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Ferromagnetic Coupling through Spin Polarization in a Dinuclear Copper(II) Metallacyclophane**

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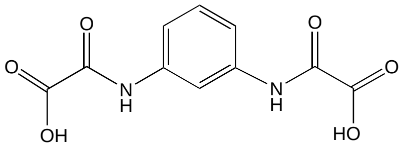
In memory of Olivier Kahn

The design and synthesis of polynuclear coordination compounds with predictable magnetic properties have always interested inorganic chemists working in the field of magnetochemistry.[1, 2] In particular, the preparation of ferromagnetically coupled dinuclear complexes appears intimately linked to the history of this relatively young discipline, namely molecular magnetism. Of the theoretical strategies to achieve a ferromagnetic spin alignment between two metal centers, those based either on orbital symmetry or spin polarization effects are the easiest ones to be managed by the synthetic chemist.[3] The second approach is particularly appealing and, however, has received more limited attention for metal complexes,[4] when compared with the extensive work concerning high-spin organic molecules (polyradicals).[5]

In our research into ligand design as a means to control the electronic and magnetic properties of polynuclear complexes,[6, 7] we prepared the new ligand H_4[**1**], the parent acid



H_4[**1**]

of *N*,*N'*-1,3-phenylenebis(oxamate). This ligand cannot act in a tetradentate manner towards a Cu^{II} center to give a monomeric four-coordinate copper(II) species, unlike the related ligand *N*,*N'*-1,2-phenylenebis(oxamate). Instead, it can self-assemble with Cu^{II} ions in a 2:2 ratio to give a dimeric copper(II) complex, $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$, where the two ligands adopt the bisbidentate coordination mode, each donating one of its oxamate donor sets to each copper. In this case, two bis(oxamate)copper(II) spin-bearing residues are bridged by two *m*-phenylene moieties, which have already proven to be very effective ferromagnetic spin-coupling units in purely organic π-conjugated polyradicals.[8] Here, we report the synthesis, crystal structure, and magnetic properties of the sodium salt of this novel oxamatocopper(II) complex of formula $Na_4[Cu_2(\mathbf{1})_2] \cdot 10\,H_2O$ (**2**).

The structure of **2** consists of noncentrosymmetric dinuclear copper(II) complex ions, $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$, sodium cations, and both coordinated and noncoordinated water molecules (Figure 1). Actually, all twelve oxygen atoms from the four oxamato groups of the dicopper anion are bound to the sodium atoms, affording an intricate two-dimensional structure. The intramolecular copper–copper separation, Cu(1)···Cu(2), is 6.822(2) Å, while the shortest intermolecular ones, Cu(1)···Cu(1″) and Cu(2)···Cu(2′), are 6.335(3) and 6.999(3) Å, respectively.

The $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$ unit is a metallamacrocycle composed of two bisbidentate oxamate ligands and two copper(II) cations. Moreover, owing to the almost parallel arrangement of the two benzene planes (dihedral angle of only 7.6(8)° and average interplanar separation of 3.4(1) Å), this dinuclear metallamacrocycle is of the cyclophane type (Figure 2a). In fact, a rather unusual near to perfect face-to-face π–π alignment of the two aromatic rings exists, such that a ring carbon atom lies just over the equivalent atom of the other ring (Figure 2b) with strong carbon–carbon contacts (C–C distances in the range 3.20(1)–3.57(2) Å). Hence, the resulting twelve-membered metallaaza-linked [3.3]metacyclophane ring system (internal cavity of ca. 3.4 × 6.8 Å) has an approximate C_{2v} symmetry, with the copper basal planes being almost perpendicular to the benzene planes (dihedral angles in the range 72.1(3)–82.0(3)°). This imposes a non-

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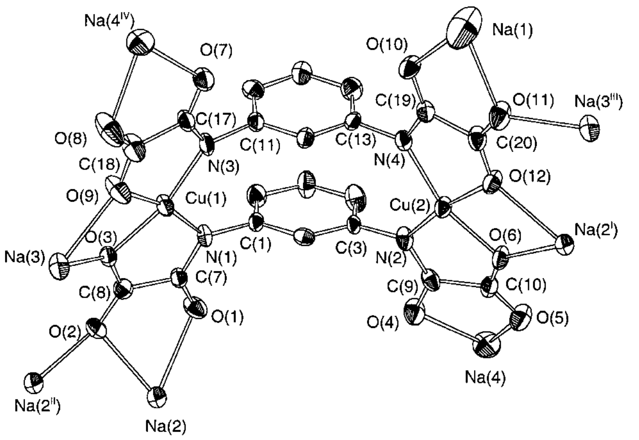

Figure 1. Perspective view of the asymmetric unit of **2**. Thermal ellipsoids are set at the 30% probability level (all hydrogen atoms and the water oxygen atoms have been omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu(1)-N(1) 1.954(5), Cu(1)-N(3) 1.925(5), Cu(1)-O(3) 1.928(4), Cu(1)-O(9) 1.963(5), Cu(2)-N(2) 1.969(5), Cu(2)-N(4) 1.952(5), Cu(2)-O(6) 1.956(4), Cu(2)-O(12) 1.995(4); N(1)-Cu(1)-N(3) 107.3(2), N(1)-Cu(1)-O(3) 84.4(2), N(1)-Cu(1)-O(9) 168.2(2), N(3)-Cu(1)-O(3) 166.3(2), N(3)-Cu(1)-O(9) 83.6(2), O(3)-Cu(1)-O(9) 85.4(2), N(2)-Cu(2)-N(4) 106.2(2), N(2)-Cu(2)-O(6) 83.3(2), N(2)-Cu(2)-O(12) 170.7(2), N(4)-Cu(2)-O(6) 162.4(2), N(4)-Cu(2)-O(12) 82.5(2), O(6)-Cu(2)-O(12) 87.4(2) (I $= -x, 1-y, 1-z$; II $= 1-x, -y, 1-z$; III $= x-1, 1+y, z$; IV $= x, y-1, 1+z$).

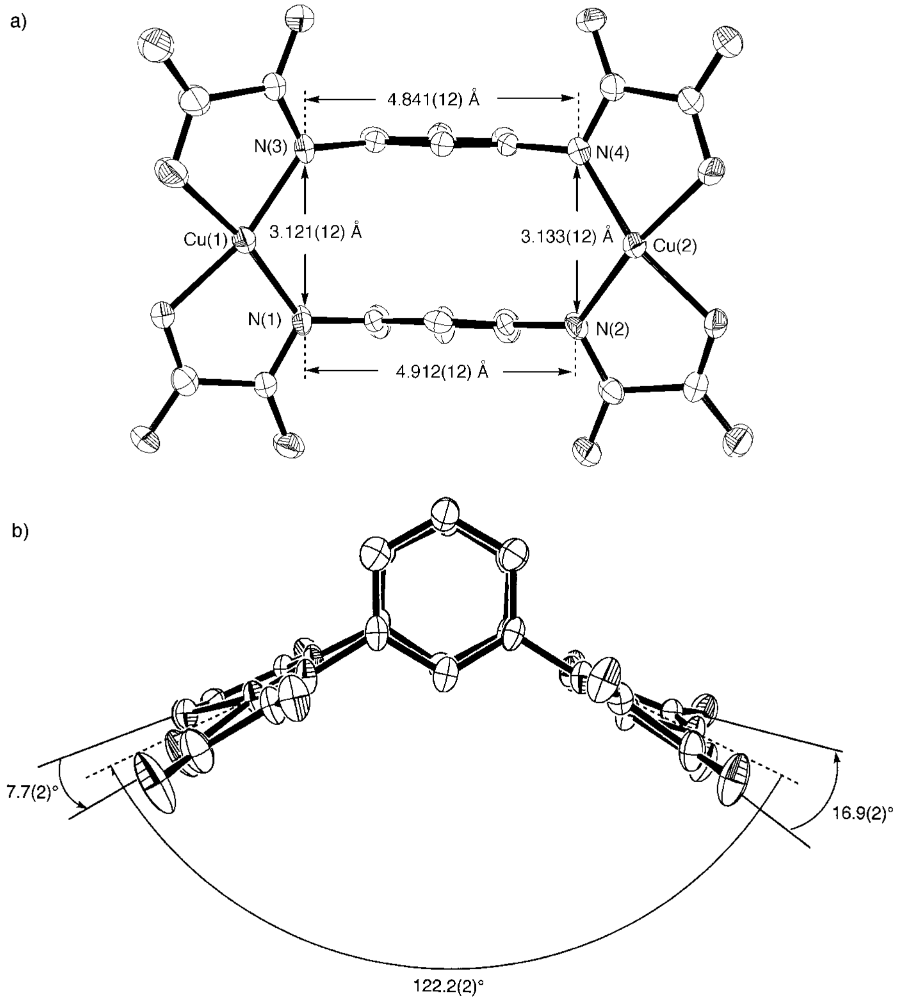

Figure 2. a) Side and b) top views of the $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$ ion of **2** with relevant dimensions for the metallamacrocyclic moiety.

planar conformation for the *N,N'*-1,3-phenylenebis(oxamate) ligands, which is the only one compatible with the square-planar environment at the metal ions. The severe distortion from planarity of these ligands is accommodated by a considerable twist of the C–N bonds between the benzene carbon and the amide nitrogen atoms (torsion angles in the range 73.6(7) – 106.3(7)°). However, the angles at the N atoms (112.4(4) – 132.1(4)°) remain close to the value expected for trigonal rather than tetrahedral hybridization.

The magnetic behavior of **2** is shown in Figure 3a as a $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility per two copper(II) ions and T the temperature. At room temperature, $\chi_M T$ is equal to 0.80 $cm^3 mol^{-1} K$, a value which is close to that expected for two magnetically noninteracting Cu^{II} ions. Upon cooling, $\chi_M T$ continuously increases until the temperature is around 5.0 K, and then remains constant between 5.0 and 1.8 K, with $\chi_M T = 1.08\ cm^3 mol^{-1} K$ (insert of Figure 3a). This behavior is characteristic of ferromagnetic coupling within the dinuclear copper(II) metallacyclophane entity in **2**. Moreover, the presence of a plateau below 5.0 K indicates that the intermolecular interactions through the sodium ions and the zero-field splitting (ZFS) of the ground triplet spin state are both negligible. Indeed, this corresponds to the temperature range where only the $S = 1$ ground state is thermally populated, with $\chi_M T = 2N\beta^2 g^2/3k$ and $g = 2.08$ (N = Avogadro's number, β = Bohr magneton, k = Boltzmann's constant, and g is the Zeeman factor). The magnetization data for **2**, at $T = 2.0$ K, are shown in Figure 3b as an M versus H plot, M being the molar magnetization per two copper(II) ions and H the applied magnetic field. As expected, the isothermal curve is well matched by the Brillouin function for an isolated triplet spin state with $g = 2.08$ and no ZFS (solid line in Figure 3b).

The least-squares fit of the susceptibility data of **2** to the Bleaney–Bowers equation gives $J = +16.8\ cm^{-1}$ and $R = 7 \times 10^{-6}$ (J is the exchange coupling parameter in the isotropic spin Hamiltonian $\mathcal{H} = -JS_1S_2$, with $S_1 = S_2 = 1/2$, and R is the agreement factor defined as $R = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2/\Sigma[(\chi_M T)_{exp}]^2$). The theoretical curve (solid line in Figure 3a) closely follows the experimental data in the whole temperature range. This exceptionally strong ferromagnetic coupling between two copper(II) ions separated by 6.8 Å cannot be explained as resulting from spin delocalization only. In this compound, the point group symmetry of the dimeric copper(II) unit $[Cu_2(\eta^2{:}\eta^2\text{-}\mathbf{1})_2]^{4-}$ is very close to C_{2v}. Then, the orbitals describing the unpaired electrons (the so-

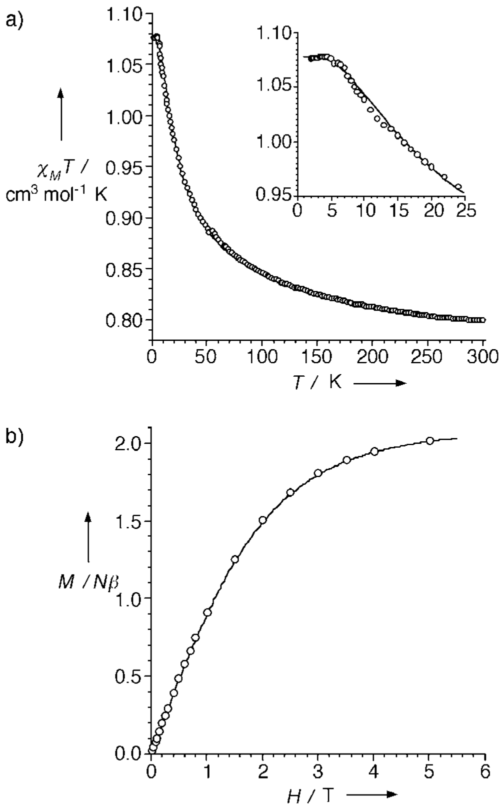

Figure 3. a) Thermal dependence of $\chi_M T$ and b) field dependence of M at 2.0 K for **2**: (○) experimental data; (——) best fit. The insert shows the thermal dependence of $\chi_M T$ in the low-temperature range.

called "magnetic orbitals") and centered on each Cu^{II} ion (built from each of the metallic d_{xy} orbitals pointing along the Cu–N and Cu–O bonds) have the same symmetry (see below). A certainly weak although non-negligible antiferromagnetic interaction should arise because of the nonzero overlap between these two nonorthogonal orbitals. Hence, the experimentally observed large ferromagnetic interaction must be a result of spin polarization effects leading to the alternation of the spin density at the double *m*-phenylenediamide bridging framework, as expected for a bridging ligand designed with this peculiar topology. To give a clear-cut answer to the spin delocalization versus the spin polarization mechanism for the propagation of the exchange interaction in **2** we have carried out density functional theory (DFT) calculations.[9]

The DFT calculations performed on the dinuclear copper(II) anionic species $[Cu_2(\eta^2:\eta^2\text{-}\mathbf{1})_2]^{4-}$ indicate a ground triplet spin state lying well below the excited singlet spin state. The calculated value of the singlet–triplet energy gap ($\Delta E_{ST} = J$) is 14.2 cm^{-1}, in very good quantitative agreement with the experimental value obtained from the fit of the susceptibility data. To qualitatively understand this result, we can now turn our attention to the nature of the singly occupied molecular orbitals (SOMOs) depicted in Figure 4a. As expected, the two SOMOs, b_1 and a_2, are nearly degenerate, with a small energy gap of 1036 cm^{-1}. They are composed by the in-phase and out-of-phase combinations, respectively, of the d_{xy} metallic orbitals of copper mixed with two π-type nonbonding molecular orbitals of *m*-phenylenediamide of

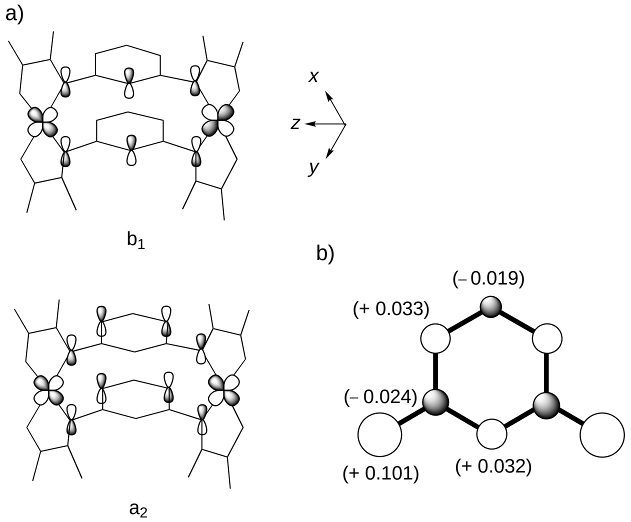

Figure 4. Schematic representation of a) the two SOMOs and b) the spin-density distribution on the bridge region for **2** on the basis of DFT calculations. Empty and full contours represent positive and negative spin densities, respectively. Calculated average atomic spin densities are given in parentheses.

appropriate symmetry. Hence, the exchange interaction is transmitted through the delocalized π system of the bridging ligands.

More importantly, an inspection of the atomic spin densities in the triplet ground state, as obtained by a Mulliken population analysis[13] (Figure 4b), provides a precise orbital picture of the exchange interaction in **2** and, concomitantly, furnishes the ultimate reason for the ferromagnetic coupling observed in this compound. The spin densities at the amide nitrogen and carboxylate oxygen atoms have the same sign as in the copper atom, indicating spin delocalization toward the donor atoms. Moreover, the delocalization of the metal spin density (average value of +0.561) toward the bridging amide N atoms is important (average value of +0.101), mainly because of the substantial covalency of the Cu–N bond resulting from the strong basicity of the amide donor group. On the other hand, the sign alternation of the spin density at the carbon atoms of the bridging benzenes agrees with spin polarization by the amide nitrogen donor atoms. This leads to significant negative spin densities at the carbon ring atoms to which they are directly attached (average value of –0.024). Given the peculiar topology (*meta* substitution pattern) of these bridges, the spin densities at both copper atoms have the same sign, and then a net ferromagnetic exchange interaction results.

In summary, complex **2**, obtained from the self-assembly of the novel benzene-substituted bis(oxamate) ligand **1** by copper(II) ions, constitutes a rare example of paramagnetic dinuclear metallacycle.[14, 15] This unique compound is, to our knowledge, the first dinuclear copper(II) complex for which the ferromagnetic spin coupling between the two Cu^{II} centers arises from spin polarization effects.[16] We are currently investigating the ability of this novel dinuclear ferromagnetic synthon to bind paramagnetic species, through the substitution of Na^I cations by first row transition and rare earth metal cations.[17] A wide variety of discrete high nuclearity complexes and extended networks can be envisaged to elaborate new supramolecular magnetic materials (high-spin molecules and molecular-based magnets).

Experimental Section

H_4[**1**]: The proligand was prepared in a standard manner[18] from the condensation of 1,3-phenylenediamine and ethyl oxalyl chloride in THF, and was isolated as the diethyl ester derivative (90%). Elemental analysis calcd (%) for $C_{14}H_{16}N_2O_6$ (308): C 54.55, H 5.19, N 9.09; found: C 54.57, H 5.18, N 9.04; ^{1}H NMR ([D$_6$]DMSO): $\delta = 1.32$ (t, 6H; 2CH_3), 4.31 (q, 4H; 2CH_2O), 7.34 (dt, 1H; 5-H of $C_6H_4N_2$), 7.50 (dd, 2H; 4-H and 6-H of $C_6H_4N_2$), 8.22 (t, 1H; 2-H of $C_6H_4N_2$), 10.83 (s, 2H; 2NH); ^{13}C NMR ([D$_6$]DMSO): $\delta = 14.17$ (2CH_3), 62.71 (2CH_2O), 113.25 (2-C of $C_6H_4N_2$), 117.45 (4-C and 6-C of $C_6H_4N_2$), 129.34 (5-C of $C_6H_4N_2$), 138.08 (1-C and 3-C of $C_6H_4N_2$), 156.13 (2-C(O)NH), 161.02 (2CO_2); IR (KBr): $\tilde{\nu} = 3349$ (N–H), 2979, 2943 (C–H), 1725, 1715, 1698 cm^{-1} (C=O); UV/Vis (THF): λ_{max} (ε) = 335 nm (800).

Complex **2** was obtained following a reported procedure[18] by reaction of the diethyl ester derivative of the ligand with Cu^{2+} ions in basic aqueous media, and isolated as its octahydrate sodium salt (85%). Elemental analysis calcd (%) for $C_{20}H_{24}Cu_2N_4Na_4O_{20}$ (859): C 27.94, H 2.79, N 6.52; found: C 27.77, H 2.62, N 6.40; IR (KBr): $\tilde{\nu} = 3423$ (O–H), 1659, 1597 cm^{-1} (C=O); UV/Vis (H_2O): λ_{max} (ε) = 645 (150), 380sh (1600), 345 nm (2650). Crystals of **2**, well-formed small dark green prisms, suitable for X-ray diffraction were obtained by slow vapor diffusion of methanol into concentrated aqueous solutions of **2** at 5 °C.

Crystal data for **2**: $C_{20}H_{28}Cu_2N_4Na_4O_{22}$, $M_r = 895.50$, triclinic, space group $P\bar{1}$, $a = 11.1489(15)$, $b = 12.8545(9)$, $c = 13.3454(19)$ Å, $\alpha = 63.855(8)$, $\beta = 78.305(12)$, $\gamma = 68.695(10)^\circ$, $V = 1597.5(3)$ Å^3, $T = 293$ K, $Z = 2$, $\rho_{calcd} = 1.862$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.485$ mm^{-1}. Lorentz and polarization effects and absorption correction. 5579 unique reflections, and 3616 observed with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS 97, and refined by the full-matrix least-squares method on F^2 using SHELXL 97. The hydrogen atoms from the organic ligand were located from a difference synthesis and refined with an overall isotropic thermal parameter, while those from the water molecules were not found or calculated. Refinement of 471 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0503$ and $R_w = 0.112$, with $S = 0.97$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157314. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Conjugated Complexes Composed of Quinonediimine and Palladium: Controlled Formation of a Conjugated Trimetallic Macrocycle[**]

Toshiyuki Moriuchi, Manabu Miyaishi, and Toshikazu Hirao[*]

π-Conjugated polymers have attracted much attention for application as electrical materials owing to their electrical properties.[1] The properties of π-conjugated polymers are considered to be modified drastically by the incorporation of metal atoms.[2, 3] Conjugated polymeric complexes in which transition metals are incorporated in the main chain represent one approach.[3] Most of the interest in these conjugated polymeric complexes has been concerned with the nature of the interactions between metal centers through a π-conjugated chain. Transition metal directed assembly is regarded as

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