Cuprophilicity, a still elusive concept: a theoretical analysis of the ligand-unsupported Cu^I–Cu^I interaction in two recently reported complexes

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Density functional theory (DFT) calculations explain the short ligand-unsupported Cu^I–Cu^I contact recently reported for the $[CuL]^+[CuCl_2]^-$ complex [L = 1,1′-bis(2-pyridyl)octamethylferrocene] by a strong electrostatic attraction (-64 kcal mol^{-1}) between the two moieties and rule out the initially suggested metallophilic interaction, but cuprophilicity might account for the dimerization occurring in a family of trimetallic complexes.

Weak attraction between transition metal atoms with closed-shell electronic configuration was first evidenced by Schmidbaur *et al.* in the cases of intra- and intermolecular Au^I–Au^I contacts.[1] The term aurophilicity was coined to describe these interactions, but it soon became clear that similar aggregation processes could also involve metal atoms other than gold, such as Tl^I or Hg^{II}.[2] These closed-shell interactions in inorganic chemistry have been reviewed by Pyykkö.[2] The occurrence of analogous metallophilic[3] effects involving lighter metal atoms and more specifically Cu^I has been the subject of a long debate due to the intramolecular character of the reported interactions.[2,4] Recently, two examples of unsupported Cu^I–Cu^I contacts with metal–metal distances of 2.905 Å[5] and 2.810 Å[6] have been tentatively assigned to cuprophilic interactions. On the theoretical side, recent studies by Pyykkö *et al.* suggest that the stabilization of the $ClCuPH_3$ model dimer due to the metallophilic interaction between the Cu^I atoms does not exceed -1.5 kcal mol^{-1} when extrapolated to the best level of theory, and is associated with a rather long metal–metal distance of 3.143 Å.[7] The goal of this study was to investigate by means of DFT and extended Hückel calculations other possible origins for the unsupported Cu^I–Cu^I interactions in the two complexes for which cuprophilicity has been addressed.

Metallophilic interactions are not easy to characterize from quantum chemical calculations. Pyykkö *et al.*[2,3] have demonstrated that metallophilicity is due to attractive dispersion forces that should overcome the Pauli repulsion between the d^{10} or the $d^{10}\,s^2$ closed shells. For metals of the third transition row, the attractive forces are greatly enhanced by relativistic effects.[2,7] Since neither *ab initio* Hartree–Fock nor DFT calculations account for dispersion-type R^{-6} terms these levels of theory unavoidably predict repulsive behaviour between unsupported metallophilic fragments.[2,3] Conversely, if these methods are able to account for an attractive interaction, it should be clear that it is not of the metallophilic type.

This is the principle of the investigations performed on $[CuL]^+[CuCl_2]^-$ [L = 1,1′-bis(2-pyridyl)octamethylferrocene] **1** for which a cuprophilic interaction had been tentatively suggested to explain the short Cu^I–Cu^I contact (2.810 Å) observed between the two copper subsystems.[6] Complex **1** has been slightly modeled by replacing octamethylferrocene with ferrocene (**1′**) and by assuming perfect C_{2v} symmetry, which implies that the coordination axes of the anion and the cation are perpendicular (Fig. 1). We then carried out a full geometry optimization of **1′** by means of gradient-corrected DFT calculations.‡ Selected geometrical parameters obtained from the calculation are reported in the caption of Fig. 1 and compared to experiment. The observed environment of the copper atoms is reproduced by the calculation with great accuracy, including the Cu–Cu bond length (calc. 2.822 Å, exptl. 2.810 Å). The interaction energy between the two fragments is calculated to be -64.1 kcal mol^{-1}, after BSSE correction. The presence of a bonding interaction at this level of theory and its order of magnitude clearly show that the attraction between the $[CuL]^+$ and the $[CuCl_2]^-$ subunits should not be assigned to cuprophilicity. Since the interaction involves charged moieties, the bonding may instead be due to Coulombic forces. Mulliken population analyses, carried out either from the extended Hückel (EHT) or from the DFT orbitals, indicate that the charge transfer between the two moieties is negligible (Table 1). The negative charge in the $(CuCl_2)^-$ fragment is distributed between the chlorine atoms while the Cu atom remains either neutral (+0.04e, DFT), or significantly positive (+0,24e, EHT). Even though the point charge distributions in the cationic fragment is noticeably different for EHT and DFT (Table 1), the $(CuCl_2)^-/(CuL)^+$ electrostatic attraction computed from the point charge model are similar (62.0 kcal mol^{-1} with EHT, -67.9 kcal mol^{-1} with DFT) and practically reproduce the fragment interaction energy obtained from DFT calculations. Other models of space partitioning[8,9] applied to the DFT wave function, however, predict some charge transfer toward the $(CuL)^+$ moiety and the fragment electrostatic energies computed from those models are scaled accordingly (Table 1).

In order to obtain an estimate of the fragment/fragment Coulombic interaction independent of space partitioning, we relied on standard energy decomposition analysis[10,11] and computed the total energy starting from the wave functions computed for the $(CuCl_2)^-$ and $(CuL)^+$ fragments assumed isolated, but occupying their geometrical positions in the complex. The interaction energy is now -69.4 kcal mol^{-1}. The difference with respect to the value of -64.1 kcal mol^{-1} reported above corresponds to the fragment relaxation energy. The fragment interaction energy is made up of: (i) the Pauli

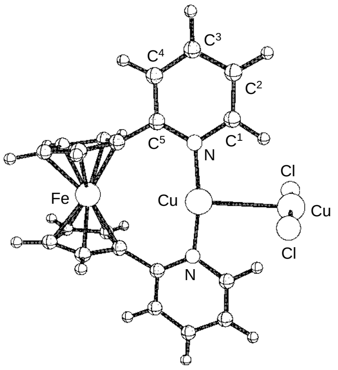

Fig. 1 Molecular structure of **1′** optimized from gradient corrected DFT calculations (C_{2v} symmetry assumed). Selected bond lengths (Å) and angles (°): Cu–Cu 2.822 (2.810); Cu–Cl 2.119 (2.095); Cu–N 1.895 (1.925); Cu···Fe 3.74; Fe–Ω 1.668 (Ω centroid of a Cp ring); N–Cu–Cu 95.0 (94.3); Cl–Cu–Cu 88.8 (89.1). Numbers in parentheses are the averaged experimental values.

Table 1 Point charge distributions (electrons) computed for **1′** using (i) the Mulliken space partitioning applied to the EHT and to the DFT wave functions, and (ii) the Hirshfeld[8] and the Voronoi[9] space partitionings, both applied to the DFT wave function. The electrostatic interaction energy between the two fragments is calculated from those point charges

Atoms	Mulliken (EHT)	Mulliken (DFT)	Hirshfeld (DFT)	Voronoi (DFT)
Fragment $(CuL)^+$:				
Cu	+0.032	+0.482	+0.247	+0.240
N	−0.336	−0.461	−0.086	−0.100
Cl + H1	+0.333	+0.352	+0.058	+0.148
C2 + H2	−0.037	+0.005	+0.034	+0.175
C3 + H3	+0.115	+0.034	+0.044	+0.052
C4 + H4	−0.038	+0.019	+0.023	−0.091
C5	+0.433	+0.178	+0.076	+0.020
Fe	−0.243	−0.012	+0.048	−0.036
Cp	+0.134	+0.119	+0.027	+0.060
Total $(CuL)^+$	+0.997	+0.962	+0.647	+0.732
Fragment $(CuCl_2)^-$:				
Cu	+0.239	+0.037	+0.111	+0.088
Cl	−0.618	−0.499	−0.379	−0.410
Total $(CuCl_2)^-$	−0.997	−0.961	−0.647	−0.732
Electrostatic interaction energy/kcal mol^{-1}				
	−62.0	−67.9	−28.9	−41.6

repulsion, +38.8 kcal mol^{-1}; (ii) the Coulombic attraction, −86.4 kcal mol^{-1}, and (iii) the energy associated with electron reorganization in the complex, which is also attractive and reaches −21.8 kcal mol^{-1}. This latter term includes the stabilization due to the mutual polarization of the two fragments which is a purely electrostatic effect that can be distinguished from charge transfer and orbital interaction.[11] This energy decomposition analysis stresses the importance of the Pauli repulsion which should not be exclusively assigned to the Cu^I–Cu^I contact, but also to the two short Cu···H1 distances (2.28 Å). It also proves, without assuming any space partitioning, the prominent influence of the Coulombic interaction.

Siemeling and colleagues[6] noted that a complex closely related to **1**, $[Cu(C_5H_3NMe_3\text{-}2,4,6)_2][CuCl_2]$ **2**,[12] does not display a similar Cu–Cu interaction. The structure of **2** is characterized by the stacking of planar $[Cu(C_5H_3NMe_3\text{-}2,4,6)_2]^+$ fragments separated by $(CuCl_2)^-$ moieties perpendicular to the N–Cu–N axis, but the Cu···Cu distance is now 3.61 Å.[12] This increase of the interfragment separation may be tentatively assigned to steric crowding induced by the presence of four Me substituents. However, providing a final answer to this problem will require the geometry optimization of models of **2**, with and without the Me substituents.

The case of $[Cu_3L'_3]_2$ {L′ = 2-[3(5)-pyrazolyl]pyridine} **3**[5] and related dimers of $Cu^I{}_3$ and $Ag^I{}_3$ complexes[13] seems more relevant to metallophilic interactions. Preliminary calculations of the extended Hückel type carried out on these molecules indicate that the Mulliken charge of the copper atoms is close to zero and confirm that no significant orbital interaction is at work between the two monomers. However, a conclusive argument proving the existence of metallophilic interactions on such large systems is at present impossible to obtain from quantum chemical calculations. It is however of interest to extrapolate from Pyykkö's calculations on $[ClMPH_3]_2$[7] the order of magnitude of the metallophilic stabilization in **3** and in its silver counterpart.

Pyykkö's potential energy curves were obtained at the *ab initio* MP2 level of calculation with very large basis sets.[7] They display energy minima at 3.208 Å for Au, 3.113 Å for Ag and 3.137 Å for Cu. The curves are however extremely shallow, especially for copper. The stabilization energy computed at the minimum is −3.07 kcal mol^{-1} but a separation of 4.5 Å still provides a favourable interaction which amounts to −1.2 kcal mol^{-1}. The crystal structure of **3** displays two short-range Cu–Cu interactions (2.905 Å) between the two monomers, but also six Cu···Cu distances between 4.44 Å and 4.75 Å.[5] Most of the metallophilic stabilization (*ca*. 60%) might then originate in these long distance interactions. However, providing a quantitative estimate for the overall stabilization energy requires caution. A comparison between MP2 calculations and more elaborate methods carried out for $[XAuPH_3]_2$ (X = H, Cl) indicates that MP2 overestimates the real stabilization energy by a factor of 2.[2,7] Scaling down accordingly the value deduced from Pyykkö's potential energy curves provides an overall stabilization of *ca*. −6 kcal mol^{-1} due to the cuprophilic effect between the two monomers, 60% of which is assigned to the intermediate range Cu···Cu interactions. A similar reasoning applied to the silver equivalent of **3** yields an estimate of *ca*. −7.5 kcal mol^{-1} for the metallophilic interaction, but in this case the intermediate range interactions account for no more than one third of the global stabilization.

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Notes and References

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‡ *Computation*: gradient-corrected DFT calculations on complex **1** have been carried out by means of the ADF program.[14] We used the local spin density approximation characterized by the electron gas exchange ($X\alpha$ with α = 2/3) together with Vosko–Wilk–Nusair[15] parametrization for correlation. Becke's nonlocal corrections to the exchange energy[16] and Perdew's nonlocal corrections to the correlation energy[17] were added. Slater basis sets of triple-ζ+ polarization quality were used to describe the valence electrons of C, N, O and H. For first-row atoms, a 1s frozen core was described by means of a single Slater function. For copper, the frozen core composed of the 1s to 2sp shells was also modelled by a minimal Slater basis; 3sp electrons were described by double-ζ Slater functions, 3d and 4s by triple-ζ functions and 4p by a single orbital.[18]

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