# Ligand-Unsupported Metal−Metal (M = Cu, Ag) Interactions between Closed-Shell d10 Trinuclear Systems

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Polynuclear molecular compounds and solid state extended lattices containing monovalent coinage metals have long demonstrated a remarkable degree of cluster-type aggregation despite the formally closed-shell d10 electronic configuration of the metals involved.[2] This behavior has been particularly well documented for gold, the term "aurophilicity" being used[3] to collectively describe Au−Au interactions, some of which are unsupported by exogenous ligands. For gold(I) sites, this attractive interaction has found its theoretical justification in the ligand-induced[4] and relativistically-supported[5] stabilization (contraction) of the 6s orbital which can favorably admix with 5d states to effectively reduce the population of the 5d valence shell. Although amply indicated in polymetallic clusters and extended solid structures,[6] the analogous cuprophilicity[7] and argentophilicity[2,7a] of the lighter congeners have been obscured by lack of sufficient experimental evidence regarding ligand-unsupported M(I)−M(I) (M = Cu, Ag) interactions in model coordination compounds. This scarcity has resulted in theoretical controversy as to the degree, if any, of stabilization offered by metal−metal contacts in ligand-supported cases. To illustrate the point, the existence of a bonding interaction reflecting the unusually short Cu(I)−Cu(I) distance (2.35 Å) found[8] in [Cu-(tolyl-NNNNN-tolyl)]3 has been both supported[9] and refuted[10,11] at various levels of theory. In our ongoing effort to develop synthetic and functional analogs of trinuclear copper sites in biological systems, we have uncovered strong evidence that weak M(I)−M(I) (M = Cu, Ag) attractive interactions *do* exist in the absence of any supportive bridging ligation. The Tl analog has also been investigated, since a similar argument concerning closed-shell Tl(I)−Tl(I) interactions has been debated,[12] following the isolation of the [((CH2Ph)5C5)Tl]2 molecular pair.[13]

Reaction of a solution of [Cu(CH3CN)4][PF6] in methanol with deprotonated 2-[3(5)-pyrazolyl]pyridine (2-(3(5)-pzH)py, **1**)[14] affords yellow-orange plates of [Cu3(2-(3(5)-pz)py)3]2·2py

(**2**, 37%)[15] upon recrystallization from pyridine. The analogous reaction of Ag(O3SCF3) with the (2-(3(5)-pz)py anion yields colorless, light-sensitive rods of [Ag3(2-(3(5)-pz)py)3]2·2py (**3**, 43%).[15] Preparation of the Tl(I) analog is accomplished by stirring Tl(OEt) and 2-(3(5)-pzH)py in EtOH followed by recrystallization from pyridine as colorless crystals of [Tl(2-(3(5)-pz)py)]n (**4**, 65%).[15]

The structure[15] of **2** (Figure 1) reveals two virtually planar triangular copper units coupled via two Cu−Cu interactions (Cu(1)−Cu(3′) = Cu(3)−Cu(1′) = 2.905(3) Å). The molecular pair resides on a crystallographically imposed inversion center. The triangle of copper atoms is nearly equilateral, with Cu···Cu distances around 3.52(5) Å. Within the trinuclear copper unit, the pyrazolato-bridged copper atoms are almost linearly coordinated to two pyrazolate rings (average N(pz)−Cu−N(pz) = 169(2)°) and more weakly to a pyridine moiety. The mean deviation of all non-hydrogen atoms from a least-squares plane fit to one trinuclear complex is 0.11 Å. The deviation of the Cu atoms from this plane (Cu(1) 0.27 Å, Cu(2) 0.08 Å, Cu(3) 0.19 Å) is clear evidence of the attractive nature of the Cu(1)−Cu(3′) and Cu(3)−Cu(1′) intertriangular interactions. These contacts are nearly orthogonal to the trinuclear planes as judged from the N−Cu−Cu bond angles.

Compound **3** (Figure 2) is isomorphous to **2**, although its structure[15] is slightly more distorted. The inversion-related triangular silver units are coupled along the longer Ag(1)···Ag(3) side (3.835 Å) by a pair of Ag−Ag contacts (3.227(2) Å), the orientation of which are more slanted with respect to the planes of the trinuclear units by comparison to **2**. The shortest interplanar Ag···N contact (Ag(3)···N(8′) = 3.038 Å) is comparable to nonbonding Ag···N distances within the triangle (Ag(1)···N(2) = 3.034 Å) and is not expected to contribute to the slanting. The enhanced overall distortion of the trinuclear silver unit versus the copper analog can also be evaluated by virtue of the mean deviation (0.155 Å) of non-hydrogen atoms from a least-squares plane fit to the trisilver complex (deviation of silver atoms: Ag(1) 0.283 Å, Ag(2) 0.151 Å, Ag(3) 0.220 Å).

It is worth noting that pyridine (solvent) does not compete with metal−metal interactions for coordination sites in the structures of **2** and **3**. 1H and 13C NMR spectra of **2** and **3** in C5D5N exhibit only one set of ligand resonances even at lower temperatures. MS spectra (CI (in C5H5N) or FAB (in glycerol)) of **2** and **3** show the molecular ion for the corresponding trinuclear complex. These results suggest that the coupling interaction does not survive in solution. Similar pyrazolato-bridged trinuclear structures have been extensively studied.[16]

In contrast, structural analysis[15] of compound **4** (Figure 3) demonstrates one-dimensional chain structures devoid of metal−

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(15) Detailed synthetic, analytical, spectroscopic, and crystallographic data have been deposited as Supporting Information. Crystal data for **1**: monoclinic, *Cc*, *a* = 11.136(1) Å, *b* = 12.462(1) Å, *c* = 11.758(1) Å, *β* = 118.127(2)°, *V* = 1439.0(3) Å3, *T* = 295 K, *Z* = 8, *R*1 = 0.0621, w*R*2 = 0.1540. For **2**: monoclinic, *P*21/*n*, *a* = 9.107(8) Å, *b* = 23.11(2) Å, *c* = 13.567(12) Å, *β* = 101.06(7)°, *V* = 2802(4) Å3, *T* = 295 K, *Z* = 2, *R*1 = 0.0850, w*R*2 = 0.2096. For **3**: monoclinic, *P*21/*n*, *a* = 9.318(4) Å, *b* = 19.682(9) Å, *c* = 15.878(9) Å, *β* = 90.28(4)°, *V* = 2912(2) Å3, *T* = 295 K, *Z* = 2, *R*1 = 0.0542, w*R*2 = 0.1283. For **4**: monoclinic, *P*21/*n*, *a* = 11.337(2) Å, *b* = 5.225(1) Å, *c* = 14.380(3) Å, *β* = 103.92(1)°, *V* = 826.8(3) Å3, *T* = 295 K, *Z* = 2, *R*1 = 0.0318, w*R*2 = 0.0711. For **5**: monoclinic, *Cc*, *a* = 8.7937(3) Å, *b* = 16.3714(5) Å, *c* = 7.9936(3) Å, *β* = 93.760(2)°, *V* = 1148.32(7) Å3, *T* = 130 K, *Z* = 4, *R*1 = 0.0263, w*R*2 = 0.0641.

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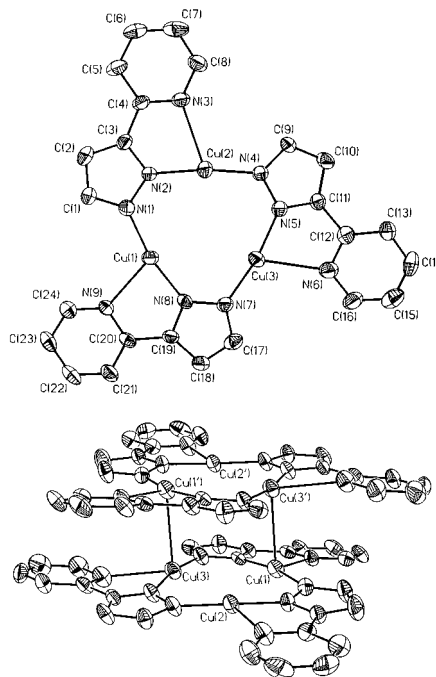
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**Figure 1.** Structure of the [Cu₃(2-(3(5)-pz)py)₃] unit (top) and the molecular pair [Cu₃(2-(3(5)-pz)py)₃]₂·2py (bottom) in **2**, showing 30% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Cu(1)−N(1) 1.867(7), Cu(1)−N(8) 1.895(7), Cu(1)−N(9) 2.317(8), Cu(2)−N(3) 2.483(8), Cu(3)−N(6) 2.522(9), N(8)−Cu(1)−N(9) 78.6(3), N(1)−Cu(1)−Cu(3′) 96.4(2), N(9)−Cu(1)−Cu(3′) 96.3(2), N(8)−Cu(1)−Cu(3′) 88.5(2).
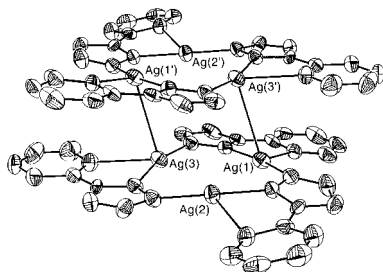


**Figure 2.** Structure of the molecular pair [Ag₃(2-(3(5)-pz)py)₃]₂·2py (**3**) showing 30% probability ellipsoids. The atom-labeling scheme is analogous to the copper compound as shown in Figure 1 (top). Selected interatomic distances (Å) and angles (deg): Ag(1)−N(1) 2.110(11), Ag(1)−N(8) 2.142(10), Ag(1)−N(9) 2.532(12), Ag(2)−N(3) 2.733(8), Ag(3)−N(6) 2.613(11), Ag(1)···Ag(2) 3.655, Ag(2)···Ag(3) 3.702, N(8)−Ag(1)−N(9) 71.9(4), N(1)−Ag(1)−Ag(3′) 114.3(2), N(9)−Ag(1)−Ag(3′) 90.5(3), N(8)−Ag(1)−Ag(3′) 65.3(2).

metal interactions. Compound **4** displays a zig-zag arrangement of pyrazolato-bridged thallium atoms, featuring a distorted trigonal pyramidal coordination geometry. The dihedral angle between alternating ligands is nearly orthogonal (81°). Intrachain and interchain Tl···Tl distances at 4.750 and 4.677 Å, respectively, provide conclusive evidence that no Tl−Tl interactions exist in this compound. A very similar one-dimensional chain is revealed in the structure of [Li(2-(3(5)-pz)py)(DMF)]ₙ (**5**).[15]

Very similar molecular pairs were recognized in the crystal lattices of the pyrazolato-bridged trimers [Cu(3,5-Me₂pz)]₃ (Cu−Cu = 2.946 Å),[17a] [Cu(3,4,5-Me₃pz)]₃ (Cu−Cu = 3.069 Å),[17b] and [Ag(pz)]₃ (Ag−Ag = 3.431 Å),[18] but their significance was not elaborated. Unsupported Ag−Ag contacts, albeit somewhat obscured by the Coulombic interaction, have been suggested
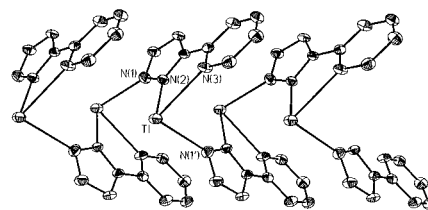


**Figure 3.** Structure of the [Tl(2-(3(5)-pz)py)₃]ₙ (**4**) extended chain showing 30% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Tl−N(2) 2.507(7), Tl−N(1′) 2.588(8), Tl−N(3) 2.762(8), N(2)−Tl−N(3) 63.5(2), N(2)−Tl−N(1A) 88.6(3), N(1′)−Tl−N(3) 81.8(3).

in the ionic [M(en)ₙ][Ag₂(CN)₄] (M = Ni, n = 3; M = Zn, n = 2)[19] and [Ag(ImH)₂][ClO₄][20] complexes. Compared to the metal−metal distances in the open-shell metallic copper (2.556 Å) and silver (2.889 Å) as well as to the rather underestimated sum of van der Waals radii (Cu−Cu = 2.80 Å, Ag−Ag = 3.44 Å),[21] the presently documented Cu−Cu and Ag−Ag distances are closer to the upper van der Waals limit but nonetheless represent genuine attractive interactions. Assignment of these metal−metal contacts to notoriously ill-defined crystal-packing forces[22] is unwarranted, since the M−M vectors demonstrate specific directionality and observed intermetallic distances commensurate with the nature of the metal involved (the covalent radii of two-coordinate Cu(I) and Ag(I) have been recently estimated[23] as 1.13 and 1.33 Å, respectively). In addition, the M−M interactions do not seem to be dictated by ligand-packing effects. No significant π-stacking interactions are apparent in the crystal structures of compounds **2** and **3** or in the hydrogen-bonded one-dimensional network of 2-(3(5)-pzH)py (**1**).[15] In contrast, ligand repulsion may actually be at work in preventing the triangles from becoming fully eclipsed to give three M−M contacts. That ligand effects are not responsible for the pairing is amply demonstrated by the crystal structure[24] of [3,5-Me₂pzH]₃ which, although it retains the planar trimeric association via hydrogen-bonding, does not display a "packing" arrangement consisting of a dimer of trimers as in [Cu(3,5-Me₂pz)]₃.[17a]

As opposed to the suggested compromise of the integrity of the d¹⁰ shell of Cu and Ag in compounds **2** and **3**, the 6s² orbital of Tl in compound **4** is apparently stereoactive, as it is clearly projecting into the empty cleft opposite to ligand coordination.

**Supporting Information Available:** Text describing synthetic procedures, analytical and spectroscopic data, ORTEP diagrams of **1** and **5**, and tables containing listings of crystal and data collection parameters, atomic coordinates and isotropic thermal parameters, interatomic distances, bond angles, and anisotropic displacement parameters for **1**−**5** (35 pages). See any current masthead page for ordering and Internet access instructions.

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