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A Perfectly Square-Planar Tetracoordinated Oxygen in a Tetracopper Cluster-Based Coordination Polymer

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S *Supporting Information*

ABSTRACT: A perfectly square-planar, D_{4h}-symmetric, tetracoordinated oxygen has been observed in a tetracopper cluster-based coordination polymer that shows an unusual magnetic moment and ESR signal. The stabilization factor of the square-planar tetracoordinated oxygen has been revealed using DFT calculations.

The realization by van't Hoff and LeBel in 1874 that tetravalent carbon prefers tetrahedral coordination laid the groundwork for understanding the spatial arrangement of molecules.[1] A century later, the theoretical studies of hypothetical planar methane and its derivatives by Monkhorst, Hoffmann, and Schleyer and Pople[2] established basic strategies for achieving planar tetracoordinate carbon (ptC) arrangements and triggered unabated experimental and computational explorations of "planar hypercoordinate" chemistry.[3] The search for examples has been extended from carbon to main-group heteroatoms such as B, N, O, Si, Cl, and P[4−7] and more recently to transition-metal elements and to much higher planar coordination.[8]

This paper focuses on planar tetracoordinate oxygen (ptO), a seemingly highly unlikely candidate. However, the solid-state lattice of niobium oxide was found to have interstitial ptO's in 1984; the ptO stabilization was attributed to Nb−Nb and Nb−Oπ^* bonding.[9] Only four additional experimental ptO examples are known, namely, $[V_4O(edt)_2Cl_8]^{2-}$ (edt = ethane-1,2-dithiolate), $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$, $[Cu_4Zr_4O_3(OPr)_{18}]$, and $H_2[Co_4O(TATB)_{8/3}]$.[6]

The theoretical discovery of the simplest square-planar μ_4-oxygen-centered global minimum, D_{4h} Al_4O, and its detailed bonding analysis revealed the importance of the $M_4^{2+}O^{2-}$ ionic character and the perimeter metal−metal interactions in such species.[10] This bonding character was illustrated further by Li et al.'s density functional theory (DFT) study of the hydrocopper $[Cu_4H_4O]^{2+}$ ptO derivative.[7a]

We have now realized a copper cluster that is closely related to Li's model. Our Cu_4O-based body-centered cubic (bcu) coordination polymer $[Cu_8O(tta)_{12}](ClO_4)_2 \cdot 2H_2O$ (tta = tetrazolate) (**1**) not only has ptO's in ideal D_{4h}-symmetric environments but also has an unusual magnetic moment and electron spin resonance (ESR) signal, possibly related to tetravalent copper. High-valent copper compounds are inherently interesting because of their superconductivity, magnetic, and electrical properties,[11] but examples are rare.[12] The discovery of new prospects and their characterization remains a challenge in solid-state physics and chemistry.

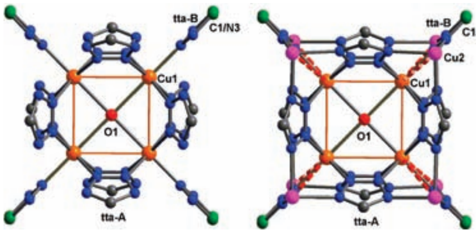

Figure 1. Views of (left) the $Cu_4O(tta)_{12}$ SBU and (right) the attachment of eight Cu2 centers to one $Cu_4O(tta)_{12}$ to form a $Cu_{12}O(tta)_{12}$ unit. Orange, purple, red, blue, gray, and green balls represent Cu1, Cu2, O1, N, C, and the indistinguishable C1/N3 atoms, respectively.

Dark-green crystals of **1** (45% yield) were obtained by hydrothermal treatment of a mixture of $CuCl_2$, tetrazole, and $HClO_4$ at 180 °C. X-ray diffraction (XRD) analysis[13] revealed that **1**, which crystallizes in the tetragonal space group $I4/m$, has a tetracopper cluster-based bcu framework with a ptO having ideal square D_{4h} symmetry. There are two crystallographically independent copper atoms. Cu1 has elongated octahedral coordination; it is ligated by two N6 and two N5 atoms in an equatorial plane and by axial N1 and O1 atoms. Cu2 also has elongated octahedral coordination; it is ligated by two N2 and two N4 atoms in an equatorial plane and two axial N7 atoms. The Cu1−O1 distance of 2.470(1) Å indicates weak Cu−O bonding. One of the two distinct tta groups (tta-A) is tetradentate, while the other (tta-B) is tridentate. The C1 and N3 atoms of tta-B are indistinguishable because of the imposed crystallographic mirror symmetry.

The four Cu1 centers in **1** form a Cu_4O cluster with Cu−Cu distances of 3.494(4) Å. As shown in Figure 1, 12 tta groups (eight tta-A and four tta-B) are attached to form a $Cu_4O(tta)_{12}$ secondary building unit (SBU). Each $Cu_4O(tta)_{12}$ SBU links eight Cu2 centers, each of which connects two $Cu_4O(tta)_{12}$ SBUs. The channels of the unusual eight-connected bcu[14] cationic framework are filled by the perchlorate anions.

A most remarkable structural feature of **1** is the ideal square D_{4h} ptO, which has the highest symmetry among the four known experimental ptO examples. The factors stabilizing the ptO in

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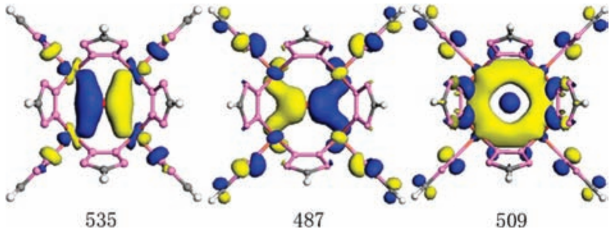

Figure 2. Important MOs of $[Cu_4O(tta)_8(tra)_4]^{6-}$ (D_{4h}) for the stabilization of square-planar oxygen. The isosurface value is 0.03 au.

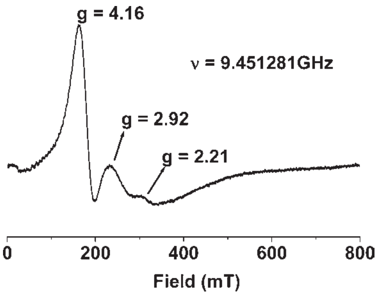

Figure 3. ESR spectrum of powdered **1** at room temperature.

1 were investigated by all-electron DFT computations of the closely related D_{4h} model complex $[Cu_4O(tta)_8(tra)_4]^{6-}$ (tra = 1,2,3-triazolate) using the DMol[3] program. Atom coordinates were extracted from the $Cu_4O(tta)_{12}$ SBU X-ray geometry, and the tta-B groups were replaced by tra groups in order to satisfy D_{4h} symmetry. The most important occupied molecular orbitals (MOs) of the resulting model complex $[Cu_4O(tta)_8(tra)_4]^{6-}$ (Figure 2) include two pairs of σ-bonding e_u MOs involving 3d valence orbitals of four copper atoms and the p_x and p_y atomic orbitals (AOs) of the ptO. As in some related cases, the perpendicular oxygen p_z "lone-pair" AO is not involved in metal bonding significantly.[6a,7a] Besides the e_u MOs in Figure 2, other e_u MOs interacting weakly with the p_x and p_y oxygen orbitals can be found in Figure S5 in the Supporting Information. The large 3.494(4) Å Cu−Cu distance in the model complex does not indicate significant direct Cu−Cu bonding. However, the two b_{1g} MOs in Figure 2 clearly show stabilizing cyclic-delocalized σ bonding around the bridged Cu−N−N−Cu perimeters.[7a] Surprisingly, no a_{1g}-symmetric bonding MO involving the 2s oxygen orbital and the Cu_4 ligands was found; this differs from the reported extended Hückel theory result for the model complex $[V_4O(SH)_4C1_8]^{2-}$.[6a] The 2s orbital of the ptO in **1** is nonbonding, since analysis shows it to be too low energetically to interact significantly with the a_{1g} MOs of the oxygen-free fragment. The p_z lone-pair orbital of the ptO also shows primarily nonbonding character, although some weak π-bonding interactions are exhibited in the 501 and 520 a_{2u} MOs. Natural bond orbital (NBO) analyses showed partial electron transfer from the surrounding copper ligands to the square ptO, as indicated by atomic charges of 1.35 for Cu and −0.86 for ptO.

Three sets of magnetic measurements using samples from different batches showed that **1** has unusually large magnetic moments. The $\chi_m T$ value of 5.29 $cm^3\ K\ mol^{-1}$ at 300 K is larger than the spin-only value for eight Cu(II) atoms, and the monotonic decrease in $\chi_m T$ upon cooling indicates antiferromagnetic coupling (Figure S6). The simulated and recorded powder XRD (PXRD) patterns matched well, eliminating the possibility of minor magnetic impurities. The ESR spectrum of a powdered sample of **1** at room temperature shows valuable information about the electronic configuration of copper (Figure 3). The strongest resonance signal appeared at 161.5 mT and had a very large g factor of 4.16. Generally, isoelectronic ions in similar symmetry environments have similar g factors, and metal ions with a $3d^7$ configuration, such as Co(II) and Fe(I), show large g factors of ~4.2.[15] Hence, the strongest ESR signal in **1** may be a clue to the presence of Cu(IV) ions with $3d^7$ configuration. With this assumption, **1** should show nonstoichiometry or defects. This supposition agrees with the observed abnormally large magnetic moment. The weak ESR signal at $g = 2.21$ could originate from Cu(II) ions. To gain further insight into the unusually large magnetic moments, X-ray photoelectron spectroscopy (XPS) for **1** was also performed; this did not provide valuable information about Cu(IV) ions but further eliminated the possibility of magnetic impurities having a $3d^7$ configuration (Figures S7 and S8). Both Cu(I) and Cu(II) signals were observed: Cu(II) has a main peak at 935.6 eV (peak II) with a shakeup satellite (peak III) at higher binding energies, and Cu(I) has a characteristic peak at 932.5 eV (peak I) with no satellite peak. Since Cu(II) ions often undergo reduction under X-ray irradiation in ultrahigh vacuum,[16] the absence of a Cu(IV) signal in the XPS data is reasonable. No cobalt or nickel peaks in the ranges 777−783 and 851−861 eV were observed, which further eliminates the presence of magnetic impurities of Co(II) or Ni(III) ions with $3d^7$ configurations.

In summary, a perfectly square planar tetracoordinate oxygen (ptO) has been observed in a tetracopper cluster-based body-centered-cubic framework. DFT computations revealed that σ-bonding interactions of the p_x and p_y orbitals of the ptO with the surrounding copper ligands and the formation of cyclically delocalized σ bonds along the Cu−N−N−Cu perimeters help stabilize the ptO. The origin of the unusual magnetic moments and ESR signals of this compound, which indicate the possible presence of tetravalent copper and nonstoichiometry, is being investigated further.

■ ASSOCIATED CONTENT

S Supporting Information. Crystal structural data for **1** (CIF); additional structural figures; PXRD, XPS, and magnetic data; and full sets of MOs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for **1**: $C_{12}H_{28}Cl_2Cu_8N_{48}O_{11}$; tetragonal, space group $I4/m$; $M_r = 1600.04$; $a = 13.1544(9)$ Å, $c = 12.0402(8)$ Å; $V = 2083.4(2)$ Å^3; $Z = 2$; $D_{calcd} = 2.551$ g cm^{-3}; $\mu = 4.248$ mm^{-1}; $F(000) = 1580$; $T_{min} = 0.3100$, $T_{max} = 0.7847$; $2\theta_{max} = 55°$; $S = 1.115$; $R_1 = 0.0663$, $wR_2 = 0.1752$.

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■ NOTE ADDED AFTER ASAP PUBLICATION

After this Communication was published ASAP March 7, 2011, details were added in the first and second paragraphs, accompanied by additional citations in refs 5 and 6. The updated version was published March 15, 2011.