The $[Cu_8Br_{15}]^{6-}$ Ion, A Crystal-Stabilized High-Symmetry Mixed-Valence Copper Complex with a Linear Halogen Bridge

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The Cu(I)−Cu(II) system is one of the most important mixed-valence systems in both biochemistry[1−9] and inorganic chemistry.[10−22] Many of the systems that have been described to date involve the delocalized $(Cu^{+1.5})_2$ unit, and we have recently shown that such a unit exists in the fundamental anion $[Cu_2Br_5]^{2-}$, which combines this delocalized intermediate oxidation level (Robin and Day class III mixed-valence system[23]) with a rare confacial tetrahedral geometry.[16] Other mixed-valence halogenocuprates that have been reported in the past include separate mononuclear systems such as $[Cu^{I}Br_3]^{2-}/[Cu^{II}Br_4]^{2-}$ (class I),[17] multinuclear complexes such as $[Cu_3Cl_6]^{2-}$ and $[Cu_4Br_{10}]^{4-}$ (class II),[18,19] and infinite chains such as $\{[Cu_2Br_4]^{-}\}_\infty$ (class II).[20] The $[Cu_2Cl_6]^{3-}$ system has been used as a model in theoretical studies,[21,22] but has not been observed experimentally.

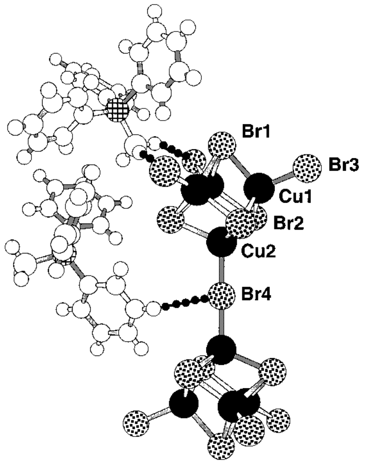

Figure 1. Structure of the anion **1** and a small part of the packing of the surrounding $MePh_3P^+$ cations in the crystal, showing one of the six cations around the waist and one of the three cations around each end of the anion. All cations are equivalent in the space group $Pa\bar{3}$. Solid spheres: Cu. Speckled spheres: Br. Dotted connections: C−H···Br hydrogen bonds. Structural parameters for **1**: symmetry S_6; Cu(1)−Br(1) 2.5259(18), Cu(1)−Br(2) 2.5779(17), Cu(1)−Br(2)′ 2.4717(15), Cu(1)−Br(3) 2.3588(17), Cu(2)−Br(2) 2.4890(14), Cu(2)−Br(4) 2.409(3), Cu(1)−Cu(1)′ 2.919(2), Cu(1)−Cu(2) 2.951(3) Å; Br(1)−Cu(1)−Br(2) 105.20(6), Br(1)−Cu(1)−Br(2)′ 108.45(6), Br(1)−Cu(1)−Br(3) 108.58(6), Br(2)−Cu(1)−Br(3) 116.52(6), Br(2)′−Cu(1)−Br(3) 113.66(7), Br(2)−Cu(1)−Br(2)′ 103.87(6), Br(2)−Cu(2)−Br(2)′ 106.03(7), Br(2)−Cu(2)−Br(4) 112.73(7), Cu(1)−Br(1)−Cu(1)′ 70.58(6), Cu(1)−Br(2)−Cu(1)′ 70.59(7), Cu(1)−Br(2)−Cu(2) 71.21(6), Cu(1)′−Br(2)−Cu(2) 73.00(6), Cu(2)−Br(4)−Cu(2)′ 179.998(1)°.

In most of the above systems, the Cu(I):Cu(II) ratio is 1:1. The only exception is in $[Cu_3Cl_6]^{2-}$,[19] where it is 2:1. Not much is known about the possible range that this ratio can take, or about the properties of mixed-valence compounds with Cu(I):Cu(II) ratios very different from unity. We report here the formation and properties of the new Cu(I)−Cu(II) mixed-valence species $[Cu_8Br_{15}]^{6-}$, **1**, in which the formal Cu(I):Cu(II) ratio is 7:1 (i.e., a Cu_8^{9+} complex), and which shows an unusual example of linear bridge bonding for one of the bromide ligands in the structure. The molecular structure of **1**, $[Br_3(\mu_3\text{-}Br_4Cu_4)(\mu_2\text{-}Br)(\mu_3\text{-}Br_4Cu_4)\text{-}Br_3]^{6-}$, S_6 symmetry (Figure 1),[24] can be considered to be derived from two Cu_4Br_8 cubane units by removing a terminal Br atom from one of the four Cu atoms in each unit and linking these two Cu atoms via a linear μ_2-Br bridge along the 3-fold axis common to both units. The six Cu(1) have a slightly distorted tetrahedral coordination environment (no local symmetry; Br−Cu−Br angles 103−117°), while the two Cu(2) also have tetrahedral coordination

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[24] Crystal data: $[MePh_3P]_6$ (**1**), dark green crystals, cubic, space group $Pa\bar{3}$, $a = b = c = 23.0997(2)$ Å, 203(2) K, $Z = 4 \times (MePh_3P)_6[Cu_8Br_{15}]$, $R = 0.0801$, $R_w = 0.0679$, GOF = 1.088.

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environments, but with C_3 local symmetry (Br−Cu−Br angles 106°, 112°). The triply bridging bromide ligands Br(1), Br(2) show bonding parameters (Cu−Br bond lengths 2.47−2.58 Å; Cu−Br−Cu angles 70−73°) that are very similar to those observed in the more familiar neutral heterocubane systems $[Cu_4Br_4L_4]$ (L = phosphine or amine ligand).[25] While cubane structures are common in neutral copper(I) and silver(I) complexes, there are no known examples of any complexes of these metals with the structure found for **1**. The only known anionic complex with a cubane structure is $[Ag_4I_8]^{4-}$.[26] The linear-bridge bonding mode for Br(4) in **1** is very unusual for halide ligands in coordination compounds. The Cu(2)−Br(4) bond length (2.404(3) Å) is significantly shorter than those involving the triply bridging bromide ligands. Although only one in eight copper atoms in the complex is formally in the (+II) oxidation state, the symmetry of the ion precludes any description in terms of localized Cu(I) and Cu(II) sites. In the polymeric $\{[Cu_2Br_4]^-\}_\infty$ system, localized alternation of Cu^{+1} and Cu^{+2} sites was proposed on the basis of a 0.1 Å difference in the Cu−Br bond lengths between the sites.[20] In the present complex, the difference between the average Cu−Br bond lengths about Cu(1) (2.484 Å) and Cu(2) (2.469 Å) is only 0.015 Å. The Cu- - -Cu distances within the cubane units are 2.919(2), 2.951(3) Å, which are at the low end of the range of values 2.8−3.5 Å found in the $[Cu_4Br_4L_4]$ heterocubane systems.[25] In view of the fact that there seems to be little Cu- - -Cu interaction at the much shorter distance of 2.36 Å in $[Cu_2Br_5]^{2-}$,[16] it is unlikely that Cu- - -Cu bonding is a significant factor in the stabilization of **1**.

The preparation of **1** is by the reaction in ethanol of a mixture of CuBr, Br^-, and $CuBr_2$ (7:6:1), or of CuBr, Br^-, and $CuCl_2 \cdot 2H_2O$ (1:1:1), 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. Although the dark green crystalline $[MePh_3P]_6$ (**1**) dissolves in acetonitrile to give a similarly green solution, the visible absorption spectrum of this solution is the same as that of a solution of $CuBr_2$ in the same solvent. The far-IR spectrum of $[MePh_3P]_6$ (**1**) shows weak, overlapping bands in the range 130−215 cm^{-1} that are assigned to the ν(CuBr) modes. The positions of these bands correspond well with those in copper(I) bromide complexes with similar Cu−Br bond lengths.[27] The Raman spectrum (514 nm Ar^+ excitation) shows a broad, unresolved ν(CuBr) band in the same region as the IR spectrum, and a very strong band at 80 cm^{-1} that is in the region expected for the symmetric deformation mode of the Cu_4Br_8 clusters.[28]

Anion **1** is encapsulated and stabilized by a crystal supramolecular array of $MePh_3P^+$ cations. The capsule of 12 cations around **1** is constructed from a single cation in the asymmetric unit of space group $Pa\bar{3}$, and is stabilized by a large number of edge-to-face Ph···Ph attractions. The cation capsule stabilizes each anion with 12 (Me)C−H···Br hydrogen bonds and 6 (Ph)C−H···Br hydrogen bonds. Special features of the crystal supramolecularity are shown in Figure 1. All surfaces of the cation fit the surfaces of the anion or of other cations, with attractive interion energies. This highly efficient crystal packing determines the charge of 6− per anion cavity, and thus the mixed valence of the anion has been crystal stabilized.

The EPR spectrum of solid $[MePh_3P]_6$ (**1**) at 77 K shows an almost isotropic signal at $g = 2.13$ without any resolved Cu hyperfine structure. This is consistent with density functional calculations on **1**,[29] which show that the SOMO is extensively delocalized over all eight Cu atoms (spin densities of 0.082, 0.088 on Cu(1,2)) and, to a lesser extent, over the Br ligands (spin densities of 0.024, 0.037, 0.008, 0.021 on Br(1,2,3,4)). The atomic charges (Mulliken population analysis) are +0.166, +0.029 on Cu(1,2) and −0.359, −0.292, −0.734, −0.182 on Br(1,2,3,4). The Cu charges and spin densities indicate that this is a class II mixed-valence system.[23] The relatively low charge on Br(4) is of some interest, since the linear bridge-bonding mode that this atom displays is very unusual. This bonding mode is also observed for the central halogen atom in trihalide ions X_3^-,[30] where the negative charge on the ion is shared mainly by terminal atoms, and the charge on the central atom is low.[31] The SOMO in this complex is an orbital of E_u symmetry, with a 2.6 eV gap to the LUMO. Major bands in the electronic absorption spectrum (obtained by diffuse reflectance spectroscopy) occur at about 300, 400, and 800 nm.

The conclusions from this work are as follows: (1) the mixed-valence complex $[Cu_8Br_{15}]^{6-}$, which has a high formal Cu(I): Cu(II) ratio, has been prepared and characterized; (2) the structure of this complex incorporates two Cu_4Br_7 units connected by a bromide ligand in an unusual linear-bridge bonding mode similar to that observed for the central atom in trihalide ions; (3) the physical properties of this complex, together with electronic structure calculations, indicate that it is a delocalized (class II) mixed-valence system with two sets of nearly equivalent Cu atoms with a formal average oxidation state of +1.125; (4) the mixed valence and the stereochemistry of the complex have been crystal stabilized and are not evident in solution.

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Supporting Information Available: The solid-state visible diffuse reflectance spectrum of $[MePh_3P]_6$ (**1**). An X-ray crystallographic file in CIF format for the structure of $[MePh_3P]_6$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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