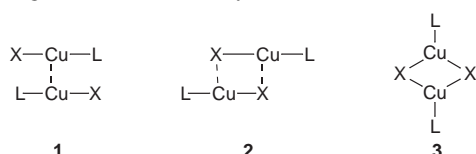# Association of two-coordinate copper(I) complexes: switching on and off Cu···Cu, ligand···ligand and Cu–ligand interactions

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A combined theoretical *ab initio* and structural database study is presented of the different interactions that allow two-coordinate copper(I) molecules to associate, from weak interactions to chemical bonds, giving rise to different structures.

Copper(I) complexes[1,2] with stoichiometry CuXL appear as bimolecular aggregates with Cu···Cu (**1**, with the two monomers in an eclipsed or a rotated conformation) or Cu···X (**2**) contacts, or forming dimers with a cyclic Cu_2X_2 core as in **3**, or

X—Cu—L   X——Cu—L   L
| | | | |
L—Cu—X   L—Cu——X   Cu
                          X   X
                          Cu
                          |
                          L

1   **2**   **3**

intermediate geometries. Also binuclear complexes with bidentate ligands bridging two copper atoms present molecular structures topologically equivalent to **1**. The Cu···Cu distances in these compounds span a large range (from 2.6 to 3.5 Å), suggesting the existence of weakly bonding interactions between the d^{10} ions, similar to those extensively studied for the related silver(I) compounds.[3–6]

The first semiempirical studies of bimolecular copper(I) aggregates,[7] based on extended Hückel calculations, proposed that mixing of the occupied d_{z^2} with the empty p_z atomic orbitals would convert the repulsion between the closed d shells into a weak bonding interaction. *Ab initio* studies have been reported for copper(I) complexes with monoatomic bridges,[8,9] and for the association between rigid monomers in $[Cu(PH_3)Cl]_2$ or in the interpenetrated networks of Cu_2O.[10,11] However, the rich structural chemistry of the [CuLX] groups outlined above has not been analyzed in detail and an explanation for the factors that determine the choice between structures **1–3** is still needed. For this reason, we present here the results of a theoretical *ab initio* MP2 (triple-ζ + polarisation basis set) study of the intermolecular interactions between two-coordinate copper(I) complexes in the model compounds $[Cu(NH_3)Cl]_2$, $[Cu(N_2)Cl]_2$ and $[Cu(PH_3)Cl]_2$, combined with a structural database analysis.‡ The structural parameters that describe the geometry of a bimolecular aggregate **4** are the bond angle β, the
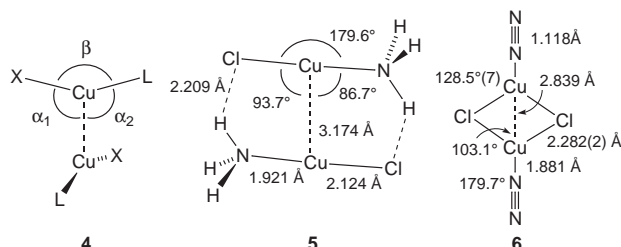
intermolecular angles Cu–Cu–Cl (α_1) and Cu–Cu–E (α_2, E = N, P), and the torsion angle Cl–Cu–Cu–Cl (τ).

The most remarkable features of the optimized structure of $[Cu(NH_3)Cl]_2$ **5** are its eclipsed conformation, a relatively long Cu···Cu distance and the existence of short intermolecular

N–H···Cl contacts. A dimer of type **3** with bridging chloro ligands was explored for $[Cu(NH_3)Cl]_2$, but no minimum was found for such a structure or for the alternative **2**, and the hydrogen-bonded structure **5** was always obtained in the optimization procedure. Nevertheless, a strong bonding interaction exists between the two bent monomers in a rhombic structure **3** of $[Cu(NH_3)Cl]_2$ [−40 kcal mol⁻¹] although the energy required to bend the monomers (17 kcal mol⁻¹ per monomer) makes the bonding energy relatively small (−7 kcal mol⁻¹). Hence, the intermolecular aggregate of type **5** with two hydrogen bonds is more stable (bonding energy −22 kcal mol⁻¹) than the rhombic form at the present level of computation. The choice of a ligand with weaker or no hydrogen bonding capabilities, such as PH_3 or N_2 in $[Cu_2L_2Cl_2]$ (L = PH_3 or N_2), makes a structure of type **1** less favorable, with only a weak Cu···Cu interaction left. Therefore, structure **3** becomes the most stable one in these cases, with dissociation energies of 17 and 18 kcal mol⁻¹ for L = PH_3 and N_2, respectively (optimized structural parameters for the latter shown in **6**). Notice that the halophosphine complexes of stoichiometry $Cu(PR_3)X$ crystallize with structure **3** (13 structures) predicted to be more stable by our calculations, except for those with the bulkiest phosphines which give isolated monomers (four structures).

We analyzed in some detail the potential energy surface of $[Cu(NH_3)Cl]$ in its staggered conformation (τ = 90°), in which both ligand···ligand and ligand···metal interactions are minimized. The interaction between two linear $[Cu(NH_3)Cl]$ monomers (with $\alpha_1 = \alpha_2 = 90°$) is found to be attractive by 1–3 kcal mol⁻¹ for all the range of distances between 2.5 and 5.0 Å. The bonding energy presents a maximum (−3.2 kcal mol⁻¹) at Cu···Cu 3.004 Å, similar to the values reported by Pyykkö *et al.* for $[Cu(PH_3)Cl]_2$ with a similar geometry,[10] and to that found for the interaction between rigid networks in Cu_2O.[11] They probably indicate the existence of a weakly bonding Cu···Cu interaction in the staggered form, which should coexist with the stronger ligand···ligand hydrogen bonding in the most stable eclipsed structure **5**. Bending the monomers does not improve the intermolecular interaction, although aggregates in which β is as small as 165° are still stable toward dissociation into linear monomers. Interestingly, the Cu···Cu distance is predicted to shorten for smaller bond angles (Fig. 1, triangles), a behavior that can be also found for the experimental data (Fig. 1, squares and circles for inter- and intra-molecular contacts, respectively).The aggregate in the eclipsed conformation is stabilized by slipping the two monomers (*i.e.* $\alpha_1 = 87°$, $\alpha_2 = 93°$ and β = 177°), while the Cu···Cu distance (2.694 Å) is significantly shortened.

Further support for the bonding nature of the Cu···Cu contact in both its eclipsed and staggered forms has been obtained from a topological analysis[12] of the calculated electron density of $[Cu(NH_3)Cl]_2$. A bond critical point was found between the two Cu atoms in $[Cu(NH_3)Cl]_2$, with electron densities of 0.017 and 0.028 for the eclipsed and staggered structures, respectively, consistent with a weak bonding interaction. The values found for all characteristic parameters of the critical points are similar to those for closed shell interactions such as the O–H···O
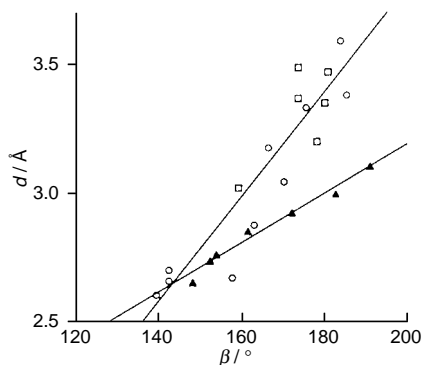
4 (structure: X—Cu—L with angles α_1, α_2, β, Cu''''X, L)

5 179.6°; Cl; 2.209 Å; 93.7°; 86.7°; 3.174 Å; H; N—H; 1.921 Å; 2.124 Å; Cl; Cu

6 N (1.118 Å); 128.5°(7); Cu 2.839 Å; Cl; Cl; 103.1° Cu; 2.282(2) Å; 1.881 Å; 179.7°; N

Fig. 1 Optimized Cu···Cu distance as a function of the bond angle β for the dimer $[Cu(NH_3)Cl]_2$ (triangles). Structural data for intermolecular (squares) and intramolecular (circles) contacts with flexible bridging ligands in an eclipsed conformation also plotted for comparison.

Fig. 2 Longest Cu···X distance as a function of the bond angle β for bimolecular aggregates $[CuLX]_2$ of types **1** and **2**, and for dimers **3**, where X = Cl (triangles, 13 structures), Br (squares, 14 structures), I (circles, 21 structures) or N (diamonds, 5 structures)

hydrogen bonds (see ref. 12, p. 292). In addition, bond critical points between the hydrogen and chlorine atoms in the eclipsed conformer confirm the existence of inter-ligand hydrogen bonds. A previous study of the electron density in a bridged silver(I) binuclear complex also showed the bonding nature of the Ag···Ag interaction.[13] It is interesting to stress that in $[Cu(NH_3)Cl]_2$ there is Cu···Cu bonding even if the copper atoms are 3.174 Å apart. In contrast, a similar analysis of the electron density of the rhombic structure of $[Cu(N_2)Cl]_2$, with a shorter Cu···Cu distance (2.839 Å), shows no bond critical point between the copper atoms. These results clearly show that it is the molecular topology, not the distance, that determines the existence of a Cu···Cu bonding interaction. Such results are consistent with the importance of the d_{z^2}–p_z hybridization[4,7] for the Cu···Cu interaction (possibly a part of the important correlation effects in post Hartree–Fock calculations[5]): in the intermolecular aggregate $[Cu(NH_3)Cl]_2$ the empty p_z orbital of Cu can participate in the Cu···Cu interaction, and a bond critical point is found between the copper atoms. In contrast, in the optimized structure of $[Cu(N_2)Cl]_2$, the p_z orbital is involved in metal–ligand bonding (corresponding to a formal sp^2 hybridization at Cu), the d_{z^2}–p_z donor–acceptor interaction should be quenched, and no Cu···Cu bond critical point is found.

The variety of structures found for the bimolecular aggregates of the [CuLX] compounds can be explained taking into account the reluctance of the monomers to bend, together with the variety of intermolecular interactions available to them: (*i*) weak Cu···Cu bonding interaction, (*ii*) intermolecular hydrogen bonds between ligands, (*iii*) new Cu–X bonds (when the X ligands have unshared electron pairs), and (*iv*) steric hindrance imposed by highly bulky ligands L that may prevent two monomers from approaching close enough to allow bonding interactions. For instance, a Cu···Cu contact at 2.810 Å is found in a staggered conformation with no supporting metal–ligand or hydrogen-bonding interactions in $[Cu(pyFc)_2][CuCl_2]$ [pyFc = 1,1′-bis(2-pyridyl)octamethylferrocene].[14] On the other hand, the hydrogen-bonded structure **5** found for our model compound has an experimental counterpart in $[Cu(Me_4pip)Br]$[15] (Me$_4$pip = 2,2,6,6-tetramethylpiperidine), which presents a N–H···Br distance of 2.653 Å and a Cu···Cu distance of 3.362 Å.

The attractive Cu···X interaction predicted in our calculations for $[Cu(L_2)Cl]_2$ (L = PH$_3$, N$_2$) that may result in the formation of a rhombic dimer of type **3** is in keeping with the coordinative unsaturation of Cu^I in two-coordinate complexes, manifested in their well known tendency to form three- or four-coordinate compounds.[1,2] In fact, one can view the different structures experimentally found as snapshots along the pathway that takes one from bimolecular aggregates of type **1** to dimers of type **3**,
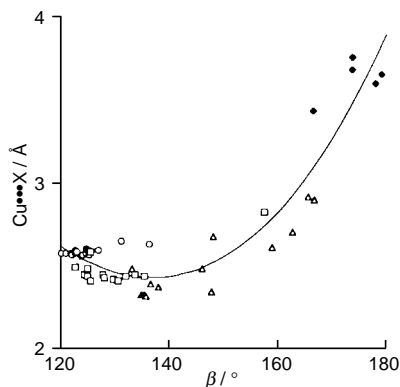
along which the Cu···X distance and the bond angle β are expected to decrease in a concerted way. This is precisely what is found (Fig. 2) for the structurally characterized dimers of type **3** and those weakly bound aggregates of type **1** or **2** (with X = Cl, Br, I or N). Alternatively, the [CuLX] monomers associate through Cu···X contacts forming chains of trigonally co-ordinated Cu atoms, that have been structurally characterized for X = L = Br.[15] When the two ligands have an unshared electron pair as in the $[CuX_2]^-$ monomers, two Cu···X contacts per molecule can be formed, thus giving chains of tetrahedrally coordinated Cu atoms, as frequently found in the salts of the $[CuX_2]^-$ anions (X = Cl, Br, or I).

Notes and References

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‡ Details of the *ab initio* calculations[16] and of the structural database search[17] can be obtained from the authors.

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