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Four alkaline earth metal complexes with structural diversities induced by cation size

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ABSTRACT

Studies concerning synthesis, structure and luminescence of four new alkaline earth metal complexes, namely, $[Mg(H_2O)_6](L)_2{\cdot}2H_2O$ (**1**), $[Ca(L)_2(H_2O)_3]_n$ (**2**), $[Sr(L)_2(H2O)_3]_n$ (**3**) and $[Ba(L)_2(H_2O)_2]_n$ (**4**) (L = 1-carboxymethylpyridinium-4-carboxylate) are reported in detail. The results of X-ray crystallographic analysis reveal that **1** is a mononuclear complex with six coordinated water molecules, which further generate a 3D supramolecular structure consisting of two types of channels through delicate hydrogen bonds. While **2** and **3** are isostructural with 2D rhombic grid structure with (4, 4) topology, which are made up of heptacoordinated metal centers and L-shaped 2-connected organic linkers. As expected, with the increase of cation size, the structure of **4** is different from those of **2** and **3**, which displays an undulated 2D network. Such 2D layers are composed of infinite 1D chains. The results indicate that the cation size, determining the geometry and coordination ability of metal centers, together with coordination mode and conformation of ligand L, have a subtle effect on the structural diversities. In addition, the solid luminescent properties of complexes **1**–**4** were also studied.

1. Introduction

Over the past decade, the design and construction of coordination supramolecules containing alkaline earth metal and organic bridging ligands have been carried out by many researchers, because of not only their fascinating structures, but also their interesting properties and potential applications as functional material in the areas of gas adsorption/separation, catalysis, molecule/ion recognition and luminescent properties [1–6]. For example, an alkaline earth porous coordination polymer $[Ba_2TMA(NO_3)(DMF)]_n$ (H_3TMA = 1,3,5-benzenetricarboxylic acid) with potential open metal sites has been reported by Kitagawa and co-workers, which is capable of CO_2/CH_4 separation in both equilibrium gas adsorption and breakthrough setup [6]. As mentioned above, the final structures of most coordination supramolecules mainly depend on the topology and geometry of both metal cation/cluster and ligand, which further determine the structure-driven properties, so rational select of metal ions and bridging ligands becomes very important for the subsequent study [7]. Group II metal ions Mg(II), Ca(II), Sr(II) and Ba(II) have been employed as metal nodes in recent years for their varied coordination geometry with increasing ion radius [8–12]. On the other hand, in contrast to limited metal ions, numerous organic linkers play more important roles in the construction of coordination supramolecules, because the flexibility of organic backbone, conformational preference and symmetry of organic ligands can lead to a remarkable series of materials bearing various structures and properties [13,14]. Among them, carboxylate ligands, especially with specific conformation, due to their various coordination modes and good coordination capacities have been widely used in recent years [15–18]. In our previous work, we have preliminarily studied the assembly of metal ions and semirigid L-shaped ligand 1-carboxymethylpyridinium-3-carboxylate and obtained some meaningful result. For instance, we have successfully obtained a novel 1D tube-like structure by utilizing Pb(II) ions as a see-saw node and 1-carboxymethylpyridinium-3-carboxylate ligand as a 4-connected linker [19]. As a continuation of our research, in this work a new semirigid L-shaped dicarboxylate ligand 1-carboxymethylpyridinium-4-carboxylate (L, Scheme 1) was used to react with alkaline earth metal salts, investigating the effect of cation size and coordination modes of ligand L on the final structure. Herein, we report the synthesis, crystal structures and luminescent properties of four new complexes $[Mg(H_2O)_6](L)_2{\cdot}2H_2O$ (**1**), $[Ca(L)_2(H_2O)_3]_n$ (**2**), $[Sr(L)_2(H_2O)_3]_n$ (**3**) and $[Ba(L)_2(H_2O)_2]_n$ (**4**).

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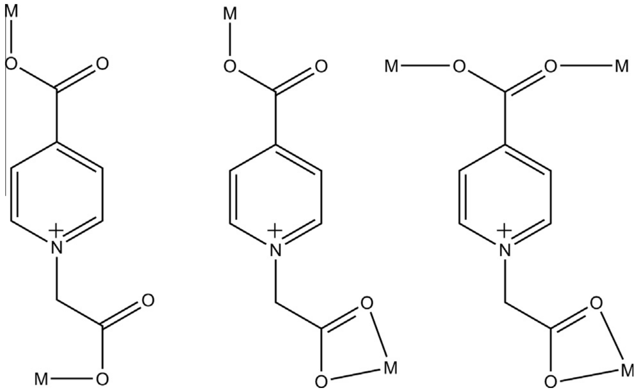

Scheme 1. Coordination modes of ligand L in the complexes **1–4**.

2. Experimental

2.1. Materials and measurements

All commercially available chemicals are of reagent grade and were used as received without further purification. The ligand L was synthesized according to the method reported previously [20]. The C, H and N microanalyses were carried out on a Perkin–Elmer 240C elemental analyser. Infrared spectra were measured on a Nicolet 380 FT-IR spectrometer in the region 400–4000 cm^{-1} using KBr pellets. The luminescent spectra for the solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrophotometer with a Xenon arc lamp as the light source, and all the measurements were carried out under the same conditions. Power X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractionmeter with graphite monochromatic Cu Kα radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 40 mA in air, with the environmental temperature of 20 °C.

2.2. Synthesis

2.2.1. Synthesis of complex $[Mg(H_2O)_6](L)_2{\cdot}2H_2O$ (**1**)

A mixture of $Mg(NO_3)_2{\cdot}6H_2O$ (102 mg, 0.4 mmol) and L (44.0 mg, 0.2 mmol) in water (4 ml) was stirred for 10 min at room temperature. Colorless crystals suitable for X-ray diffraction analysis were isolated by slow diffusion of acetone into the clear filtrate for two weeks. Yield: 50%. *Anal.* Calc. for $C_{16}H_{28}MgN_2O_{16}$: C, 36.35; H, 5.34; N, 5.30. Found: C, 36.41; H, 5.27; N, 5.31%. IR (KBr, cm^{-1}): 3358 (s), 1614 (vs), 1565 (s), 1381 (vs), 1196 (w), 785 (m), 714 (m), 655 (m), 493 (m), 473 (m), 448 (m), 434 (m), 424 (m), 416 (m).

2.2.2. Synthesis of complex $[Ca(L)_2(H_2O)_3]_n$ (**2**)

Compound **2** was prepared in the same way as **1**, using corresponding $CaCl_2$ (44.4 mg, 0.4 mmol) instead of $Mg(NO_3)_2{\cdot}6H_2O$. Yield: 68%. *Anal.* Calc. for $C_{16}H_{18}CaN_2O_{11}$: C, 42.29; H, 3.99; N, 6.17. Found: C, 42.31; H, 4.06; N, 6.10%. IR (KBr, cm^{-1}): 3428 (vs), 3121 (s), 3069 (s), 3012 (s), 1683 (vs), 1620 (vs), 1563 (s), 1454 (m), 1377 (vs), 1303 (s), 1205 (m), 1111 (m), 972 (w), 919 (m), 836 (w), 789 (m), 722 (s), 659 (s), 478 (m), 442 (m).

2.2.3. Synthesis of complex $[Sr(L)_2(H_2O)_3]_n$ (**3**)

Compound **3** was prepared in the same way as **1**, using corresponding $Sr(NO_3)_2$ (84.6 mg, 0.4 mmol) instead of $Mg(NO_3)_2{\cdot}6H_2O$. Yield: 32%. *Anal.* Calc. for $C_{16}H_{18}SrN_2O_{11}$: C, 38.29; H, 3.61; N, 5.58. Found: C, 38.33; H, 3.57; N, 5.64%. IR (KBr, cm^{-1}): 3427 (vs), 3118 (s), 3069 (s), 3006 (s), 1682 (vs), 1625 (vs), 1562 (s), 1464 (m), 1381 (vs), 1308 (s), 1205 (m), 1111 (m), 976 (w), 919 (m), 877 (w), 825 (w), 794 (m), 716 (s), 6659 (s), 477 (m), 436 (m).

2.2.4. Synthesis of complex $[Ba(L)_2(H_2O)_2]_n$ (**4**)

Compound **4** was prepared in the same way as **1**, using corresponding $BaCl_2{\cdot}2H_2O$ (97.2 mg, 0.4 mmol) instead of $Mg(NO_3)_2{\cdot}6H_2O$. Yield: 70%. *Anal.* Calc. for $C_{16}H_{16}BaN_2O_{10}$: C, 36.01; H, 3.02; N, 5.25. Found: C, 35.97; H, 3.13; N, 5.21%. IR (KBr, cm^{-1}): 3456 (s), 3365 (s), 3266 (s), 3120 (s), 3053 (vs), 1631 (vs), 1568 (vs), 1469 (m), 1370 (vs), 1298 (m), 1204 (m),

Table 1
Crystallographic data and refinement parameters for complexes **1–4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{16}H_{28}MgN_2O_{16}$	$C_{16}H_{18}CaN_2O_{11}$	$C_{16}H_{18}SrN_2O_{11}$	$C_{16}H_{16}BaN_2O_{10}$
Formula weight	528.71	454.40	501.94	533.65
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/c$
a (Å)	6.6926(19)	23.174(2)	23.3486(19)	8.5766(17)
b (Å)	19.715(5)	7.0480(7)	7.0420(6)	20.853(4)
c (Å)	17.464(5)	13.7553(14)	13.9641(12)	10.807(2)
α (°)	90	90	90	90
β (°)	91.260(4)	126.410(1)	126.465(8)	112.16(3)
γ (°)	90	90	90	90
V ($Å^3$)	2303.7(11)	1808.1(3)	1846.5(3)	1790.0(6)
Z	4	4	4	4
D_{calc} ($g\ cm^{-3}$)	1.524	1.669	1.806	1.980
μ (mm^{-1})	0.161	0.416	2.988	2.281
T (K)	296	296	293	296
F (000)	1112	944	1016	1048
θ_{max} (°)	55	56.88	50	54
Independent reflections	5235	2281	1636	3886
Data/restraints/parameters	5235/0/373	2281/0/148	1636/2/147	3886/0/278
R_{int}	0.0573	0.0200	0.0592	0.0324
Goodness-of-fit (GOF) on F^2	1.026	1.049	1.078	1.221
R_1[a] $[I > 2\sigma(I)]$	0.0435,	0.0328	0.0309	0.0214
wR_2[b] $[I > 2\sigma(I)]$	0.1229	0.0870	0.0703	0.0587
R_1[a] (all data)	0.0528	0.0370	0.0359	0.0235
wR_2[b] (all data)	0.1320	0.0902	0.0725	0.0695

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.