

- (MAGH); C, 34.32; H, 3.29; N, 17.15; Cu, 12.97 (MAHH). Found: C, 27.91; H, 3.48; N, 13.02; Cu, 15.14 (MAGH); C, 34.16; H, 3.47; N, 17.03; Cu, 13.11 (MAHH).
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- (23) On the basis of similar potentiometric measurements, the acid dissociation and formation constants of GGH and its 1:1 Cu(II) complex were estimated: $\text{p}K_{\text{COOH}} = 2.84$, $\text{p}K_{\text{im}} = 6.87$, $\text{p}K_{\text{NH}_3^+} = 8.22$, $\log K_1 = 5.32$, and $\text{p}K_{2c} = 8.37$.
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Studies of the Cubane Cluster of Copper(I). A Modified Self-Consistent Charge and Configuration Molecular Orbital Investigation of the Cluster Containing the $\text{Cu}_8\text{S}_{12}^{4-}$ Core

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A molecular orbital study of the modified self-consistent charge and configuration type (SCCC) was performed on a model of a general class of cube copper clusters containing the nuclear core $\text{Cu}_8\text{S}_{12}^{4-}$, where the sulfur atoms are distributed (in a distorted cuboctahedral manner) above the edges of a cube formed by copper atoms. In the study the basis set was chosen to consist of copper 3d, 4s, and 4p and sulfur 3s and 3p atomic orbitals. The results of the calculations, which are compared with those of the observed electronic spectrum, show no net bonding Cu-Cu interaction with this model. The predicted lowest energy electronic transition is charge transfer, of the type $\text{S}(3\text{p}) \rightarrow \text{Cu}(4\text{s}, 4\text{p})$. The highest filled molecular orbitals are sulfur in character and are antibonding. The lowest energy empty orbital is primarily a mixture of copper 4s and 4p and sulfur 3p orbitals. A cyclic voltammetric study of one tetraanionic cluster shows numerous high redox potential peaks. However, none are reversible and the cluster appears to decompose after repeated redox cycles, with the concomitant deposition of the oxidized ligand.

Introduction

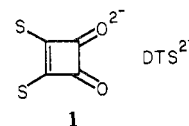
The appearance of relatively short intermetallic separations in reported structures of copper(I) cluster complexes¹ has posed the intriguing question "Are there metal-metal bonds in such d^{10} systems?" A simple view which recognizes that closed-shell repulsions preclude attractive interactions suggests the absence of such bonds.² Yet at the 2.38-Å Cu-Cu separation found in (4-methyl-2-cupriobenzyl)dimethylamine,^{1a} which is nearly 0.2 Å shorter than bond lengths in copper metal,³ it seems likely that attractive interactions exist. However, given that all reported Cu clusters possess bridging ligands, it is not clear what role the stereochemical requirements of the ligands play in producing the apparent M-M interactions.

To improve our own understanding of the bonding in these multinuclear d^{10} systems, we performed a modified self-consistent charge and configuration (SCCC) molecular orbital study of one particular class of copper clusters,⁴ those containing the core $\text{Cu}_8\text{S}_{12}^{4-}$. A study on copper(I) dimeric clusters has been recently performed by Mehrotra and Hoffmann.⁵

Slater and Johnson²¹ briefly describe an $X\alpha$ calculation on the neutral unit Cu_8 . Since copper atoms in this case appear to have the configuration d^{10} s, some difficulty arises in direct comparison to our work. However, the general features of a closely spaced d band are similar.

The general class of octanuclear clusters which possess the Cu_8S_{12} core consists of at least three structurally characterized^{6,7} members, $\text{Cu}_8(i\text{-MNT})_6^{4-}$, $\text{Cu}_8(\text{DED})_6^{4-}$, and $\text{Cu}_8(\text{DTS})_6^{4-}$, where $i\text{-MNT}^{2-} = 1,1\text{-dicyanoethylene-2,2-dithiolate}$, $\text{DED}^{2-} = \text{dicarboethoxy-2,2-ethylenedithiolate}$, and

$\text{DTS}^{2-} = \text{dithiosquarate}$, **1**. In each of these complexes eight



copper(I) ions are arranged at the corners of a nearly perfect cube which is inscribed into a distorted cuboctahedron defined by the 12 sulfur atoms from six dithiolate ligands. In all cases the shortest Cu-Cu distances are approximately 2.8 Å. Since the central core Cu_8S_{12} can be viewed to have the point symmetry O_h (if one approximates the sulfur atoms to be situated directly above the edges of the cube), the theoretical study of such an esthetically intriguing class of compounds is considerably simplified by the use of group theory.

Hollander and Coucouvanis⁷ presented an interesting structural view of the stability of such clusters. Presently, we will attempt to deal with the problem in the context of molecular orbital theory. In order to help visualize the Cu_8S_{12} geometry contained in these "cubane" clusters, an ORTEP stereodrawing of the $\text{Cu}_8(\text{DTS})_6^{4-}$ with its approximate T_h symmetry is presented in Figure 1.

Method of Calculation

The bonding model to be discussed idealizes the clusters in the following way. The sulfur atoms are considered to be cuboctahedrally arranged above the edges of a cube of copper atoms, thus forming the hypothetical species $\text{Cu}_8\text{S}_{12}^{4-}$, of point group O_h , where the remaining portion of the ligand is ignored. The basis set consists of 120 atomic orbitals (AO), distributed

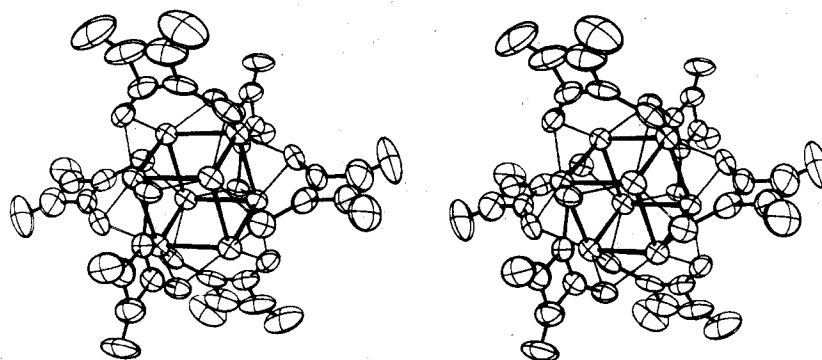


Figure 1. Stereopair ORTEP drawing of the dithiosquarate anionic "cubane" cluster $\text{Cu}_8(\text{DTS})_6^{4-}$ reported by Hollander and Coucouvanis.⁷

Table I. Reducible Representations Generated by the Atomic Orbitals

	O_h	E	C_3	C_2'	C_4	C_4^2	i	S_4	S_6	σ_h	σ_d
metal	$\Gamma_s = \Gamma_{p_z} = \Gamma_{d_{z^2}}$	8	2	0	0	0	0	0	0	0	4
	$\Gamma_{p_x, p_y} = \Gamma_{d_{x^2-y^2}, d_{xy}} = \Gamma_{d_{xz}, d_{yz}}$	16	-2	0	0	0	0	0	0	0	0
ligand	Γ_{p_x}	12	0	-2	0	0	0	0	0	4	-2
	Γ_{p_y}	12	0	-2	0	0	0	0	0	-4	2
	$\Gamma_{p_z} = \Gamma_s$	12	0	2	0	0	0	0	0	4	2

among 20 atoms, and includes minimum-set HF-SCF copper 3d ("double ζ "), 4s, and 4p orbitals⁸ and sulfur 3s and 3p Slater-type orbitals.⁹

The treatment can be resolved into the following steps: (1) choosing a convenient local coordinate system for each of the 20 atoms; (2) determining the irreducible representations spanned in O_h by the AO's in the basis of the local coordinate systems; (3) generating linear combinations of atomic orbital (LCAO) functions which are adapted to the irreducible representations necessary to span the orbitals; (4) deducing the analytical expressions for the Hamiltonian elements in the symmetry-adapted (SA) LCAO basis, using a Wolfsberg-Helmholtz method (WHM)¹⁰ with k fixed at 2; (5) reducing the coordinate-system-dependent (CSD) diatomic overlaps which are used to construct the Hamiltonian elements into linear combinations of σ , π , and δ types suitable for calculation by standard methods; (6) obtaining from atomic spectroscopic data¹¹ the valence orbital ionization potentials (VOIP), which are functions of charge and configuration and which place the Hamiltonian elements on an absolute energy scale, and then partially adding the Madelung-type electrostatic potential to the VOIP's; (7) solving the secular matrices, independently for each irreducible representation, by means of matrix diagonalization; (8) performing Mulliken configuration and overlap population analysis on the occupied eigenvectors; (9) comparing the calculated and starting atomic charges and configurations and refining the calculation iteratively to self-consistency with respect to these parameters; and (10) varying a parameter which introduces electrostatic effects (in lieu of the customary procedure of varying the WHM constant) when fitting the observed electronic bands.

Two Fortran IV computer programs, SALC and CUS12, were written to perform the various steps in the calculation.⁴

The local coordinates, shown in Figure 2, were chosen in a way that simplified both the SA-LCAO expressions and the reduction process of the CSD diatomic overlaps. The various internuclear distances in the model were taken from the structure of $\text{Cu}_8(i\text{-MNT})_6^{4-}$: $\text{Cu}_1\text{-Cu}_2 = 2.83$ and $\text{Cu}_1\text{-S}_1 = 2.25$ Å. The consequences of the simplification of the chosen geometry place $\text{S}_1 \cdots \text{S}_2$ at 3.75 Å, similar to that found in $\text{Cu}_8(\text{DTS})_6^{4-}$.

In the model, all possible Cu-Cu interactions in the cube were considered ($\text{Cu}_1\text{-Cu}_2$, $\text{Cu}_1\text{-Cu}_3$, $\text{Cu}_1\text{-Cu}_7$). The metal-ligand interactions were confined to nearest-neighbor type

Cu_8S_{12}

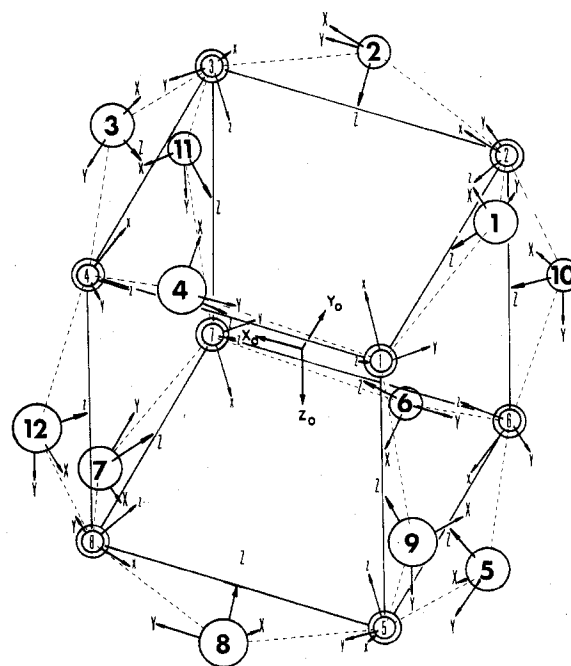


Figure 2. Model geometry. All the atomic z axes point to the center of the cube. The orientations of the metal x and y axes are such that y_1, y_2, y_3 and y_4 lie in one plane and y_5, y_6, y_7 and y_8 lie in another plane, parallel to the first; all the x axes point to the fourfold axis intersecting these planes. The ligand x axes of atoms 1, 2, 3 and 4 and 5, 6, 7 and 8 point to two common points, respectively along the same fourfold axis mentioned above. The ligand x and z axes of atoms 9, 10, 11 and 12 lie in a plane parallel to the two other planes mentioned.

($\text{Cu}_1\text{-S}_1$, $\text{Cu}_1\text{-S}_4$, $\text{Cu}_1\text{-S}_9$). Also included for consideration were the nearest-neighbor S-S interactions ($\text{S}_1\text{-S}_2$, $\text{S}_1\text{-S}_4$, $\text{S}_1\text{-S}_9$, $\text{S}_1\text{-S}_{10}$).

Using standard group-theoretical procedures,¹² the reducible representations spanned by the metal and ligand orbitals are presented in Table I, while the decomposition to irreducible components is summarized in Table II. As is shown in the latter table, one has so far by the application of group theory,

Table II. Irreducible Components Generated by the Atomic Orbitals in O_h Symmetry

	atomic orbitals	irreducible representations								
		A_{1g}	A_{2u}	E_g	E_u	T_{1g}	T_{2u}	T_{2g}	T_{1u}	A_{2g}
metal	s	x	x					x	x	
	p_z	x	x					x	x	
	d_{z^2}	x	x					x	x	
	(p_x, p_y)			x	x	x	x	x	x	
	(d_{xz}, d_{yz})			x	x	x	x	x	x	
	$(d_{x^2-y^2}, d_{xy})$			x	x	x	x	x	x	
ligand	p_x			x	x	x		x	x	
	p_y		x		x	x		x	x	
	p_z	x		x		x	x	x		
	s	x		x		x	x	x		

reduced a 120×120 Hamiltonian matrix to a diagonal set of much smaller submatrices, the largest of which (T_{1u}) is only 10×10 . To utilize this simplification, one must reexpress the atomic orbitals in terms of LCAO's which are adapted to the necessary representations (Table II) and thus form bases for

each of the submatrices. This procedure has already been described by us.¹³ The results are summarized in Table III. In this table α and β refer to members of irreducible pairs of atomic orbitals, such as $(d_{x^2-y^2}, d_{xy})$ or (p_x, p_y) . This is a consequence of the definitions of the local coordinate systems.

The details of the derivation of the Hamiltonian elements may be found elsewhere.⁴ The key point in the method is that such elements are linear functions of diatomic overlaps.

To evaluate overlaps in a general coordinate system, such as the complicated one we have here, one first transforms the local coordinates, a pair of centers at a time, to a standard two-center system where overlaps are of the σ -, π -, and δ -type only.¹⁷ For example, $S(4s(\text{Cu}_1), 4s(\text{Cu}_2)) = S_\sigma$, $S(4p_z(\text{Cu}_1), 4p_z(\text{Cu}_2)) = 1/3 S_\sigma + 2/3 S_\pi$, and $S(3d_{xz}(\text{Cu}_1), 3d_{xz}(\text{Cu}_2)) = 1/6 S_\sigma + 5/18 S_\pi + 5/9 S_\delta$. This procedure is similar to the method of angular overlap.¹⁵ That is, the overlap between two centers should not depend on the particular type of coordinate system chosen. The standard-orientation overlaps were evaluated using master formulas of the Milliken type,¹⁶ some of which had to be derived for this calculation.⁴ With the type of radial functions chosen^{8,9} some typical values of overlaps found are $S_{3d\sigma}(\text{Cu}_1, \text{Cu}_2) = 0.064$, $S_{3d\pi}(\text{Cu}_1, \text{Cu}_2) = 0.033$,

Table IIICoefficients of *Metal* SA-LCAO Orbitals^a for $\text{Cu}_8\text{S}_{12}^{4-}$

irreducible representation	orbital type	atomic centers															
		1^α	2^α	3^α	4^α	5^α	6^α	7^α	8^α	1^β	2^β	3^β	4^β	5^β	6^β	7^β	8^β
$A_{1g}(A_{2u})$	Z	1	1	1	1	1	1	1	1								
$T_{2g}(T_{1u})$	Z^ξ	3	-1	-1	-1	-1	-1	3	-1								
	Z^η		2	-1	-1	-1	-1		2								
	Z^ζ			1	-1	1	-1										
$E_g(E_u)$	$(X,Y)^u[(A,B)^u]$	1	1	1	1	1	1	1	1								
$T_{1g}(T_{2u})$	$(X,Y)^v[(A,B)^v]$									1	-1	1	-1	-1	1	-1	1
	$(X,Y)^x[(A,B)^x]$	$\sqrt{3}$	1	-1	-1	-1	-1	1			1	-1	-1	-1	1	-1	-1
	$(X,Y)^y[(A,B)^y]$								1								
$T_{2g}(T_{1u})$	$(X,Y)^z[(A,B)^z]$																
	$(X,Y)^\xi[(A,B)^\xi]$		1	-1	-1	-1	-1	1									
$T_{2g}(T_{1u})$	$(X,Y)^\eta[(A,B)^\eta]$	1	-1	1	-1	1	-1	1		$\pm\sqrt{3}$							
	$(X,Y)^\zeta[(A,B)^\zeta]$	1	-1	1	-1	1	-1	1			$\pm\sqrt{3}$						
	$(X,Y)^\xi[(A,B)^\xi]$	1	1	-1	-1	-1	-1	1				$\pm\sqrt{3}$					
$T_{2g}(T_{1u})$	$(X,Y)^\eta[(A,B)^\eta]$	1	-1	1	-1	1	-1	1		$\pm\sqrt{3}$							
	$(X,Y)^\zeta[(A,B)^\zeta]$	1	-1	1	-1	1	-1	1			$\pm\sqrt{3}$						
	$(X,Y)^\xi[(A,B)^\xi]$	1	-1	1	-1	1	-1	1				$\pm\sqrt{3}$					

Coefficients of *Ligand* SA-LCAO Orbitals for $\text{Cu}_8\text{S}_{12}^{4-}$

irreducible representation	orbital type	atomic centers											
		1	2	3	4	5	6	7	8	9	10	11	12
A_{1g}	Z	1	1	1	1	1	1	1	1	1	1	1	1
$A_{2g}[A_{2u}]$	X[Y]	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
	$X^u[Y^u]$	2	1	2	1	2	1	2	1	-1	1	-1	1
$E_g[E_u]$	$X^v[Y^v]$				1		1		1		1		-1
	Z ^u	2	-1	2	-1	2	-1	2	-1	-1	-1	-1	-1
	Z ^v		1		1		1		1	-1	-1	-1	-1
$T_{1g}[T_{1u}]$	$X^x[Y^x]$	1		-1		-1		1					
	$X^y[Y^y]$		1		-1		-1		1				
	$X^z[Y^z]$									1	1	1	1
	$Y^x[X^x]$	2	1		1		-1	-2	-1	-1	1	1	-1
T_{1u}	$Y^y[X^y]$		3		-1		-2	1	-3	-1	-3	1	3
	$Y^z[X^z]$			1	1		-1		1		1		-1
	Z ^x	2	1		1		-1	-2	-1	1	1	-1	-1
	Z ^y		3	2	-1	-2	1	-3	-3	1	3	-1	-1
$T_{2g}[T_{2u}]$	Z ^z			1	1		-1			-1			1
	$Y^\xi[X^\xi]$	2	-1		-1		1	-2	1	1	-1	-1	1
	$Y^\eta[X^\eta]$		3	-2	-1	2	1	-3	3	1	-3	-1	-1
T_{2u}	$Y^\zeta[X^\zeta]$			1	-1	-1	1			1			-1
	Z ^{xi}	1		-1		-1		1					
	Z ^{eta}		1		-1		-1		1				
	Z ^{zeta}									1	-1	1	-1
T_{2u}	Z ^{xi}	2	-1		-1		1	-2	1	-1	-1	1	1
	Z ^{eta}		3	-2	-1	2	1	-3	3	1	-3	-1	3
	Z ^{zeta}			1	-1	-1	1			1			
	Z ^{xi}										1	-1	

^a Coefficients for representations in parentheses can be obtained by multiplying the coefficients at center (2,4,5,7) ^{α,β} by -1. Orbital types related by a slash are differentiated by the signs +/- at the β centers. Brackets relate isomorphic representations. Watanabe's¹⁴ symbolism is used to differentiate SA-LCAO functions whose representations are doubly and triply degenerate. The superscripts α and β have the same meaning as in the text.

Table IV. Results^a of the Modified-SCCC Molecular Orbital Calculation on the Cluster $\text{Cu}_8\text{S}_{12}^{4-}$

		result no.		
		1	2	3
-VOIP +	4p(Cu)	-27.1	-17.4	-7.5
κV_e ,	4s(Cu)	-65.5	-56.6	-47.6
$\text{cm}^{-1} \times 10^3$	3d(Cu)	-98.4	-90.8	-83.5
	3p(S)	-73.7	-70.4	-68.0
	3s(S)	-144.6	-141.2	-138.9
κ		0.2	0.3	0.4
config and charge on Cu atoms	fd	9.996	10.009	10.008
	fs	0.527	0.451	0.385
	fp	0.029	0.019	0.016
	Q	+0.447	+0.521	+0.592
	fd	9.995	9.999	10.003
	fs	0.528	0.461	0.385
	fp	0.030	0.019	0.016
	Q	+0.447	+0.521	+0.595
	Mulliken overlap popula- tion			
	Cu-Cu	-0.063	-0.075	-0.081
	Cu-S	+0.168	+0.157	+0.144
$E_{3e_u} - E_{3a_{1g}}$,		6.0	12.5	18.8
$\text{cm}^{-1} \times 10^3$				

^a V_e is the point-charge electrostatic potential. There are 128 valence electrons under consideration. The valence shell configuration for copper is $3d^{10}4s^14p^0$. The highest occupied MO is $3e_u$, while the lowest unoccupied MO is $3a_{1g}$. See text.

$S_{3d\sigma}(\text{Cu}_1, \text{Cu}_2) = 0.005$, $S_{4s\sigma}(\text{Cu}_1, \text{Cu}_2) = 0.294$, and $S_{4p\sigma}(\text{Cu}_1, \text{Cu}_2) = 0.396$. Generally, the largest overlaps occurred between sulfur 3s and 3p orbitals and copper 4s and 4p orbitals, as would be expected.

No attempt was made to vary the Wolfsberg-Helmholz constant, k , and its value was set to 2.0 throughout the calculation. The departure from the standard SCCC method occurred with the introduction of an electrostatic potential of the Madelung type into the Hamiltonian matrix. It was calculated on the basis of the residual atomic charges after a Mulliken population analysis was performed.¹⁸ That is, the potential experienced by an electron is taken to be the sum of all the residual charges divided by the distance the charges are from the particular electron. Rather than simply adding such a potential to the Hamiltonian, we decided to introduce it fractionally, and proceeded to examine the consequences. The fraction introduced is denoted as κ , which ranges from 0.0 to 1.0.

Before the Hamiltonian matrix in the SA-LCAO basis was diagonalized, it was orthogonalized by the Lowdin¹⁹ procedure. After diagonalization it was deorthogonalized in order to preserve the original SA-LCAO basis.

Experimental Section

The method of Fackler and Coucouvanis²⁰ was used to prepare orange crystals of $(\text{Pr}_4\text{N})_4[\text{Cu}_8(\text{i-S}_2\text{CC}(\text{CN})_2)_6]$. Visible and ultraviolet spectra of ethanol solutions of the compound were taken on the Cary 14 spectrophotometer. Reflectance spectra were measured on the Beckman DK-2 instrument. For the electrochemical investigations a Hewlett-Packard Model 3300A function generator and a Model 7035B X-Y recorder, along with a potentiostat designed and built locally by Mr. Wayne Huhak, were used. For cyclic voltammetric measurements the working electrode was a revolving platinum wire (1 cm) and the reference was a saturated calomel electrode.

Results and Discussion

The results of three calculations where κ was varied are presented in Table IV. Figure 3 shows the effects of continuous variation of κ on the molecular orbitals in the vicinity of the d band. The introduction of a partial component of the point-charge electrostatic field (κ being the fractional factor) has the effect of increasing the electrostatic contribution to

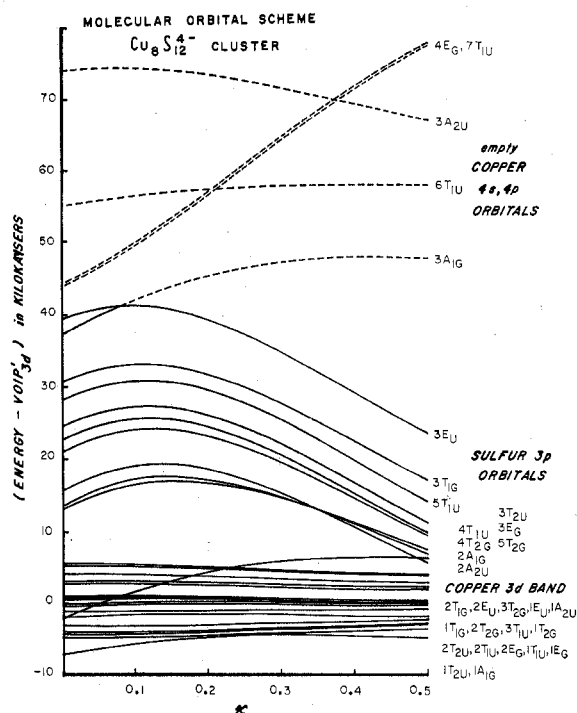


Figure 3. Molecular orbital level diagram for the $\text{Cu}_8\text{S}_{12}^{4-}$ model compound, calculated as a function of the partial introduction of the point-charge electrostatic potential.

the Cu-S, Cu...Cu, and S...S interactions and decreasing the covalency of such interactions. As κ increases, the residual charge on the copper atoms (Table IV) also increases. The gap between the d-orbital band and the highest filled MO's, which are dominantly sulfur in character, decreases (Figure 3). This is interpreted as a diminished interaction due to decreased covalency by the introduction of electrostatic effects. For $\kappa > 0.1$, a diamagnetic closed-shell configuration is obtained. The highest filled molecular orbital is $3e_u$ and it is composed 91% of ligand p_y SA-LCAO (Figure 4B). From Table III this orbital is composed of $p_y(\text{S}_2) + p_y(\text{S}_4) + p_y(\text{S}_6) + p_y(\text{S}_8) + p_y(\text{S}_9) - p_y(\text{S}_{10}) + p_y(\text{S}_{11}) - p_y(\text{S}_{12})$. In Figure 2 one notes that the sulfur p_y orbitals are all collinear with the edges of the cube in this function. The antisymmetric SA-LCAO is disposed above two faces of the cube (Cu_1 - Cu_4 - Cu_8 - Cu_5 and Cu_2 - Cu_3 - Cu_7 - Cu_6) and is antibonding as shown in Figure 4B. The next two filled MO's are similar in character (Figure 4C, D). The first empty MO is $3a_{1g}$, and it has the copper 4s and 4p atomic orbitals oriented for maximal positive overlap with the sulfur 3p atomic orbitals (Figure 4A). It is thus a strongly bonding molecular orbital. The first symmetry-allowed transition thus is predicted to be the $\text{S}(3p) \rightarrow \text{Cu}(4s, 4p)$ charge transfer. It should be intense. The absorption spectrum contains the first intense band at about $20 \times 10^3 \text{ cm}^{-1}$, which is the value we calculate for the $5t_{1u} \rightarrow 3a_{1g}$ transition if we choose $\kappa = 0.27$. Table V contains further details of possible transitions.

The net Cu-Cu overlap population from Mulliken-type analysis is predicted to be slightly negative and principally arises from 4s-4p and 3d-3d interactions. A very slight positive contribution comes from 4p-3d- and 4s-3d-type interactions. Most of the valence electron density rests in the copper-sulfur bonds.

The residual atomic charges (Table IV) suggest a transfer of electron density from the sulfur orbitals to the copper 4s orbitals.

The filled copper d orbitals do not interact very much in the bonding scheme. The d band in Figure 3 is principally of a localized nature.

Table V.^a Symmetry-Allowed^b Calculated Transitions (under $40 \times 10^3 \text{ cm}^{-1}$)

initial confign [eigenvector components ^c]	final confign [eigenvector components ^c]	calcd	$\Delta E, \text{cm}^{-1} \times 10^3$		
			reflectance	obsd bands, ($\epsilon, \text{M}^{-1} \text{cm}^{-1}$)	
				EtOH soln	acetone soln
$3e_u[p^L]$	$3a_{1g}[p^L, S, Z, Z^2]$	10.2 ^b	11.2 w	not obsd ^d	not obsd ^d
$3t_{1g}[p^L, (xz, yz), (x^2-y^2, xy)]$	$3a_{1g}[p^L, S, Z, Z^2]$	17.5 ^b	13.4 w	not obsd ^d	not obsd ^d
$5t_{1u}[p^L S]$	$3a_{1g}[p^L, S, Z, Z^2]$	19.6	19.6 vs	24.8 (2.3×10^4)	25.3
$3t_{1g}[p^L, (xz, yz), (x^2-y^2, xy)]$	$6t_{1u}[p^L, S, Z]$	28.3	26.0 vs	31.2 (1.8×10^4)	
$4t_{1u}[p^L, S, Z^2]$	$3a_{1g}[p^L, S, Z, Z^2]$	31.3			
$3t_{1g}[p^L, (xz, yz), (x^2-y^2, xy)]$	$7t_{1u}(x, y)$	32.6			
$5t_{1u}[p^L, S]$	$4e_g(x, y)$	34.5		35.1 sh (1.2×10^4)	
$3e_g[p^L]$	$6t_{1u}[p^L, S, Z]$	35.5			
$5t_{2g}[p^L, S]$	$6t_{1u}[p^L, S, Z]$	36.6		41.0 (1.1×10^4)	
$3t_{2u}[p^L]$	$4e_g(x, y)$	38.3			
$3e_g[p^L]$	$7t_{1u}(x, y)$	39.8		49.8 sh (1.7×10^4)	

^a This calculation is with $\kappa = 0.266$. ^b The calculated symmetry-forbidden transitions whose energies are less than that of the first allowed transition are also listed in this table. ^c The eigenvector components are listed in decreasing order. Those with values less than 0.1 are not included. Symbolism: $p^L = p_x$ or p_z SA-LCAO on sulfur; the rest refer to initial SA-LCAO components, $z = p_z, z^2 = d_{z^2}$, etc. ^d Not observed in saturated solutions.

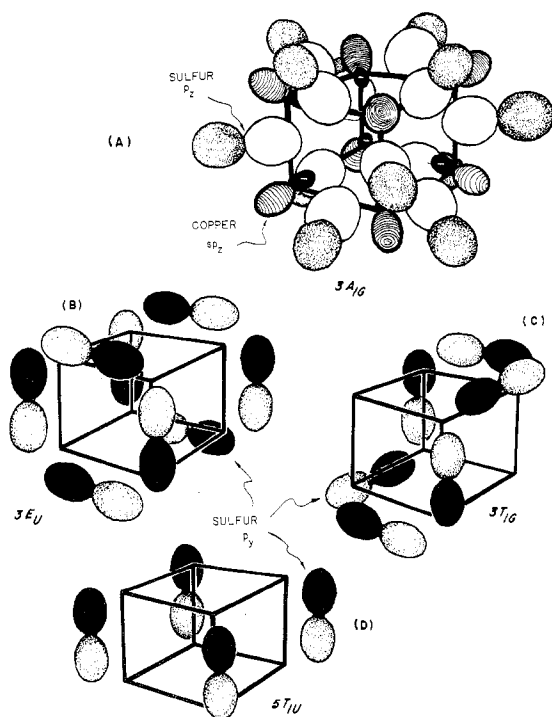


Figure 4. Molecular orbital diagrams. The first empty orbital (A) is of a_{1g} symmetry and is principally of bonding character: $\psi_{3a_{1g}} = -0.5[\psi_{Cu}^{SA-LCAO}(4s) + \psi_{Cu}^{SA-LCAO}(4p_z)] + 0.2\psi_{Cu}^{SA-LCAO}(3d_{z^2}) + 0.8\psi_S^{SA-LCAO}(3p_z)$. All the sulfur p-type orbitals point to the center of the cube while the copper spd-type orbitals point out from the center of the cube, thus favoring overlap. The three highest filled MO's, $3e_u$ (B), $3t_{1g}$ (C), and $5t_{1u}$ (D), are principally sulfur 4p in character and are antibonding: $\psi_{3e_u} = -0.1\psi_{Cu}^{SA-LCAO}(3d_{xy}, 3d_{yz}) + 1.0\psi_S^{SA-LCAO}(3p_x)$, $\psi_{3t_{1g}} = -0.2\psi_{Cu}^{SA-LCAO}(3d_{xz}, 3d_{yz}) + 0.1\psi_{Cu}^{SA-LCAO}(3d_{x^2-y^2}, 3d_{xy}) + 1.0\psi_S^{SA-LCAO}(3p_y)$, $\psi_{5t_{1u}} = -0.1\psi_{Cu}^{SA-LCAO}(4s) + 1.0\psi_S^{SA-LCAO}(3p_x)$.

Electrochemical Study. Cyclic voltammetric scans, at 100–150 mV/s, of the compound in dichloromethane (0.25 M supporting electrolyte, $n\text{-Bu}_4\text{NClO}_4$) showed only irreversible peaks. The positions and intensities depended highly on the scan range and the number of scans performed. For anodic scans in the range 0.0–1.5 V (vs. SCE), typically, two peaks occurred at 490 and 850 mV in the forward scan and at 380 and 9 mV in the reverse process. Similar irreversible behavior was observed for cathodic scan. If the anodic scans were allowed to continue for about 3 min, a dark yellow solid began to form on the working electrode. Under similar conditions cyclic voltammetric scans of $\text{K}(i\text{-S}_2\text{CC}(\text{CN})_2)_2$ so-

lutions also produced a dark yellow solid, suggesting that the ligand in both cases was being oxidized, possibly into a neutral disulfide compound.

Conclusion

The calculated results appear reasonable and give a semi-quantitative interpretation of the observed electronic spectrum for the $\text{Cu}_4\text{S}_{12}^{4-}$ cluster. Metal-metal bonding does not appear to be important in this study. The stability of the cluster appears to be related to the stereochemical dictates of the dianionic bidentate sulfur ligands. Virtually all of the bonding electron density rests in the Cu-S bonds. The observed spectrum is primarily that of $L \rightarrow M$ charge transfer.

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Registry No. $(\text{Pr}_4\text{N})_4[\text{Cu}_8(i\text{-S}_2\text{CC}(\text{CN})_2)_6]$, 66758-51-8.

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

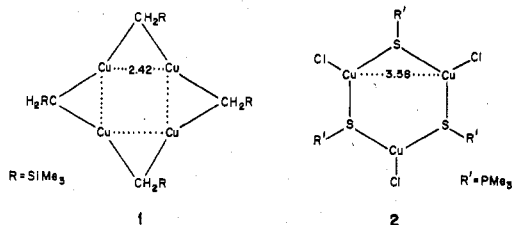
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The interaction between Cu(I) centers is studied by means of molecular orbital calculations on Cu_n^{n+} , $n = 2-4$, model dimers with phosphonium ylide bridges, and tetramers with alkyl bridges. In the absence of metal s and p functions the expected 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-workers⁶ 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

distance, Å	3d orbitals alone		3d, 4s, 4p orbitals	
	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