Three Azamacrocycle-Based Coordination Complexes Bearing a New Triazine Derived Carboxylic Ligand Via In Situ Ligand Hydrolysis: The Trap of Resonance Structure

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The in situ ligand hydrolysis reaction of 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine and macrocyclic complexes yields three coordination complexes bearing new triazine derived carboxylic ligands, namely, \((\text{NiL}_1)(\text{L}_0)-\text{DMF})_n\) (1), \((\text{NiL}_2)(\text{L}_0)-\text{DMF}-\text{H}_2\text{O})_n\) (2), and \([\text{NiL}_3][\text{NiL}_3](\text{L}_0)_2\cdot\text{H}_2\text{O})_n\) (3) \((\text{L}_0 = 4\text{-}(6\text{-Hydroxy-4-oxo-4,5-dihydro-}[1,3,5\text{-triazine-2-}oxy])\text{-benzoic acid, }\text{L}_1 = 1,4,8,11\text{-tetraazacyclotetradecane, }\text{L}_2 = 1,8\text{-dimethyl-1,3,6,8,10,13-hexaazacyclotetradeca and }\text{L}_3 = 1,3,6,9,11,14\text{-hexazatricyclooctadecane.}\)

Single-crystal X-ray diffraction analyses reveal that 1 and 2 exhibit a one-dimensional (1D) chain structure, which is further connected into a three-dimensional (3D) supramolecular structure by hydrogen bonds. In complex 3, a ion-pair structure, which is connected into a 2D \(4\text{i}\) hydrogen bonded supramolecular structure. The results indicate the subtle difference of azamacrocycle may lead to diverse structures. Importantly, in complexes 1–3, the resonance structure is trapped in crystals 1–3.

Keywords: azamacroyclic complex, crystal structure, in situ ligand hydrolysis, resonance structure

Introduction

Coordination complexes have made rapid progress due to their intriguing structural variety and interesting functional properties, such as luminescence, magnetism, ferroelectric, adsorption, and catalysis.\(^1\) Over the past decade, much effort has been put in the rational design and controllable synthesis of desired structures and properties. However, it is still a great challenge to construct target coordination complexes, because many factors, such organic ligand, reagent ratio, solvent, pH value, temperature, and so on, may affect the final results.\(^6\)–\(^10\) To obtain desired coordination complexes, we always chose the suitable building block to simplify the construction. Metal ion, metal cluster, and some other metal ligand have been chosen as building blocks. In recent years, azamacrocyclic complex that contains two axial vacant coordination sites has aroused scientists’ interest. Two axial vacant coordination sites can bind carboxylic ligand to build new coordination complexes. Hence, azamacroyclic complex also can be regarded as building blocks to construct new discrete coordination complexes and coordination polymers. Comparatively less attention has been paid to this area.\(^11\)–\(^15\) Very recently, based on azamacrocyclic complex, we used tripodal carboxylic ligands, 4,4',4''-triazine-1,3,5-triytrimino benzoic acid and 4,4',4''-[1,3,5-benzenetriyltris(carbonylimino)]-trisbenzoic acid to synthesize two microporous coordination polymers.\(^16\) Along this idea the tripod ligand 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine (TCPT) was utilized. Unexpectedly, during the reaction, in situ ligand hydrolysis happened, three azamacrocycle based coordination complexes, namely, \((\text{NiL}_1)(\text{L}_0)-\text{DMF})_n\) (1), \((\text{NiL}_2)(\text{L}_0)-\text{DMF}-\text{H}_2\text{O})_n\) (2) and \([\text{NiL}_3][\text{NiL}_3](\text{L}_0)_2\cdot\text{H}_2\text{O})_n\) (3)

Experimental

The macrocyclic precursors \([\text{NiL}_1])(\text{ClO}_4)_2\)\(^17\), \([\text{NiL}_2])(\text{ClO}_4)_2\)\(^18\) and \([\text{NiL}_3])(\text{ClO}_4)_2\)\(^19\) and TCPT\(^20\) ligand were prepared according to the literature. All other chemicals are commercially available and were used without further purification. The IR spectra were measured from KBr pellets on a Nicolet Avatar 370 FT-IR spectrometer. Elemental analyses were performed using a Vario ELIII CHNS/O elemental...
The powder X-ray diffraction measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer.

Synthesis of \{(\text{Ni}L_1)(L_0)\cdot\text{DMF}\}_n \ (1)

\[\text{[NiL}_1\cdot\text{(ClO}_4)_2\ (0.2 \text{ mmol, 91.4 mg)}, \text{TCPT (0.1 mmol, 48.9 mg)}, \text{and triethylamine (52 \mu L, 0.3 mmol)} \text{ were added to} 20 \text{ mL DMF:H}_2\text{O (V/V = 1:1) mixed solution with stirring, and then filtration and slow evaporation of the resulting solution gave purple crystals within two weeks. Yield: 80\% based on [NiL}_1\cdot\text{(ClO}_4)_2\]. Anal. Calcd. for C\text{23H}\text{36N}_8\text{NiO}_6\ (%): C, 47.69; H, 6.26; N, 19.34. Found (%): C, 47.64; H, 6.26; N, 19.33. IR (cm}^{-1}): 3355(s), 3189(s), 2919(w), 2775(m), 1677 (s), 1614(s), 1484(s), 1398(s), 1382(s), 1371(s), 1286(m), 1041 (s), 985(s), 877(m), 792(m), 624(m).\]

Synthesis of \{(\text{Ni}L_2)(L_0)\cdot\text{DMF}\cdot\text{H}_2\text{O}\}_n \ (2)

\[\text{[NiL}_2\cdot\text{(ClO}_4)_2\ (0.2 \text{ mmol, 97.4 mg)}, \text{TCPT (0.1 mmol, 48.9 mg}), \text{and triethylamine (52 \mu L, 0.3 mmol)} \text{ were added to} 20 \text{ mL DMF:H}_2\text{O (V/V = 1:1) mixed solution with stirring, and then filtration and slow evaporation of the resulting solution gave purple crystals within three weeks. Yield: 60\% based on [NiL}_2\cdot\text{(ClO}_4)_2\]. Anal. Calcd. for C\text{23H}\text{40N}_10\text{NiO}_7\ (%): C, 44.04; H, 6.43; N, 22.33. Found (%): C, 44.10; H, 6.37; N, 22.42. IR (cm}^{-1}): 3465(s), 3207(s), 2927(s), 2859(w), 1670(s), 1616(s), 1562(s), 1473(m), 1371(s), 1255(m), 1157(m), 1022(s), 856(m), 798(m), 729(m), 549(m).\]

Synthesis of [\text{NiL}_3]/[\{(\text{Ni}L_3)(L_0)\cdot\text{2H}_2\text{O}\}_n \ (3)

\[\text{[NiL}_3\cdot\text{(ClO}_4)_2\ (0.2 \text{ mmol, 102.2 mg)}, \text{TCPT (0.1 mmol, 48.9 mg}), \text{and triethylamine (52 \mu L, 0.3 mmol)} \text{ were added to} 20 \text{ mL DMF:H}_2\text{O (V/V = 1:1) mixed solution with stirring, and then filtration and slow evaporation of the resulting solution gave purple crystals within one week. Yield: 45\% based on [NiL}_3\cdot\text{(ClO}_4)_2\]. Anal. Calcd. for C\text{44H}\text{66N}_18\text{Ni}_2\text{O}_{12}\ (%): C, 45.70; H, 5.75; N, 21.80. Found (%): C, 45.90; H, 5.56; N, 21.97. IR (cm}^{-1}): 3465(s), 3136(s), 2931(s), 1677 (s), 1643(s), 1443(s), 1336(s), 1311(m), 1186(s), 1037(s), 1012(s), 854(m), 798(m), 729(m), 549(m).\]

Results and Discussion

Synthesis and In Situ Ligand Hydrolysis

At first, we aimed to obtain porous coordination polymers based on macrocyclic precursors and 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine (TCPT) ligand. Unexpectedly, the hydrolysis of tricarboxylic acid ligand happened. A new

Sch. 1. The hydrolysis of the 2,4,6-tris-(4-carboxyphenoxy)-1,3,5-triazine ligand.
triazine derived carboxylic ligand was isolated after the hydrolysis of the TCPT. Based on Park and Suh[24] and Zhu et al.'s[25] work, the TCPT was stable under high temperature and in the water solution. Combined with our experiments, the only difference is the addition of macrocyclic precursors, indicating there may be a macrocyclic complex catalysis process in existence. Therefore, parallel experiments were designed to study the mechanism of the hydrolysis. Without the macrocyclic precursors, no Lo ligand was detected after several days. Hence, the hydrolysis of TCPT was ascribed to the macrocyclic complex catalysis.

The hydrolyzed product may have four different resonance structures (α, β, γ, δ), including full and partial resonance conformations (Scheme 2 is the simplified diagram). The precise structure of Lo is confirmed by the bond distance of triazine ring, C-O/C=O distance, charge balance and the rationality of hydrogen bond. In 1–3, two C-N bond distances in the triazine ring are larger than the unprotonated tri-

Table 1. Crystal data and structure refinement parameters for 1–3

|       | 1       | 2       | 3       |
|-------|---------|---------|---------|
| Chemical formula | C_{23}H_{36}N_{8}NiO_{6} | C_{23}H_{40}N_{10}NiO_{7} | C_{44}H_{56}N_{18}Ni_{2}O_{12} |
| Formula weight  | 579.29  | 627.36  | 1156.53 |
| Crystal system  | Triclinic | Triclinic | Triclinic |
| Space group     | P-1     | P-1     | P-1     |
| a (Å)           | 8.9661(18) | 9.6857(19) | 8.5893(17) |
| b (Å)           | 10.854(2)  | 11.456(2) | 9.4118(19) |
| c (Å)           | 15.277(3)  | 15.288(3) | 15.935(3) |
| α (°)           | 91.28(3)   | 68.90(3)  | 82.73(3)  |
| β (°)           | 105.48(3)  | 72.88(3)  | 83.44(3)  |
| γ (°)           | 112.19(3)  | 70.95(3)  | 87.58(3)  |
| Volume (Å³)     | 1314.0(6)  | 1465.5(6) | 1269.0(4) |
| Z, Dc (Mg/m³)   | 2, 1.464  | 2, 1.417  | 1, 1.513  |
| Absorption coefficient(mm⁻¹) | 0.793 | 0.721 | 0.822 |
| F(000)          | 612      | 660      | 608      |
| Reflections collected | 11342 | 12671 | 12543 |
| Independent reflections | 5094 | 5675 | 5758 |
| GOF             | 1.00     | 1.06     | 1.06     |
| Final R indices [I>2sigma(I)] | R₁ = 0.0421, wR₂ = 0.1334 | R₁ = 0.0490, wR₂ = 0.1609 | R₁ = 0.0365, wR₂ = 0.1014 |
| Largest diff. peak and hole (e.Å⁻³) | 1.41 and –0.41 | 0.59 and –0.96 | 0.63 and –0.55 |

Sch. 2. Four different resonance structures and the number of related complexes in the CSD database.
Fig. 1. The molecular structure diagram of complex 1 with the selected atom-labeling scheme (A: $2 - x, -y, -z$, B: $1 - x, -y, 1 - z$).

Fig. 2. Two kinds of hydrogen bonds within a chain of complex 1.

Fig. 3. Hydrogen bonds between 1D chain of complex 1 (A: $3 - x, -y, 1 - z$).
azine ring, one of the C-O bond distance located in the double bond range, and the other C-O bond distance in the scope of single bond range. Hence, the precise structure of L₀ can be regarded as the β mode. Importantly, the proton on triazine ring can be found from Fourier maps (H1N in complex 1, H1N in complex 2, and H1N in complex 3). From the Cambridge Structural Database (CSD) database, the number of ligands derived from the four resonance structures is 180, 8, 16, and 268, respectively, indicating a difficult task to characterize the resonance intermediate through the crystallization of single crystal. However, partial resonance conformation of L₀ were observed in 1–3 demonstrated that coordination complexes may serve as platform to trap the resonance structure.

Crystal structure

The crystal structure of 1 is triclinic, space group P-1, with the asymmetric unit consisting of one L₀ anion, one [NiL₁]²⁺ cation (half [Ni(1)L₁]²⁺ and half [Ni(2)L₁]²⁺), and one DMF.
Ni(1) atom is in a slightly distorted \([\text{NiN}_4\text{O}_2]\) octahedral coordination geometry, where four nitrogen atoms come from the azamacrocyclic ligand, two oxygen atoms come from hydroxyl group of \(L_0\) ligand. The average Ni(1)-N and Ni(1)-O bond distances are 2.0636 Å and 2.1562 Å, respectively. Those bond distances are close to those observed in similar complexes. Similarly, Ni(2) atom is also in a distorted \([\text{NiN}_4\text{O}_2]\) octahedral coordination geometry, however, where four nitrogen atoms come from the azamacroyclic ligand, two oxygen atoms come from carboxylic group. The average Ni(1)-N and Ni(1)-O bond distances are 2.0733 Å and 2.1296 Å respectively. Each \(L_0\) ligand binds two Ni(II) ions in a bis-monodentate mode, which results in a zigzag 1D coordination polymer chain. Hydrogen bonds interactions play crucial roles in the formation of supramolecular structures. Within a chain, two kinds of hydrogen bonds were formed, (a) hydrogen-bonding interaction between the -COO\(^-\) group and the -NH- group on the macrocyclic ligand and (b) hydrogen-bonding interaction between N atom on triazine and the -NH- group on the macrocyclic ligand (Figure 2). The former one is usually observed in azamacrocycle based coordination complexes. To the best of our knowledge, the later one is never been observed before. Furthermore, zigzag chains are held together through interchains hydrogen bonds (Figure 3), giving rise to a 2D supramolecular layer.

As shown in Figure 4, single-crystal X-ray diffraction analysis reveals that the complex 2 consists of one \(L_0\) anion,
one [NiL₂]²⁺ cation, one DMF and one water molecule. The general structure of complex 2 is similar to complex 1. The coordination geometry around nickel(II) is described best by a slightly [NiN_4O_2] distorted octahedron with four Ni-N bonds from the macrocycle and two Ni-O bonds from L₀ ligands. The average Ni(1)-N and Ni(1)-O bond distances are 2.0615/2.0571 Å and 2.1369/2.1394 Å, respectively, which range in the normal distance. Each L₀ binds two Ni(II) ions in a monodentate mode, which results in a zigzag 1D coordination polymer chain. Similarly, two kinds of hydrogen bonds are observed within a chain (Figure S1). Those zigzag chains are further held together through inter-chains hydoro-

Fig. 8. Hydrogen bonds between 2D supramolecular layer of complex 3.

Fig. 9. The simulated and experimental XRD patterns of complexes 1–3.
gen bonds and π--π stacking (Figure 5), giving rise to a 2D supramolecular structure.

The molecular structure of complex 3 with atom labeling is shown in Figure 6. The complex 3 consists of two discrete units: [NiL3]2+ and [(NiL3)(L0)2]2-. Compared with L1 and L2 macrocyclic ligands, the discrete [Ni(1)L3]2+ fragment locates in the crystal maybe due to the steric hindrance of L3 macrocycle. Similar to complexes 1 and 2, the Ni(2) atoms sit on an coordination center, which displays distorted [NiN4O2] octahedral geometry, with four secondary nitrogens from the macrocycle and two oxygens from carboxylates. The average Ni(1)-N and Ni(1)-O bond distances are 2.0719 Å and 2.1477 Å, respectively, which range in the normal distance. In the [(NiL3)(L0)2]2- anion, the hydrogen bond between the -COO- group and the -NH- group on the macrocyclic ligand is also observed (Figure S2). Two different ion pairs are connected by the hydrogen bonds between tertiary amine and protonated triazine, secondary amine (-NH-) and triazine (Figure 7). It is deserved to note that the hydrogen bond between tertiary amine and protonated triazine is never been observed before. When we treat as [NiL3]2+ a 4-connected node and [NiL3](L0)2- as linker, the hydrogen bonded framework can be simplified to a 2D 44-network (Figure S3). Furthermore, the 44-layer is linked by hydrogen bond between water and L0, which form a twelve membered ring (Figure 8).

It had been clearly shown that the crystallization of complexes was significantly influenced by pH, the reaction temperature, solvent, metal cation, the conformation of ligand and so on. As described previously, complexes 1-3 were synthesized under the same external experimental environment except for the macrocyclic ligand, however, they exhibit huge structural changes. Very recently, such peripheral macrocycles regulated drastic different structures had been observed by our group. Complexes are air-stable and insoluble in water and common organic solvents. The simulated and experimental XRD patterns of complexes obtained are shown in Figure 9. Their peak positions are in good consistency with each other, indicating the phase purity of the synthesized sample.

Conclusion

In summary, three entire different nickel(II) coordination complexes based on various azamacroyclic precursors and a new triazine derived ligand were obtained and characterized. The results indicate the subtle difference of azamacrocycle may lead to diverse structures. In additional, our research shows the resonance structure can be trapped in coordination complex. This phenomenon may provide a straightforward approach to characterize the unstable resonance structure.

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Supplementary Material

Supplemental data for this article can be accessed at the publisher’s website. CCDC-1018670 (for 1), 1018671 (for 2), and 1018672 (for 3) contain the supplementary crystallographic data for this paper. These date can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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