR (KBr, ν, cm^{-1}): 3419(w), 3057(w), 2913(w), 1635(s), 1600(s), 1572(s), 1528(s), 1498 (s),1466(s), 1449(s), 1387(m), 1322(m), 1262(m), 1127(m), 901 (m), 854(m), 751(s), 621(s), 473(m).

$[Er_2(HL)_2(NO_3)_4]\cdot 4CH_3CN$ (**4**) The empirical formula and the molecular weight is $C_{40}H_{42}Er_2N_{12}O_{18}$ and 1313.38 respectively. Yield: 37 mg, 57% based on $Er(NO_3)_3\cdot 6H_2O$). *Anal.* Calc. for C, 36.58; H, 3.22; N, 12.80; Found: C, 36.49; H, 3.20; N, 12.84%; IR (KBr, ν, cm^{-1}): 3358(m), 2927 (m), 2854 (w), 1655 (s), 1608 (s), 1594 (s), 1563 (m), 1477(s), 1309 (s), 1238 (m), 1024 (m), 768 (s).

2.4. X-ray single-crystal diffraction analysis

Single crystals of dimensions 0.26 × 0.22 × 0.16 mm^3 for **1**, 0.32 × 0.20 × 0.10 mm^3 for **2**, 0.32 × 0.28 × 0.26 mm^3 for **1** and 0.16 × 0.06 × 0.04 mm^3 for **4** was mounted on a glass rod. The crystal data were collected with a Bruker SMART CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. A hemisphere of data was collected in



Scheme 1. The synthetic route of the ligand.