Synthesis and structural diversity of complexes with new isomeric tripodal ligands

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ABSTRACT

Four new complexes $[Ni(L3)_2] \cdot (ClO_4)_2$ (**1**), $[Cu(L3)(H_2O)] \cdot (ClO_4)_2$ (**2**), $[Cu_2(L4)_2(Cl)] \cdot (ClO_4)_3 \cdot 2H_2O$ (**3**), and $[Cu(L4)(NO_3)(H_2O)] \cdot (NO_3) \cdot H_2O$ (**4**) with new tripodal ligands N^1-(2-Amino-ethyl)-N^1-pyridin-3-ylmethyl-ethane-1,2-diamine (L3) and N^1-(2-Amino-ethyl)-N^1-pyridin-4-ylmethyl-ethane-1,2-diamine (L4) have been synthesized. Interestingly, complex **1** shows mononuclear structure, complex **2** displays 1D *zig-zag* chain structure, complex **3** exhibits 1D ladder structure, and complex **4** presents less waved 1D *zig-zag* chain structure in comparison with complex **2**. The results clearly showed that the variation of the N-donor orientation of the ligands, metal ions, and anions, has remarkable impact on the frameworks of the complexes.

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1. Introduction

In the past few years, the construction of coordination polymers has attracted great interest, for not only the intriguing structural topologies like zero-, one-(1D), two-(2D), and three-dimensional(3D) coordination architectures, but also the versatile properties such as magnetism, gas adsorption, biomimic functions, and so on [1–3]. It is well known that the self-assembly process of the complexes is influenced by many factors such as the nature of the ligands, metal ions, anions, pH, temperature, etc. Among which, the design of organic ligands is particularly crucial, since subtle modification on the ligand like the flexibility, the length, the spacer and so on, may lead to dramatic changes on the ultimate structures and properties of the coordination frameworks [4–6]. Recently, we focus our attention on the polyamine tripodal ligands, which have two symmetric amino groups and one imidazole-containing arm, and are proved excellent to construct varied frameworks with various properties [7]. However, up to now, similar tripodal ligands bearing one pyridine arm are seldom, so it is of great interest to investigate the kinds of organic ligands and their derivates [8]. Here, as an extension of our previous work, we designed two new isomeric pyridine-containing tripodal ligands, namely N^1-(2-Amino-ethyl)-N^1-pyridin-3-ylmethyl-ethane-1,2-diamine (L3) and N^1-(2-Amino-ethyl)-N^1-pyridin-4-ylmethyl-ethane-1,2-diamine (L4), which have the same frame structure except

distinct N-donor orientation on the pyridine arm, with 3-position N-donors of L3 while 4-position ones of L4 (Scheme 1). Further, we reported four complexes $[Ni(L3)_2] \cdot (ClO_4)_2$ (**1**), $[Cu(L3)(H_2O)] \cdot (ClO_4)_2$ (**2**), $[Cu_2(L4)_2(Cl)] \cdot (ClO_4)_3 \cdot 2H_2O$ (**3**), and $[Cu(L4)(NO_3)(H_2O)] \cdot (NO_3) \cdot H_2O$ (**4**) under the same synthesis conditions (Scheme 2).

2. Experimental

2.1. Synthesis of the tripodal Ligands

The NH_2 groups of diethylenetriamine were protected by phthalic anhydride as described previously [7c]. The protected product (1.80 g, 5 mmol) was allowed to react with pyridine-3-aldehyde (0.53 g, 5 mmol) in methanol (50 ml) followed by reduction using sodium cyanoborohydride (0.32 g, 5 mmol) in small portions in three hours. After the resulting solution had been stirred for one day at room temperature, the solution was evaporated under reduced pressure. The residual was extracted by CH_2Cl_2 from aqueous phase, and the organic phase was dried over Na_2SO_4 and evaporated to give pale oil. Then concentrated hydrochloric acid (30 ml) was added, and the mixture was boiled for 8 h, and filtered. The filtrate was evaporated to dryness, after recrystallization from ethanol, L3·3HCl was obtained as white powder (1.10 g, 73%). ^{1}H NMR: (D_2O, 500 MHz): δ = 8.79 (s, 1H), 8.70 (s, 1H), 8.61 (s, 1H), 8.03 (s, 1H), 3.97 (s, 2H), 3.14 (t, 4H), 2.84 (t, 4H) ppm. ESI-MS: [L3+H⁺] calc. for $C_{10}H_{19}N_4$: 195.3; found 195.4 (100%), [L3+Na⁺] calc. for $C_{10}H_{18}N_4Na$: 217.3; found 217.3 (25%). L4·3HCl was obtained as white powder with similar method except that pyridine-4-aldehyde was used (0.85 g, 56%). ^{1}H NMR: (D_2O, 500 MHz):

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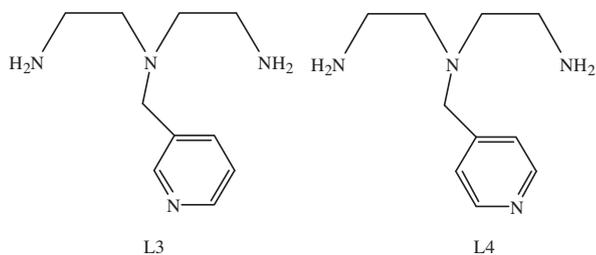
Scheme 1. The tripodal ligands L3 and L4.
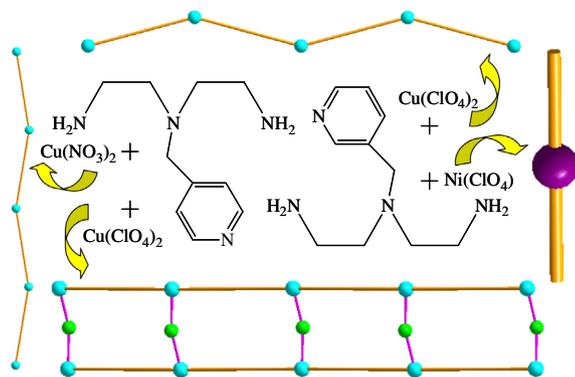
Scheme 2. Schematic drawing for formation of complexes **1–4** with isomeric tripodal ligands.

δ = 8.69 (s, 2H), 8.03 (s, 1H), 4.03 (s, 2H), 3.12 (t, 4H), 2.85 (t, 4H) ppm. ESI-MS: [L4+H$^+$] calc. for $C_{10}H_{19}N_4$: 195.3; found 195.4 (100%), [L4+Na$^+$] calc. for $C_{10}H_{18}N_4Na$: 217.3; found 217.3 (18%).

2.2. Synthesis of the complexes

2.2.1. Synthesis of [Ni(L3)$_2$]·(ClO$_4$)$_2$ (1)

An aqueous solution (3 ml) of L3·3HCl (0.0151 g, 0.05 mmol) was added to an aqueous solution (3 ml) of Ni(ClO$_4$)$_2$·6H$_2$O (0.0177 g, 0.05 mmol), and the resulted solution was adjusted to pH ca. 9 with 0.5 M NaOH while stirring and acetonitrile (5 ml) was added. The solution was filtered about 15 min later, and the filtrate was evaporated slowly in air for several days, violet crystals

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1–4**.

1			
Ni1–N1	2.146(3)	Ni1–N2	2.196(2)
Ni1–N3	2.129(3)		
N1–Ni1–N2	99.1(1)	N1–Ni1–N3	90.7(1)
N2–Ni1–N3	82.1(1)		
2			
Cu1–N1	1.980(5)	Cu1–N2	2.070(4)
Cu1–N3	2.003(5)	Cu1–N4#1	2.046(4)
Cu1–O1	2.261(6)		
N1–Cu1–N2	84.5(1)	N1–Cu1–N4#1	90.9(2)
N1–Cu1–O1	103.0(3)	N2–Cu1–N3	85.8(2)
N2–Cu1–O1	97.2(2)	N3–Cu1–N4#1	96.3(2)
N3–Cu1–O1	93.2(3)	N4–Cu1–O1#1	92.2(2)
3			
Cu1–N1	2.009(4)	Cu1–N2	2.068(4)
Cu1–N3	2.012(4)	Cu1–N4#2	2.034(4)
Cu1–Cl1	2.603(1)		
N1–Cu1–N2	83.4(2)	N1–Cu1–N4#2	97.0(2)
N2–Cu1–N3	84.2(2)	N2–Cu1–Cl1	103.8(2)
N3–Cu1–N4#3	92.4(2)	N3–Cu1–Cl1	93.4(2)
N4–Cu1–Cl1#3	92.6(2)		
4			
Cu1–N1	2.003(2)	Cu1–N2	2.046(2)
Cu1–N3	1.992(2)	Cu1–N4#3	2.026(2)
Cu1–O1	2.587(2)		
N1–Cu1–N2	85.8(1)	N1–Cu1–N4#3	95.4(1)
N1–Cu1–O1	84.3(1)	N2–Cu1–N3	84.6(1)
N2–Cu1–O1	90.1(1)	N3–Cu1–N4#3	94.4(1)
N3–Cu1–O1	87.5(1)	N4–Cu1–O1#3	92.5(1)
N1–Cu1–O2	86.5(1)	N2–Cu1–O2	92.6(1)
N3–Cu1–O2	101.9(1)	N4–Cu1–O2#3	84.9(1)

Symmetry transformation used to generate equivalent atoms: #1 1/2 + x, 1/2 − y, z; #2 1/2 + x, 1/2 − y, 1/2 + z; #3 1 + x, 1/2 − y, 1/2 + z.

were obtained. Yield: (60%). *Anal.* Calc. for $C_{20}H_{36}Cl_2NiN_8O_8$: C, 37.18; H, 5.62; N, 17.34. Found: C, 37.29; H, 5.43; N, 17.46%. IR: (KBr, cm^{-1}): 3236 (s), 3151 (s), 2930 (m), 2883 (m), 1601 (m), 1476 (m), 1428 (m), 1357 (w), 1082 (vs), 894 (m), 802 (m), 723 (m), 628 (m).

2.2.2. Synthesis of [Cu(L3)(H$_2$O)]·(ClO$_4$)$_2$ (2)

The single crystal of **2** was obtained by the same method for **1** except Cu(ClO$_4$)$_2$·6H$_2$O was used. Blue block crystals were

Table 1
Crystallographic data for complexes **1–4**.

Complex	**1**	**2**	**3**	**4**
Empirical formula	$C_{20}H_{36}Cl_2NiN_8O_8$	$C_{10}H_{20}Cl_2CuN_4O_9$	$C_{20}H_{40}Cl_4Cu_2N_8O_{14}$	$C_{10}H_{22}CuN_6O_8$
Formula weight	427.08	474.75	885.48	417.89
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$Pna2_1$	$C2/c$	$P2_1/c$
a (Å)	9.167(3)	15.404(6)	17.651(6)	11.9341(18)
b (Å)	11.438(4)	13.289(5)	15.090(6)	10.9626(17)
c (Å)	16.558(6)	8.387(3)	13.545(5)	17.3693(19)
α (°)	88.050(5)	90.00	90.00	90.00
β (°)	68.728(6)	90.00	109.874(4)	131.552(6)
γ (°)	71.181(6)	90.00	90.00	90.00
V (Å^3)	696.8(5)	1716.9(11)	3393(2)	1700.6(4)
Z	1	4	4	4
D_{calc} (g cm^{-3})	1.540	1.837	1.733	1.632
μ (mm^{-1})	0.947	1.639	1.643	1.338
R_{int}	0.0095	0.0784	0.0314	0.0192
R_1 ($I > 2\sigma(I)$)[a]	0.0448	0.0602	0.0545	0.0305
wR_2 (all data)[b]	0.1300	0.1651	0.1543	0.0826
Goodness-of-fit (GOF) on F^2	1.038	1.053	1.066	1.043

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