A Giant Antiferromagnetic Interaction through the Bihydroxide Bridge ($H_3O_2^-$)

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Despite the great number of hydrated hydronium salts which have been characterized,[1] only a few examples of structural characterization of compounds containing the corresponding hydrated hydroxide anion ($H_3O_2^-$) have been reported.[2] The shortest O···O distance known (2.29(2) Å) is observed in the discrete $H_3O_2^-$ entity, whereas a significant O···O lengthening (2.41–2.54 Å) occurs when it acts as a bridging ligand between metal ions in polynuclear compounds. This very short distance is consistent with a strong hydrogen bond made by a central proton surrounded by two hydroxide groups, [HO- -H- -OH]⁻. The fact that $H_3O_2^-$ can act as a ligand led us to investigate the possibility to use it as a bridging group between copper(II) ions in order to explore its ability to transmit magnetic interactions between paramagnetic centers and to compare this ability with that of parent triatomic bridging ligands. In relation to this, it deserves to be noted that values of J (singlet–triplet energy gap) up to -94 cm^{-1} were determined for asymmetric hydrogen-bonded [O–H···O] dinuclear copper(II) complexes.[3]

In the framework of our research work on the preparation and structural and magnetic characterization of polynuclear complexes between copper(II) and 2,2′-bipyrimidine (bpm),[4] we obtained single crystals of a novel copper(II) complex of formula $[Cu_2(bpym)_2(H_3O_2)(H_2O)_2](ClO_4)_3$ (**1**) which contains both bpm and bihydroxide as bridging ligands. It was obtained by recrystallization of the parent chain $[Cu(bpm)(H_2O)_2](ClO_4)_2{\cdot}H_2O$ (**2**)[4c,5a] in water. Only a few crystals of **1** (small pale blue-greenish parallelepipeds very small in one dimension) separated together with a mixture of **2** (blue needles) and the dinuclear $[Cu_2(bpm)_3(H_2O)_4](ClO_4)_4$ (**3**)[4c] (rhombohedral blue crystals) and mononuclear $[Cu(bpm)_2(H_2O)](ClO_4)_2{\cdot}2H_2O$ (**4**)[4c,5b] (blue parallelepipeds) complexes. Hand-picked crystals of **1** were characterized by elemental analysis, EPR and magnetic measurements, and X-ray structural analysis.[6]

The crystal structure of **1** consists of cationic 1D chains of bpm-bridged copper(II) ions (Figure 1a) which are held together by bihydroxide groups acting as bridging ligands between the metal ions (Figure 1b) to yield a 2D network. The electroneu-

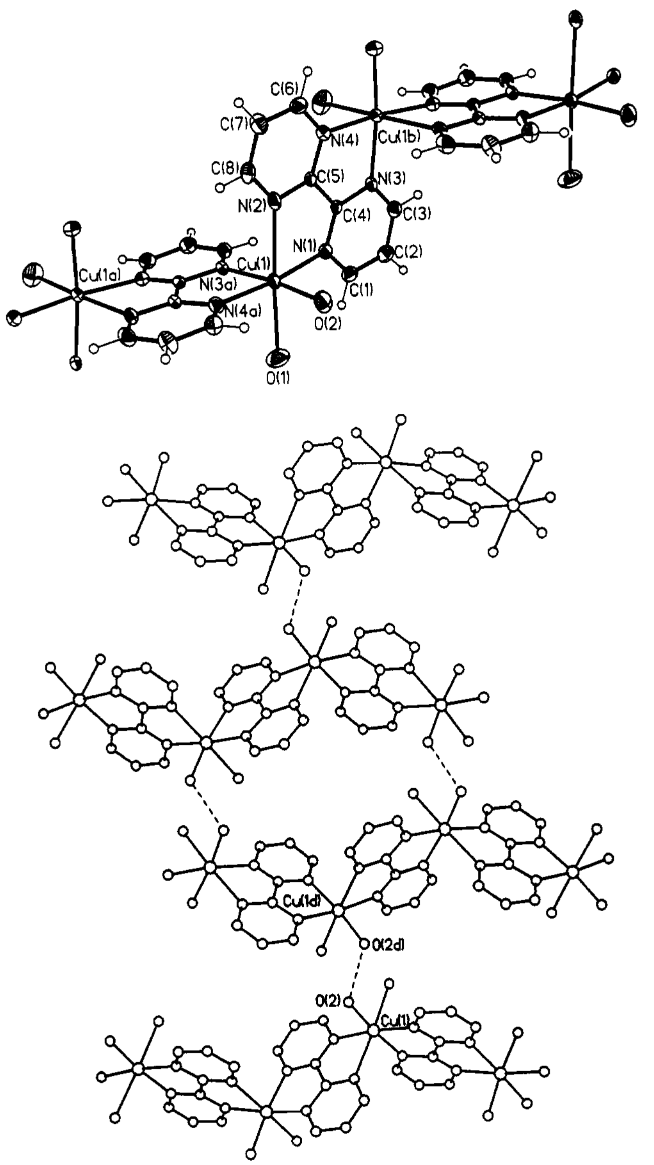

Figure 1. Structure of **1** (ellipsoids drawn at the 30% probability level): (a, top) view of the bpm-bridged copper(II) zigzag chain showing the atom numbering; (b, bottom) arrangement of the chains in the *xy* plane (perchlorate anions omitted for clarity). Selected bond distances (Å) and angles (deg) with standard deviations in parentheses: Cu(1)–N(1) = 2.079(6), Cu(1)–N(2) = 2.290(6), Cu(1)–N(3a) = 2.040(5), Cu(1)–N(4a) = 2.030(6), Cu(1)–O(1) = 2.321(8), Cu(1)–O(2) = 1.930(7); N(1)–Cu(1)–O(2) = 89.0(3), N(1)–Cu(1)–N(3a) = 95.1(2), N(1)–Cu(1)–O(1) = 97.7(3), N(1)–Cu(1)–N(2) = 76.6(2), N(1)–Cu(1)–N(4a) = 173.1(2), O(2)–Cu(1)–N(4a) = 95.2(3), O(2)–Cu(1)–O(1) = 86.8(3), O(2)–Cu(1)–N(2) = 93.8(3), O(2)–Cu(1)–N(3a) = 173.4(2), N(3a)–Cu(1)–N(4a) = 81.2(2), N(3a)–Cu(1)–O(1) = 87.6(2), N(3a)–Cu(1)–N(2) = 92.0(2), N(4a)–Cu(1)–O(1) = 88.0(3), N(4a)–Cu(1)–N(2) = 97.6(2), O(1)–Cu(1)–N(2) = 174.3(3). Symmetry code: (a) $^1/_2 - x$, $^1/_2 + y$, z; (b) $^1/_2 - x$, $y - {}^1/_2$, z.

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(6) Crystal data: $C_{16}H_{19}N_8Cl_3Cu_2O_{16}$ (fw = 812.8), orthorhombic, space group *Aba*2, $a = 15.349(2)$ Å, $b = 9.954(1)$ Å, $c = 18.029(2)$ Å, $V = 2754.5(5)$ Å^3, $Z = 4$, $D_c = 1.960$ g cm^{-3}, $\mu = 19.3$ cm^{-1}, 2θ range 3–54°, crystal size 0.18 × 0.19 × 0.41 mm^3, $F(000) = 1632$, 1776 collected reflections, 1568 unique, and 1382 assumed as observed with $I > 3\sigma(I)$, 196 parameters, $R(F_o) = 0.0459$, $R_w(F_o) = 0.0525$, and $S = 1.36$ with $w^{-1} = \sigma^2(F_o) + 0.002000(F_o)^2$.

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trality is achieved by uncoordinated perchlorate anions. The polymeric chain runs parallel to the *y*-axis, and the resulting layer grows in the *xy* plane. Each copper atom is in a distorted octahedral environment: two oxygen atoms occupying one axial and one equatorial position and four nitrogen atoms from two bpm ligands filling the remaining axial and equatorial sites define the metal environment. The copper atom is displaced by 0.015(1) Å from the mean basal plane toward the axial N(2) atom. The bpm group acts in an asymmetrical bis-bidentate fashion and is bound to the metal ion in a cis configuration (the equatorial Cu–N(bpm) distances are in the range 2.030(6)–2.079(6) Å whereas the axial Cu–N(2) bond length is 2.296(6) Å). The structure of the resulting chain is very close to that of **2**, the only difference being the formal substitution of an equatorially bound water molecule by a hydroxo group. Along the polymeric chain, alternate bpm mean planes are parallel with an interplane separation of 3.29 Å (3.86 Å in **2**).

A comparison between the related Cu–O bond distances in **1** and **2** shows that the axial copper–oxygen distance remains practically unchanged (2.331(8) versus 2.325(11) Å) whereas the equatorial one is significantly shorter (1.930(7) versus 2.001(9) Å). In the light of these data, it would be reasonable to assume that this shorter distance corresponds to the copper–hydroxo bond, but charge balance considerations dictate that only one hydroxo group can be present per two copper(II) ions, and this would require that the same equatorial position were alternatively occupied by an hydroxo anion and a water molecule. Occupational disorder is usually associated with relatively high temperature factors, while, in our case, the U_{eq} value of O(2) is almost equal to that of O(1). This apparent inconsistency may be overcome by considering the interaction between neighboring chains. Indeed, there is a very strong hydrogen bond between the O(2) atoms from different chains: the O(2)···O(2d) [(d) = $-x$, $-y$, z] distance is 2.42(1) Å, a very short value which most likely corresponds to a symmetrical hydrogen bond (unfortunately, our experimental data are affected by the disorder involving one of the perchlorate anions and do not allow the localization of the hydrogen atoms). Therefore, it seems reasonable to suppose that two equatorial O(2) atoms from neighboring chains are held together by a symmetrical hydrogen bond of the type Cu(1)–(HO)(2)···H···(OH)(2d)–Cu(1d) in which, formally, a water molecule and a hydroxo group are involved to form an $H_3O_2^-$ anion. This explanation accounts for the presence of only one hydroxo group per two copper(II) ions, while occupational disorder may be excluded. The metal–metal separations through bpm and bihydroxide bridges are 5.613(1) (5.597(3) Å in **2**) and 5.123(1) Å, respectively. The Cu(1)–O(2)–O(2d) angle is 119.3°, and the dihedral angle between the Cu(1)O(2)O(2d) and Cu(1d)O(2d)O(2) planes is 111°.

1 is diamagnetic at room temperature, and no EPR signal could be observed. These features support the occurrence of a very strong antiferromagnetic coupling between copper(II) ions ($-J$ larger than 1000 cm^{-1}). Exchange pathways through both bridges are possible in the present compound. However, the fact that the value of J in **2** was found only as -62 cm^{-1} reveals that the bihydroxide pathway is responsible for the giant coupling found in **1**. This strong magnetic interaction can be understood taking into account that the HOMO of the bihydroxide is essentially a nonbonding σ_u level (Figure 2) according to MO calculations through the CACAO program.[7] The next deeper molecular orbitals are π_g and π_u levels (the energy gap between the σ and π levels is only 0.3 eV). It is very interesting to compare this orbital scheme with that of a related triatomic bridging ligand such as the azide anion (the distance between the terminal nitrogen atoms in N_3^- is very close to that of O···O in $H_3O_2^-$). The HOMO in the azide[8] is of π_g symmetry, and the next deeper molecular orbital, which is a σ_u level, is at 1.3 eV (a much greater energy gap than in the preceding case). Because the small energy gap between the HOMO σ_u and π_g and π_u levels in $H_3O_2^-$, one can expect that both levels would participate in the exchange pathway. It is clear that the σ pathway is dominant when α approaches 180° whereas the π one is enhanced as far as α approaches 90°. The value of β does not affect the σ pathway. For the experimental value of α in **1**, 119.3° for Cu(1)–O(2)–O(2d), theoretical calculations show that both σ and π contributions are important. However, the σ contribution is practically negligible in the case of azide for similar angles. This is due to the fact that the σ level is deeper (about 1.3 eV) than the π one. This probable participation of the σ level in the exchange pathway through $H_3O_2^-$ could account for the larger coupling in **1** respect to the single end-to-end azido-bridged copper(II) complexes ($J = -308.6$ cm^{-1}).[9] It is worthwhile noting that double end-to-end azido bridges between copper(II) ions are required in order to achieve practically diamagnetic copper(II) dinuclear species.[10]

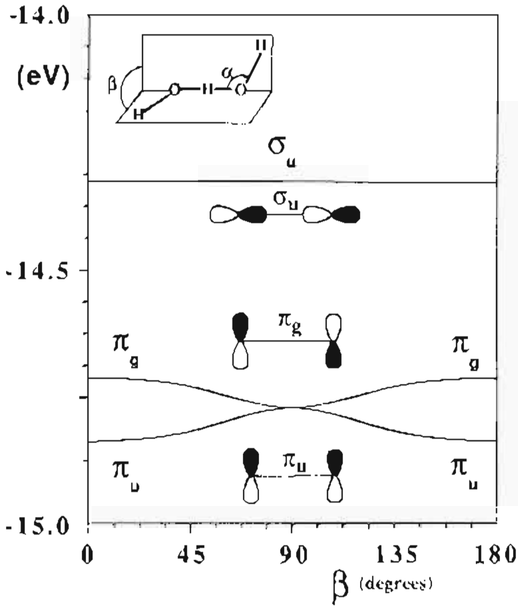

Figure 2. Walsh diagram of the three HOMO's of the $H_3O_2^-$ anion.

The remarkable ability of $H_3O_2^-$ to transmit electronic effects makes necessary more theoretical and magneto-structural studies concerning bihydroxide-bridged copper(II) complexes (work in progress) in order to check the proposed exchange pathway mechanism. To conclude, these results illustrate how the relevant role that hydrogen bonding plays from a structural point of view can also be determinant as far as the magnetic properties are concerned.

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Supplementary Material Available: Tables listing crystal data, atomic coordinates and temperature factors for non-hydrogen atoms, hydrogen atom coordinates and temperature factors, intramolecular bond distances and angles, and least-squares planes (Tables S1–S6) and a description of the X-ray structure analysis of **1** (9 pages). Ordering information is given on any current masthead page.

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