J. Am. Chem. Soc. **1988**, *110*, 7077-7083

Experimental and Theoretical Studies of the Copper(I) and Silver(I) Dinuclear *N*,*N'*-Di-*p*-tolylformamidinato Complexes

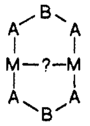
F. A. Cotton,* Xuejun Feng, Marek Matusz, and Rinaldo Poli

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. Received March 2, 1988

Abstract: This work addresses the question raised by many compounds in which short metal–metal distances might be taken to imply the existence of M–M bonds, but first-order, qualitative bonding theory is ambiguous, the answer depending on the degree of participation of outer (s,p) valence orbitals. The two compounds $M_2(form)_2$, where M = Cu^I or Ag^I and form represents p-$CH_3C_6H_4NCHNC_6H_4$-p-CH_3, have been prepared and characterized by X-ray crystallography and visible spectroscopy. Their electronic structures in the ground state have been investigated by SCF-Xα-SW molecular orbital calculations. Although the metal–metal distances are short (Cu–Cu = 2.497 (2) and Ag–Ag = 2.705 (1) Å), we conclude that there is little or no direct metal–metal bonding in these molecules. Valence shell s and p orbitals of the metals play a prominent role in metal–ligand bonding but do not provide a basis for metal–metal bonding. Crystallographic data are as follows: $Cu_2(C_{15}H_{15}N_2)_2$ (**1**), space group *Pccn*, a = 13.187(2) Å, b = 29.073 (5) Å, c = 7.140 (2) Å, V = 2737 (1) Å^3. $Ag_2(C_{15}H_{15}N_2)_2$ (**2**), space group *Pnaa*, a = 7.0397 (8) Å, b = 13.689 (2) Å, c = 29.039 (3) Å, V = 2799 (1) Å^3.

Metal–metal bonds of orders 1 to 4 are well established in hundreds of transition-metal compounds.[1] They are generally formulated in terms of d–d overlaps giving rise to σ, π, and δ bonding and antibonding orbitals, and so long as there are fewer electrons occupying the antibonding orbitals than there are in the bonding orbitals, no ambiguity arises as to the bond order. For M_2 units formed by elements toward the right side of the d block, the occupation of antibonding orbitals eventually becomes complete, as in compounds such as $Pd_2(RNCHNR)_4$ and $Ni_2(RNCHNR)_4$; in these and related cases, the usual formal, qualitative treatment of the M–M bonding would result in assigning a bond order of zero. However, the M–M distances in such compounds are usually short enough to raise the question of whether direct M–M bonding might not exist because the participation of s and/or p orbitals (e.g., 5s and 5p for Pd) could provide a surplus of occupied M–M bonding molecular orbitals. In a recent study[2a] of such compounds, we reached the conclusion that this is not the case, although there is some participation of outer s and p orbitals in metal–ligand bonds.

In the work reported here, we have extended this type of enquiry to the case of some Cu^I–Cu^I and Ag^I–Ag^I compounds, where the question of metal–metal bonding appears in a form that is similar in principle, though different in detail, to that outlined above. The question we are dealing with here concerns compounds of type I, where the bridging ligands ABA^- are each forming one electron pair donor bond (formally speaking) to each metal ion, and the metal ions are d^{10} ions such as Cu^+ and Ag^+. Since there is no possibility of d–d metal–metal bonding, and yet (as will be seen) the M–M distances are rather short, we are inquiring whether M–M bonds are formed by use of metal s or p orbitals.



I

Experimental Section

The compounds $Cu_2(form)_2$, **1**, and $Ag_2(form)_2$, **2**, where form represents the anion of (p-tol)NCHNH(p-tol), were prepared according to a literature procedure.[3] $Cu_2(form)_2$ was recrystallized from toluene to give pale yellow crystals. $Ag_2(form)_2$ was purified by dissolving it in CH_2Cl_2 and filtering through a short Celite column to obtain a clear solution. To this solution hexane was added. Evaporation afforded pure $Ag_2(form)_2$ as a colorless crystalline solid.

X-ray quality crystals of **1** were grown by vapor diffusion of ether into a dichloromethane solution of it. The acicular crystals were as much as a few millimeters long but very thin. A small piece of one of the long needles was broken and used for X-ray crystallography. Crystals of **2** were grown by slow evaporation, in the dark, of a dichloromethane–ether solution of $Ag_2(form)_2$. They were platelike in nature.

Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer 783 spectrometer. $Cu_2(form)_2$: 1610 w, 1580 s, 1550 s, 1510 s, 1470 s, 1380 m, 1345 s, 1310 w, 1230 s, 1180 w, 1118 w, 980 m, 938 w, 825 s, 775 w, 723 m, 640 w, 532 s, 475 w, 405 w. $Ag_2(form)_2$: 1610 w, 1580 s, 1550 s, 1510 s, 1460 m, 1360 s, 1310 w, 1238 s, 1185 m, 1125 w, 1045 w, 980 m, 940 w, 830 s, 770 w, 722 m, 660 w, 635 m, 545 w, 530 m, 509 w.

UV-vis spectra were recorded on CH_2Cl_2 solutions (HPLC grade, Aldrich) with a Cary 17D spectrometer (800–240 nm). $Cu_2(form)_2$: λ = 380 nm (sh), λ = 324 nm (ϵ = 34 300 M^{-1} cm^{-1}), λ = 258 nm (ϵ = 37 720 M^{-1} cm^{-1}). $Ag_2(form)_2$: λ = 325 nm (sh), λ = 307 nm (ϵ = 35 800 M^{-1} cm^{-1}), λ = 245 (sh).

X-ray Crystallography. Single crystals were glued on top of glass fibers. Preliminary investigation revealed the crystals to be orthorhombic. The Laue class and the axial dimensions were confirmed with oscillation photographs. From the systematic absences, the space group was uniquely determined to be *Pccn* (no. 56) for $Cu_2(form)_2$. For $Ag_2(form)_2$, a nonstandard setting of *Pccn* (*Pnaa*) was used. Data processing was routine to our laboratory. Lorentz, polarization, and absorption corrections[4] were applied. The structure of $Ag_2(form)_2$ was partially solved by the direct methods of the SHELX-86 package.[5] Remaining non-hydrogen atoms were found by alternating least-squares cycles and difference Fourier maps. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to phenyl rings at calculated distances, assigned a common thermal parameter, and included in the refinement. Methyl groups were refined as rigid bodies, with hydrogen atoms having an assigned common thermal parameter also included in the refinement. The hydrogen atom on the bridging carbon atom was treated like the phenyl hydrogen atom.

The refinement of the $Cu_2(form)_2$ structure was initiated with the metal atom position taken from the above structure. The refinement proceeded routinely. Because of the smaller number of data available, only Cu, N(1), N(2), and C(1) were refined anisotropically. The phenyl rings and methyl group were treated isotropically. Hydrogen atoms were added at calculated distances to the phenyl rings and to the methyl group, which were refined as rigid bodies. Two thermal parameters were as-

---

[1] Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; John Wiley and Sons: New York, 1982.

[2] (a) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144. (b) A previous study of Cu^I–Cu^I interactions in different compounds, using the extended Hückel method, concluded that mixing of metal s and p orbitals lead to "a slight attraction". Cf. Mehrotra, P. K.; Hoffman, R. *Inorg. Chem.* **1978**, *17*, 2187.

[3] Bradley, W.; Wright, I. *J. Chem. Soc.* **1956**, 640.

[4] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

[5] Sheldrick, G. M. SHELXS-86; Institut für Anorganische Chemie der Universitat: Göttingen, F.R.G., 1986.

0002-7863/88/1510-7077$01.50/0

Table I. Crystallographic Data for $Cu_2(form)_2$, **1**, and $Ag_2(form)_2$, **2**

formula	$Cu_2N_4C_{30}H_{30}$	$Ag_2N_4C_{30}H_{30}$
formula weight	573.68	662.34
space group	*Pccn*	*Pnaa* (nonstandard for *Pccn*)
systematic absences	$0kl$, $h0l$: $l \neq 2n$; $hk0$: $h + k \neq 2n$	$0kl$, $k + l \neq 2n$; $h0l$, $hk0$: $h \neq 2n$
a, Å	13.187 (2)	7.0397 (8)
b, Å	29.073 (5)	13.689 (2)
c, Å	7.140 (2)	29.039 (3)
α, deg	90.0	90.0
β, deg	90.0	90.0
γ, deg	90.0	90.0
V, Å^3	2737 (1)	2799 (1)
Z	4	4
d_{calcd}, g/cm^3	1.397	1.572
cryst size, mm	0.6 × 0.1 × 0.07	0.5 × 0.5 × 0.1
μ (Mo Kα), cm^{-1}	15.877	14.097
data collectn instrument	P3	Enraf-Nonius CAD-4
radiatn (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
orientatn reflcns, no.; range (2θ)	25, $12 < 2\theta < 30$	25, $18 < 2\theta < 28$
temp, °C	22	20
scan method	ω	ω
data col. range, 2θ, deg	4, 45	4, 50
no. unique data, total	1360	2460
with $F_o^2 > 3\sigma(F_o^2)$	849	1430
no. of params refined	101	163
trans. factors, max., min.	0.9904, 0.8810	0.9964, 0.7776
R^a	0.0516	0.0449
R_w^b	0.0617	0.0609
quality-of-fit indicator[c]	1.163	1.501
largest shift/esd, final cycle	0.08	0.30
largest peak, e/Å^3	0.41	1.639[d]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$. [d] Second largest peak was 0.944 e/Å^3.

signed to hydrogen atoms (one for phenyl hydrogens, one for methyl hydrogens) and included in the refinement. The hydrogen on the bridging carbon atom was treated as an aromatic hydrogen. Both structures were refined with SHELX-76.[6] Relevant crystallographic and procedural data are presented in Table I.

Computational Procedures. A model system, $M_2(HNCHNH)_2$, was used for each calculation instead of the real $M_2(form)_2$ molecule. For both model molecules the calculations were carried out by the SCF-Xα-SW method.[7] The atomic coordinates used in the calculations were derived from the averaged bond distances and bond angles based on the crystal structure data of the real compounds. However, the metal–metal distances used were exactly those in the real compounds, and the N–H and C–H bond distances were chosen as 1.06 and 1.08 Å, respectively. For both molecules a strict D_{2h} symmetry was assumed, and all atoms in the molecules were put in the XZ plane with the two metal atoms lying on the Z axis.

The initial molecular potentials for the SCF procedure were constructed from Cu(+1.0) or Ag(+1.0), N(−0.4), and C(−0.2) Herman–Skillman atomic potentials and H 1s radical functions. The α values used for each atom were taken from the compilation of Schwarz.[8] The partial wave basis consisted of s-, p-, and d-type spherical harmonics on the Cu and Ag atoms, s and p on the N and C atoms, and s only on the H atoms. For the outer sphere $l = 4$ was used. The SCF calculations for both molecules were considered to be converged when the shift in the molecular potential was less than 0.001 Ryd.

Under the D_{2h} symmetry of the molecule both d_{z^2} and $d_{x^2-y^2}$ orbitals as well as the s orbitals of the metals span the a_g and b_{1u} representations. To make clear the roles of the individual d orbitals in bonding, LCAO representations of the converged numerical Xα-SW molecular orbitals were generated for all such orbitals by projecting onto a Slater-type atomic orbital basis set.[9] The basis set includes a double-ζ function for the d orbital and single-ζ functions for the s and p orbitals of the metal.

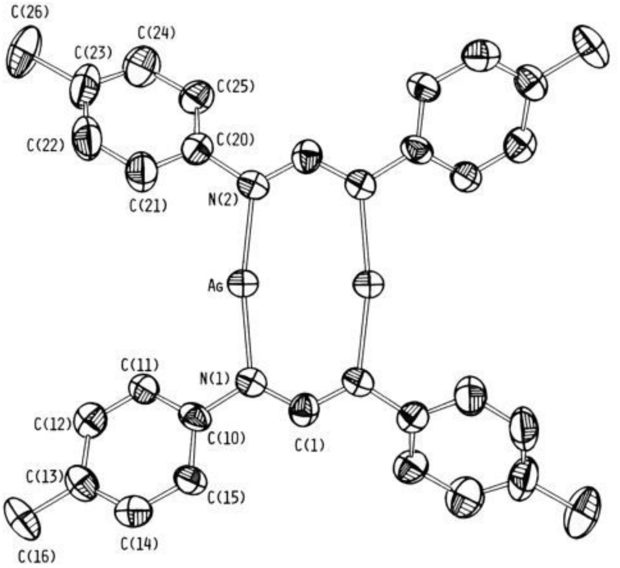


Figure 1. ORTEP plot of $Ag_2(form)_2$ at 50% probability level. Hydrogen atoms have been omitted for clarity.

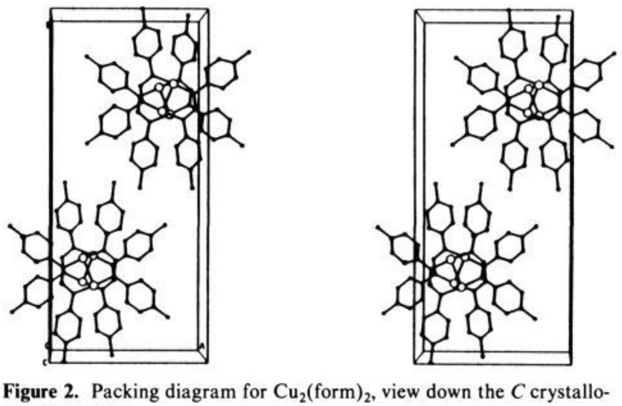


Figure 2. Packing diagram for $Cu_2(form)_2$, view down the *C* crystallographic axis.

Results

The $M_2(form)_2$ compounds are easily prepared and stable in air. They form isotypic crystals, but since the structures were determined by different persons, the lattices were indexed differently, causing one of them to be handled in space group *Pccn* and the other in a nonstandard setting of the same space group, viz., *Pnaa*. The two compounds are strictly isotypic, and the intermolecular contacts and packing in the two cases are qualitatively the same. No unusual nonbonded contacts occur. The two sets of coordinates are related by the trivial relationship $[x, y, z]_{Ag} = [z, x + {}^1/_2, y + {}^1/_2]_{Cu}$. The positional parameters and isotropic equivalent thermal displacement parameters for **1** and **2** are listed in Table II. In each case a crystallographic 2-fold axis passes through the midpoint of the molecule. The entire central group, $M_2(NCN)_2$, is essentially planar, and the planes of the tolyl groups are only slightly tilted out of this plane. These features are all clearly displayed in Figure 1, which shows the $Ag_2(form)_2$ molecule. The $Cu_2(form)_2$ molecule is very similar, differing mainly in the considerably shorter metal–metal distance. The atom numbering follows the same pattern in both cases. Tables III and IV provide the principal bond lengths and bond angles for **1** and **2**, respectively. The crystal packing in these

---

(6) Sheldrick, G. M. SHELX-76; University of Cambridge: Cambridge, England 1976.

(7) (a) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1974; Vol. IV. (b) Johnson, K. H. *Adv. Quantum Chem.* **1973**, *7*, 143.

(8) Schwartz, K. *Phys. Rev. B* **1972**, *5*, 2466; *Theor. Chim. Acta* **1974**, *34*, 225.

(9) Bursten, B. E.; Fenske, R. F. *J. Chem. Phys.* **1977**, *67*, 3138.

Table II. Positional Parameters and Their Estimated Standard Deviations for Cu$_2$(form)$_2$ and for Ag$_2$(form)$_2$

atom	*x*	*y*	*x*	*B* (Å^2)
		Cu$_2$(form)$_2$		
Cu	0.2144	0.2101	0.1276	3
N(1)	0.0856	0.2384	0.1320	2
N(2)	0.3465	0.1877	0.1296	3
C(1)	0.0736	0.2820	0.1320	2
C(10)	−0.0026	0.2093	0.1250	2[a]
C(11)	0.0021	0.1662	0.2073	2[a]
C(12)	−0.0813	0.1378	0.2085	3[a]
C(13)	−0.1713	0.1506	0.1272	3[a]
C(14)	−0.1746	0.1929	0.0376	3[a]
C(15)	−0.0928	0.2226	0.0353	3[a]
C(16)	−0.2632	0.1188	0.1297	4[a]
C(20)	0.3679	0.1397	0.1488	2[a]
C(21)	0.4495	0.1227	0.2480	3[a]
C(22)	0.4629	0.0752	0.2675	4[a]
C(23)	0.3965	0.0453	0.1834	4[a]
C(24)	0.3165	0.0618	0.0847	4[a]
C(25)	0.3034	0.1097	0.0667	3[a]
C(26)	0.4109	−0.0063	0.2087	6[a]
		Ag$_2$(form)$_2$		
Ag	0.1143 (1)	0.71271 (4)	0.70687 (2)	4.69 (2)
N1	0.1201 (8)	0.5756 (4)	0.7404 (2)	3.6 (1)
N2	0.1209 (8)	0.6407 (4)	0.8136 (2)	3.8 (1)
C1	0.125 (1)	0.5674 (5)	0.7846 (2)	3.3 (1)
C10	0.117 (1)	0.4915 (5)	0.7118 (2)	3.4 (1)
C11	0.201 (1)	0.4962 (5)	0.6687 (2)	3.5 (1)
C12	0.203 (1)	0.4164 (5)	0.6401 (2)	3.8 (2)
C13	0.122 (1)	0.3270 (5)	0.6532 (2)	3.9 (2)
C14	0.035 (1)	0.3255 (5)	0.6963 (2)	4.0 (2)
C15	0.031 (1)	0.4037 (5)	0.7251 (2)	3.7 (2)
C16	0.129 (1)	0.2385 (6)	0.6222 (3)	5.6 (2)
C20	0.1424 (9)	0.8770 (5)	0.6375 (2)	3.3 (1)
C21	0.058 (1)	0.8134 (6)	0.6070 (3)	4.9 (2)
C22	0.081 (1)	0.8274 (7)	0.5604 (3)	5.9 (2)
C23	0.185 (1)	0.9027 (7)	0.5424 (3)	5.8 (2)
C24	0.265 (1)	0.9656 (6)	0.5735 (3)	5.6 (2)
C25	0.247 (1)	0.9552 (5)	0.6204 (2)	4.2 (2)
C26	0.210 (2)	0.9122 (9)	0.4903 (3)	8.8 (3)

[a] Atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(^4/_3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Selected Bond Distances in Å and Bond Angles in deg for Cu$_2$(form)$_2$[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
Cu	Cu	2.497 (2)	N(1)	C(10)	1.438 (11)
Cu	N(1)	1.886 (7)	N(2)	C(1)	1.368 (11)
Cu	N(2)	1.859 (7)	N(2)	C(20)	1.426 (11)
N(1)	C(1)	1.276 (11)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cu	Cu	N(1)	86.2 (2)	C(1)	N(1)	C(10)	118.9 (8)
Cu	Cu	N(2)	88.5 (2)	Cu	N(2)	C(1)	119.6 (6)
N(1)	Cu	N(2)	174.5 (3)	Cu	N(2)	C(20)	121.9 (6)
Cu	N(1)	C(1)	122.8 (6)	C(1)	N(2)	C(20)	118.3 (7)
Cu	N(1)	C(10)	118.2 (5)	N(1)	C(1)	N(2)	122.9 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Selected Bond Distances (Å) and Angles (deg) for Ag$_2$(form)$_2$[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
Ag	Ag′	2.705 (1)	N1	C10	1.420 (8)
Ag	N1	2.116 (5)	N2	C1	1.310 (8)
Ag	N2	2.094 (5)	N2	C20	1.448 (8)
N1	C1	1.289 (7)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ag′	Ag	N1	84.7 (1)	C1	N1	C10	120.9 (5)
Ag′	Ag	N2	84.4 (2)	Ag	N2	C1	123.5 (4)
N1	Ag	N2	168.8 (2)	Ag	N2	C20	116.2 (4)
Ag	N1	C1	122.5 (4)	C1	N2	C20	120.0 (5)
Ag	N1	C10	116.6 (4)	N1	C1	N2	124.9 (6)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

compounds deserves some comment. It is qualitatively the same in both cases, since the compounds are isotypic. Figure 2 shows a stereoview of the unit cell of the copper compound. There are infinite sheets of molecules in planes perpendicular to the crystallographic *c* axis. Alternatively, one may describe the packing as consisting of stacks of molecules parallel to the *c* axis. There is no indication of any unusual intermolecular interactions. Within the sheets, the contacts are normal van der Waals contacts between tolyl groups, while the sheets are separated by 3.570 Å in the Cu case and 3.520 Å in the Ag case, these being precisely *c*/2 and *a*/2, respectively. The criss-cross pattern of M$_2$ units in the stacks seems clearly to be caused by the packing of the slightly tilted tolyl groups; the angles between the projected M–M axes of adjacent layers is almost exactly 45°. The shortest intermolecular (i.e., interlayer) M–M contacts are as follows: Cu–Cu, 3.687, 4.250 Å and Ag–Ag, 3.665, 4.320 Å.

In both compounds the metal–metal distances are unusually (though not uniquely, vide infra) short. We shall make comparisons with other compounds later. It may be noted here, however, that the Ag···Ag distance, though longer in an absolute sense then the Cu···Cu distance (by 0.208 Å) is shorter in proportion to the sizes of the atoms. Pauling gives R_1 radii for Cu and Ag of 1.176 and 1.342 Å, respectively, which means that Ag···Ag and Cu···Cu distances might have been expected to differ by 0.33 Å purely on the basis of the inherent atomic size difference. Indeed, for the silver compound, the actual Ag···Ag separation, 2.71 Å is but slightly greater than twice the single bond radius (viz., 2.68 Å) for that metal.

Because of these short interatomic distances, the question naturally arises whether there is metal–metal bonding. Since Cu$^{\rm I}$ and Ag$^{\rm I}$ are d^{10} systems, this could only be the case if significant s–s and or p$_z$–p$_z$ overlap comes into play. Molecular orbital calculations were carried out for both compounds to see what light they might throw on this point.

Bonding in Cu$_2$(HNCHNH)$_2$. The results of the molecular orbital calculation are summarized in Table V. In addition to the MOs described in Table V, there are ten more at lower energy, all of which are completely ligand-based and hence of no direct interest here. A search for the lowest lying virtual orbitals was made, employing the converged molecular potential, up to an energy of −0.5 eV. Four such orbitals were found, viz., 3b$_{2u}$, 7a$_g$, 6b$_{1u}$, and 8a$_g$, all of which are diffuse with most of their amplitude located in the intersphere and outersphere regions. The LUMO is the 3b$_{2u}$ orbital, and it lies 2.64 eV above the HOMO, 2a$_u$.

Before turning to detailed discussion of the results in Table V, it will be helpful to employ simple group-theoretical analysis to determine the representations to which molecular orbitals of different functional types must belong. We shall use the subscripts i and o to designate orbitals whose amplitude is (at least mainly, but in some cases rigorously) *in* the molecular plane (i) or *out* of it (o). The results of this analysis are presented in Table VI.

A single, well-defined bonding or antibonding function for each of the 18 MOs listed in Table V is fairly easy to assign for Cu$_2$(HNNNH)$_2$. Let us first deal with Cu–N bonding. For the σ bonds it is the 3b$_{1u}$, 4a$_g$, 3b$_{2g}$, and 4b$_{3u}$ orbitals that clearly have this as their main role. Contour diagrams for these four orbitals are presented in Figure 3. The Cu–N σ bonding is fairly polar, with the electron density being, on average, twice as concentrated on the N atoms as on the Cu atoms. It is of particular importance to note that for the 3b$_{2g}$ and 4b$_{3u}$ orbitals the metal contributions consist of 95% and 85%, respectively, metal 4p$_x$ orbitals. The other two Cu–L σ orbitals have smaller but still significant (20–30%) contributions from the 4s orbital.

Metal–ligand π bonding is not strong. All four of the orbitals that can most reasonably be assigned that role have low or fairly

Table V. Upper Valence Molecular Orbitals for $Cu_2(HNCHNH)_2$

		% contribution					Cu angular contribution			
D_{2h} level	energy, eV	2Cu	4N	2C	4H	2H				
$2a_u$	-4.7013	38	62	0	0	0			100%d_{xy}	
$5b_{1u}$	-5.3121	93	6	0	1	0	17%s	3%p	33%$d_{x^2-y^2}$	47%d_{z^2}
$2b_{3g}$	-5.6983	6	94	0	0	0				
$2b_{1g}$	-6.3158	87	5	8	0	0			100%d_{xy}	
$4b_{2g}$	-6.3579	98	1	0	1	0			100%d_{xz}	
$6a_g$	-6.4788	98	2	0	0	0	22%s		76%$d_{x^2-y^2}$	2%d_{z^2}
$1b_{3g}$	-6.4904	99	1	0	0	0			100%d_{yz}	
$4b_{1u}$	-6.5260	100	0	0	0	0	1%s		49%$d_{x^2-y^2}$	50%d_{z^2}
$5b_{3u}$	-6.7145	97	2	0	1	0			100%d_{xz}	
$2b_{2u}$	-6.9431	99	1	0	0	0			100%d_{yz}	
$5a_g$	-7.2891	100	0	0	0	0	11%s	1%p	88%d_{z^2}	
$1a_u$	-7.3726	77	23	0	0	0			100%d_{xy}	
$4b_{3u}$	-8.4762	20	55	9	6	10		85%p	15%d_{xz}	
$1b_{2u}$	-8.8044	3	64	33	0	0				
$1b_{1g}$	-9.0894	21	54	25	0	0			100%d_{xy}	
$3b_{2g}$	-9.5429	18	69	2	11	0		95%p	5%d_{xz}	
$4a_g$	-10.1914	34	37	10	6	13	32%s		55%$d_{x^2-y^2}$	12%d_{z^2}
$3b_{1u}$	-10.2272	33	52	0	15	0	20%s		59%$d_{x^2-y^2}$	21%d_{z^2}

Table VI. Symmetry Classification of Molecular Orbitals in $M_2(HNNNH)_2$ Molecules of D_{2h} Symmetry[a]

M-M Bonding and Antibonding			
σ(MM)	α_g	σ^*(MM)	b_{1u}
π_0(MM)	b_{2u}	π_0^*(MM)	b_{3g}
π_i(MM)	b_{3u}	π_i^*(MM)	b_{2g}
δ(MM)	b_{1g}	δ^*(MM)	a_u
M-N Bonding Orbitals			
σ(MN)	a_g, b_{2g}, b_{1u}, b_{3u}		
π(MN)	b_{1g}, b_{3g}, a_u, b_{2u}		

[a] Axis system: Z coincides with M-M and X is in the molecular plane.

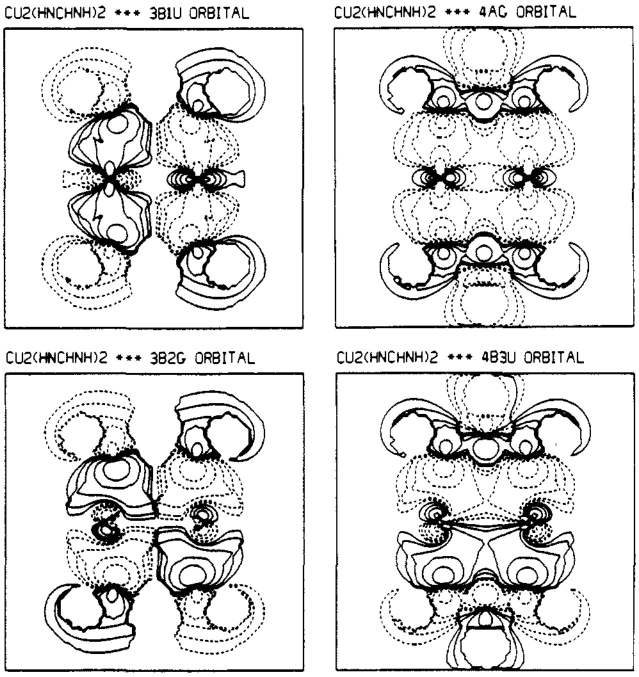


Figure 3. Contour diagrams of the four molecular orbitals mainly concerned with Cu-N σ bonding in $Cu_2(HNCHNH)_2$: $3b_{1u}$, $4a_g$, $3b_{2g}$, and $4b_{3u}$.

low metal contributions, viz., $1b_{1g}$ (21%), $1b_{2u}$ (3%), $2b_{3g}$ (6%), and $2a_u$ (38%).

Turning now to the various components of Cu-Cu interaction, we can begin with the π and π^* MOs. There are two types of each: the inplane (π_i, π_i^*) and the out-of-plane (π_o, π_o^*). Assignment of the MOs in Table V to these roles is not difficult. We have for π_o and π_i the almost equienergic $2b_{2u}$ and $5b_{3u}$ orbitals, which consist almost totally (99% and 97%, respectively) of the appropriate d orbitals, namely, d_{yz} and d_{xz}, respectively. Their antibonding counterparts are $1b_{3g}$ (π_o^*, 99% d_{yz}) and $4b_{2g}$ (π_i^*, 98% d_{xz}). There is clearly no net π bonding. These four MOs are physically equivalent to having $d_{xz}{}^2d_{yz}{}^2$ configurations on each of the metal atoms.

The Cu-Cu δ interactions are also easily identifiable. The $2b_{1g}$ orbital which has 87% d_{xy} character is the δ orbital and the $1a_u$ orbital (77% d_{xy} character) is the δ^* orbital. Actually the $1a_u$ and $2a_u$ orbitals interact and mix δ^* and Cu-N π character to some extent, and it is for this reason that the δ^* ($1a_u$) orbital lies below (by ca. 1 eV) the δ ($2b_{1g}$) orbital. However, it is clear that no net δ bonding occurs; even a slight imbalance of δ and δ^* effects would be of little importance since the δ overlap is inherently very small.

We have now accounted for most aspects of the copper-ligand and Cu-Cu bonding (showing that the former is essentially polar σ bonding benefitting from $4p_x$ and 4s orbital participation) and that the latter is nonexistent as far as π and δ components are concerned. It now remains only to consider Cu-Cu σ and σ^* interactions. These are provided by the $5a_g$ and $6a_g$ σ orbitals and the $4b_{1u}$ and $5b_{1u}$ σ^* orbitals.

The $5a_g$ orbital is formed mainly by a d_{z^2}-d_{z^2} overlap, modified slightly by a small admixture of 4s orbital; it is shown in Figure 4. It provides a good Cu-Cu σ bonding interaction. The $6a_g$ orbital arises mainly by $d_{x^2-y^2}$-$d_{x^2-y^2}$ overlap supplemented by some s-s overlap. The former provides very little bonding since it is effectively a δ type interaction. This orbital is shown from two points of view in Figure 4. It is clear that it is practically nonbonding in the Cu-Cu sense. Both the $4b_{1u}$ and $5b_{1u}$ orbitals are Cu-Cu σ antibonding. Each of these can best be regarded as involving the overlap of d_{z^2}-$d_{x^2-y^2}$ hybrids so that $4b_{1u}$ consists of a $d_{z^2-y^2}$-$d_{z^2-y^2}$ combination, while the $5b_{1u}$ is formed from a $d_{z^2-x^2}$-$d_{z^2-x^2}$ combination supplemented by a small 4s-4s contribution. These two orbitals are shown as contour diagrams in Figure 5. It is clear that the net amount of Cu-Cu σ bonding appears to be about zero.

In summary, for $Cu_2(HNCHNH)_2$ our Xα calculation leads to the conclusion that the $4p_x$ orbitals contribute to Cu-N σ bonding and the 4s orbitals make small contributions to both σ and σ^* Cu-Cu interactions. The other potential contributors to Cu-Cu bonding, namely p_z (to σ) and p_y (to π) have no significant involvement. Thus, the net result of bringing two d^{10} Cu^I atoms together is shown to be *no net Cu-Cu bond formation.*

Bonding in $Ag_2(HNCHNH)_2$. While the overall picture here is grossly similar to that for the copper compound, there are many differences in detail. Again, we can employ the classification in Table VI to structure our discussion of the results summarized in Table VII.

We shall again begin by examining the metal-ligand bonding. There is less 5s and 5p participation than in the Cu case. The

Table VII. Upper Valence Molecular Orbitals for $Ag_2(HNCHNH)_2$

D_{2h} level	energy, eV	% contribution					Ag angular contribution			
		2Ag	4N	2C	4H	2H				
$2a_u$	−5.3748	11	89	0	0	0			100%d_{xy}	
$2b_{3g}$	−5.8128	2	98	0	0	0				
$5b_{1u}$	−6.6484	72	24	1	0	3	25%s	2%p	36%$d_{x^2-y^2}$	37%d_{z^2}
$6a_g$	−7.6937	71	20	3	2	4	54%s	1%p	44%$d_{x^2-y^2}$	1%d_{z^2}
$5b_{3u}$	−7.8116	23	55	6	7	9		57%p	43%d_{xz}	
$2b_{1g}$	−8.3299	44	34	22	0	0			100%d_{xy}	
$4b_{2g}$	−8.6279	61	32	0	7	0		11%p	89%d_{xz}	
$2b_{2u}$	−9.0329	8	61	31	0	0				
$4b_{1u}$	−9.1059	100	0	0	0	0			36%$d_{x^2-y^2}$	64%d_{z^2}
$1b_{3g}$	−9.1434	100	0	0	0	0			100%d_{yz}	
$3b_{2g}$	−9.5585	56	39	2	3	0		10%p	90%d_{xz}	
$1a_u$	−9.6293	95	5	0	0	0			100%d_{xy}	
$4b_{3u}$	−9.7900	90	5	3	0	2			100%d_{xz}	
$1b_{2u}$	−9.8426	96	3	1	0	0			100%d_{yz}	
$5a_g$	−10.0625	96	2	1	0	1	4%s		26%$d_{x^2-y^2}$	70%d_{z^2}
$1b_{1g}$	−10.1535	71	21	8	0	0			100%d_{xy}	
$4a_g$	−10.8235	63	18	6	4	9	1%s		56%$d_{x^2-y^2}$	43%d_{z^2}
$3b_{1u}$	−11.5379	48	39	0	13	0	4%s		75%$d_{x^2-y^2}$	21%d_{z^2}

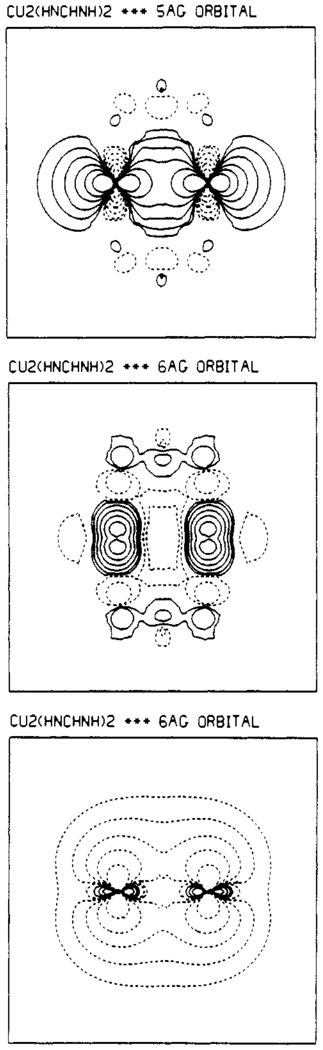


Figure 4. Contour diagrams of the principal Cu–Cu σ orbitals, $5a_g$ and $6a_g$ (the latter shown projected both in the molecular plane and perpendicular to the molecular plane).

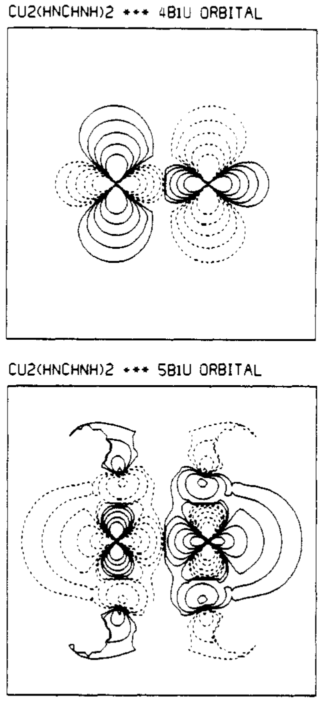


Figure 5. Contour diagrams of the principal Cu–Cu σ^* orbitals, $4b_{1u}$ and $5b_{1u}$.

$3b_{1u}$ orbital is a major player in Ag–N σ bonding and is fairly similar to the $3b_{1u}$ orbital in the Cu case, but it has a nearly negligible 5s contribution. The $4a_g$ orbital is again not only involved in M–N σ bonding but also contributes to Ag–Ag bonding to a far greater extent than was the case with the Cu compound. The b_{2g} contribution to Ag–N σ bonding is shared between the $3b_{2g}$ and $4b_{2g}$ orbitals, instead of being confined mainly to $3b_{2g}$ orbital as in the Cu case; also the 5p contribution is much smaller. Finally, it is the $5b_{3u}$ orbital which makes the b_{3u} contribution to Ag–N bonding, whereas in the Cu case it was the $4b_{3u}$ orbital. The $5b_{3u}$ orbital of $Ag_2(HNCHNH)_2$ has the largest 5p contribution (57%) of any MO, but it is still smaller than that (85%) of the $4b_{3u}$ Cu–N σ orbital. Figure 6 shows contour diagrams for the $3b_{1u}$, $4a_g$, and $5b_{3u}$ MOs of $Ag_2(HNCHNH)_2$.

Silver–nitrogen π bonding resembles Cu–N π bonding in being weak. There are some differences, however. For the Ag case it is the $2b_{1g}$, $2b_{2u}$, $2a_u$, and $2b_{3g}$ orbitals that can be primarily assigned to this, in contrast to $1b_{1g}$, $1b_{2u}$, $2a_u$, and $2b_{3g}$ in the Cu case. Again, the metal contributions are all small (percentages, respectively, of 44, 8, 11, and 2) with but one exception.

Next we look at the Ag–Ag π and π^* orbitals. Here the situation again closely resembles that in the Cu compound, although some of the orbitals have different relative energies. We have two nearly degenerate π orbitals, $1b_{2u}$ (96% d_{yz}) and $4b_{3u}$ (90% d_{xz}); which provide π_o and π_i bonding, respectively. We then have a corresponding filled orbital, $1b_{3g}$ (π^*_o, 100% d_{yz}), but the π_i^* antibonding function is split between the $3b_{2g}$ and $4b_{2g}$ orbitals (which also split their contributions to the role of Ag–N σ

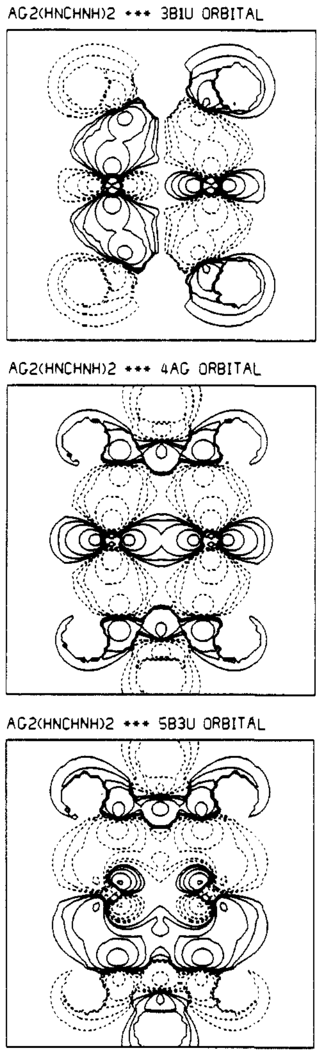


Figure 6. Contour diagrams of three of the orbitals that are the main contributors to Ag–N σ bonding in $Ag_2(HNCHNH)_2$: $3b_{1u}$, $4a_g$, and $5b_{3u}$.

bonding). However, despite the differences in detail, the final conclusion is still the same as in the Cu case, namely, that there is no net π bonding.

Turning now to the Ag–Ag δ interactions, we find a situation slightly different from that in the Cu compound but just as unambiguously indicative of no net δ bonding. In this case the pertinent orbitals are the $1b_{1g}$ (70% d_{xy}) and $1a_u$ (95% d_{xy}). Here we have the δ and δ^* orbitals in the conventional order but again off-setting each other.

Once again, we have dealt with the metal–ligand bonds (σ and π) and shown that metal–metal interactions of the π and δ types are essentially nonbonding. It remains, therefore, only to deal with those MOs that will be involved in Ag–Ag σ and σ^* interactions. Some of the pertinent orbitals that we shall now discuss are shown in Figure 7. As already mentioned, the $4a_g$ orbital makes a small contribution to Ag–Ag σ bonding, but the $5a_g$ orbital, consisting almost entirely of metal d_{z^2} orbitals, is a major source of Ag–Ag σ bonding. The $6a_g$ orbital also makes a major contribution and is about one-half metal 5s in parentage. Thus, there is a substantial amount of Ag–Ag σ bonding. However, offsetting this are three σ^* orbitals of b_{1u} symmetry. The $3b_{1u}$ orbital (already noted as a major factor in Ag–N σ bonding) has a modest Ag–Ag σ^* role, tending to oppose the modest bonding effect of the $4a_g$ orbital. The $4b_{1u}$ orbital is strongly Ag–Ag σ^* in character and should effectively cancel the bonding effect of the $5a_g$ orbital. Finally, the $5b_{1u}$ orbital, which consists of a mix of d_{z^2} and $d_{x^2-y^2}$ parentage as well as appreciable 5s (25%) character, should approximately counteract the bonding effect of the $6a_g$ orbital. Thus, as in the Cu case, we again conclude that no important amount of net Ag–Ag bonding emerges.

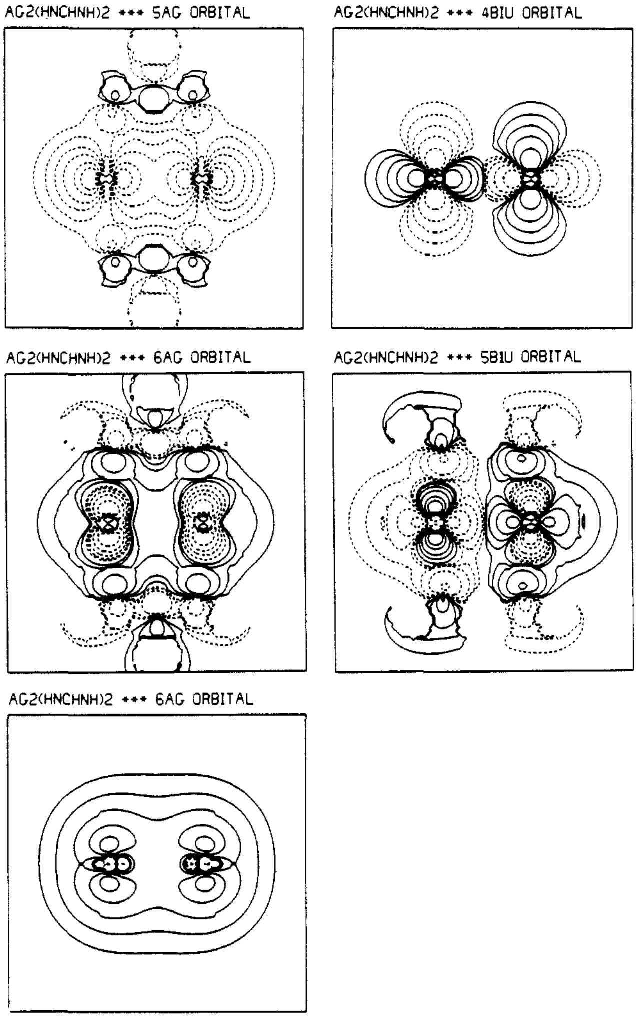


Figure 7. Contour diagrams of the four orbitals principally concerned with Ag–Ag σ and σ^* interactions: $5a_g$, $6a_g$ (two views), $4b_{1u}$, and $5b_{1u}$.

Discussion

The $M_2(form)_2$ and $M_2(HNCHNH)_2$ Compounds. The crystal structures show discrete, noninteracting $M_2(form)_2$ molecules, which are nearly planar and which we therefore believe are faithfully modeled by the rigorously planar (D_{2h}) $M_2(HNCHNH)_2$ species. The results of the MO calculations on both of the model compounds have been presented and discussed in detail. One point of comparison between the MO results for the model compounds and the properties of the real molecules concerns the UV–vis spectra. The observed bands have been listed in the Experimental Section, and the spectrum of the copper compound is shown in Figure 8. The spectrum of Hform itself shows absorptions at 320 and 285 nm, and both of the complexes display peaks at or near these wavelengths. Since the MO calculations showed in each case a large HOMO–LUMO gap, 2.5–3 eV, it is not inconsistent that no absorption bands are seen below 3.2 eV for $Cu_2(form)_2$ and 4.0 eV for $Ag_2(form)_2$.

Comparison of the Cu–Cu Distance in $Cu_2(form)_2$ with Others. The metal–metal contact in the $Cu_2(form)_2$ compound is among the shortest known, although there is at least one which is shorter. The literature is quite large, and rather than make any attempt to cover it completely we shall deal only with a few compounds that seem especially pertinent.

Perhaps the closest analogue to $Cu_2(form)_2$ is $Cu_2(PhNNNPh)_2$, which also has, effectively, D_{2h} symmetry. Its crystal structure was determined many years ago[10] and is relatively inaccurate by present standards. The Cu–Cu distance is reported as 2.45 ± 0.02

---

(10) Brown, I. D.; Dunitz, J. D. *Acta Crystallogr.* **1961**, *14*, 480.

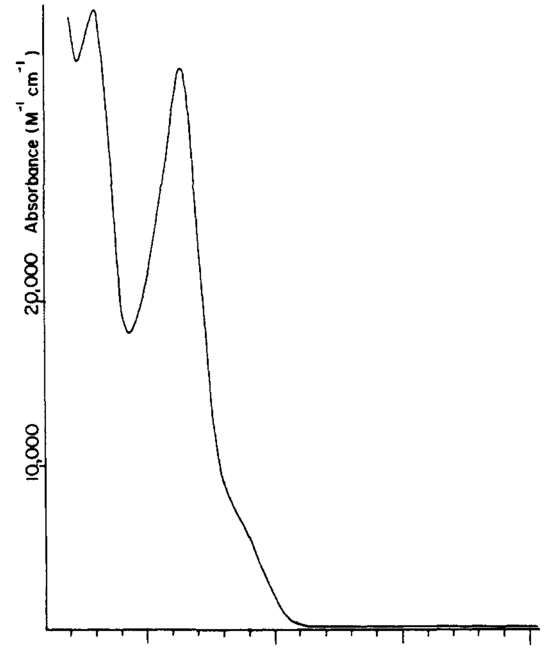


Figure 8. The electronic absorption spectrum of $Cu_2(form)_2$ in CH_2Cl_2 solution.

Å. Treating 0.02 Å as an esd, this value is less than 3σ from the one, 2.497 (2) Å, that we find in $Cu_2(form)_2$. Very likely, however, it truly is at least a little bit shorter. It is interesting that the copper(I) 1,3-dimethyltriazinato compound, where steric hindrance is much less, is a tetramer, $[Cu(MeNNNMe)]_4$, with Cu–Cu separations in the range of 2.64–2.68 Å for adjacent pairs.[11]

The structures of several copper(I) carboxylates, which are easily synthesized[12] have been determined. Copper(I) benzoate forms tetramers in which the closest Cu–Cu contacts are 2.719 (4) Å.[13] Crystalline copper(I) acetate forms dimers similar to $Cu_2(form)_2$, but these link up by oxygen-atom bridging to give infinite chains in which the closest Cu–Cu distances are 2.544 (4) Å.[14] However, according to an electron diffraction study of gaseous copper(I) acetate,[15] where separated $Cu_2(O_2CCH_3)_2$ molecules persist, the Cu–Cu distance drops to 2.491 (3) Å, which is not significantly different from what we have found in $Cu_2(form)_2$.

The compound $Cu_2[o\text{-}(Me_3Si)_2CC_5H_4N]_2$ contains essentially planar $M_2(NCC)_2$ head-to-tail units[16] in which the Cu–Cu distance is 2.412 (1) Å. This is unambiguously shorter than that in $Cu_2(form)_2$. However, we would venture the guess that there is still no clearly defined Cu–Cu bonding, because of the general similarity of the molecule to $Cu_2(form)_2$.

Comparison of the Ag–Ag Distance in $Ag_2(form)_2$ with Others. In this case, there appear to be two compounds previously described that have slightly shorter Ag–Ag distances than that in $Ag_2(form)_2$. These are the silver analogue of the copper compound just mentioned, $Ag_2[o\text{-}(Me_3Si)_2CC_5H_4N]_2$, in which an Ag–Ag distance of 2.654 (1) Å is found,[16] and $Ag_2(PhNNNPh)_2$ where the Ag–Ag distance is 2.669 (1) Å.[17] The few silver(I) carboxylate dimers whose structures have been done all appear to have considerably longer Ag–Ag distances. There are $Ag_2(O_2CCF_3)_2$[18] and $Ag_2(O_2CCF_2CF_2CF_3)_2$[19] with silver–silver separations of 2.967 (3) and 2.90 (2) Å; the latter structure was fairly crude, and the Ag–Ag distance is the only one reported with an esd. Silver benzoate, $Ag_2(O_2CC_6H_5)_2$, and silver p-hydroxybenzoate, $Ag_2(p\text{-}HO\text{-}C_6H_4COO)_2\cdot 2H_2O$, were prepared and structurally characterized.[20] The metal–metal distances are again long, 2.902 (3) and 2.915 (8) Å, respectively.

A final point of interest is that in the $M_2[o\text{-}(Me_3Si)_2CC_5H_4N]_2$ compounds[16] the gold compound is also known and has a very short (2.672 (1) Å) Au–Au distance. In fact, it was stated that stability in this group of compounds increases in the order Cu > Au > Ag. In the case of $M_2(form)_2$ compounds, we have been unable to isolate a gold compound, and thus the stability series must be Cu $\approx$ Ag $\gg$ Au. We do not know the reason for this difference.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Full tables of bond distances, bond angles, and anisotropic displacement parameters for $Cu_2(form)_2$ and $Ag_2(form)_2$ (4 pages); tables of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

---

(11) O'Connor, J. E.; Janusonis, G. A.; Corey, E. R. *Chem. Commun.* **1968**, 445.

(12) Lockhart, T. P.; Haitko, D. A. *Polyhedron* **1985**, *4*, 1745.

(13) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1977**, 299.

(14) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Chem. Commun.* **1973**, 124.

(15) Iijima, K.; Itoh, T.; Shibata, S. *J. Chem. Soc., Dalton Trans.* **1985**, 2555.

(16) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 3085.

(17) Beck, J.; Strahle, J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 4.

(18) Griffin, R. G.; Ellett, J. D., Jr.; Mehring, M.; Bullitt, J. G.; Waugh, J. S. *J. Chem. Phys.* **1972**, *57*, 2147.

(19) Blakeslee, A. E.; Hoard, J. L. *J. Am. Chem. Soc.* **1956**, *78*, 3029.

(20) Usubaliev, B. T.; Movsumov, E. M.; Amiraslanov, I. R.; Akhmedov, A. I.; Musaev, A. A.; Mamedov, K. H. S. *Zh. Strukt. Khim.* **1981**, *22*, 98.