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In Situ C−C Coupling and Formation of a Heptanuclear Copper(II) Cluster

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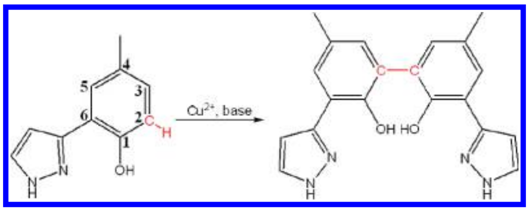
The reaction of $CuCl_2$ with H_2Meppz and a base under low temperature gave rise to a heptanuclear copper compound, in which a novel ligand 2,2′-bis(H_2Meppz) (H_4L') was obtained through in situ C−C coupling.

As an effective method for the synthesis of novel organic ligands that cannot be obtained through conventional organic synthesis, in situ metal/ligand reactions have been attracting increasing interest in recent years. In the process of in situ reactions, the metal ions are usually believed to be a highly efficient catalyst and meanwhile take part in the formation of various coordination compounds with diverse functions.[1] Up to now, most of the in situ reactions leading to novel ligands include C−C coupling, hydroxylation [2 + 3] cycloaddition, oxidation, and decarboxylation and occurred only under hydro(solvo)thermal conditions.[1,2]

Recently, we introduced the ligands 3-(2-hydroxyphenyl)-pyrazole (H_2ppz) and 3-(2-hydroxy-5-methylphenyl)pyrazole (H_2Meppz) to construct several one-dimensional manganese(III) compounds and hexadecanuclear and heneicosanuclear copper(II) clusters that showed attractive magnetic properties.[3] As a successive work, a new heptanuclear copper(II) compound, $[Cu_7(H_2L')(HL')_2(Meppz)(H_2O)Cl_4]$ (**1**), was obtained by the reaction of H_2Meppz with $CuCl_2$ under low temperature. What is more interesting is that a novel ligand H_4L' was also in situ synthesized through C−C coupling (Scheme 1). Here we report the synthesis and magnetic properties of the heptanuclear compound and the possible mechanism of in situ ligand formation.

Scheme 1. Formation of Ligand H_4L' from H_2Meppz



An acetone solution of H_2Meppz and NEt_3 was laid upon a methanol solution of $CuCl_2$ in a test tube at a temperature below 10 °C and produced black crystals of $[Cu_7(H_2L')(HL')_2(Meppz)(H_2O)Cl_4]\cdot x(CH_3)_2CO\cdot yH_2O$ ($\mathbf{1}\cdot x(CH_3)_2CO\cdot yH_2O$) in 4 weeks. The crystals lost guest solvents in the air, and stable solvent-free crystals of **1** were obtained under vacuum overnight for X-ray and magnetic studies.

Single-crystal X-ray structural analysis[4] of **1** revealed that the crystals crystallized in space group *Pbca*, and the molecular structure is shown in Figure 1. The whole entity can be viewed as a $[Cu_4O_4]$ cubane connected to three peripheral Cu^{II} ions through the $H_2L'^{2-}$, HL'^{3-}, and $Meppz^{2-}$ bridges, respectively. The ligand $Meppz^{2-}$ coordinates to Cu^{II} ions in an $\eta^2:\eta^1:\eta^1\text{-}\mu_3$ mode (Scheme 2a),[3c] while the in situ synthesized ligand H_4L' coordinates to Cu^{II} ions in two modes, which are $\eta^1:\eta^3:\eta^2:\eta^1\text{-}\mu_4$ ($H_2L'^{2-}$; Scheme 2b) and $\eta^1:\eta^1:\eta^3:\eta^2:\eta^1\text{-}\mu_5$ (HL'^{3-}; Scheme 2c), respectively. In the $[Cu_4O_4]$ core, the Cu1 atom locates in a pseudo square pyramid, with O3 and N5 atoms from the HL'^{3-} ligand, O2′ from another one, and O4 from the $Meppz^{2-}$ ligand shaping the highly distorted basal plane and a weakly bound O2 atom (Cu1−O2 2.465 Å) occupying the apical position. The Cu2 atom is coordinated by one N atom and four O atoms to form a square-pyramidal entity, whose apical O3 atom is weakly bound to Cu2 (2.411 Å). In the basal plane, the O1 atom comes from the $H_2L'^{2-}$ ligand, the O2 and N3 atoms from the HL'^{3-} ligand, and O3′ from another one. The coordination environment of Cu3 is similar to that of Cu2, with the O1 atom occupying the apical position (Cu3−O1 2.435 Å), while in the basal plane, the O1′ and O2 atoms come from the

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(4) Crystal data for **1**: $C_{70}H_{56}N_{14}O_8Cl_4Cu_7$, M_r = 1807.87, orthorhombic, space group *Pbca*, a = 22.666(1) Å, b = 20.678(1) Å, c = 32.502(1) Å, V = 15233.1(9) Å^3, Z = 8, T = 173(2), D_c = 1.577 g·cm^{-3}, μ = 2.119, GOF = 0.839, R1 = 0.0587, wR2 = 0.1521.

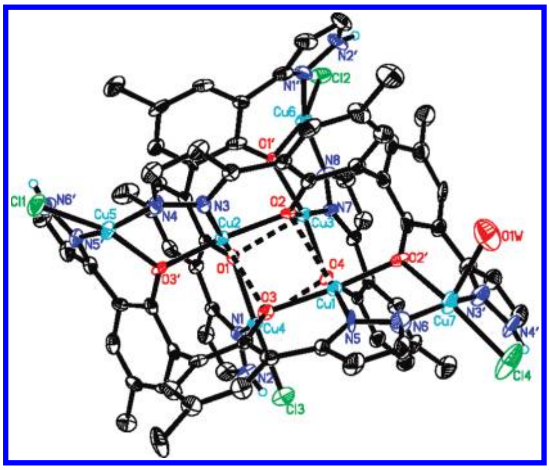
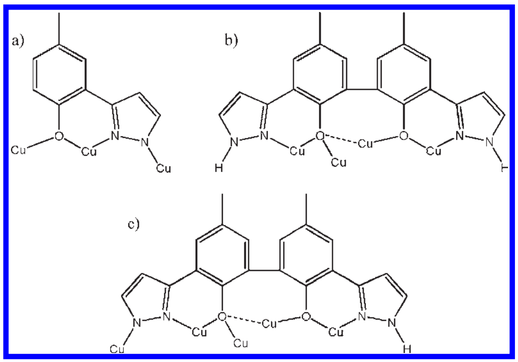


Figure 1. ORTEP drawing of **1** at the 35% probability level with atom labeling. Selected bond distances (Å) and angles (deg): Cu1−O2 2.465(5), Cu1−O2′ 1.994(6), Cu1−O3 2.021(5), Cu1−O4 1.954(5), Cu1−N5 1.867(6), Cu2−O1 1.989(5), Cu2−O2 1.996(5), Cu2−O3 2.411(5), Cu2−O3′ 1.942(5), Cu2−N3 1.918(6), Cu3−O1 2.435(5), Cu3−O1′ 1.937(5), Cu3−O2 2.011(5), Cu3−O4 1.970(5), Cu3−N7 1.900(6), Cu4−O1 2.075(5), Cu4−O3 1.964(5), Cu4−O4 2.475(6), Cu4−N1 1.893(6), Cu4−Cl3 2.264(3), Cu5−O3′ 1.922(5), Cu5−N4 1.947(7), Cu5−N5′ 1.971(7), Cu5−Cl1 2.238(2), Cu6−O1′ 1.942(5), Cu6−N1′ 1.976(7), Cu6−N8 1.947(7), Cu6−Cl2 2.230(2), Cu7−O2′ 1.945(5), Cu7−N3′ 1.974(8), Cu7−N6 1.946(8), Cu7−Cl4 2.313(3), Cu7−O1W 2.315(8); Cu1−O3−Cu4 102.4(2), Cu1−O4−Cu3 104.5(2), Cu2−O2−Cu3 102.0(2), Cu2−O1−Cu4 100.8(2), Cu1−O2′−Cu7 112.0(2), Cu2−O3′−Cu5 114.9(2), Cu3−O1′−Cu6 114.2(2).

Scheme 2. Coordination Modes of H_2Meppz (a) and H_4L' (b and c) in **1**[a]



[a] The dotted lines represent a weak coordination bond.

$H_2L'^{2-}$ and HL'^{3-} ligands, respectively, and the remaining O4 and N7 atoms are from the Meppz^{2-} ligand. The Cu4 atom is coordinated by O1, N1 ($H_2L'^{2-}$), and O3 (HL'^{3-}) atoms and a terminal chloride ion (Cu4−Cl3 2.264 Å) to give a highly distorted coordination square. The O4 atom is weakly bound to Cu4 (Cu4−O4 2.476 Å), so that the coordination geometry of Cu4 can be viewed as a pseudo-square-pyramidal one. The Cu1, Cu2, and Cu3 atoms are bridged to three peripheral Cu7, Cu5, and Cu6 atoms, respectively, by both phenolate and pyrazolate groups with Cu−O−Cu bond angles of 112.0°, 114.9°, and 114.2°, respectively, which are larger than those within the [Cu_4O_4] core (100.8−104.5°). Among the three peripheral Cu^{II} atoms, both the Cu5 and Cu6 atoms locate in a highly distorted square environment, the Cu5 atom is coordinated by one Cl$^-$ ion (Cl1), one N atom (N4) from the HL'^{3-} ligand, and one N atom and one O atom (O3′ and N5′) from another one, whereas the Cu6 atom is coordinated by one Cl$^-$ ion (Cl2), one N atom (N8) from the Meppz^{2-} ligand, and one N atom and one O atom (O1′ and N1′) from the $H_2L'^{2-}$ ligand. The Cu7 atom is five-coordinated, with the water molecule (O1W) occupying the apical position of the square pyramid, whose basal plane is completed by one Cl$^-$ ion (Cl4), one N atom (N6) from the HL'^{3-} ligand, and one N atom and one O atom (O2′ and N3′) from another one. The average Cu−O bond length, except that of Cu−O$_{\text{apical(square pyramid)}}$, is 1.976 Å, and the Cu−N bond length is 1.934 Å, which are similar to those in the hexadecanuclear copper(II) compound.[3c]

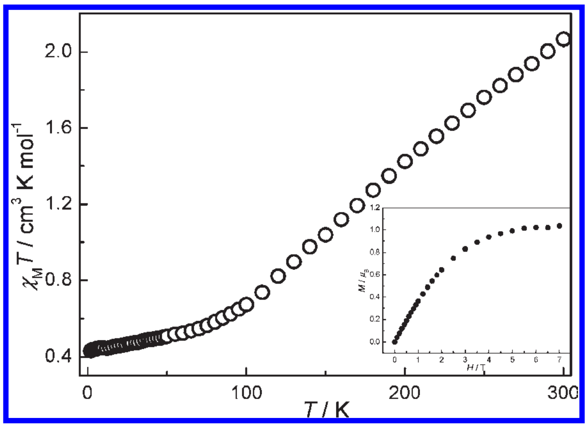


Figure 2. Temperature-dependent susceptibilities of **1** under an applied field of 1000 Oe. Inset: Field-dependent magnetization at 2 K.

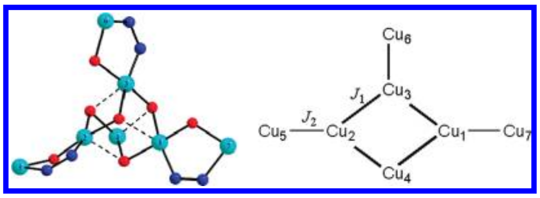


Figure 3. Simplified Cu_7 unit (left) and a coupling model (right) of **1**.

The direct-current magnetic susceptibilities of **1** shown in Figure 2 were measured in the temperature range of 2−300 K. The $\chi_M T$ value at room temperature is 2.065 cm^3 K mol^{-1}, which is much smaller than the theoretical one (2.625 cm^3 K mol^{-1}) for seven uncoupled Cu^{II} ions ($g = 2$). Upon cooling, the $\chi_M T$ value quickly decreases and reaches a minimum value (0.431 cm^3 K mol^{-1}) at 2 K, indicating dominant intramolecular antiferromagnetic interactions. The saturated magnetization value at 7 T is 1.04 μ_B, which confirms the antiferromagnetic properties of the compound. Generally, copper phenoxo compounds show ferromagnetic properties when the Cu−O−Cu angles are less than 99° and antiferromagnetic beyond this.[5] A further investigation of the core structure of **1** reveals that in the [Cu_4O_4] cubane the exchanges in this manner with Cu−O distances longer than 2.4 Å are negligible (dotted lines in Figure 3, left). Because other Cu−O distances are shorter than 2.1 Å, the [Cu_4O_4] cubane can be viewed as a square in which the average Cu−O−Cu angle is 102.4° (Figure 3, right) and the average Cu−O−Cu angle between the peripheral and cubane Cu atoms is 113.7°, both

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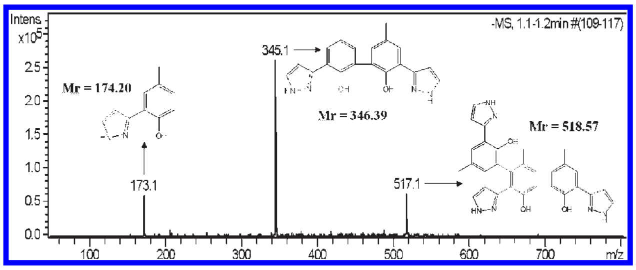

Figure 4. ESI-MS spectra collected in the negative-ion mode. Calculated *m*/*z* values for $HMeppz^-$, $H_3L'^-$, and $H_5L''^-$ are 173.20, 345.40, and 517.57, respectively. The ortho−meta trimer is just a proposed structure.

implying antiferromagnetic exchanges between Cu atoms. We tried to simulate the susceptibilities with *MAGPACK*,[6] which, however, did not give reasonable results. From a structural point of view, because the Cu−O−Cu angles between the peripheral and cubane Cu atoms are larger than those within the cubane, the coupling parameter $|J_2|$ is believed to be larger than $|J_1|$.

In order to verify the C−C coupling reaction in the synthesis process of **1**, an electrospray ionization mass spectrometry (ESI-MS) experiment was carried out (Figure 4). To a stirred MeOH/acetone (3/10 mL) solution of H_2Meppz (0.1 mmol) and NEt_3 (0.1 mmol) was added solid $CuCl_2 \cdot 2H_2O$ (0.1 mmol). This mixture was stirred for 1 h at room temperature, and then a $(NH_4)_2S$ solution was added to precipitate the Cu ions, the solution was filtered, and the filtrate was characterized in the negative-ion mode of the ESI source. The main peak with a weight of 1 less than the molecular weight of H_4L' ($M_r = 346.39$) clearly indicates the existence of $H_3L'^-$, which results from a C−C coupling reaction, while the weak ion peak with a weight of 173.1 corresponds to the H_2Meppz molecule losing one H atom. Another weak peak with a weight of 517.1 may be ascribed to the coupled H_2Meppz trimer (M_r = 518.57), which loses one H atom (Figure 4, inset).

The C−C coupling reaction is very important in organic syntheses.[7] In recent years, increasing interest has been focused on the development of transition-metal-catalyzed C−H bond activation and C−C bond formation to effectively construct biaryl scaffolds.[8] So far, several metal catalysts have already been utilized, such as ruthenium, rhodium, and palladium.[9] The present in situ ligand formation of H_4L' belongs to one of the C−C coupling reactions, the dimerization of phenols. It is a long-standing historical reaction for building metal−organic frameworks[10] and a basic approach to synthesizing natural products.[11] The mechanism of phenol dimerization is believed to involve either two one-electron or one two-electron oxidations to form an aryl−aryl-coupled dimer through the ortho and/or para position(s).[12]

$FeCl_3 \cdot 6H_2O$[13] and especially a large number of copper(II) amine compounds[14] have been proven to be efficient catalysts in the oxidative coupling of two aryl C−H bonds of phenol or naphthol molecules. In the process of H_4L' formation, the H_2Meppz ligand may first chelate Cu ions by its phenol O atom and pyrazole N atom to form an intermediate compound that successively activates its own C−H bond (2 site; Scheme 1) and dimerizes. In addition, the C−H bond at the 5 site of the H_2Meppz ligand may also be activated and lead to the formation of the H_2Meppz trimer, as indicated by the ESI-MS results.

In conclusion, we have reported a heptanuclear copper(II) compound with an in situ synthesized ligand; the present C−C coupling reaction is very uncommon in phenol pyrazolate compounds.

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Supporting Information Available: Experimental details and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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