

Theoretical analysis of the geometry of weak Cu(II)..H-C bonds in planar complexes

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Introduction. Weak M..H–C interaction has been reported in several square planar d^8 and d^9 complexes.¹ Metal complexes of biologically important ligands, like ephedrine derivatives² or polypeptide chains, can also show such interaction with electron-rich metal ions. The nature of the M..H–C interaction is still unclear, and it is debated if it is an agostic or weak hydrogen bond. The geometry (angle) of the M..H–C bond is often cited as an argument for the presence of agostic interaction. However, the reasons for the particular geometry are generally not carefully examined. Also, the spectroscopic properties (H-NMR shift, UV-VIS) suggest only weak or non-existent orbital interaction between the metal ion and the alkyl chain, which is more consistent with a weak hydrogen bond-like interaction. In this talk we report a systematic theoretical study on a series of square planar Cu(II) and Pd(II) complexes with R alkyl side chain (R: ethyl (Et), n-butyl (Bu), 2,2-dimethylpropyl (Dmp) and 2-methylbutyl (Mbu)) previously experimentally characterized by Yamauchi et al.³ These complexes are structurally as well as spectroscopically very well characterized examples showing M..H close contacts. Using DFT methods, we studied the geometry and spectroscopic properties of the complexes, focusing on the factors that determine the position of alkyl C-H compared to the metal.

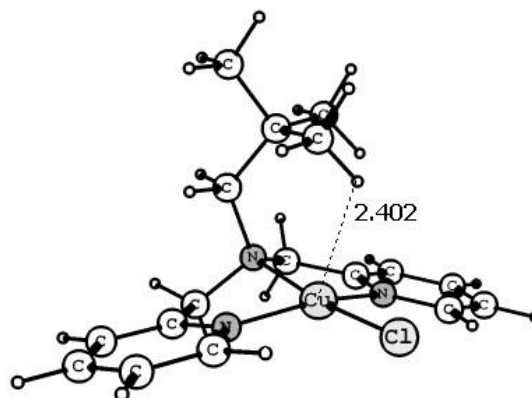


Fig. 1. Interaction between Cu(II) and 2,2-dimethylpropyl side chain with the distance in Å.

Methods. The calculations were carried out at B3LYP/SDD level with Gaussian 03 program suit. For optimizations, “Tight” convergence criterion was used with “Ultrafine” integration grids. To account for the solvent (methanol and acetonitrile) background, Polarizable Continuum Model (PCM) was used.

Results. Geometry optimizations showed that all of the complexes has two distinct potential energy minima: an “open” conformation, which corresponds to an approximate “anti” position of the alkyl side chain far from the M(II) ion, and a “closed” conformation with short M(II)..H–C distance. The geometry of Cu and Pd complexes was similar when the complexes with same ligand are compared. All the experimental X-ray crystallographic structures³ could be assigned with either of “open” or “closed” conformation. In “closed” conformation the complexes with Et and Bu formed a 5-member ring through the M(II)..H–C bonds, leading to a M..H bond distance of 2.73–2.87 Å and an M(II)..H–C angle of 105–110°. In complexes with Dmp and Mbu, however, a 6-member ring could be formed (Fig 1.), resulting in a much shorter M..H bond distance of 2.35–2.40 Å and an M(II)..H–C angle of 120–140°. In Cu(II) complexes with such short M..H contact the interaction energy can reach 3–4 kcal/mol according to the DFT calculations.

The energy barriers between the potential minima can be derived from steric and hyperconjugation effects in the ligand. The M..H interaction is relatively weak in the complexes, therefore the position

of the energy minima, thus the geometry, is primarily controlled by the ligand conformation energies in all the studied complexes (see in Figure 2. for the Cu(II) with ethylene sidechain), and not by the M..H bond.

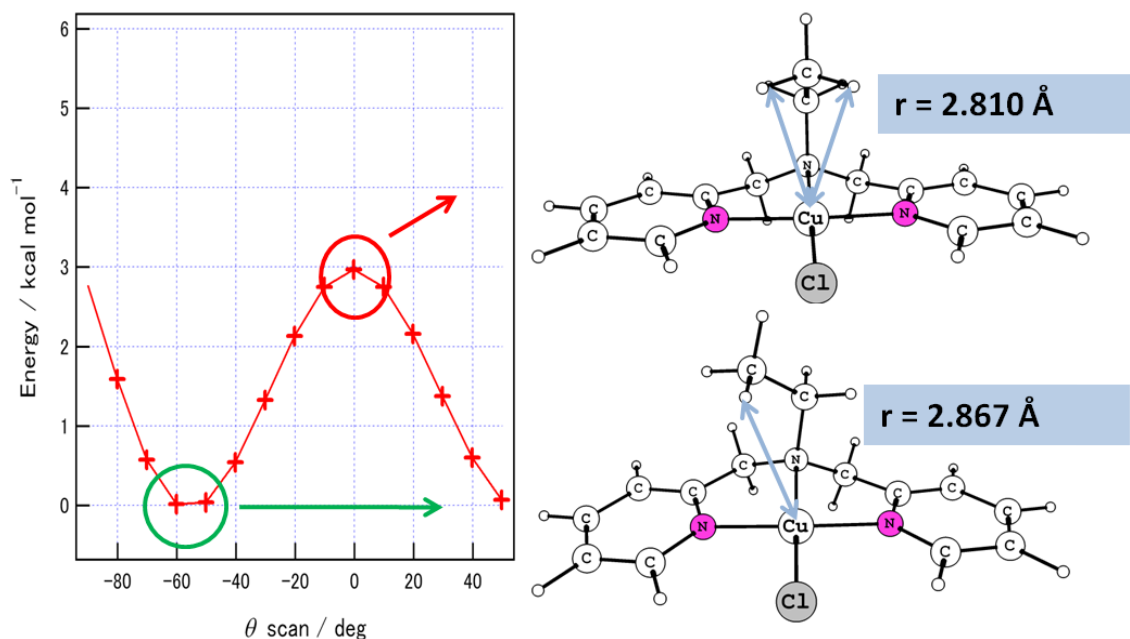


Fig. 2. Interaction between Cu(II) and ethyl side chain upon relaxed rotation of the side chain: corresponding energy in vacuum (left), short distances between Hs and Cu(II) (right).

Further analysis showed that in both the Pd(II) and Cu(II) complexes the orbitals with significant d_{z^2} contribution are essentially non-bonding, and there is no sign of orbital interactions between the H and d_{z^2} on the metal ions. In agreement with these findings, TD-DFT calculations predict that the excitation energies corresponding to the promotion of an electron from d_{z^2} orbitals to $d_{x^2-y^2}$ orbitals are insensitive to the structure and position of the R group when complexes with the same metal ion are compared. In other words, the M..H interaction has only very weak influence on the d orbital energies. On the other hand, we found a strong polarization of the H, due to the charge density on the metal. This polarization is in good agreement with the H-NMR shift observed on the alkyl chain H upon close contact, and it indicates a primarily electrostatic, closed-shell interaction in the M..H-C bond.

Summary. In summary, our calculations suggest that the M(II)..H-C(alkyl) bond (M: Cu, Pd) is similar to the weak hydrogen bond in d^8 metal-complexes with M(II)..H-N(amin) interaction.

References:

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