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A Short but Weak Cu−Cu Interaction in $[Cu_2Br_5]^{2-}$, a Crystal Engineered $(Cu^{1.5+})_2$ Confacial Bitetrahedral Complex

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Among mixed valence copper compounds, the delocalized $(Cu^{1.5+})_2$ pair has recently been reported in bimetal complexes of octaaza macrocyclic and macrobicyclic ligands,[1] and in the Cu_A electron transfer sites of cytochrome *c* oxidase (CCO)[2] and nitrous oxide reductase (N_2OX)[2f] and well-characterized compounds which model the Cu_A active site.[3]

We report here the formation and properties of a new type of $(Cu^{1.5+})_2$ pair, in the fundamental anion $[Cu_2Br_5]^{2-}$, **1**, which combines the fully delocalized intermediate oxidation level (Robin and Day class III[4]) with the rare confacial tetrahedral geometry.[5] For copper this geometry is known only for Cu^+ with I^- bridging ligands,[6] including but one instance of a bimetal complex with a single pair of confacial tetrahedra.[7] The molecular structure of **1** (Figure 1) has D_{3h} symmetry, and can be described as a trigonal bipyramid of Br atoms (Br^{ax}, Br^{eq}) with a Cu atom in each pyramid: each Cu atom is C_{3v} tetrahedral (Br−Cu−Br angles 118° and 100°), and the Cu−Cu distance is 2.36 Å.[8,9] The delocalized mixed valence of **1** is distinct from the localized alternation of Cu^+ and Cu^{2+} in $\{[Cu_2Br_4]^-\}_\infty$.[10]

The preparation of **1** is by the reduction of $CuBr_2$ by 2-propanol/HBr or by Cu, or from stoichiometric mixture of CuBr, $CuBr_2$, and Br^-, but only in the presence of $MePh_3P^+$. This is because **1** occurs only in the crystalline state, trapped in cavities in a lattice formed by $MePh_3P^+$ cations. We have no evidence that **1** exists in solution: crystalline $(MePh_3P^+)_2{\cdot}\mathbf{1}$ is intense red, but crystallizes from less intense green solutions, and dissolution of $(MePh_3P^+)_2{\cdot}\mathbf{1}$ discharges its color. All attempts to isolate **1** with cations other than $MePh_3P^+$ have yielded other anionic species.

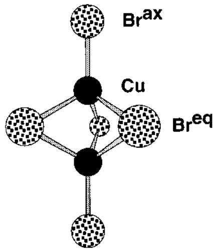

Figure 1. The $[Cu_2Br_5]^{2-}$ ion **1** in $(MePh_3P^+)_2{\cdot}\mathbf{1}$: symmetry D_{3h}; Cu−Br^{ax} 2.28 Å, Cu−Br^{eq} 2.51 Å, Cu−Cu 2.36 Å; Br^{ax}−Cu−Br^{eq} 118°, Br^{eq}−Cu−Br^{eq} 100; Cu−Br^{eq}−Cu 56°.

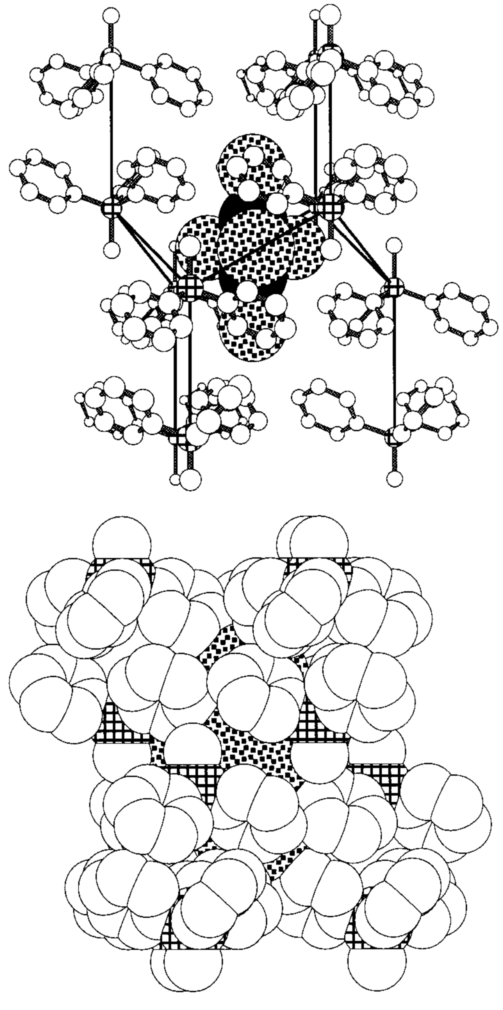

Figure 2. The HA6PE lattice of $(MePh_3P^+)_2{\cdot}\mathbf{1}$: Cu black, Br speckled, P hatched, C white, H atoms omitted. (a) The central anion (exaggerated in size) at a D_3 (32) site surrounded by 12 cations in six 6PE (vertical gray lines) and a single puckered hexagon. (b) Space-filling representation of the same atoms, revealing the many edge-to-face local interactions of the multiple phenyl embraces, and the total enclosure of **1**. The shortest distance between centroids of the anions is 11.3 Å.

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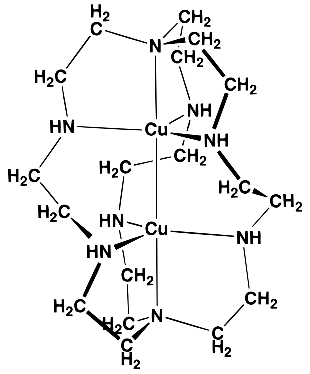
The crystal lattice of $MePh_3P^+$ cations which traps and stabilizes **1** is the hexagonal array of 6-fold phenyl embraces (HA6PE), which we have identified and described previously.[11] In this high-symmetry rhombohedral lattice the $MePh_3P^+$ cations engage in attractive 6-fold phenyl embraces (6PE) aligned with the 3-fold axis, and these 6PE are arranged in a puckered hexagonal array that allows additional Ph••Ph and Ph••Me supramolecular attractions around the hexagonal nets. The $MePh_3P^+$ cations constitute a pseudodiamondoid array, maintained by supramolecular *attractions* between cations. The cations surround cavities which must accommodate 2− anions. Figure 2 shows the 12 $MePh_3P^+$ cations enclosing **1**. The crystallization of this HA6PE lattice engineers the capture of **1** from solutions in which it is at most a minor constituent.

This entrapment of **1** in its $MePh_3P^+$ HA6PE lattice is comparable with the encapsulation of $(Cu^{1.5+})_2$ in macrobicyclic ligands, as in complex **2**: these complexes also impose 3-fold symmetry on $(Cu^{1.5+})_2$ but without bridging ligands, and the Cu−Cu distances range from 2.36 to 2.45 Å.[1c−e] At the protein-enclosed Cu_A sites of CCO (and N_2OX) two $Cu^{1.5+}$ atoms are bridged by two cysteine ligands and separated by 2.5 to 2.7 Å.[2a,b,d,3c]



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The ESR of solid $(MePh_3P^+)_2{\cdot}\mathbf{1}$ at 77 K does not resolve the Cu hyperfine structure. The $g_{||} = 2.060$ and $g_\perp = 2.17$ values are similar to those[1d] of three complexes of type **2**, and indicate that the singly occupied orbital has d_{z^2} character. This is consistent with density functional calculations[12] of **1** (D_{3h}), which show that the SOMO is Cu−Cu σ^* (ca 55% Cu d_{z^2}), with a 3.9 eV gap to the LUMO. Underlying orbitals with major copper composition and Cu−Cu σ or σ^* symmetry are 1.12 (σ), 2.17 (σ^*), and 2.37 eV (σ) below the SOMO.

A significant characteristic of **1** is the flatness of its energy surface for compression or elongation along the 3-fold axis. As shown in Figure 3, the calculated total energy for this concertina distortion (involving concomitant optimization of the Cu−Br bond distances, and variation of the Cu−Br−Cu angle, maintaining D_{3h} symmetry) increases by less than 5 kcal mol^{-1} for Cu−Cu distances up to 0.25 Å shorter than the optimum, and by less than 1 kcal mol^{-1} for elongation of Cu−Cu by 0.3 Å. The energy surface of **1** is calculated to be remarkably flat (<5 kcal mol^{-1}) for a variation of the Cu−Cu distance by 0.6 Å. Since the Cu−Br bond lengths are virtually constant, ΔE for variation of the Cu−Cu distance is compensated mainly by ΔE for $Cu-Br^{eq}-Cu$ variation, which is estimated to be of order 1 kcal mol^{-1} for a 0.2 Å change in Cu−Cu.[13] Therefore we conclude that the Cu−Cu interaction is energetically weak and soft. This conclusion is reinforced by the sensitivity of the Cu−Cu distance to temperature: on temperature reduction from 294 to 203 K the change in the Cu−Cu distance, −0.045 Å, is substantially larger than the changes in $Cu-Br^{ax}$ (−0.011 Å) and $Cu-Br^{eq}$ (−0.002 Å). The flatness of the energy surface is also evident in the low vibrational frequencies of **1**. There is good agreement between the observed (IR and Raman) frequencies and density functional calculated frequencies, and the vibrational structure of **1** is well understood: the coupled Cu−Cu stretching and $Cu-Br^{ax}$ stretching modes are at 100 and 250 cm^{-1}. These results are consistent with an earlier description of soft Cu^+-Cu^+ attractions.[14] Density functional calculations show a similarly flat energy surface for variation of the Cu−Cu distance in **2**.

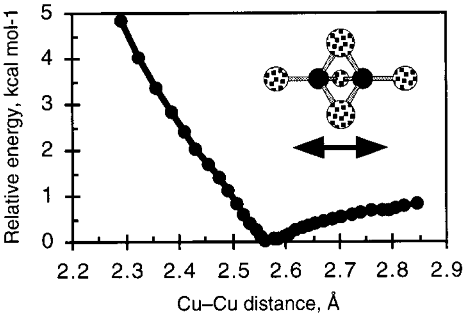

Figure 3. Plot of the change in total energy of **1** versus the Cu−Cu distance, obtained during energy minimizations starting at geometries with the Cu−Cu distance 0.3 Å shorter or longer than the optimum distance. The discrepancy between the calculated Cu−Cu distance at the minimum and the observed distance is a consequence of a small systematic underbinding by the density functional methods used, and the flatness of the energy surface.

The conclusions and insight deriving from this work are the following: (1) a discrete confacial tetrahedral bicopper complex is possible with Br^- ligands, which are smaller and geometrically more demanding than the I^- ligands in the previous instances of this unusual stereochemistry;[5,6c,7] (2) the fully delocalized $(Cu^{1.5+})_2$ class III[4] redox state readily forms with a third type of ligand system, simply Br^-; (3) the crystallographic data and density functional results show that the short Cu−Cu interaction is electronically adequate for full σ delocalization, but is surprisingly weak energetically; and (4) the HA6PE lattice, as a supramolecular lattice synthon, is useful and has potential for the trapping of unusual and possibly unstable anions.

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Supporting Information Available: X-ray experimental details with positional parameters, ORTEP representation, and bond distances and angles (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(8) Crystal data: $(MePh_3P^+)_2{\cdot}\mathbf{1}$, deep red crystals, trigonal, space-group $R\bar{3}c$, $a = b = 10.775(2)$ Å, $c = 60.398(12)$ Å, 294 K, $z = 6 \times (MePh_3P)_2[Cu_2Br_5]$, $R = 0.034$, $R_w = 0.043$, GOF = 1.58. At 203 K, $a = b = 10.7475(3)$ Å, $c = 60.047(2)$ Å, $R = 0.053$.

(9) The X-ray diffraction data do not support a disordering of geometrically different Cu^I and Cu^{II} sites in $[Cu_2Br_5]^{2-}$, because the refined thermal ellipsoids of Cu and Br^{ax} are oblate rather than prolate along the 3-fold axis, and the rms displacements of anion atoms are of similar magnitude to those of the cations. Analysis of the details of the calculated anisotropies indicates that the D_{3h} $[Cu_2Br_5]^{2-}$ anion wobbles from the crystallographic 3-fold axis by ca. 3° at 294 K (1.3° at 203 K). This thermal motion of the anion is also consistent with the shape of its cage, formed by the cations.

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