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Anionic Tuning of the Dimensionality in Copper Oximato Chemistry

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Control of the dimensionality and nuclearity in pyraziloximato-copper(II) chemistry has been achieved by tuning of the donor properties of the counteranions.

R_1-2-{R_2}pyridyloximate ligands (Chart 1) have demonstrated to be versatile donors capable of generating medium-to-high nuclearity clusters in the bottom-up approach by the self-assembly of metal oximato fragments.[1] These kinds of ligands are able to act as bidentate ligands when neutral or to link up to three or four metallic centers in their deprotonated anionic form. A series of high-nuclearity clusters, such as, for example, Ni_{12} and Ni_{14},[2] Fe_{12},[3] or Mn_{12},[4] exhibiting in some cases a single-molecule-magnetic response, have been characterized by us and other groups in recent years.

2-Pyridyloximate, (py)C(H)NOH, is the basic unit on which a variety of modifications[1] have been made in order to modulate its donor properties: coordination compounds have been reported by varying the R_1 group (H, Me, Ph), introducing a donor function in the same R_1 position (py, OH, NH_2), or placing a second oximate group in R_2, giving the 2,6-pyridyldioximate family of ligands[1,5] (Chart 1).

Analysis of CCDC-reported structures shows that copper oximato chemistry is prone to generating some characteristic topologies such as the double oximato bridge (Chart 2A), which tends to generate dinuclear systems with a very strong antiferromagnetic coupling[6] (typically $-J > 500\ cm^{-1}$) and triangular systems containing one central μ_3-hydroxo or alkoxo donor. Typically, in these triangular arrangements,[7] the anions bind axial coordination sites of pentacoordinated copper atoms, displaying two defined shapes: on opposite faces of the triangle for carboxylato or similar anions (Chart 2B) or a tridentate linkage on the same face of the triangle for tetrahedral anions such as sulfate or perchlorate (Chart 2C).

Chart 1. (Left) 2-Pyridyloximate Ligand Indicating the Main Positions Adequate for the Introduction of New Functions; (Right) (pz)C(Me)-NOH Ligand

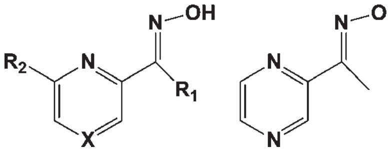
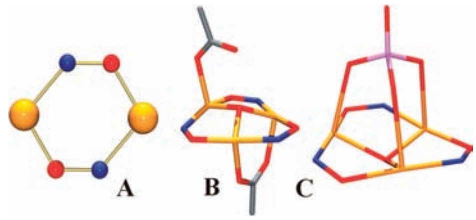


Chart 2. Typical Arrangements for the Copper(II) Oximato System[a]



[a] Color code: Cu, orange; O, red; N, blue.

In the present work, we introduce a synthetic strategy comprising two main changes with respect to the reported systems: the first one consists of a new modification on the pyNOH ligand, consisting of the addition of a second nitrogen-donor atom on the aromatic ring, leading to the 2-pyrazilaldoximato ligand, (pz)C(Me)NOH (Chart 1). In parallel, we introduce the first systematic exploration of the

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influence of the donor properties of the axial ligand (good donors vs poorly coordinating anions), with the aim of promoting supramolecular architectures based on interlinked clusters, which are unprecedented in metal oximato chemistry without the help of additional bridging ligands. To our knowledge, the only related ligand reported until now is pyrazinohydroxamato, for which some discrete Cu_5La and Cu_5Gd derivatives have been reported.[8]

The (pz)C(Me)NOH ligand was obtained by the conventional reaction of acetylpyrazine and hydroxylammonium chloride in a basic (NaOH) medium. Compounds **1**−**5** were obtained by the reaction of the corresponding copper(II) salt, (pz)C(Me)NOH, and Et_3N in a 1:1:1 ratio. When the resulting blue solutions were layered with diethyl ether, X-ray-quality **1**−**5** compounds were obtained.

For salts containing anions with good donor properties, the complexes follow the reported trends and the preferred shape was based in the typical triangular structure with the axial coordination sites of the copper atoms occupied by the corresponding anion, as was found for the acetate or chloride derivatives. Complex[9] $[Cu_3(OH)((pz)C(Me)NO)_3(AcO)_2]$ (**1**) consists of a triangular arrangement of copper oximato ligands in the typical topology shown in Chart 2B, in which the noncoordinated carboxylato oxygen atom forms a strong hydrogen bond with the μ_3-OH group.

The new complex $[Cu_6(MeO)_2((pz)C(Me)NO)_6(Cl)_3]Cl$ (**2**) containing μ_3-methoxo groups instead of hydroxo ligands; Figure 1) exhibits the same pattern as in Chart 2B, but in this case, the bridging ability of the chloride ligand promotes a hexanuclear compound in which the two triangles are linked by one chloride donor.

These compounds, among others, give a clear indication that the very stable triangular structure with axial anionic donors is preferred over coordination of the neutral pyrazinic nitrogen atom. The new complex $[Cu_6(OH)_2((pz)C(Me)NO)_6(NO_3)_3(MeOH)_2]_n(NO_3)_n$ (**3**), which also contains the same kinds of trinuclear units, was synthesized starting from copper nitrate. In contrast with the above-described compounds **1** and **2**, one of the axial coordination sites is occupied by one pyrazinic ligand from the neighboring triangle, giving chains of trimers (Figure 2). The remaining axial sites are linked by one monodentate nitrato anion, one solvent molecule, and a second nitrato ion in the very rare μ_4-O,O,O′O″-coordination mode (Figure 2), which links the chains of trimers, giving a two-dimensional (2D) network.

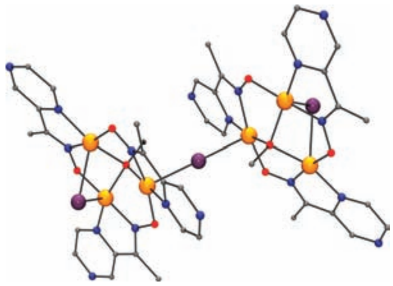

Figure 1. Plot of the structure of the hexanuclear compound **2**. Cu−O−Cu bond angles are 107.3(6)°, 105.6(5)°, and 99.3(5)°, giving an isosceles triangle, with the MeO^- group placed 0.825 Å above the Cu_3 plane.

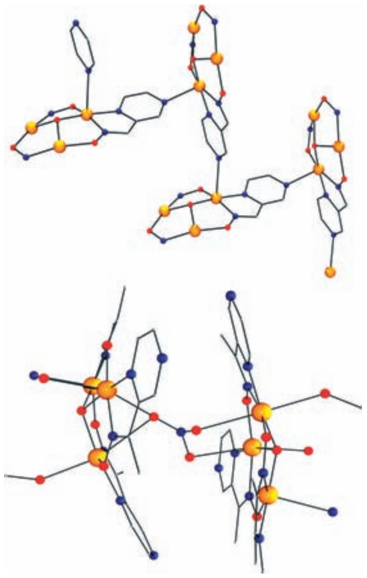

Figure 2. (Top) Plot of the one-dimensional arrangement of trinuclear units linked by the pyrazil groups found for compound **3**. These chains are linked between them by μ_4-NO_3^- counteranions (bottom), giving a 2D system. The Cu−O−Cu bond angles lie between 106.8(2)° and 112.3(3)°, with the OH^- groups placed 0.603/0.648 Å above the Cu_3 planes.

The above compounds confirm two main features: that coordinating anions stabilize the triangular arrangement of copper(II) oximato ligands and that the pyrazinic nitrogen atom is capable of expanding the dimensionality of the system. In light of these results, our strategy was to try to obtain new derivatives starting from noncoordinating anions such as triflate and tetrafluoroborate with the aim of reducing the stability of the triangular arrangement. Using as starting reagents the corresponding copper(II) salts, compounds $[Cu_2((pz)C(Me)NO)_2]_n(CF_3SO_3)_{2n}$ (**4**) and $[Cu_3(OH)_{0.5}(O)_{0.5}((pz)C(Me)NO)_3]_n[Cu_2((pz)C(Me)NO)_2]_{1.5n}(BF_4)_{4.5n}$ (**5**) were obtained.

Compound **4** consists of two nonequivalent dimers with double oximato bridges (Chart 2A, local topology). Both units deviate largely from planarity, with the Cu−N−O−Cu torsion angles around 20°/30° for each nonequivalent subunit. An equatorial CuN_3O environment around the copper

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[9] Crystal data for **1**: $2(C_{22}H_{24}Cu_3N_9O_8)\cdot 7(CH_3OH)$ (1690.54), triclinic, $P\bar{1}$, a = 11.731(6) Å, b = 12.592(4) Å, c = 13.272(6) Å, α = 72.23(3)°, β = 74.24(3)°, γ = 83.43(2)°, V = 1795(1) $Å^3$, Z = 1, T = 223(2) K, λ(Mo Kα) = 0.710 73 Å, 13 824 reflections collected, 7296 unique (R_{int} = 0.0436), R1 = 0.0508, wR2 = 0.1463. Crystal data for **2**: $C_{38}H_{42}Cl_4Cu_6N_{18}O_8$ (1402.00), monoclinic, $C2/c$, a = 14.333(6) Å, b = 24.720(10) Å, c = 18.872(7) Å, β = 97.28(1)°, V = 6633(5) $Å^3$, Z = 4, T = 100(2) K, λ(Mo Kα) = 0.710 73 Å, 15 152 reflections collected, 2591 unique (R_{int} = 0.177), R1 = 0.085, wR2 = 0.225. Crystal data for **3**: $C_{38}H_{44}Cu_6N_{22}O_{22}$ (1542.19), monoclinic, Cc, a = 24.315(11) Å, b = 10.174(5) Å, c = 26.310(8) Å, β = 117.52(1)°, V = 5772(4) $Å^3$, Z = 4, T = 293(2) K, λ(Mo Kα) = 0.710 73 Å, 22 006 reflections collected, 12 482 unique (R_{int} = 0.0596), R1 = 0.0618, wR2 = 0.1982. Crystal data for **4**: $C_{18}H_{18}Cu_3N_9O_3$ (599.06), monoclinic, $P2_1/c$, a = 14.0966(5) Å, b = 14.1845(7) Å, c = 24.671(1) Å, β = 92.511(1)°, V = 4928.2(4) $Å^3$, Z = 4, T = 100(2) K, λ(Mo Kα) = 0.710 70 Å, 46 681 reflections collected, 10 113 unique (R_{int} = 0.052), R1 = 0.0635, wR2 = 0.1872. Crystal data for **5**: $C_{36}H_{36}Cu_6F_{1.35}N_{18}O_7$ (1239.78), trigonal, $R\bar{3}$, a = 29.758(2) Å, b = 29.758(2) Å, c = 11.824(1) Å, γ = 120°, V = 9068(1) $Å^3$, Z = 6, T = 100(2) K, λ(Mo Kα) = 0.710 73 Å, 92 696 reflections collected, 4186 unique (R_{int} = 0.069), R1 = 0.071, wR2 = 0.233. CCDC numbers 780202−780206. The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

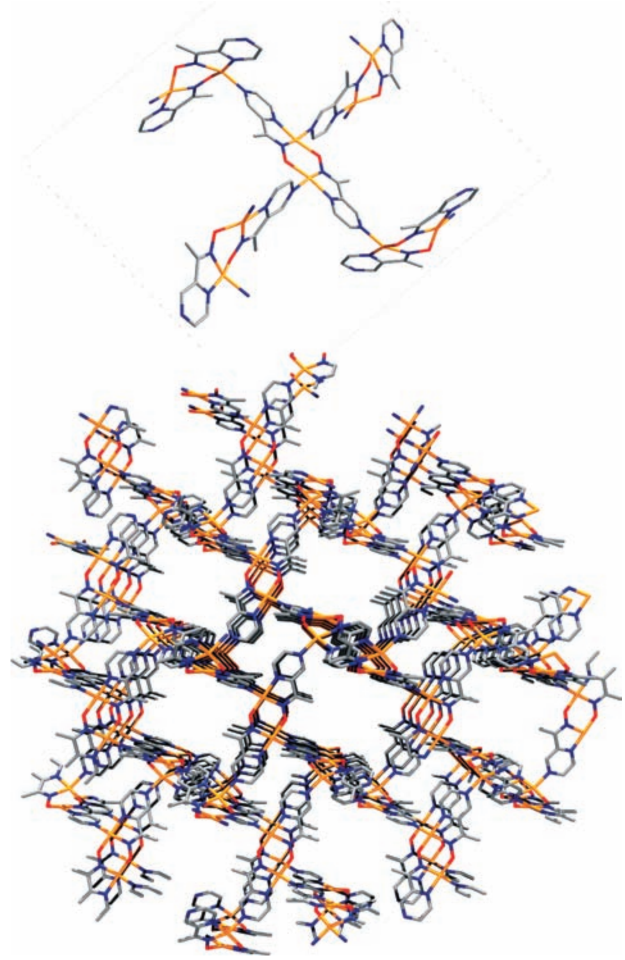

Figure 3. (Top) Plot of the network linked by means of the pyrazil groups of dinuclear subunits found for compound **4**. (Bottom) View along the *b* direction of the channels containing the triflate counteranions and solvent molecules.

atoms is achieved by coordination of one (pz)C(Me)NO$^-$ ligand, one bridging oxygen atom from the neighboring oximato group, and one pyrazinic nitrogen atom from the other dinuclear entity. This pattern of interactions generates a three-dimensional (3D) network of dimers (Figure 3). The structure is porous (the calculated density of the network is 0.8 g cm^{-3}), exhibiting channels along the three axes of the structure.

Compound **5** is a surprising system that combines the topologies of the previous compounds: it consists of one 3D network of equivalent dimers (similar to compound **4**), a templated, built around equilateral triangular units. Interaction of the 3D network and the triangles is provided by the axial coordination of all of the pyrazil nitrogen atoms of the triangular units (Figure 4). In this case, the channels containing the Cu_3 units and the counteranions appear only in the *c* direction. The diameter of these hexagonal channels is 17.5 Å.

Susceptibility measurements performed between 2 and 300 K indicate strong antiferromagnetic coupling for compounds **1**−**5**. The $\chi_M T$ product versus T for compounds **1**−**3** tends to the expected value for the $S = {}^1/_2$ ground state around 150 K (J values lie between −300 and −500 cm^{-1}), and below this temperature, it decreases because of antisymmetric interactions in the equilateral triangles, derived from frustration effects. The $\chi_M T$ product versus T for compound **4** quickly tends to zero, evidencing strong antiferromagnetic coupling with $J = -504$ cm^{-1}, as is usual in doubly bridged copper oximato systems.[6] Compound **5** behaves as the sum of the dinuclear plus trimer components. The axial view of the structure shows a Kagome-like network[10] built from dinuclear units, but the strong antiferromagnetic coupling in these dimeric subunits excludes network frustration effects.

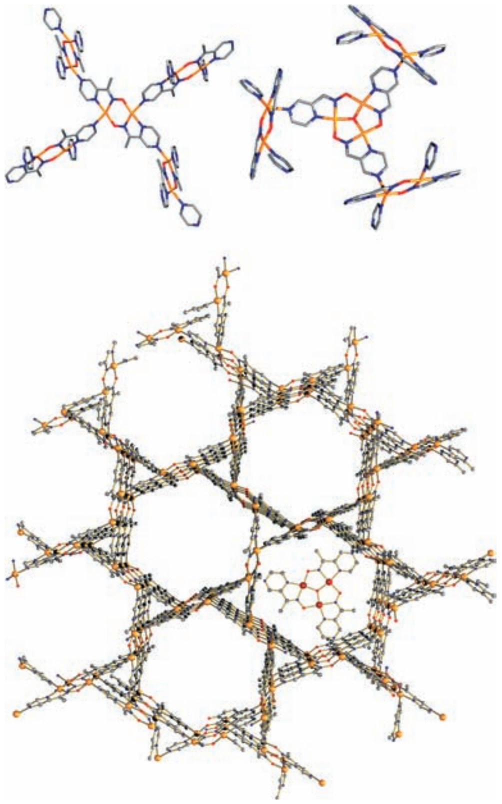

Figure 4. (Top) Plot of the linkage by means of the pyrazil groups of dinuclear subunits and dinuclear−trinuclear interactions. (Bottom) View along the *c* direction of the channels containing the pillared trinuclear units and the BF_4^- counteranions. Only one Cu_3 triangle has been depicted for clarity.

In conclusion, it should be pointed out that the reported compounds are the first metallic complexes derived from the ligand (pz)C(Me)NOH and that the reported 3D compounds are unprecedented in metal oximato chemistry. We emphasize that we have shown how the linkage of the oximate ligands and the nuclearity or dimensionality of these systems can be tuned by the adequate design of the functionalized oximato ligand and control of the donor properties of the anions. A description of the full series of characterized complexes and their chemistry with other cations will be published in forthcoming papers.

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Supporting Information Available: Plots of the structure of **1**, views along the [100] and [001] directions for **4**, preliminary magnetic measurements for **1**−**5**, and 4 K electron paramagnetic resonance spectra for **1** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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