Inorg. Chem. 2008, 47, 7969−7971

Inorganic Chemistry
Communication

Di-2-pyridyl Ketone/Benzoate/Azide Combination as a Source of Copper(II) Clusters and Coordination Polymers: Dependence of the Product Identity on the Solvent

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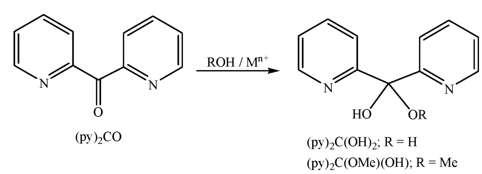
Received June 30, 2008

The reactions of di-2-pyridyl ketone with $Cu(O_2CPh)_2$ in the presence of NaN_3 and LiOH have led to an antiferromagnetically coupled ($S = 0$) Cu^{II}_6 cluster with a novel core and to $(Cu^{II}_8)_n$ and $(Cu^{II}_2)_n$ coordination polymers (the former 1D and the latter 2D) with interesting structures. The cluster or polymer formation depends on the reaction solvent.

Molecular clusters[1] and coordination polymers[2] of paramagnetic 3d transition metals continue to be a major research theme of many groups around the world because of their fascinating physical properties, their potential applications, and the aesthetic beauty and complexity of their structures.

The chances of identifying new clusters and polymers will benefit from the development of new reaction systems with suitable organic ligands. A popular such ligand is di-2-pyridyl ketone, $(py)_2CO$ (Chart 1).[3] Water and alcohols (ROH), among other[4] nucleophiles, have been shown to add to the carbonyl group *upon coordination* of the carbonyl oxygen and/or the 2-pyridyl rings, forming the ligands $(py)_2C(OH)_2$ [the *gem*-diol form of $(py)_2CO$] and $(py)_2C(OR)(OH)$ [the hemiacetal form of $(py)_2CO$], respectively (Chart 1). The immense structural diversity displayed by the complexes reported stems, in part, from the ability of $(py)_2C(OR)O^-$ (R = H, Me, Et,...) and $(py)_2CO_2^{2-}$ to exhibit no less than nine distinct bridging modes ranging from μ_2 to μ_5.[3] Employment of carboxylates ($R'CO_2^-$) and/or inorganic anions with a coordination capability as ancillary ligands in the reaction mixtures gives an extraordinary structural flexibility in the mixed-ligand systems, allowing the synthesis of a variety of 3d metal clusters[5] (and occasionally of coordination polymers[6]).

Chart 1. Ligands Discussed in the Text[a]



[a] Note that $(py)_2C(OR)(OH)$ and their anions do not exist as free species but exist only in their respective metal complexes (M^{n+} = metal ion; $n = 2$ and 3).

We have been exploring the ternary $(py)_2CO/R'CO_2^-/N_3^-$ (R' = H, Me, Ph,...) ligand combination ("blend") in 3d metal chemistry as a means to high-nuclearity species. Studies with Mn,[7] Fe,[8] Co,[9] and Ni[10] have been very encouraging. We have thus decided to extend the exploration of this general ligand combination in copper(II) chemistry. We herein report that the $Cu^{II}/(py)_2CO/PhCO_2^-/N_3^-$ reaction system has provided access to one hexanuclear cluster and two, one 1D and the other 2D, coordination polymers [the first polymeric complexes from the $(py)_2CO/R'CO_2^-/N_3^-$ combination for any metal].

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Published on Web 08/12/2008

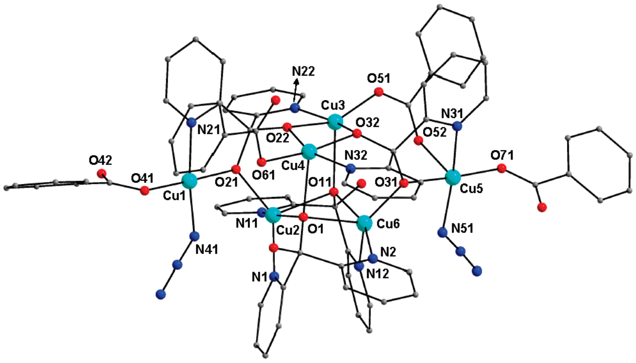

Figure 1. Molecular structure of **1**. Color scheme: Cu^{II}, sky blue; O, red; N, dark blue; C, gray.

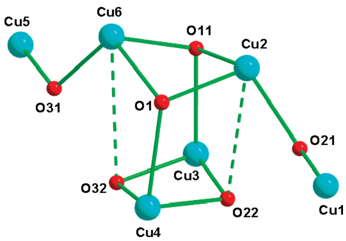

Figure 2. $[Cu^{II}_6(\mu_3\text{-OR}'')_2(\mu\text{-OR}'')_4]^{6+}$ core of **1**, emphasizing the central defective cubane subcore (green thick lines). The green dashed lines represent the two missing edges of the cubane unit. Color scheme: Cu^{II}, sky blue; O, red.

The reaction of $Cu(O_2CPh)_2\cdot 2H_2O$, $(py)_2CO$, LiOH, and NaN_3 in a 2:1:1:1 molar ratio in MeCN gave a dark-green solution, which upon layering with Et_2O gave dark-green crystals of $[Cu_6(O_2CPh)_4(N_3)_2\{(py)_2CO_2\}_2\{(py)_2C(OH)O\}_2]\cdot 2H_2O\cdot 4.5MeCN$ (**1**$\cdot 2H_2O\cdot 4.5MeCN$) in 55% yield; the product analyzed satisfactorily as **1**$\cdot 2H_2O$. The hexanuclear molecule[11] (Figure 1) is held together by two 4.2211 (Harris notation[12]) $(py)_2CO_2^{2-}$ ligands, two 3.3011 $(py)_2C(OH)O^-$ groups, and a single *syn,anti*-2.11 $PhCO_2^-$ group. Peripheral ligation is provided by three monodentate (1.10) $PhCO_2^-$ groups and two terminal (1.100) N_3^- ligands. The novel core (Figure 2) consists of four, square-pyramidal Cu^{II} atoms [Cu(2,3,4,6)] located at four alternate vertices of a central defective cubane unit (a cubane missing two opposite edges), two μ_3 O atoms (O1, O11) from the 3.3011 $(py)_2C(OH)O^-$ groups, and two μ O atoms (O22, O32) from two different 4.2211 $(py)_2CO_2^{2-}$ ligands (these four O atoms occupy the remaining vertices of the cube), two additional satellite Cu^{II} atoms (Cu1 is square planar; Cu5 is square pyramidal) across the missing edges, and two μ O atoms (O21 and O31) that belong to the two different $(py)_2CO_2^{2-}$ groups, and each links the cubane unit with a satellite metal ion. Complex **1** joins a very small family of hexanuclear Cu^{II}_6/N_3^- clusters.[13] This nuclearity is the second highest in copper(II) azide chemistry after the impressive $(Cu^{II}_7)_2/N_3^-$ cluster synthesized by Thompson's group.[14]

(11) Crystal structure data for **1**$\cdot 2H_2O\cdot 4.5MeCN$: $C_{81}H_{71.5}Cu_6N_{18.5}O_{18}$, M_w = 1973.31, triclinic, space group $P\bar{1}$ with a = 16.289(8) Å, b = 17.295(8) Å, c = 18.125(8) Å, α = 69.870(10)°, β = 69.18(2)°, γ = 73.48(2)°, V = 4404(4) Å^3, T = 298 K, Z = 2, R1 [$I > 2\sigma(I)$] = 0.0711, wR2 = 0.1396 (F^2, all data). Crystal structure data for **2**: $C_{38}H_{32}Cu_4N_{16}O_8$, M_w = 1094.96, monoclinic, space group $P2_1/c$ with a = 21.690(10) Å, b = 12.867(9) Å, c = 16.810(10) Å, β = 114.46(2)°, V = 4270(4) Å^3, T = 298 K, Z = 4, R1 [$I > 2\sigma(I)$] = 0.0446, wR2 = 0.1079 (F^2, all data). Crystal structure data for **3**: $C_{19}H_{16}Cu_2N_8O_4$, M_w = 547.48, monoclinic, space group $P2_1/n$ with a = 12.994(6) Å, b = 8.630(4) Å, c = 19.302(9) Å, β = 102.13(3)°, V = 2116.2(17) Å^3, T = 298 K, Z = 4, R1 [$I > 2\sigma(I)$] = 0.0703, wR2 = 0.1330 (F^2, all data).

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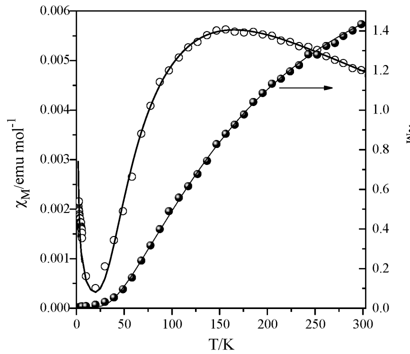

Figure 3. χ_M vs T (open cycles) and $\chi_M T$ vs T (solid cycles) plots for **1**$\cdot 2H_2O$ in a 1 kG field. The solid lines are the fit of the data; see the text for the fit parameters.

Solid-state direct current magnetic susceptibility (χ_M) data on dried **1**$\cdot 2H_2O$ were collected in an 0.1 T field in the 2.0−300 K range and are plotted as $\chi_M T$ vs T and χ_M vs T in Figure 3. χ_M increases from 48 × 10^{-4} emu mol^{-1} at room temperature to a maximum value of 56 × 10^{-4} emu mol^{-1} at 170 K and then decreases drastically to a minimum of 3 × 10^{-4} emu mol^{-1} at 20 K, before increasing again to the value of 21 × 10^{-4} emu mol^{-1} at 6 K. On the basis of the room-temperature $\chi_M T$ value of 1.43 emu mol^{-1} K, which is lower than the value expected for six $S = {}^1/_2$ uncoupled spins (2.25 emu mol^{-1} K with g = 2.0) and the maximum in the χ_M vs T plot at 170 K, we conclude that strong antiferromagnetic exchange interactions between the Cu^{II} atoms are operative within the cluster. The Curie tail in the low-temperature susceptibility data reveals the existence of a paramagnetic, possibly monomeric, impurity. According to the core (Figure 2), a simplified spin Hamiltonian that describes the exchange interactions in **1** is

$$H = -2J_1(S_1\cdot S_2 + S_5\cdot S_6) - 2J_2S_2\cdot S_6 - 2J_3S_3\cdot S_4 \quad (1)$$

Best-fit (solid lines in Figure 3) parameters are J_1 = −94(5) cm^{-1}, J_2 = −110(5) cm^{-1}, J_3 = −116(5) cm^{-1}, g = 2.05, and ρ = 0.15%, leading to an overall S = 0 ground state. A fourth exchange parameter (J_4) incorporating the S_2S_3, S_2S_4, S_3S_6, and S_4S_6 magnetic interactions was not considered because the relevant Cu···Cu distances are rather long (3.56−3.73 Å); incorporation of J_4 leads to significant correlations between the fitted parameters.

The same preparative and crystallization procedure as that of **1** but employing MeOH instead of MeCN gave a mixture of dark-green plate- and needle-like crystals, crystallographically characterized[11] as the 1D and 2D polymers $[Cu_4(O_2CPh)_2(N_3)_4\{(py)_2C(OMe)O\}_2]_n$ (**2**) and $[Cu_2(O_2CPh)(N_3)_2\{(py)_2C(OMe)O\}]_n$ (**3**), respectively; the nonoptimized yields were ~20% (**2**) and ~10% (**3**). Mainly because of the identical Cu/$PhCO_2^-/N_3^-/(py)_2C(OMe)O^-$ (2:1:2:1) ratio present, the two complexes could not be isolated separately.

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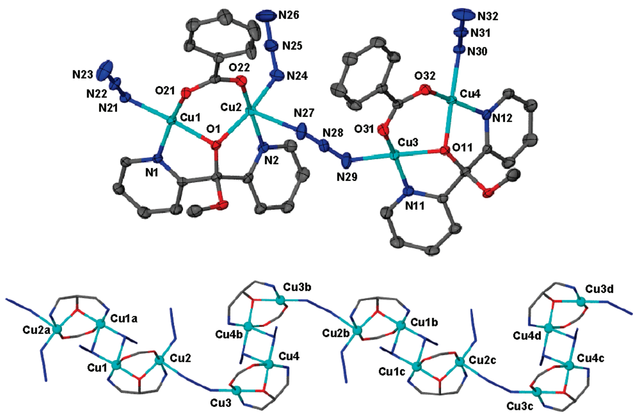

Figure 4. ORTEP view of the asymmetric unit of **2** at the 30% probability level (top) and a view (with many atoms omitted) of one infinite zigzag chain of the AABB repeating units running along the *ac* diagonal (bottom). Color scheme as in Figure 1.

The asymmetric unit of **2** (Figure 4, top) consists of two similar $Cu^{II,II}_2$ subunits A (Cu1 and Cu2) and B (Cu3 and Cu4) bridged by a single end-to-end (EE or $\mu_{1,3}$) N_3^- ligand through the square-pyramidal Cu2 and the square-planar Cu3 ions. The two Cu^{II} centers within each dinuclear unit are bridged by one 2.2011[12] $(py)_2C(OMe)O^-$ ligand and one *syn,syn*-2.11 $PhCO_2^-$ group. Two end-on (EO or $\mu_{1,1}$) N_3− ligands bridge two Cu1 atoms from two dinuclear units A. Similarly, two dinuclear units B are bridged through two EO N_3^- ligands via two Cu4 centers. Both Cu1 and Cu4 are in square-pyramidal environments with azido N atoms at the apical positions. Thus, tetranuclear units A═A and B═B form, while one EE azido ligand bridges the tetranuclear units A═A and B═B, giving rise to an octanuclear repeating unit of −A═A−B═B−, where "═" and "−" denote double EO and single EE azide bridges, respectively. The AABB repeating unit forms an infinite zigzag chain running along the *ac* diagonal (Figure 4, bottom). Therefore, chemically **2** is best formulated as $[Cu_8(O_2CPh)_4(N_3)_8\{(py)_2C(OMe)O\}_4]_n$.

The asymmetric unit of **3** consists of dinuclear $[Cu_2(O_2CPh)(N_3)_2\{(py\}_2C(OMe)O\}]$ moieties, where the two square-pyramidal Cu^{II} centers (Cu1 and Cu2) are bridged (as in **2**) by one 2.2011 $(py)_2C(OMe)O^-$ ligand and one *syn,syn*-2.11 $PhCO_2^-$ group. The dinuclear units assemble with two EO azido ligands that bridge the Cu2 atoms to form a tetranuclear unit (Figure 5, top). The latter are linked through the Cu1 centers via four EE azido ligands to form a 2D layer along the (1, 0, −1) plane (Figure 5, bottom). The 2D layer of **3** adopts the "herringbone" or "parquet floor" architecture. The familiar herringbone network is based on T-shaped 3-connected nodes bridged by linear spacers (Figure 6, left), while in **3**, each tetranuclear unit serves as two fused 3-connected nodes that self-assemble to create the herringbone architecture (Figure 6, right). To the best of our knowledge, **3** joins only a handful of extended 2D networks that adopt the herringbone architecture that is *not* based on T-shaped nodes.[15]

Complex **3** could have derived from **2** if the terminal azide ligand on Cu2 in **2** (Figure 3) had bridged the Cu3 atom in an EE fashion (see the Supporting Information). Complexes **2** and **3** are the first copper(II) coordination polymers with any $(py)_2CO$-based ligand/N_3^- combination.

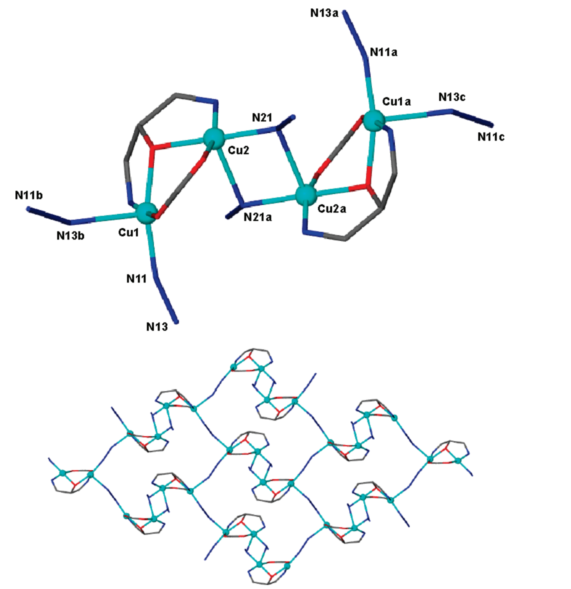

Figure 5. Assembly of two dinuclear units (top) of **3** and the 2D layer running along the (1, 0, −1) plane (bottom). Symmetry code: a, 2 − *x*, −*y*, −*z*; b, 1.5 − *x*, 0.5 +*y*, 1.5 − *z*; c, 0.5 + *x*, −0.5 − *y*, 0.5 + *z*. Color scheme as in Figure 1.

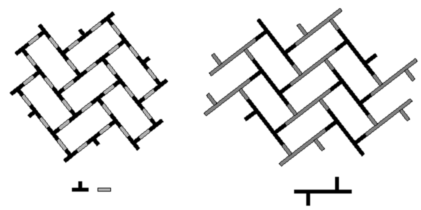

Figure 6. Familiar herringbone motif based on T-shaped 3-connected nodes and spacers (left) and the herringbone architecture of **3** based on the tetranuclear units that serve as two fused 3-connected nodes (right).

In summary, the use of both $(py)_2CO$ and N_3^- in reactions with $Cu(O_2CPh)_2$ has led to a hexanuclear cluster with a novel core and to one 1D coordination polymer and one 2D coordination polymer with interesting structural features. The products provide an example of the dependence of the structural type (cluster vs polymer) on the reaction solvent. The combination of $(py)_2CO$, carboxylate, and azide ligands with a host of other 3d transition elements promises to deliver many new and exciting clusters and polymers.

Acknowledgment. Financial support from the program PYTHAGORAS I (Grant b.365.037) and the Special Account for Research Grants (SARG) of the University of Athens is gratefully acknowledged.

Supporting Information Available: Full synthetic procedures and elemental analyses of complexes **1**−**3**, coordination modes of the ligands discussed in the text, several views of the three complexes, and crystallographic data for **1**·2H$_2$O·4.5MeCN, **2**, and **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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