Tuning metal–metal distances through ligands

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Abstract. Metal–metal distances in polynuclear metal complexes are often controlled by factors other than favourable metal–metal (M–M) interactions. Recently metal cluster topology has been identified as a major factor in controlling Cu–Cu distances in tetrahedral copper clusters. The more obvious ligand control in M–M distances was shown to play a secondary role. In order to probe ways to tune metal–metal distances in clusters, a study of clusters with similar ligands around the metal has been taken up. Two broad classes were identified: Clusters in which there are two-electron two-centre bonds, and a second class where multicentre multielectron bridging is involved.

Clusters held together by two-electron two-centre bonds can be analysed fairly effectively using a test electrophile like the proton. This is illustrated by analysing structures available in the literature. The sensitivity of the method to detect M–M interactions will be illustrated with examples from gold clusters where relativistic interactions cause gold $d^{10} - d^{10}$ interactions to be attractive. Among the latter class $Cu_3P_6X_2$ core makes a specially interesting case study. The capping ligand X determines the extent of Cu–Cu interaction present in the cluster. Simple EHT calculations on the cluster reveal that Cu–Cu reduced overlap populations change significantly with the extent of π-donation or acceptance of the ligand.

Keywords. Metal–metal distances; clusters; ligand control; EHT calculations.

1. Introduction

Metal–metal bonds are considered an essential feature of metal clusters (Cotton and Wilkinson 1988). Indeed, in several metal clusters one of the major forces is the metal–metal bond. Hence in some instances the chemistry of a metal cluster is said to be determined by the strength of metal–metal bonds. However in many polynuclear metal complexes, where comparable short metal–metal distances exist, metal–metal bonds are nonexistent or questionable at best (Cotton *et al* 1988). Although short metal–metal contacts exist in these compounds, suggesting at first sight that there are attractive forces between the metal centres, analysis of the M–M bond order reveals that there is no net bonding between the two atoms. A few examples of such compounds are listed in figure 1. One must then answer the question, why do these compounds adopt short metal–metal distances? The answer to this question might be sought in the type of bridging ligands present in these complexes. Indeed in polynuclear copper(I) complexes where repulsive $d^{10} - d^{10}$ interactions rule out M–M bonding, bridging ligands appear to play a major role in determining M–M distances (Abraham *et al* 1993). In this study we show that the methodology developed by them can be used, not only to rule out the presence of an M–M bond but also to confirm the presence of
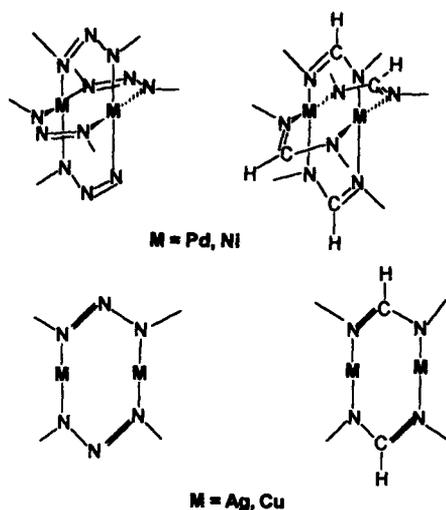
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Figure 1. Metal complexes with an M–M bond order of zero.

attractive M–M interactions. Furthermore the possibility of tuning of M–M attractions through electron deficient multicentre bonding can be predicted through simple Extended Huckel Theoretical (EHT) calculations (Hoffman 1963).

2. Results and discussion

Most polynuclear metal complexes containing d^{10} metal atoms are held together by the presence of bridging ligands except for a few examples of polynuclear gold complexes which have short M–M contacts in the absence of bridging ligands (Park and Kanatzidis 1990). Such unsupported short contacts are not known with other d^{10} metal ions. A careful analysis of the various polynuclear d^{10} clusters shows that there are two types of bridges holding the metal centres together. The first type involves metal centres bridged by the ligand through two-centre two-electron bonds. The second type involves monoatomic bridges formed by atoms such as S and Cl. The role of these bridges in determining M–M distances in oligomeric complexes has to be discussed separately.

2.1 *Electron precise metal–ligand bridging*

In complexes where the metal centres are bridged by a ligand through two different atoms, each donating a pair of electrons, the distances between the donor sites could have an influence on the distances between the metal atoms. This might be independent of the attractive or repulsive forces between the metal centres. An example of such a control is obvious when one compares the series of complexes illustrated in figure 1. In all cases the N–C–N bridged metal centres (Cotton *et al* 1988) are further apart than the N–N–N bridged clusters (Corbett *et al* 1975). This distance between the ligating atoms, which is the geometric distance between the coordinating atoms (r_g) could be taken as a parameter for judging the extent to which different ligands influence the metal–metal distance. However, consider a hypothetical ligand where the two electron donor sites, L and L', are separated by a distance r_g, the electron pair available for donation to the metal on L could be directed away from the other atom L' as shown in

Figure 2. Variation of r_e and r_g.

figure 2 (centre). In this situation the M–M distance dictated by the ligand could be much larger than r_g. Alternatively the electron pair could be directed in the direction of L′ (figure 2, right). The latter situation would force the metal atoms to come close to one another. In either of these situations the geometric distance between the ligating atoms is not indicative of the metal–metal distance dictated by the ligand. One reaches a wrong conclusion about M–M interactions from the value of r_g. This was first pointed out by Hoffman and coworkers (Merz and Hoffman 1988).

Of greater significance are the angles subtended by the non-bonded pair of electrons on the ligating atoms. This allows one to define electronic bite angles which would help one to discern the extent to which the ligands control the M–M distances. The presence of M–M interactions, if any, would be apparent from the deviations from these ligand-determined bite angles. A reliable estimate of the bite angles can be obtained from semi-empirical calculations available in the MOPAC package (Abraham *et al* 1993). Using the MNDO/III program (Stewart 1990) the preferred direction of approach of a test electrophile (H^+) towards the ligating atoms of the bridging ligand can be estimated. The advantage of using the proton as a test electrophile is that by doing so, one eliminates all the complications and bias that arise due to metal–metal interactions, So also, by optimizing the position of the proton, the preferred approach of the test electrophile could be obtained. One could, in principle, use the alkali metal ion, modelled by a positive charge "sparkle" in the MNDO program, as a test electrophile. However the geometrical parameters related to the sparkle cannot be optimised.

For a particular ligand, the bite requirements are obtained by carrying out the calculation with the ligand fixed in the geometry found in the crystal structure of the metal complex. Optimising the bond distance and angles of proton attached to the ligating atom reveals the directionality of the non-bonded electron pair. It is instructive to compare the bite angles for a typical hard donor N and a soft donor S. The ideal bite angle at an sp^2 N using this procedure is calculated to be 121°, while that at RS^- is much smaller, 102°. These values are consistent with the computed and experimental geometries of acid-base complexes involving N and S donor molecules (Smith *et al* 1982; Rajappa *et al* 1989). It is important to note the variation of the energy as a function of the bite angles. The energy loss on deviating from the predicted bite angle is much larger at N. The flatness of the electrophilic surface near the sulphur atom is compatible with its softness (Pearson 1990). This flatness indicates that the electrophile may approach the donor sulphur atom at a wide range of angles. The Cu–S–Cu bridging angles involving the sulphide ligand for example, vary from about 70° to about 135° in various crystallographically characterised copper complexes. The donor orbitals of the polarizable sulphur atom can accommodate the approaching electrophile in a wide range of angles.

The ideal coordination angles computed for various ligands found in polynuclear copper complexes show that Cu(I)–Cu(I) distances are determined by the bite angles of the ligands (Abraham 1994). Although these results are entirely consistent with the

conclusions of other workers in this area (Cotton *et al* 1988; Lee and Trogler 1990), one needs to show that the procedure adoped is indeed capable of identifying cases where M−M bonds are involved. Hence a study of gold complexes has been taken up. In view of the predicted flatness of the potential energy surface of ligating S atoms, one would expect the sulphur coordinated gold complexes to show the greatest deviations if any from predicted bite angles.

2.2 *The d^{10} gold(I) system*

An intriguing phenomenon in gold chemistry which has received attention in both theoretical and experimental studies is the propensity for gold(I) atoms (Pyykko *et al* 1994; Assmann *et al* 1995; Jones *et al* 1995) to cluster due to the weak bonding interactions between the closed shell metal ions. Numerous gold(I) complexes with metal–metal separations of 2·78 Å to 3·25 Å which are less than the van der Waal's radius for gold are known to exist (Khan *et al* 1988; Nakamoto *et al* 1993; Mingos *et al* 1995). Other studies on multinuclear gold complexes have also shown that these attractive gold(I)–gold(I) interactions persist even in solution (Narayanaswamy *et al* 1993). The strength of gold–gold interactions has been estimated to be around 5–15 kcal/mol (Assefa *et al* 1995).

Fackler and coworkers have synthesized a series of dinuclear bridged complexes and a tetranuclear complex all of them bridged by sulphide ligands (figure 3). These complexes provide an excellent framework for the study of weak metal–metal interactions which are said to be brought about by relativistic contraction of the orbitals on Au. Compound 3·1 [$Au_2(\mu\text{-}S(CH_2)_3S(\mu\text{-dppm})$] (dppm = *bis*(diphenylphosphinomethane)) has a close gold–gold distance of 3·128 Å. While nearly linear S–Au–P angles are observed, the slight deviation (6–10°) from linearity is probably due to the twist of the propylene chain which is needed to maintain gold–gold contacts. This compound is also found to be luminescent under UV radiation. Fackler and others conclude that the presence of attractive M−M interactions is indicated by comparison of the S–S bite distance (4·122 Å) which is considerably longer than the corresponding metal–metal distance (3·128 Å) in the complex. Similarly, the metal–metal distance for complex 3·2, [$Au_2(\mu\text{-}S_2C_2(CN)_2)(PPh_3)_2$] (3·116 Å) is significantly shorter than the corresponding S–S distance (3·490 Å). So also, the S–S distance (3·399 Å) in complex (3·3) [$Au_2(\mu\text{-}S_2C_6H_4)(PPh_3)_2$] is much larger than
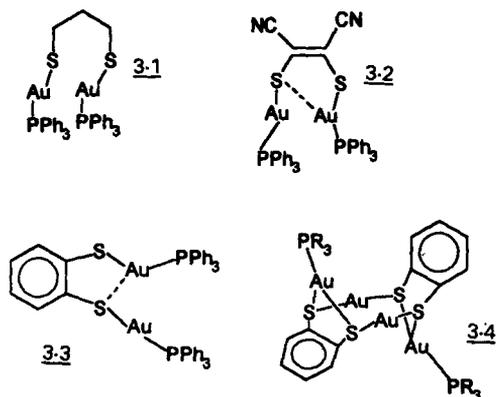

Figure 3. Thiolate bridged gold(I) complexes.

the gold–gold separation of 3·149 Å. These distances are shown in table 1. At first sight, the data would seem to imply the presence of bonding interactions between the metal centres. However, as detailed earlier, concluding that Au–Au interactions are responsible for the shorter metal–metal distances rather than the S–S distances, one could be making a dangerous over-simplification. The geometric bite does not take into account the directionality of the donor orbitals. On the other hand, the true bite requirements of the ligand would be better represented by the electronic bite angles of the ligand.

Again the test electrophile, the proton, was employed to determine the preferred direction of approach of metals of the coordinating atoms of the ligands in the gold complexes. The ideal coordination angles computed for the ligand and for those found in the complex are listed in table 1. A striking difference in the results obtained from the calculations performed on the gold(I) system as compared to those carried out on the copper(I) system is evident from the observed deviations. It may be recalled that in the copper(I) system, the preferred geometry of the protons obtained by MNDO calculations was almost the same as that in which the metals were present. In the case of the gold(I) system, the calculated ideal bite angles of the ligand were in the range of the angles present in the crystal geometry of the complex. However, the ideal dihedral angles calculated by the MNDO method were considerably different from the value observed for the metal in the complex (deviations up to 95° are observed). It is not the bite angle requirements of the ligand that dictate the position of the metals in these complexes! This deviation from the ideal geometry can be explained by the presence of attractive interactions between the gold(I) centres.

Table 1. Reduced overlap populations for gold dimers

Complex	Inter-atomic distances		Reduced overlap populations	
	S–S	Au–Au	Core	Complex
3·1	4·122	3·128	0·027	0·036
3·2	3·490	3·116	0·028	0·015
3·3	3·399	3·149	0·025	0·010
3·4	3·399	3·099	0·029	0·008

Table 2. Observed and calculated ligand bite angles.

Complex	Crystal geometry		MNDO optimised geometry	
	Au–S–C	Au–S–C–C′	H–S–C	H–S–C–C′
3·1	107·3	100·9	98·9	167·4
	104·3	130·0	99·5	170·5
3·2	106·4	6·5	101·8	101·3
	103·9	71·0	99·5	140·9
3·3	107·9	− 2·4	101·9	− 22·8
	99·7	− 85·3	99·0	− 100·7
3·4	106·8	6·1	96·6	66·6
	105·3	54·4	98·4	54·4

EHT calculations were also performed on this system and the reduced overlap populations (ROP) of the core and complex are listed in table 2. Though the values are not large, they do indeed reveal that there are metal–metal interactions. A significant feature is that, in the first case, the ROP values actually increase (≈ 0.01) upon the introduction of the ligand, unlike the other three complexes where there is a decrease (≈ 0.01–0.02) in the ROP values. In the first case, it is possible that this is a case where the ligand has induced metal–metal interaction. The ligand helps in increasing the bonding interactions between the metal centres through 3-centre-2-electron bonding. The ROP values of this complex are significantly higher than the other three complexes even though the metal–metal distances are comparable, which means that there are probably two effects, metal–metal relativistic interactions as well as ligand mediated metal–metal interactions. These two effects act in a concerted fashion to bring about the observed short(I)–Au(I) distances. The potential of the procedure in predicting the presence of metal–metal interactions in d^{10} systems with short metal–metal distances is well illustrated by these studies on gold dithiolate complexes.

2.3 *Ligand induced metal–metal interactions*

The analysis is slightly more complicated in the case of ligands which bridge two metal centres through a single atom. It has been shown for example that a measure of the preferred angle between the donor lone pairs on sulphur could be obtained by placing two protons with various HSH angles about the ligand. Full optimization at the MNDO level of the parameters related to the protons gave an angle of 96° which may be considered to be the ideal M–S–M angle in the absence of additional electronic effects. Examination of the M–S–M bridges characterised to date reveal a rather complex situation. Both acute and obtuse bridges have been observed. In the case of two nearly identical clusters, one had an acute angle and short metal metal distances (Abraham *et al* 1993) and the other had angles close to 90° and longer Cu–Cu distances (Narasimhamurthy *et al* 1989). However in the tetrahedral clusters (Abraham *et al* 1993), it was shown that there was an additional complicating feature. The topology of the Cu_4^+ unit spanned by four 3-atom ligand bridges dictated the presence of acute Cu–S–Cu angles.

To determine the effect of the M–X–M angle on metal–metal interactions, EHT calculations were performed on a single model system with various X^- ligands bridging a Cu_2^{2+} unit. For a given fixed a Cu–Cu distance of 2·8 Å, the system was found to be destabilized on the basis of sum of one-electron energies as the Cu–X–Cu angle was decreased from acute to obtuse angles. This is primarily due to the loss in Cu–X bonding. Interestingly, the Cu–Cu ROP values are higher at more acute angles as given in table 3. For example, for $X^- = RS^-$, the metal–metal ROP is as large as 0·06 at an angle of 65°. However, the value becomes negative, taking a value of -0.01 at 8°, indicating antibonding interactions. Another interesting variation is the extent of antibonding in these complexes which increases with increased π donation by the ligand. Thus reduced overlap populations between the two copper centres are greater when they are bridged by OH^- than when O^{2-} is present as a bridge. A comparison of O^{2-} and S^{2-} suggests that bridging atoms which are larger decrease the M–M interactions more effectively. Furthermore, pure σ donors such as H^- are extremely efficient in increasing the reduced overlap population between the metal centres. The hydride bridge presents a special case as there is no π type of orbital on the bridge and

Table 3. Reduced overlap populations ($\times 10^3$) computed from EHT calculations

Bridge angle	System studied									
	Cu–Cl–Cu		Cu–OH–Cu		Cu–O–Cu		Cu–S–Cu		Cu–H–Cu	
	Cu–Cu	Cu–Cl	Cu–Cu	Cu–OH	Cu–Cu	Cu–O	Cu–Cu	Cu–S	Cu–Cu	Cu–H
82·3	7	437	31	183	25	170	7	598	74	188
80·6	11	411	32	165	27	153	10	572	73	177
78·9	14	386	33	148	29	138	13	545	72	166
77·3	17	360	34	133	31	123	16	519	71	155
75·8	21	336	35	118	32	109	20	493	70	145
74·2	24	311	35	104	33	97	23	467	68	134

reduced overlap populations between two Cu–Cu centres are large even with obtuse angles. Due to the smaller Cu–H distances, the induced Cu–Cu bonding is more effective at short Cu–H distances and obtuse Cu–H–Cu angles. This indeed to be expected from the molecular orbital description of the bonding (*vide infra*). Thus, there is a direct connection between the acute bridging angles and the short metal–metal distances in d^{10} clusters.

The above results are entirely consistent with previous studies (Cui and Kertesz 1990; Alemany and Alvarez 1992; Subramanian and Hoffmann 1992) and can be interpreted in terms of the nature of Cu–X–Cu bonding. In analogy to the bonding patterns in boranes, two extreme descriptions of closed and open C-centre bonding models have been proposed. If the angle at the bridging ligand is acute, a closed 3-centre 2-electron bond is indicated (figure 4). In this arrangement, the metal–metal interaction is attractive. On the other hand, an open 3-centre bond has been invoked for bridges with wider Cu–X–Cu angles. The interaction involves a p type lone pair on X and an antisymmetric combination of metal orbitals. As the overlap becomes more effective, the interaction between the metal atoms becomes correspondingly antibonding. Ligands such as a hydride can only have closed 3-centre 2-electron bonding and hence will result in short Cu–Cu distances. This has indeed been experimentally observed (Ho and Bau 1983, 1984). Increasing the effectiveness of π donation would increase the antibonding interactions between the copper atoms and reduce the ROPs. Thus in most cases both the closed and open bonding interactions are generally possible resulting in the reduced Cu–Cu ROPs with inclusion of ligands.

The importance of ligand induced metal–metal interactions in determining metal–metal separations would be best exposed in systems where ligands are involved in 3-centre 2-electron or orbital-rich bridges. A rather ubiquitous trinuclear fragment $M_3(dppm)_3$ qualifies for this study. Figure 5 gives some of the complexes where $M_3(dppm)_3$ clusters are capped by various bridges. The variation of metal–metal distances with various caps shows how the bridging ligand clearly influences the metal–metal distances. In order to probe if the reduced M–M distances are due to attractive M–M interactions, an EHT study was taken up in the case of the $Cu_3(dppm)_3$ clusters. Some of these clusters are doubly capped (figure 6) and crystallographic results are available for several of them. These complexes synthesized earlier (Diez *et al* 1993) have a basic framework of an isosceles triangle of copper(I) atoms with a dppm ligand bridging each edge to form a roughly planar Cu_3P_6 core. These *triangulo* copper(I) complexes are either mono or bicapped ligands. The bridging acetylide ligand for example, coordinates to the three coppers in an asymmetric $\mu_3\eta^1$ fashion. The monocapped species adopts a bent orientation which notably reduces the formal distance of the acetylene $C\beta$ atom to the Cu_3^{3+} plane. The distance between the coordinating atoms and the coppers are significantly different in each case. The most

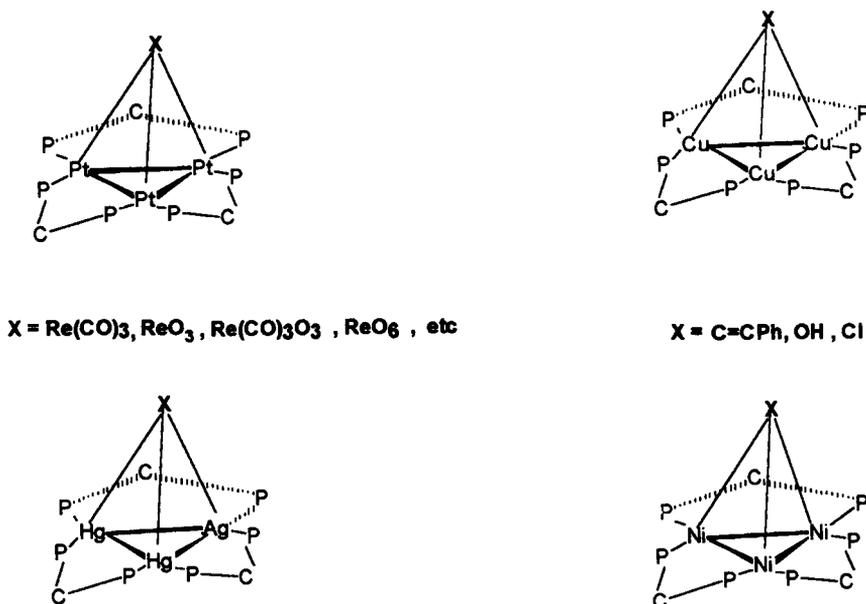**Figure 4.** Three-centre bonding in metal complexes.

X = Re(CO)₃, ReO₃, Re(CO)₃O₃ , ReO₆ , etc

X = C≡CPh, OH , Cl

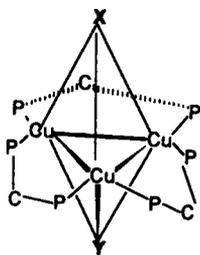**Figure 5.** Triangular clusters bridged by dppm.

Figure 6. Bicapped tricopper clusters.

striking feature is that the monocapped alkynyl complex shows among the three complexes the larger Cu–Cu distances but the shortest Cu–C distance. In contrast the introduction of one additional chloride or acetylide ligand to form a bicapped system leads to the shortening of the copper–copper distance while the copper–carbon distances are increased. The Cu–Cu distances in the bicapped complexes, with two Cl⁻ ligands, and in the one with OH⁻ are the longest. It was precisely this observation that led to the suspicion that this was indeed a case of ligand mediated metal–metal interaction. The bonding in this sytem has been described as a 4c–2e bridge in the case of the monocapped species or a 5c–4e bridge in the case of the bicapped species. In either case, one might expect the outcome of having an orbital-rich situation to be similar to the Cu_2X system.

Table 4. Reduced overlap populations ($\times 10^3$) computed from EHT calculations for triangular copper clusters.

Complex		Reduced overlap populations		
X	Y	Cu–Cu	Cu–X or Cu–Y	Comments
		0·062		ROP of the core
C ≡ C–H		0·071	0·261	Monocapped core
C ≡ C–H		0·069	0·270	Tilted monocapped
C ≡ C–H	C ≡ C–H	0·036	0·240	Dicapped core
C ≡ C–H	C ≡ C–H	0·071	0·170	Dicapped core
CO		0·071	0·250	Monocapped π acceptor
Cl		0·052	0·130	Monocapped π donor
Cl	Cl	− 0·021	0·327	Dicapped core

The results of the EHT calculations are given in table 4. The effect of capping ligands on the bonding interactions in the cluster is probed using a method of analysis similar to the one used for the study on the tetrameric and hexameric copper(I) complexes. In order to have a highly symmetrical system which would make the interpretation of the results less involved, an equilateral triangle of copper atoms was employed in the study. The bridging ligand(s) were placed perpendicular to the plane containing the metal atoms and were bonded to the metal atoms in a symmetrical $\mu_3\eta^1$ fashion. The bridging dppm ligands were not included to help assess the role of only the mono- and bicapped ligands in bringing about metal–metal interactions. All the complexes were modelled using the program Insight II[1]. The interactions between the metal centres placed at a distance of 2·60 Å in the triangulo Cu_3^{3+} core were first computed. One acetylide ligand was then introduced to cap the tricopper plane at a distance of 2·12 Å from it and the Reduced Overlap Populations (ROPs) were then determined. An increase in the ROP (ca. 0·01) reveals that the introduction of the ligand enhances the interaction between the metal centres and is greater than the interactions in the naked Cu_3^{3+} core. When this acetylide ligand was tilted by 10° to the tricopper plane, the metal–ligand interactions increased at the expense of the metal–metal interactions as seen by the decrease in the ROP between the metal centres and an increase in the M–L ROPs. Next, the second ligand was introduced to cap the tricopper plane from below, again at the same distance. Contrary to the expectation based on experimental observation where the copper–copper distances decreased, the introduction of the second ligand actually lowered the ROPs by a factor of 0·02. However, a closer examination of the Cu–C distances in the bicapped cluster shows that the Cu–C distances increased to 2·32 Å making the bridges more acute. When the calculations were repeated at this Cu–C distance of 2·32 Å, the ROPs increased significantly.

Next, the role of the strong π donor ligands in influencing the metal–metal interactions were investigated. When two chlorides were introduced to form the bicapped species, the reduced overlap populations between the metal centres actually became negative, indicating antibonding interactions between the metal centres, that showed bonding interactions for the bicapped acetylide complex at the same metal–metal distances. Similarly the

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OH^- ligand also reduced the metal–metal attractive interactions. Both the OH^- and the Cl^- ligands have π-donor and σ-donor capabilities and they do not help in enhancing metal–metal interactions. If this were to be true, a carbonyl ligand or a hydride which has predominantly sigma bonding properties and π acid properties will promote metal–metal attractive interactions as did the acetylide ligand. This was found to be true with the reduced overlap populations being as high as in the acetylide case. Thus depending upon the π-acceptor and σ-donating capabilities of the ligands, the metal–metal interactions can either be enhanced to have bonding interactions between metal centres or efficiently destroyed to have only antibonding interactions. These results clearly demonstrate how the ligand mediates in bringing about positive interactions between the metal centes.

Synthesis of a complex with a specific capping ligand, however, is not always easy. In fact some of the clusters studied theoretically such as the hydride capped Cu_3 cluster may not be formed for the simple reason that there are not enough electrons for skeletal bonding if one assumes it is a 16-valence electron complex. Skeletal bonding in the case of metals which form 16-valence electron complexes has been worked out (Mingos 1984). The copper cluster requires that there be 48 valence electrons when it is capped on both sides and 46 valence electrons when it is capped on one side. A six-electron donor such as the OH^- leads to an isosceles triangle of copper atoms when it forms a monocapped structure since the electron count indicates a *nido* structure. Attempts to prepare the carbon monoxide capped trimer have not been successful to date (Bera *et al* unpublished work). In retrospect, this is not surprising since CO is a very poor π donor. Preliminary results from an X-ray crystallographic study suggest that the Cu–Cu distances in the $Cu_3(dppm)_3$ core bridged by two aryloxide ligands are in the range predicted by the above analysis (Wycliff *et al*, unpublished results). Further, a planar Cu_4 cluster, bridged by hydrides, appears to have short Cu–Cu distances (Sekhar *et al* unpublished results). Tuning metal–metal distances with ligands indeed appears to be a feasible goal.

Acknowledgements

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