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# Hydrothermal In Situ Synthesis and Characterization of Cu(II) Complexes

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The hydrothermal in situ Cu(II)/2,3-pyrazine dicarboxylic acid reactions at 100 and 140 °C result in Cu(II) 3-hydroxy-2-pyrazinecarboxylate and oxalate complexes, respectively. This is the first example of a combination of experimental and theoretical study on in situ metal/ligand reactions under hydro- and solvothermal conditions.

In situ metal/ligand reactions under hydro(solvo)thermal conditions have generated great attention in the past decade because the in situ ligand synthesis results in the generation of novel coordination compounds exhibiting structural diversity and unique properties for potential applications.[1] A variety of novel coordination complexes synthesized in situ have been documented, and many types of in situ reactions have been used in which the carboxylic acid ligands play an essential role.[2] Decarboxylation and hydroxylation took place when the in situ Cu(II)/1,2,3-benzenetricarboxylic acid reaction was carried out using the hydrothermal method and $[Cu_2(ipO)(4,4'-bpy)]_n$ (ipO = 2-hydroxyisophthalate, 4,4'-bpy = 4,4'-bipyridine) was formed.[3] J. Y. Lu et al. reported the first oxalato and isonicotinato mixed-ligand guest-inclusion open-frame-
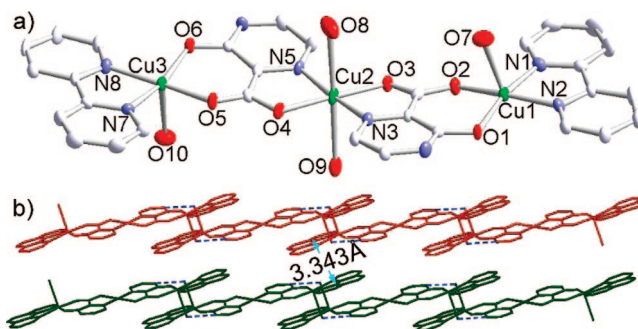
Figure 1. (a) Coordination environment of Cu(II) in complex **1** drawn at 50% probability level. All hydrogen atoms, nitrate ions, and lattice–water molecules are omitted for clarity. (b) 1D ladderlike chains in complex **2** showing hydrogen bonds and $\pi-\pi$ interactions.

work coordination polymer $[Zn_2(oxa)(IN)_2(H_2O)_2]_n \cdot 2nH_2O$ (oxa = oxalate, IN = isonicotinate), in which the oxalate came from pyridinecarboxylate.[4] The hydrothermal synthesis of $[Ln_2(C_2O_4)_2(pyzc)_2(H_2O)_2]_n$ (Hpyzc = 2-pyrazinecarboxylic acid; Ln = Pr, Er) in which Hpyzc decomposes into an oxalate anion was reported in 2006.[5] However, such a reaction that requires further understanding and characterization of the mechanism has proven to be a big challenge. Herein, we report the synthesis and reaction mechanism of four copper complexes obtained from the in situ Cu(II)/2,3-pyrazine-dicarboxylic acid reaction under hydrothermal conditions at different temperatures and first explicate mechanism of the conversion from aromatic dicarboxylic acid to hydroxycarboxylate or oxalate.
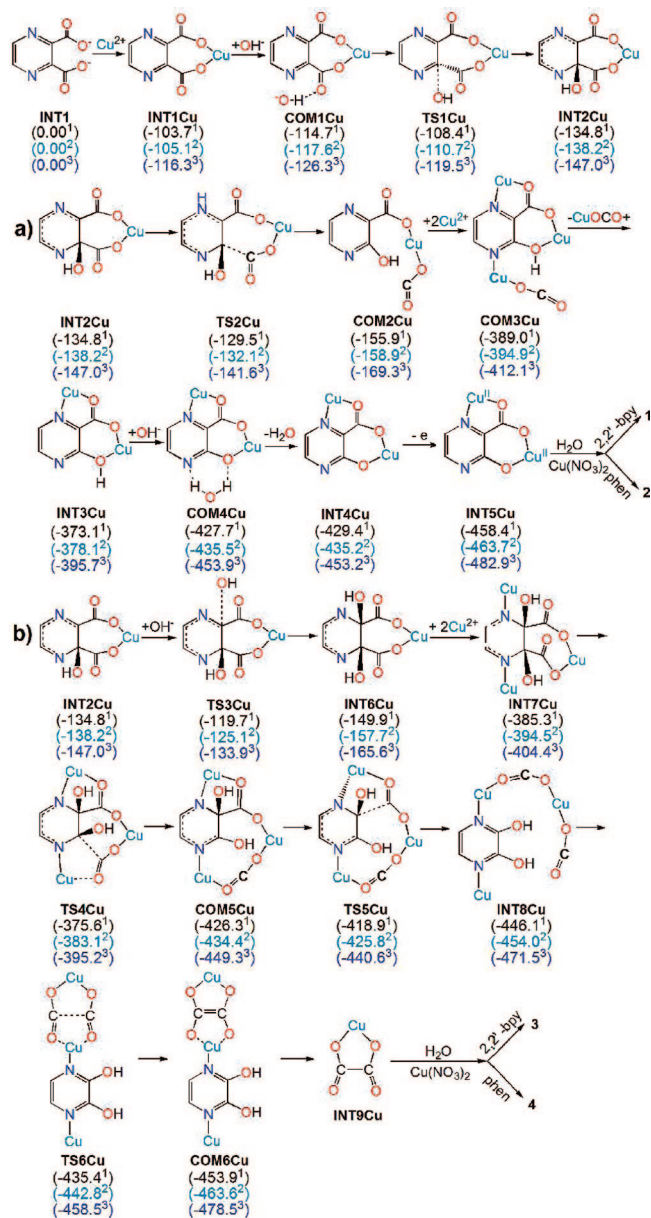
Trinuclear Cu(II) complexes, $[Cu_3(opza)_2(2,2'-bpy)_2(H_2O)_4](NO_3)_2 \cdot H_2O$ (**1**) and $[Cu_3(opza)_2(phen)_2(H_2O)_2](NO_3)_2 \cdot 2H_2O$ (**2**) (opza = 3-hydroxy-2-pyrazinecarboxylate; 2,2'-bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline), were prepared in the hydrothermal in situ reaction of $Cu(NO_3)_2 \cdot 3H_2O$, H2pzda (2,3-pyrazinedicarboxylic acid), 2,2'-bpy (or phen) in H_2O and aqueous NaOH in a Parr Teflon-lined steel vessel at 100 °C for 72 h.[6] The opza ligand was derived from the decarboxylation and hydroxylation of H2pzda, while

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Figure 2. Reaction scheme and relative energies in kilocalories per mole. (a) Formation of complexes **1** and **2**, and (b) the formation of complexes **3** and **4**. (1) SCRF-B3LYP/6-31+G* (Cu atom using a LanL2DZ basis set) in H_2O solution, with 0.96 scaling factor for zero-point energy (ZPE) correction.[14] (2) The same as 1 but without ZPE correction, and (3) SCRF-B3LYP/6-311+G* (for all atoms)//6-31+G* (Cu atom using a LanL2DZ basis set) in H_2O solution, without ZPE correction.

H_2opza has not been prepared using organic synthesis. At a synthesis temperature of 140 °C, a change of H_2pzda to oxalate occurs, and $[Cu_3(oxa)_2(2,2'\text{-bpy})_3(H_2O)_2](NO_3)_2$ (**3**) and $[Cu(oxa)(phen) H_2O] \cdot H_2O$ (**4**) (oxa = oxalate) were subsequently obtained.[6] Complexes **3** and **4** could not be obtained using reaction mixture of $Cu(NO_3)_2$, H_2pzda and 2,2'-bpy (phen) under normal conditions.

X-ray diffraction studies of complex **1**[7] reveals that **1** is a linear trinuclear Cu(II) complex (see Figure.1a). There are three crystallographically independent Cu centers, but Cu1 and Cu3 are in a very similar coordination environment

(Figure 1a). Both Cu1 and Cu3 are five-coordinate to two oxygen atoms from the carboxyl and hydroxyl groups of an opza ligand, two nitrogen atoms from 2,2'-bpy and one oxygen atom from a coordinated water molecule. Cu2 is six-coordinate. The equatorial positions are occupied by two oxygen atoms and two nitrogen atoms from two opza ligands. The axial positions are both coordinated to water molecules. The trinuclear entities overlap and display $\pi-\pi$ stacking of the parallel aromatic rings. The hydrogen bonds between the coordination water and lattice–water, NO_3^-, and carboxylate oxygen atoms link the linear trinuclear Cu(II) entities into a 3D network. The structure of complex **2**[8] is similar to that of complex **1**. However, there are only two crystallographically independent Cu atoms, and the Cu1 atom in the middle position of the trinuclear center is four-coordinate in square planar geometry. The trinuclear units form a ladderlike 1D chain along the [111] direction via the hydrogen bonds established by uncoordinated nitrogen atom of opza ligand and an oxygen atom of coordinated water molecule. The $\pi-\pi$ interaction occurs between phen molecules in the adjacent chains resulting in a 3D supramolecular network (see Figure 1b). The structure of **3** is the same as that of the Cu complex prepared by evaporation of a hot solution of the $[Cu(2,2'\text{-bpy})(NO_3)_2]$ precursor and $Li_2C_2O_4$, which was reported by M. Julve et al.[9] The structure of **4** is the same as the Cu complex reported by P. Cheng et al., which was synthesized through the evaporation of $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$ and phen in ethanol solution.[10]

To characterize the mechanisms for the formation of complexes **1–4**, density functional theory (DFT)[11] calculations employing the SCRF-B3LYP/6–31+G(d) method (where the LANL2DZ basis set was used for Cu atoms) have been carried out to mimic the experimental conditions, using the polarized continuum model (PCM) (water as solvent).[12] To get better results, single-point SCRF-B3LYP/6–311+G* (for all atoms)//SCRF-B3LYP/6–31+G* (LANL2DZ for Cu) calculations have also been performed. The geometric parameters of all possible stationary points attempted have been located and characterized by the number of imaginary frequencies, as implemented in the Gaussian 03 program.[13] For manageable calculations, the auxiliary ligands were omitted to model the mechanism (see Figure 2). In alkaline solution, the reactant H_2pzda loses its two acid hydrogen atoms to form the anionic **INT1** (pzda^{2-}), which coordinates

(6) The yields of complexes **1**, **2**, **3**, and **4** were 69.2%, 72.0%, 77.3%, and 79.5%, respectively. The residues are unknown compounds.

(7) Crystal data for **1**: $C_{30}H_{30}Cu_3N_{10}O_{17}$, M = 993.26, monoclinic, space group Cc, T = 294(2) K, a = 22.114(4) Å, b = 16.830(3) Å, c = 10.4238(18) Å, β = 105.035(3)°, V = 3746.6(1) Å^3, Z = 4, ρ_{calcd} = 1.761 g·cm^{-3}, R_1 = 0.0788, R_2 = 0.0935.

(8) Crystal data for **2**: $C_{34}H_{28}Cu_3N_{10}O_{16}$, M = 1023.28, triclinic, space group $P\bar{1}$, T = 294(2) K, a = 8.252(2) Å, b = 10.377(2) Å, c = 12.503(2) Å, α = 100.519(3)°, β = 107.988(3)°, γ = 106.490(3)°, V = 932.5(3) Å^3, Z = 1, ρ_{calcd} = 1.822 g·cm^{-3}, R_1 = 0.0812, R_2 = 0.1414.

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Figure 2 structures and labels:

INT1 (0.00[1]) (0.00[2]) (0.00[3])
INT1Cu (-103.7[1]) (-105.1[2]) (-116.3[3])
COM1Cu (-114.7[1]) (-117.6[2]) (-126.3[3])
TS1Cu (-108.4[1]) (-110.7[2]) (-119.5[3])
INT2Cu (-134.8[1]) (-138.2[2]) (-147.0[3])

a)
INT2Cu (-134.8[1]) (-138.2[2]) (-147.0[3])
TS2Cu (-129.5[1]) (-132.1[2]) (-141.6[3])
COM2Cu (-155.9[1]) (-158.9[2]) (-169.3[3])
COM3Cu (-389.0[1]) (-394.9[2]) (-412.1[3])

INT3Cu (-373.1[1]) (-378.1[2]) (-395.7[3])
COM4Cu (-427.7[1]) (-435.5[2]) (-453.9[3])
INT4Cu (-429.4[1]) (-435.2[2]) (-453.2[3])
INT5Cu (-458.4[1]) (-463.7[2]) (-482.9[3])

b)
INT2Cu (-134.8[1]) (-138.2[2]) (-147.0[3])
TS3Cu (-119.7[1]) (-125.1[2]) (-133.9[3])
INT6Cu (-149.9[1]) (-157.7[2]) (-165.6[3])
INT7Cu (-385.3[1]) (-394.5[2]) (-404.4[3])

TS4Cu (-375.6[1]) (-383.1[2]) (-395.2[3])
COM5Cu (-426.3[1]) (-434.4[2]) (-449.3[3])
TS5Cu (-418.9[1]) (-425.8[2]) (-440.6[3])
INT8Cu (-446.1[1]) (-454.0[2]) (-471.5[3])

TS6Cu (-435.4[1]) (-442.8[2]) (-458.5[3])
COM6Cu (-453.9[1]) (-463.6[2]) (-478.5[3])
INT9Cu

with Cu^{2+} ion to form **INT1Cu**. As shown in Figure 2, **INT2Cu** could be formed via a transition state, **TS1Cu**, by OH^- attack, with an energetic barrier of ∼6.3 kcal/mol, and here, Cu(II) is reduced to Cu(I). Extensive search on the potential energy surfaces indicates that two competitive pathways, a and b, have been proposed, in which pathway a will lead to crystals **1** and **2** and pathway b will form crystals **3** and **4**. Other proposed pathways are less likely because most of them are of higher energy or because some important stationary points could not be located (see Supporting Information, Figures S1 and S2).

Under normal circumstances, it is improbable that attack by OH^- on the pyrazine ring results in the departure of a COO^- (S_N2 reaction). However, the reaction becomes accessible with the assistance of Cu^{2+}, in which the energetic barrier is calculated to be ∼5.3 kcal/mol on going from **INT2Cu** to **COM2Cu** in pathway a.

It is shown in Figure 2a that only Cu^{2+} can form the crystals because there are several reaction steps that involve the inclusion of OH^- and bring more negative charges, in which the electron transfers from OH^- to Cu^{2+} takes place to disperse the negative charges. For example, Cu in **INT2Cu**, **TS2Cu**, and **COM2Cu** should be monovalent Cu(I), as observed from the calculated spin densities of near zero, and it will be oxidized back to Cu(II) in **INT3Cu**. However, one of the Cu atoms in **INT4Cu** becomes Cu(I) again with the inclusion of interaction with OH^-, which then loses an electron to become Cu(II) in **INT5Cu**. In the final crystals **1** and **2**, all three Cu atoms should be Cu(II).

The formation of crystals **3** and **4** are much more complicated, as illustrated in Figure 2b, because there are two COO^- groups that leave the pyrazine ring to form oxalate. The insertion of a second OH^- into the **INT2Cu** ring is more difficult than that of the first (from **COM1Cu** to **INT2Cu**) because the energy barriers for both processes are 15.1 and 6.3 kcal/mol, respectively, as indicated in Figure S3. This may be the reason why the reaction only proceeded to crystals **1** and **2** at 100 °C, and the crystals **3** and **4** were crystallized out when the reaction was carried out at 140 °C in our experiments.

At first, one may image that **INT6Cu** might directly result in oxalate. However, it turns out that the two carboxyl groups cannot be directly broken from **INT6Cu** (see Supporting Information, Figure S2). A putative mechanism is proposed in Figure 2b, from which one can observe that **INT9Cu** is the structure from which the final crystals **3** and **4** are formed. The relative energies for two competitive reaction pathways a and b (see Figure.2) are shown in Figure S3. The numbering system of some optimized stationary points, some optimized Cartesian coordinates, frequencies of some stationary points, and total energies, Gibbs free energies, zero-point energies, relative energies, and relative Gibbs free energies for the formation of key structures in complexes **1**-**4** at UB3LYP/6–-31+G* (except LanL2DZ for Cu) level in aqueous solution are shown in Figure S4 and Tables S2−S4, respectively. The calculated spin densities of **INT2Cu**, **TS2Cu**, **COM2Cu**, **INT3Cu**, **INT4Cu**, etc., are shown in Table S11. These findings are useful toward understanding and supporting the reaction mechanism.

In conclusion, $Cu_3(opza)_2^{2+}$ and $Cu_3(oxa)_2^{2+}$ complexes were synthesized when a Cu(II)/H_2pzda mixture was hydrothermally heated to 100 and 140 °C, respectively. The theoretical study reveals that the electron transfer from OH^- to Cu^{2+} plays an important role in the processes of $pzda^{2-}$ → $opza^{2-}$ and $pzda^{2-}$ → oxa^{2-}. These findings are helpful in understanding the mechanism of the formations of the four title Cu(II) complexes and Cu(II) analogues formed in situ metal/ligand reactions under hydrothermal condition.

Supporting Information Available: CIF, crystallographic data, and structure refinements, elemental analysis of complexes **1**–**4**, and all of the geometries, energies, and frequencies reported here. This material is available free of charge via the Internet at http://pubs.acs.org.

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