Journal of Molecular Structure 1119 (2016) 340–345

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Three interesting coordination compounds based on metalloligand and alkaline-earth ions: Syntheses, structures, thermal behaviors and magnetic property

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ARTICLE INFO

Article history:
Received 17 February 2016
Received in revised form
6 April 2016
Accepted 11 April 2016
Available online 30 April 2016

Keywords:
Coordination compounds
Metalloligand
Crystal structure
Alkaline-earth ions
Magnetic property

ABSTRACT

Based on metalloligand L^{Cu} ($[Cu(2,4\text{-pydca})_2]^{2-}$, 2,4-pydca^{2-} = pyridine-2,4-dicarboxylate) and alkaline-earth ions (Ca^{2+}, Sr^{2+}, and Ba^{2+}), three interesting coordination compounds, $[Ca(H_2O)_7][L^{Cu}\cdot H_2O]\cdot H_2O$ (**1**), $\{Sr[L^{Cu}\cdot H_2O]\cdot 4H_2O\}_n$ (**2**), and $\{Ba[L^{Cu}\cdot H_2O]\cdot 8H_2O\}_n$ (**3**), have been synthesized and well-characterized by elemental analysis, infrared spectroscopy, thermogravimetric and single-crystal X-ray diffraction analysis. X-ray crystallographic studies reveal that **1** features a discrete 0D coordination compound, while **2** and **3** exhibit the 2D network and 1D chain structures, respectively. Compound **2** is constructed from $\{L^{Cu}\}_2$ dimers connected with $\{Sr_2\}$ units, which is fabricated by two Sr^{2+} ions bridged via two μ_2-O bridges, while compound **3** is formed by 1D $\{Ba\}_n$ chain linked with metalloligands L^{Cu} and exhibits an interesting sandwich like chain structure. It is noted that the coordination numbers of alkaline-earth ions are in positive correlation with their radiuses. Moreover, the magnetic property of compound **2** has been studied.

1. Introduction

During the past decade, coordination compounds have attracted a great deal of attention not only for their interesting molecular structures [1–3] but also for the potential applications as functional materials [4–6]. It has been found that the judicious choices of synthetic approach are of significance to the architectures and physical properties of coordination compounds [7–11]. In recent years, the application of metalloligands has been developed to an important strategy for the construction of coordination compounds [12–20]. For example, building blocks $[M(CN)_8]^{3-/4-}$ (M = W, Mo, Nb) and $[MS_4]^{2-}$ (M = W, Mo) have been regarded as ideal metalloligands for the construction of coordination compounds with magnetic and non-linear optical properties, respectively [21]. Recently, a new metalloligand $[Cu(2,4\text{-pydca})_2]^{2-}$ built from the ligand 2,4-pydca (pyridine-2,4-dicarboxylate) has been developed. Shin-ichiro Noro and his co-workers have reported several heterometallic coordination compounds with novel structures based on the metalloligand $[Cu(2,4\text{-pydca})_2]^{2-}$ [22]. To the best our knowledge, the investigation on such kind of metalloligand is still rare [23–27].

From the synthetic point of view, the construction of coordination compounds can also be affected by several factors, such as pH values, solvent polarities, auxiliary ligands, and the metal centers. Among these factors, the metal center plays an important role to the structures and physical properties of coordination compounds due to the various coordination modes and diverse chemical valences. It is well known that a large number of 3d and 4f transition metals have been employed as the metal centers in the fabrication of coordination compounds [28,29]. Compared with transition metal ions, alkaline-earth ions are rare used as metal centers in the construction of coordination compounds due to the fact of that the alkaline-earth ions are hard to be coordinated [30–34]. To extend the alkaline-earth-based coordination compounds, three alkaline-earth ions Ca^{2+}, Sr^{2+}, and Ba^{2+} will be invited as the metal centers.

In the present work, three new coordination compounds,

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http://dx.doi.org/10.1016/j.molstruc.2016.04.034
0022-2860/

$[Ca(H_2O)_7][L^{Cu}\cdot H_2O]\cdot H_2O$ (**1**), $\{Sr[L^{Cu}\cdot H_2O]\cdot 4H_2O\}_n$ (**2**), and $\{Ba[L^{Cu}\cdot H_2O]\cdot 8H_2O\}_n$ (**3**), have been prepared from metalloligand L^{Cu} and alkaline-earth ions. Single-crystal X-ray diffraction analysis reveals that compound **1** contains metalloligand L^{Cu} with $[Ca(H_2O)_7]^{2+}$ as a counterion, while compounds **2** and **3** consist of polymeric 2D network and 1D chain, respectively. The network of compound **2** is constructed from $\{L^{Cu}\}_2$ dimers connected with $\{Sr_2\}$ units, which is built by two Sr^{2+} ions bridged through two μ_2-O bridges, while the sandwich like chain structure of compound **3** is formed by metalloligands L^{Cu} linked with 1D $\{Ba\}_n$ chain, which is fabricated by Ba^{2+} ions connected with each other via μ_2-O bridges. Interestingly, the coordination numbers of alkaline-earth ions in these compounds are in positive correlation with their radiuses. Thermal behaviors of all three compounds have been investigated in the temperature range of 25–800 °C. Moreover, the magnetic property of compound 2 has also been studied.

2. Experimental section

2.1. Materials and methods

All the chemicals were commercially available and used without further purification. Pyridine-2,4-dicarboxylate acid and metalloligand L^{Cu} were synthesized according to the literature [22]. Element analyses for C, H and N were performed with a Perkin–Elmer 240C system. Infrared spectra were recorded in the region 400–4000 cm^{-1} with a Nicolet Nexus 470 spectrometer (Germany) with samples as KBr disks. Thermogravimetric analysis (TGA) measurements were carried out with a Perkin–Elmer Pyis 1 system in a nitrogen purge with a heating rate of 10 °C min^{-1}.

2.2. Preparation of $[Ca(H_2O)_7][L^{Cu}\cdot H_2O]\cdot H_2O$ (1)

A methanol solution (1 mL) of $Ca(NO_3)_2\cdot 4H_2O$ (24 mg, 0.1 mmol) and 1 mL blank aqueous solution were carefully put onto an aqueous solution (1 mL) of L^{Cu} (62 mg, 0.1 mmol) in a little straight glass tube. Blue crystals of **1** were obtained in dark after several days. Yield: 21 mg (36% based on Cu). Anal. Calcd for $C_{14}H_{24}CaCuN_2O_{17}$ (595.98): C, 28.19; H, 4.03; N, 4.70. Found: C, 28.13; H, 4.02; N, 4.68. IR (KBr, cm^{-1}): 3765(w), 3661(m), 3396(s), 2931(m), 2366(m), 1648(s), 1611(s), 1550(m), 1464(w), 1384(m), 1335(m), 1262(w), 1188(w), 1089(w), 1035(w), 783(m), 734(m), 697(m), 630(m), 562(m), 519(m), 470(m), 427(m).

2.3. Preparation of $\{Sr[L^{Cu}\cdot H_2O]\cdot 4H_2O\}_n$ (2)

2 was obtained as blue block crystals by the same way as that of **1** except that $Ca(NO_3)_2\cdot 4H_2O$ was replaced by $Sr(NO_3)_2$ (21 mg, 0.1 mmol). Yield: 30 mg (52% based on Cu). Anal. Calcd for $C_{14}H_{16}SrCuN_2O_{13}$ (571.45): C, 29.42; H, 2.80; N, 4.90. Found: C, 29.31; H, 2.81; N, 4.86. IR (KBr, cm^{-1}): 3759(w), 3439(s), 2359(m), 1659(s), 1591(m), 1542(m), 1475(w), 1389(m), 1334(m), 1254(w), 1095(w), 1033(w), 916(w), 843(w), 788(w), 738(m), 689(m), 560(m), 469(m).

2.4. Preparation of $\{Ba[L^{Cu}\cdot H_2O]\cdot 8H_2O\}_n$ (3)

A mixed solution (methanol/water = 2:1, 1 mL) of $Ba(NO_3)_2$ (26 mg, 0.1 mmol) and 1 mL blank aqueous solution were successively added on the aqueous solution (1 mL) of L^{Cu} (62 mg, 0.1 mmol) in a little straight glass tube. The resulting solution was placed in the dark and allowed to diffuse slowly at room temperature. Blue crystals of **3** were obtained after several days. Yield: 15 mg (17% based on Cu). Anal. Calcd for $C_{14}H_{24}BaCuN_2O_{17}$ (693.23): C, 24.24; H, 3.46; N, 4.04. Found: C, 24.37; H, 3.45; N, 4.05. IR (KBr, cm^{-1}): 3764(w), 3457(s), 3384(s), 2365(m), 1665(s), 1597(m), 1543(m), 1475(w), 1389(m), 1334(m), 1254(w), 1095(w), 1027(w), 904(w), 836(w), 782(w), 738(m), 695(m), 572(m), 475(m).

2.5. Crystal structure determination

Single crystals with high qualities of all three compounds were chosen directly from glass tubes and mounted on glass fibes. All measurements were made on a Rigaku Saturn 724^+ CCD diffratometer with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293K. Structures were solved by direct methods, and non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELX-97 package [35–37]. All the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. All the hydrogen atoms were placed at the calculated positions and refined following the riding model. Details of the crystal parameters, data collection and refinement of coordination compounds **1**–**3** are summarized in Table 1, while the selected bond lengths of coordination compounds **1**–**3** are listed in Table 2.

3. Results and discussion

3.1. Synthetic method

All three compounds **1**–**3** were synthesized under similar reaction conditions with the inter-diffusion method. The reaction of metalloligand L^{Cu} and alkaline-earth salts $Ca(NO_3)_2\cdot 4H_2O$/$Sr(NO_3)_2$/$Ba(NO_3)_2$ in a 1:1 M ratio in methanol/aqueous solution at room temperature gave rise to the crystals of coordination compounds **1**, **2**, and **3**. Compared to the direct synthetic approach, the inter-diffusion method here plays an important role in the crystallization of compound **1**–**3**. It has been found that the blank solution used in the reaction process can provide a stable environment for the reaction of two different kinds of reactive components [21]. The structure difference in compounds **1**–**3** may be attributed to different coordination modes of alkaline-earth ions.

3.2. Crystal structure of 1

Compound **1** was synthesized from the reaction of metalloligand L^{Cu} and $Ca(NO_3)_2\cdot 4H_2O$ in the molar ratio of 1:1. Single-crystal X-ray diffraction analysis reveals that **1** consists of seven-coordinated cation $[Ca(H_2O)_7]^{2+}$ and metalloligand L^{Cu} (Fig. 1). As displayed in Fig. 1, Cu atom is coordinated with two N atoms and three O atoms from one water molecule and two pyridine-2,4-dicarboxylate, which form a distorted tetragonal pyramid geometry. Bond lengths of Cu–N range from 1.981(3) to 1.984(3) Å, while the distances of Cu–O bond are in the range of 1.971(3) to 2.238(4) Å. The bond lengths of Cu–O between Cu atoms and O atoms from water molecules are larger than the values between Cu atoms and O atoms from carboxylates. Bond lengths of Ca–O are in the range of 2.348(3) to 2.451(3) Å. As shown in Fig. 2, the cations $[Ca(H_2O)_7]^{2+}$ connect with each other to form a supramolecular double chain along *a* axis through the O–H···O hydrogen bonds (Table S1). These chains are further extended to a 3D supramolecular structure via the multiple hydrogen bonds (Fig. S1). Hydrogen bonds between water molecules and carboxilates and π-π interactions (3.38–3.50 Å) between pyridine-carboxylates enhance the stability of such 3D supramolecular structure. The shortest distance between Ca^{2+} ions is 5.070(1) Å, while the shortest distance between Ca^{2+} and Cu^{2+} is 6.103(1) Å.