Structure, bonding, and magnetic behavior of bis(?-chloro)-and (?-bromo)-bridged Cu(II) dimers

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It has been previously reported that dimeric compounds of the general formula [L3Cu(II)]2(?-Cl)2 exhibit a correlation between their magnetic coupling constant J and the bridging Cu-Cl-Cu angle. A full survey of the published structural and magnetic data on these compounds confirms this correlation but leads to the conclusion that its physical significance is questionable. EHMO calculations on Cu2Cl84- and its bromo analog show that the molecular orbitals responsible for the magnetic behavior of the dimers are not the orbitals responsible for the bonding interactions in these dimers. Therefore, they are very weakly affected by variations of the molecular structure, and no significant correlation between J and any of the structural parameters is theoretically predicted. However, this situation changes when the coordination around the Cu atoms is strongly and dissymmetrically pyramidalized.