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# Cu(I)-Cu(I) Interactions. Bonding Relationships in d^{10}-d^{10} Systems

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The interaction between Cu(I) centers is studied by means of molecular orbital calculations on Cu_n^{n+}, $n = 2$–4, model dimers with phosphonium ylide bridges, and tetramers with alkyl bridges. In the absence of metal s and p functions the expected closed-shell repulsion between the d^{10} centers is evident. Mixing of metal s and p orbitals converts this repulsion into a slight attraction in Cu(I) clusters of any size. A severe perturbation is caused by the introduction of the bridging ligands, which impose their own stereochemical requirements. Nevertheless, weak attractive Cu(I)–Cu(I) interactions remain.

In the last few years numerous synthetic and structural studies have been reported on organocopper(I) compounds containing Cu_n cluster units. At present examples are available of structures where n ranges from 2 to 8.[1-6,7] Some of these structures have been recently reviewed.[8] There is no question that there is a tendency for the Cu(I) centers to cluster together. But are there direct Cu–Cu bonds in these molecules? A simplistic approach would make one wonder about the possibility of attraction between two d^{10} centers, formally closed shells. The present contribution, in conjunction with a related study of Pt(0)–Pt(0) interactions,[9] approaches the problem of bonding in these molecules.

A range of Cu–Cu distances is found in the structures available to date. Typical of the short and long extremes are the tetranuclear and trinuclear structures **1**[3a] and **2**.[2b] There are structures with longer and even shorter[3b] Cu–Cu separations, but most distances are intermediate.[1-7]
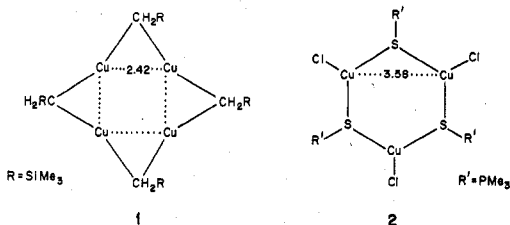
Clearly the longer distances, such as those in **2**, do not even hint at direct metal–metal interaction. Contraction of a metal–metal separation by itself is not a sign of metal–metal bonding, especially when bridging atoms are present, as they are in all the Cu(I) structures. Thus, in the course of another detailed study of binuclear complexes of the M_2L_6 type we found that direct metal–metal bonding took third place as a determinant of geometry, behind the geometrical preferences of the monomer unit and the symmetry-conditioned coupling capabilities of the bridging atoms.[10] However, Cu–Cu distances as short as 2.38 Å cannot be ignored nor can be the general tendency to cluster.

The problem is studied by means of extended Hückel calculations,[11] with parameters given in the Appendix. We also direct the reader's attention to a preceding extensive molecular orbital investigation of the Cu_8 cluster by Avdeef and Fackler.[8c,12] Their study found a slightly negative net copper–copper overlap population. Coucouvanis and co-workers[6] have advanced structural arguments for attractive

Table I. Cu_2^{2+} Binding Energies (Relative to Two Isolated Cu^+ Ions) and Overlap Populations as a Function of Cu–Cu Separation

	3d orbitals alone		3d, 4s, 4p orbitals	
distance, Å	binding energy,[a] eV	overlap population	binding energy,[a] eV	overlap population
3.18	+0.002	−0.0002	−0.026	+0.0078
2.98	+0.005	−0.0005	−0.058	+0.0173
2.78	+0.014	−0.0013	−0.120	+0.0364
2.58	+0.023	−0.0031	−0.228	+0.0705

[a] A positive value indicates repulsion; a negative value, attraction.

interactions between Cu atoms in cluster structures.

The Interaction of Two to Four Cu(I) Centers

We begin by constructing an interaction diagram for a Cu_2^{2+} molecule at a separation of 2.58 Å, within the range of distances found in the Cu(I) clusters. If one allows only 3d orbitals on Cu, then the situation shown at left in Figure 1 is obtained. The inclusion of overlap in the extended Hückel calculation leads to the typical result that the antibonding MO's are destabilized more than the bonding ones are stabilized, both relative to the 3d orbitals of an isolated copper atom. With all 10 orbitals occupied in the d^{10}–d^{10} system we have a typical case of conjugative destabilization.[13]
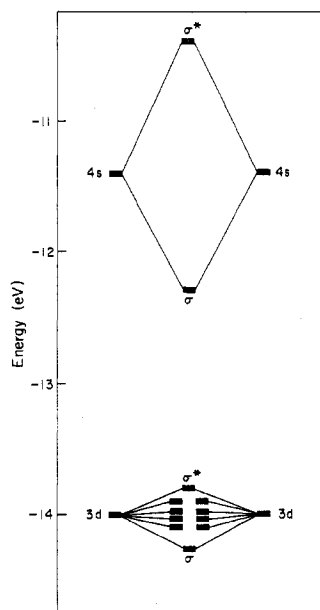
The repulsive nature of unmitigated d^{10}–d^{10} interaction is reflected in two further ways in Table I, which shows the binding energy and overlap populations in Cu_2^{2+}, relative to two isolated Cu^+ centers, as a function of distance. The interaction of two Cu^+ ions is repulsive, as judged by both the increasingly positive binding energy and the increasingly negative overlap population with decreasing distance.

All this is without metal 4s and 4p orbitals. When these are included, as they must be, the situation changes dramatically. Table I shows that with Cu 4s and 4p orbitals there is an attractive interaction between two Cu^+ centers approaching each other, as indicated by both the negative binding energy and the growing positive overlap population. Figure 2 shows the energy levels at 2.58 Å, and the d block of Figure 2 is repeated in Figure 1 at right to allow a direct comparison of the occupied orbitals with and without s and p functions.

The mechanism by which 4s and 4p orbitals stabilize the dimer is well understood. From the 4s functions one generates σ and σ^* orbitals, and from 4p σ, π, π^*, and σ^* are generated. These mix into the occupied 3d combinations of proper

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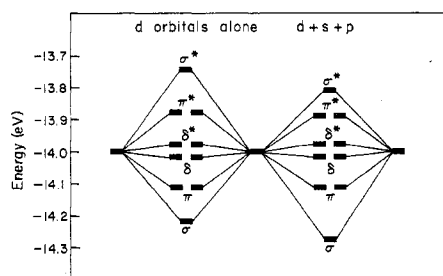
Figure 1. Energy levels of the d block of Cu_2^{2+} at a separation of 2.58 Å. At left are the results of a calculation with 3d orbitals alone; at right are results for 3d along with 4s and 4p on each center.

Table II. Binding Energies for Cu_3^{3+} and Cu_4^{4+} with 3d, 4s, and 4p Orbitals

Cu–Cu distance, Å	binding energy, eV	overlap population
	Cu_3^{3+} (D_{3h})	
2.98	−0.175	0.018
2.78	−0.359	0.038
2.58	−0.674	0.075
2.38	−1.131	0.132
	Cu_4^{4+} (D_{4h})	
2.83	−0.417	0.032
2.57	−0.984	0.080
2.44	−1.469	0.124

Figure 3. Total energy (top) and Cu–Cu overlap population (bottom) for a $(CuCH_3)_4$ tetramer as a function of external C–Cu–C angle. The energy scale markings are in eV.

Figure 2. Energy levels of Cu_2^{2+} at 2.58 Å with 3d, 4s, and 4p levels on the metal centers. The 4p combinations are not shown but lie at still higher energy.

symmetry, and, of course, in such a way as to stabilize the 3d σ and σ* orbitals. The details of the mixing are shown in **3** and **4** for the σ and σ* orbitals. The comparison of the two
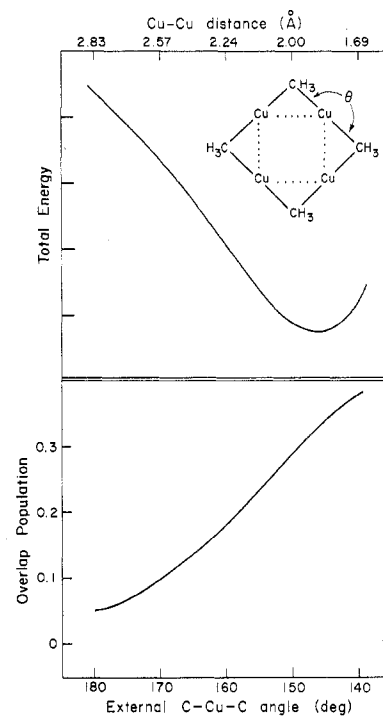

3, σ*   **4**, σ
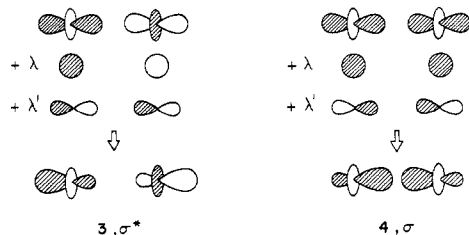
parts of Figure 1 shows that these are most affected by the inclusion of 4s and 4p orbitals in the basis set. The σ orbital becomes more bonding and the σ* less antibonding, moving partway to a lone-pair combination, **3**.

Similar results are obtained for three or four Cu⁺ atoms, as shown in Table II.

A closed-shell repulsion has been converted into an attraction by the inclusion of unfilled orbitals of the proper symmetry. This is, of course, a general phenomenon. The assumption that filled shells, be they s^2, p^6, or d^{10}, repel is an oversimplification. Whether bonding does or does not occur depends on the location in energy and extent in space of unfilled orbitals. In the case of He, for instance, the mixing of 2s and 2p into repelling 1s shells is never large enough to produce attraction or condensation, no matter what the degree of clustering be. Beryllium, on the other hand, is not bound

as a diatomic Be_2 but does form a metal. Its 2p orbitals are lower relative to the occupied 2s than in the He case. SCF calculations indicate that the smallest Be cluster that is strongly bound is Be_4.[14,15] p–d interactions very similar to those discussed here are behind the stacking of four-coordinate square-planar d^8 complexes. Also the same phenomenon is at work in the formation of Pt(0) clusters,[9] including an L_2PtPtL_2 dimer [$L_2 = (t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2$] which has no bridges and yet a 2.765 Å Pt–Pt separation.[16]

The Effect of Bridging Ligands vs. Cu–Cu Bonding

The previous section dealt with bare Cu(I) ions. While there are slightly bonding interactions between these, it remains to be seen if the bonding to other ligands, especially bridging ones, is not responsible for the short metal–metal contacts. We have studied in some detail a model, **5**, for the tetranuclear clusters of type **1** and a dimer **6** as a model for the phosphonium ylide complex of Schmidbaur and co-workers.[1a]
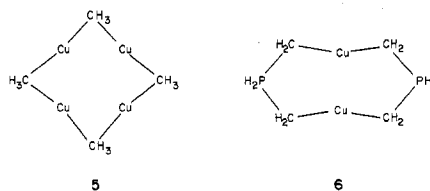

5   **6**

Table III. Extended Hückel Parameters

orbital	H_{ii}, eV	Exponents[a]	
		ζ_1	ζ_2
Cu 4s	−11.4	2.200	
Cu 4p	−6.06	2.200	
Cu 3d	−14.0	5.950 (0.5933)	2.300 (0.5744)
H 1s	−13.6	1.300	
C 2s	−21.4	1.625	
C 2p	−11.4	1.625	
P 3s	−18.6	1.600	
P 3p	−14.0	1.600	

[a] Two Slater exponents are listed for the 3d functions. Each is followed in parentheses by the coefficient in the double ζ expansion.

For **5** we varied the C–Cu–C angle while keeping the Cu–C distance fixed at 2.00 Å. The results are shown in Figure 3. The experimental structure, with bridging $CH_2Si(CH_3)_3$ instead of CH_3, shows a C–Cu–C angle of 164°. The calculated minimum is at an angle of $\sim 145°$, which is too small. It may thus be that our calculations overestimate the attractive Cu–Cu interactions.

The levels of the cluster may be constructed by interacting four CH_3^- groups with a preformed Cu_4^{4+}. The perturbation in this interaction is a serious one, but not so much on the d band as on the higher orbitals of the cluster which are hybrids of 4s, 4p, and 3d orbitals. These interact strongly with the bridging methyl groups. Note that the Cu–Cu overlap population keeps increasing as the energy minimum is passed. The Cu–Cu interactions are clearly attractive and the minimum appears to be set, not quite correctly, by the balance of these interactions with the angularly dependent bonding requirements of the bridging ligand.

Similar results are obtained for **6**. The computed Cu–Cu distance optimizes at 2.7 Å, which is somewhat shorter than the observed 2.84 Å in the phosphonium ylide complex.[1a] Positive Cu–Cu overlap populations keep growing as the Cu–Cu separation is decreased past the minimum. This would seem to indicate attractive Cu–Cu interactions. However, a model calculation on monomeric $CH_3CuCH_3^-$ in precisely the same geometry as the PCH_2CuCH_2P piece of the dimer also shows a bending at the copper. So the ligand stereochemistry acts to bring the copper atoms together, at least in this case, and so do the direct interactions.

In practice it will be difficult to distinguish the effects of direct Cu–Cu interaction and the stereochemical demands of the ligand set around the copper atoms. As was noted in our previous study of M_2L_6 systems,[10] the latter will depend on the particular ligand set, especially the bridging atoms. Our calculations do provide support for a soft attractive Cu(I)–Cu(I) interaction, overlaid on top of the ligand set requirements.

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Appendix

The calculations performed were of the extended Hückel type[11] with parameters listed in Table III. These parameters were taken from previous studies on M_2L_6 transition-metal dimers;[10] they are listed in Table III. The modified Wolfsberg–Helmholz formula was used.[17]

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