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Ligand orientation effects on metal–metal, ligand–ligand and metal–ligand interactions

Santiago Alvarez *, Ana A. Palacios, Gabriel Aullón

Departament de Química Inorgànica and Centre de Recerca en Química Teòrica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

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Abstract

A number of chemical and physical properties of transition metal complexes can be explained by fundamental chemical criteria such as bond order, electron configuration, ligand or metal electronegativity, or the idealized coordination polyhedron. However, variations in the properties of similar compounds are associated with subtle differences in the spatial arrangement of the ligands, as revealed by combined structural database and molecular orbital studies. Combined theoretical and structural database studies show how

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* Corresponding author. Tel.: +34-93-4907725; fax: +34-93-4409975.
E-mail address: salvarez @kripto.qui.ub.es (S. Alvarez)

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ligand orientation affects the weak magnetic exchange coupling interactions in ligand-bridged binuclear complexes. Metal–ligand and ligand–ligand bonds in M_2X_2 cores of double-bridged binuclear complexes are also sensitive to the relative position of the ligands as seen, among other cases, in the relative stabilities of the oxo and peroxo isomers of the synthetic analogues of oxy-hemocyanin.

Keywords: Structural correlations; Molecular orbitals; Stereochemistry

1. Introduction

In this contribution we review some results of our combined theoretical and structural database studies on the stereochemistry, bonding, and properties of transition metal compounds. By using both theoretical analysis and structural data one can obtain not only a better insight on the properties of particular compounds, but also a wider perspective than can be achieved by using each of these tools separately. While science ultimately relies on experimental facts (read in this case molecular or crystal structure), the use of quantum chemical studies of structure and bonding can be of great help as a complement to the experimental information for several reasons: (a) if properly used, they may be useful to provide explanations for unusual behaviors. (b) Theoretical studies allow one to isolate the effect of different parameters that cannot be separated in the experiment, thus providing hints as to the relative importance of each factor. (c) They can predict experimental trends that had gone unobserved before. (d) As a result, one may decide on interesting new synthetic targets.

There is also a tension between two poles: the quest for accuracy and the need for understanding. The former can nowadays be achieved in most cases through ab initio or density functional calculations if one has some technical background and especially enough computer time available, although for the bigger molecules some models must usually be adopted. Understanding, however, requires the scientist to build explanations based on the fundamental concepts shared by the community of researchers, often more interested in trends than in the accuracy of the results or the technicalities of the calculations.

In the realm of coordination chemistry, the fundamental concepts used to interpret most structural, chemical and physical properties are basically (a) the molecular topology, expressed through the coordination polyhedron, (b) the number of d electrons associated to a particular metal ion, (c) the donor properties of the ligands (hard/soft, π-donor/π-acceptor), and (d) the nature of the transition metal ion (ionization potentials, atomic size). Associated with these are the bonding characteristics of the d orbitals, or the electron counting rules so useful in organometallic or cluster chemistry. The aim of the present contribution is to offer a few examples of how an often neglected factor, the spatial orientation of the ligands, may be crucial in determining the chemical and physical properties of coordination compounds. Experimentally, one can in some way tailor the spatial arrangement of the ligands by introducing substituents, changing the size of some atoms (hence the bond lengths), or constraining the conformation by using bidentate or macrocyclic ligands. In theoretical studies one can mimic such effects in simplified model compounds by imposing on the ligands a particular orientation, even if it does not correspond to the calculated energy minimum. An account of the conceptual framework for the structure correlation analysis has been published by Bürgi and Dunitz [1]. Most of the structural correlation studies in the field of coordination chemistry have dealt with the rearrangement of the coordination sphere, as in the Berry pseudorotation interconversion of ML_5 complexes [2], or with rearrangements of the metallic skeleton of clusters [3], but not with the mutual influence of coordination sphere rearrangement and metal–metal, metal–ligand or ligand–ligand interactions.

In modeling *complicated* ligands such as ethylenediamine, cyclam or triphenylphosphine with simpler ones, such as NH_3 or PH_3, one must be conscious that the electronic structure of the real molecule is best represented by a molecular geometry of the model molecule which does not necessarily correspond to its energy minimum and may even be a high energy form of the model compound. Consider the case of ethylenediamine. When coordinated to first row transition metal atoms in octahedral complexes, the average N–M–N bond angle within the chelate ring is 84.7° (value obtained from 747 independent rings of 364 compounds). In the analogous NH_3 complexes, the average *cis* N–M–N bond angle is 90.0° (value obtained from 430 independent pairs of NH_3 ligands in 68 compounds). Clearly, any quantum chemical calculation that puts two ammonia ligands at 85° will give a higher energy than at 90°, yet the first geometry would best represent the electronic structure of the ethylenediamine compound. But not all models have such a clear energetic effect. In many instances, the theoretical molecule can be taken away from the optimum structure by weak *packing* forces, such as interactions with counterions, intra- or intermolecular hydrogen bonds, or even steric repulsions between the real ligands. In all these situations, the use of an idealized molecule can offer highly useful information on a family of related compounds with a variety of substituents or ligand constraints, provided one explores those parts of the potential energy surface away from the minimum that are likely to become thermally accessible by the effect of the neglected substituents.

Two main topics are covered by this review, the ligand orientation effect on the spin coupling in binuclear complexes (often referred to as magneto-structural correlations), and the relationship between ligand orientation and through-ring bonding in double-bridged complexes with M_2X_2 core. Other ligand orientation effects studied by us that will not be discussed here include those in small carbonyl clusters of the iron group [4,5], the reorientation of the coordination sphere that accompanies dimerization of copper(I) linear complexes [6], and the stereo-electronic effects associated with orientation of the ligands in tricoordinate amido complexes [7].

2. Some magneto-structural correlations

It has long been recognized [8,9] that some structural parameters can be held responsible for the varying degree of magnetic coupling between paramagnetic centers in binuclear compounds. For a magneto-structural correlation to be established from experimental information, one needs to synthesize a relatively large number of compounds, solve their crystal structures if good quality crystals can be obtained, and measure the temperature dependence of their magnetic susceptibilities. The compounds must belong to the same family, but at the same time must be different enough as to present sizable differences in their structural parameters and magnetic behavior. In this way, one needs not only good experimental skills, but time (probably a few years) and good luck to establish a new magneto-structural correlation. It is thus no surprise that the theoretical study of the exchange coupling problem has been seen with much interest by coordination chemists.

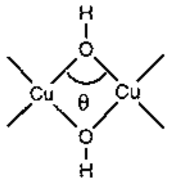
Given the computational limitations that made binuclear transition metal complexes untractable by ab initio calculations until recently, the qualitative model of Hay, Thibeault and Hoffmann has been widely exploited [10–15]. In essence, the exchange coupling constant is decomposed as a sum of a ferromagnetic and an antiferromagnetic contribution. For the simple case of two unpaired electrons, the coupling constant measures the difference in energy between the singlet and triplet states and can be approximated by Eq. (1), where the ferromagnetic term depends on a two-electron exchange integral (K_{ab}), and the antiferromagnetic term depends on the square of the gap between the two single-occupied molecular orbitals (SOMOs), and on the inverse of a two-electron term ($J_{aa} - J_{ab}$):

$$E_S - E_T = J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{J_{aa} - J_{ab}} \tag{1}$$

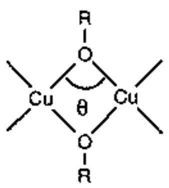
By assuming that the two-electron terms remain approximately constant within a family of similar compounds, one can associate the variations of the coupling constant with a particular structural parameter by just looking at the dependence of the energy gap on that structural parameter. In this way, Hay, Thibeault and Hoffmann were able to explain the variation of J with the ring angle θ in the family of hydroxo-bridged Cu(II) complexes (**2a**). Although such analysis explains the main trend, that the coupling constant becomes more antiferromagnetic as θ increases, a ligand orientation effect was not detected, which was also neglected in the analysis of the structural data.

Recently we have reported density functional calculations that reproduce to a good approximation the experimental coupling constants for binuclear complexes [16–20]. When attempting to reproduce the experimental values for hydroxo- and alkoxo-bridged complexes, it was found that the calculated J was far away from the experimental values for small angles: those compounds with $\theta \approx 96°$ were predicted to be antiferromagnetic ($J \approx -200$ cm^{-1}), in contradiction with quite strong ferromagnetic behavior experimentally found (Fig. 1). If the position of the substituent in the OR bridges is varied, though, two important effects are found: (a) the value of θ is correlated to the degree of out of plane displacement of the substituent (τ), and (b) a more positive value of J results, yielding calculated values in excellent agreement with experimental ones [16]. Since the bridging hydroxo groups are often involved in hydrogen bonding with the counterions, it was deduced that these affect the value of τ, hence the ring angle θ, and ultimately determine the value of the magnetic exchange constant. Interestingly, the families of end-on azido-bridged complexes of Cu(II), Ni(II) and Mn(II) [19], show a similar dependence of J on θ, but are practically insensitive to the out of plane displacement of the bridging N_3 ligands.

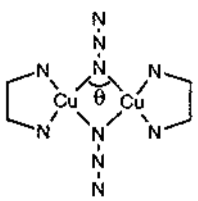
Other ligand orientation effects on the exchange interaction will not be discussed in detail here, but we summarize the essential data in Fig. 2. There, we show the values of $(\varepsilon_1 - \varepsilon_2)^2$ that are obtained by some structural variation for different families of binuclear Cu(II) compounds (indicated in **2a**–**2f**), and represent the calculated values of J as a function of that parameter.



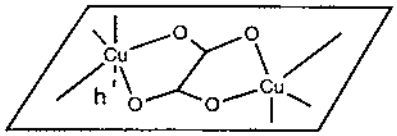
2a



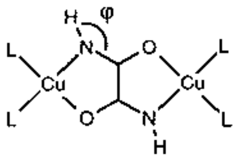
2b



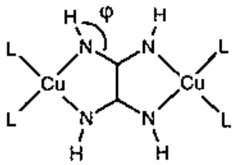
2c



2d



2e



2f

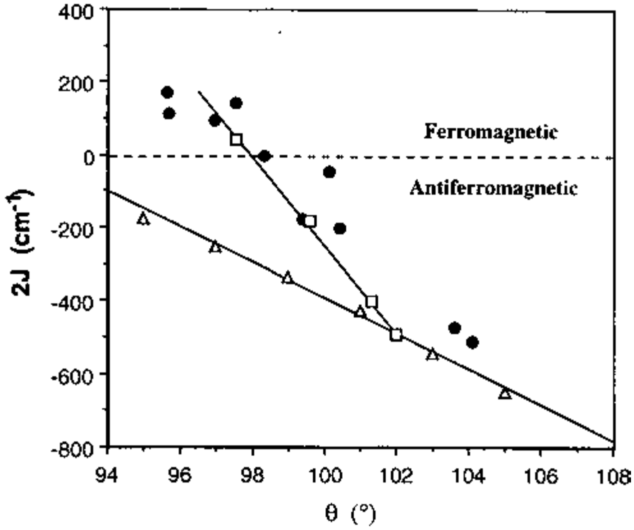


Fig. 1. Exchange coupling constant calculated for hydroxo-bridged Cu(II) complexes as a function of the Cu–O–Cu bond angle (θ), with the hydrogen atom in the Cu_2O_2 plane (triangles), and with θ optimized for different out of plane angles (white squares). The black circles represent the experimental data. Adapted from Ref. [16].

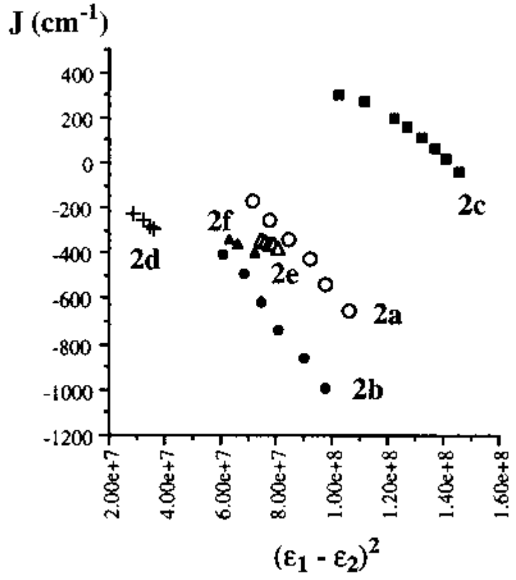


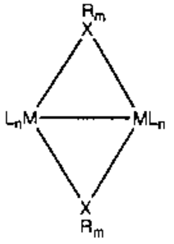
Fig. 2. Calculated exchange coupling constants for the bridged Cu(II) binuclear complexes **2a**–**2f**, represented as a function of the energy gap between the two SOMOs calculated varying the structural parameter indicated in **2a**–**2f**.

At first sight one can distinguish that there are two groups of compounds: those with a polyatomic bridge, such as oxalate, and those with a monoatomic bridge, such as hydroxide. In the first case, the orbital gap can be only slightly modified with the studied variations of ligand orientation. Consequently, the values of J vary within a narrow range for these compounds. Conversely, for the monoatomic-bridged systems, the structural variations induce large changes in the orbital gap and correspondingly large variations in the J values. Another interesting conclusion that can be drawn from Fig. 2 is that the different magnetic behavior of the hydroxo- and azido-bridged complexes cannot be attributed to structural effects and the corresponding changes in orbital energies, but stems from different two-electron exchange interactions.

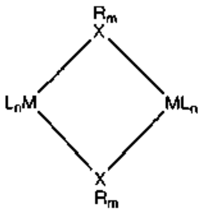
3. Forming and breaking bonds across a ring

3.1. Framework orbitals and electrons

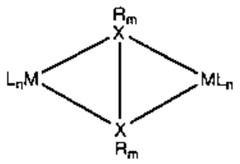
There is an intriguing problem in the structural chemistry of the late transition elements. When these metals form double-bridged binuclear complexes of general formula $[M_2(\mu\text{-}XR_m)_2L_{2n}]$ they may appear in any of three different isomeric forms, **3a**–**3c**.



3a



3b



3c

In general, structure **3b** should be expected [21,22] whenever the number of electrons available for M–X bonding (i.e. the framework electron count, or FEC) is eight. But when fewer framework electrons are available (six or four), structures with either an M–M (**3a**) or an X–X (**3c**) bond across a the M_2X_2 ring is to be expected.

In counting framework electrons, one has to adopt some convention, namely that each ML_n fragment is an electronically saturated group able to act as a four electron acceptor toward the two bridging ligands. Thus, for a tetrahedral coordination sphere around a metal atom, a d^{10} electron configuration is assumed, consistent with the 18-electron rule. For a square planar coordination sphere, on the other hand, the appropriate electron configuration is d^8, according to the 16-electron rule. In that way, all the electrons participating in framework bonding are provided by the bridging atoms (disregarding those involved in X–R bonding or in the outwards-pointing lone pairs) together with any extra electrons required by the molecular charge. Notice that for such compounds different molecular structures may appear depending on how the valence electrons are distributed between the non-bonding metal d orbitals and the framework molecular orbitals. Furthermore, it will be shown in this section that important ligand orientation changes are associated with the different structures of the M_2X_2 frameworks. Conversely, adequate manipulation of the topology of the coordination sphere, e.g. through ligand design, should allow one to control both the thermodynamics and the kinetics of the isomerization process.

3.2. Rhodium–rhodium bonds in phosphido bridged complexes

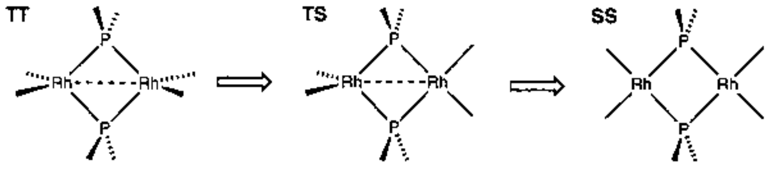
As a first example we focus on the compounds such as $[Rh_2(\mu\text{-}PR_2)_2(CO)_4]$ and their isoelectronic analogues, whose most relevant structural data are collected in Table 1, [36–44]. Counting the electrons assigned to the metal d orbitals and those contributed by the bridging ligands, the overall number of valence electrons (VE) for these complexes is 24. Similar compounds with 20–22 electrons and short metal–metal distances across the ring (**3a**) are also known [23–33] and a reduced species, $[Rh_2(\mu\text{-}PR_2)_2(CO)_4]^{2-}$, with 26 VE has also been reported [34]. For the time being, we focus only on the 24 VE systems and will briefly comment on the 20–22 VE compounds later. A detailed theoretical study was reported by Albright et al. [35], and a thorough discussion of the qualitative aspects of the bonding in the M_2X_2 framework was presented by Alemany [21] and Aullón [22]. The reader may have already noticed that there is an ambiguity in the definition of the FEC for those compounds, since one must first decide whether to consider tetrahedral or square planar RhX_2L_2 coordination spheres. Let us then analyze the three different ways in which the orientation of the terminal ligands can be found (**3d**): two tetrahedral metal atoms (abbreviated TT), one tetrahedral and one square planar metal atom (TS), and two square planar metal atoms (SS).

Table 1
Some binuclear compounds of the type $[M_2(\mu\text{-}XR_2)L_4]$[a] with 24 valence electrons

	M–M	Δ_{MM}	α_1	α_2	Structure[b]	Refcode	Ref.
$[Fe_2(\mu\text{-}P\{CF_3\}_2)_2(NO)_4]$	2.747	0.07	122	122	TT	fmpnfe	[36]
$[Fe_2(\mu\text{-}PMe_2)_2(NO)_4]$	2.712	0.03	123	126	TT	mpntfe	[37]
$[Fe_2(\mu\text{-}PPh_2)_2(NO)_4]$	2.711	0.03	122	122	TT	ppntfe	[37]
	2.689	0.01	125	125	TT		
$[Ru_2(\mu\text{-}PPh_2)_2(NO)_2(PPh_2Me)_2]$	2.628	−0.17	98	98	TT	dpprun10	[38]
$[Co_2(\mu\text{-}PMe_2)_2(PMe_3)_4]$	2.360	−0.30	99	99	TT	jaklow	[39]
$[Rh_2(\mu\text{-}P^tBu_2)_2(CO)_2(PMe_3)_2]$	2.555	−0.35	85	85	TT	cecsei	[40]
$[Rh_2(\mu\text{-}P^tBu_2)_2(CO)_4]$ (triclinic)	2.748	−0.15	110	91	TS	cabdue01	[41]
$[Rh_2(\mu\text{-}P^tBu_2)_2(CO)_4]$ (monoclinic)	2.761	−0.14	112	89	TS	cabdue	[42]
$[Rh_2(\mu\text{-}P^tBu_2)_2(CO)_4]$	3.717	0.82	90	90	SS	cabfam	[42]
$[Rh_2(\mu\text{-}As^tBu_2)_2(CO)_4]$	3.884	0.98	93	93	SS	daslak10	[43]
$[Ir_2(\mu\text{-}As^tBu_2)_2(CO)_4]$	3.895	1.26	93	93	SS	fuphed	[44]

[a] Δ_{MM} is the difference between the M–M distance and the sum of the atomic radii; α_1 and α_2 are the L–M–L bond angles for the two metal atoms. All distances (Å), angles (°).

[b] Coordination geometry of each transition metal atom (T, tetrahedral; S, square planar; see **3d**).



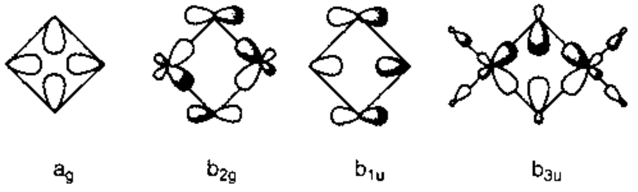
	TT	TS	SS
FEC =	4	6	8
Metal configuration	d^{10}/d^{10}	d^{10}/d^{8}	d^{8}/d^{8}
Bridge	R_2P^+	R_2P	R_2P^-

3d

With the electron counting convention just discussed, we assign a d^{10} electron configuration to each metal atom in the TT structure. This would leave positively charged R_2P^+ bridges, but this is only for electron counting purposes with no implications whatsoever for the oxidation states and charge distributions. Each R_2P^+ group contributes two electrons to the framework bonding, resulting in a total FEC of four and an expected short M–M distance across the ring. To allow for comparison of compounds with different metal atoms, we define Δ_{MM} as the difference between the experimental M–M distance and the sum of the atomic radii (Table 1). A look at the values of this parameter shows that all the TT isomers present M–M distances roughly equal to or shorter than the sum of the atomic radii.

For the TS structure, the tetrahedral metal atom should be assigned a d^{10} and the square planar metal a d^8 configuration, leaving six framework electrons. Again, one should expect a short M–M distance, if somewhat longer than for the analogous TT isomers (with FEC = 4), as actually found in the structural data of Table 1. Finally, the two metal atoms in the SS structure should be ascribed a d^8 configuration, leaving a FEC of eight, for which a square framework with no through-ring bonding is predicted, in excellent agreement with the experimental data.

In summary, the rotation of the terminal ligands results in the formation or cleavage of the through-ring M–M bond. Such geometrical rearrangement is associated with an electron drift indicated by the formal attribution of a d^{10} or d^8 configuration to the metal atoms, and can be easily described in terms of the framework molecular orbitals. For an SS isomer there are two groups of molecular orbitals (MOs) which are relevant for the present discussion. On one hand there are four non bonding MOs per metal atom [45] with major contributions from the metal d orbitals, which we represent in Fig. 3 as a d-block.



3e

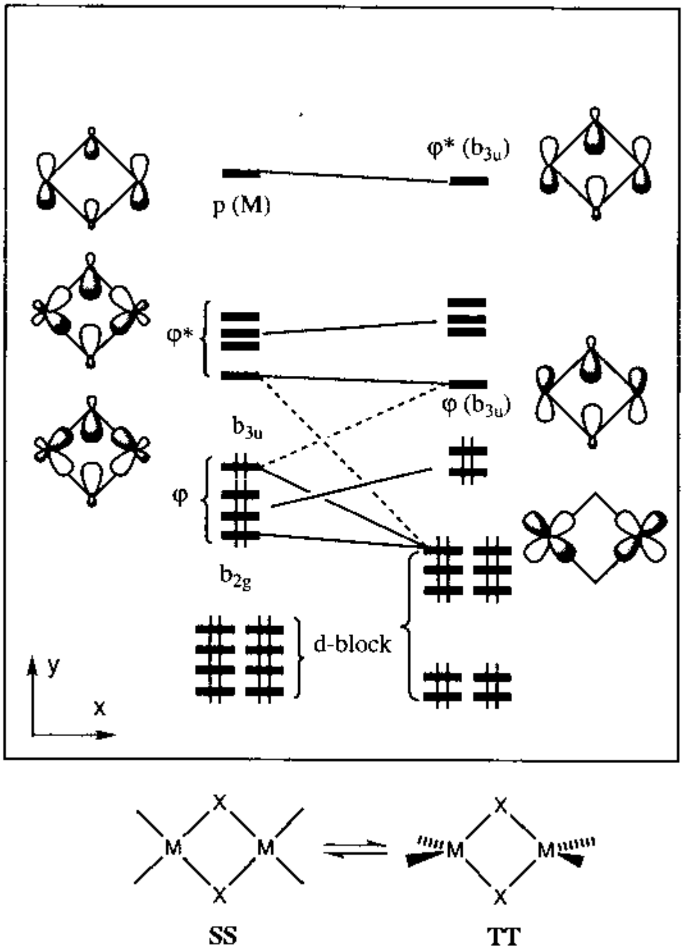


Fig. 3. Qualitative correlation diagram for the d-block and framework (φ and φ*) orbitals of a $[M_2(\mu\text{-}XR_m)_2L_4]$ complex in the TT and SS structures (see **3d**). The orbital occupation shown corresponds to, e.g. M = Rh, $XR_m = PR_2$, and L = neutral ligand.

On the other hand, there are four framework bonding MOs (labeled φ from here on), sketched in **3e**, two of which (b_{2g} and b_{3u}) have major contributions from the high-lying d_{xy} orbitals (with M–L σ* character). The four corresponding M–X antibonding combinations (φ*) appear at higher energies and are empty. The main effect of the rotation of the terminal ligands on such orbitals is that the antibonding interaction with those ligands is lost (**3f**) and the d_{xy} orbitals become mostly localized at the metal atoms, as depicted in Fig. 3 for b_{3u}.

3f

3g

In this situation, sp^3 hybrid orbitals of the metal atoms combine with the orbitals of the bridging ligands to form the corresponding φ and φ^* orbitals. But the net effect of the SS $\rightleftarrows$ TT conversion is that four electrons occupying framework bonding orbitals in the SS form become localized in metal d orbitals in the TT form, with the corresponding change in metal electron configuration (from d^8 to d^{10} at both metal atoms) and in framework electron count (FEC = 8 to 4). Once one is left with only four framework electrons, the squeezing of the ring with a resulting X–X or M–M short distance is favored [21,22]. In this case, the short M–M distance is most favored because the metal–metal π^* character of the now localized d_{xy} orbitals can be minimized by hybridizing them as sketched in **3g**. The changes in the localization of the occupied molecular orbitals when going from the TT to the TS and SS structures and the associated geometry changes can be formally described by the electron configurations given in **3d**, although one should be careful not to ascribe much physical significance to those formal charges.

Associated with the rotation of the terminal ligands is an opening of the L–M–L bond angles, since in the square planar geometry these should be close to 90°, whereas bond angles close to 109° should be expected for a tetrahedral coordination sphere. Such qualitative trends are clearly encountered in the structural data (Table 1), where the bond angles are smaller than 93° for all square planar metal atoms and larger than 98° for practically all tetrahedral metal atoms. The exception corresponds to $[Rh_2(\mu\text{-}P^tBu_2)_2(CO)_2(PMe_3)_2]$, in which the Rh atoms are tetrahedrally coordinated but with quite small L–M–L bond angles. Such behavior should undoubtedly be attributed to the important steric interactions between the bridging and terminal phosphine ligands. As a corollary, these data suggest that the control of the L–M–L angle (e.g. by using bidentate terminal ligands or by modulating steric or chemical interactions between terminal and bridging ligands) might provide an excellent way to favor tetrahedral or square planar coordination, hence induce at will the presence of a short metal–metal distance.

3.3. Ligand–ligand bonds: electron localization or delocalization

After discussing the case in which the orientation of the terminal ligands is associated with the existence or not of through-ring metal–metal bonding, let us focus on two different groups of compounds in which isomers with or without ligand–ligand bonds can appear. The changes in electronic structure associated with the **3a** $\rightleftarrows$ **3b** $\rightleftarrows$ **3c** isomerization processes will be described first in a general way with the aid of a simplified orbital model [22,46]. Then, the experimental and theoretical data for the two families of compounds will be presented and discussed in the light of the qualitative bonding model.

The framework bonding in the M_2X_2 rings can be described as discussed above by four MOs with M–X bonding character and their four antibonding counterparts. Although the contribution of the metal atoms to the b_{3u} and b_{2g} MOs may be mostly of d character for square planar or octahedrally coordinated metal atoms, and essentially of p character for tetrahedrally coordinated metal atoms, we will focus in what follows only in the former case. For a ‘regular’ framework with no short distance across the ring, the topologies of the framework bonding orbitals are those shown in Fig. 4. If the ring is distorted by approaching the two bridging atoms, the b_{3u} orbitals are recombined, thus accumulating the σ^*(X–X) character in the empty MO and the d_{xy} character in the occupied MO (Fig. 4, right). In a similar way, the bonding $\varphi(b_{2g})$ orbital is destabilized due to the enhanced π^*(X–X) interaction and recombines with $\varphi^*(b_{2g})$ finally giving localized π^*(X–X) and $(d_{xy} + d'_{xy})$ orbitals. It is important to stress two aspects of such an orbital picture which can be summarized by the electron configuration changes indicated in **3h**.

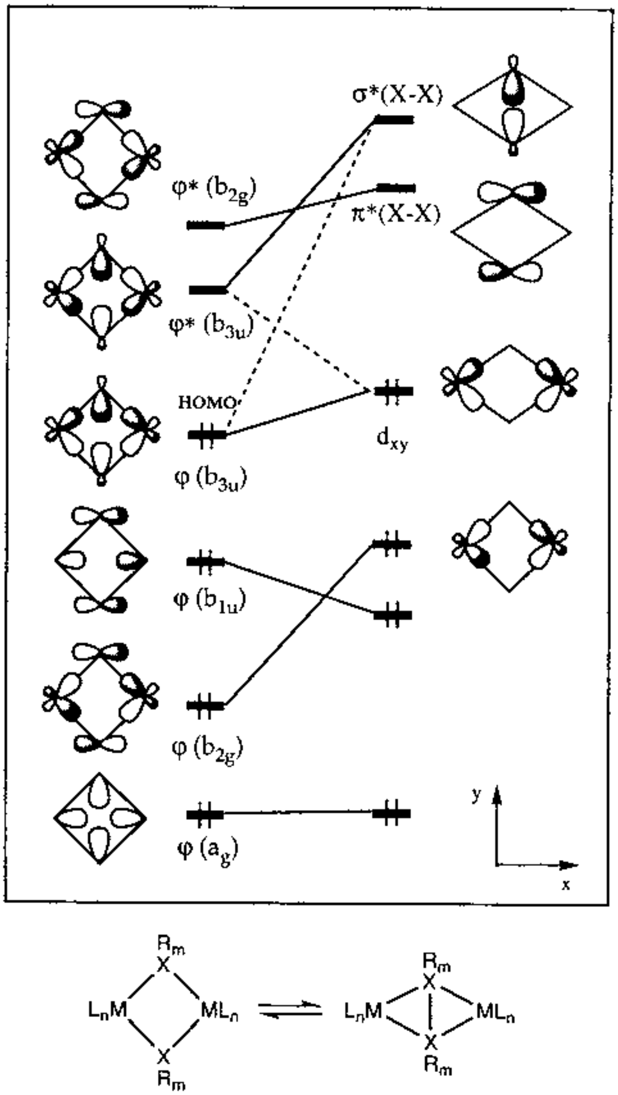
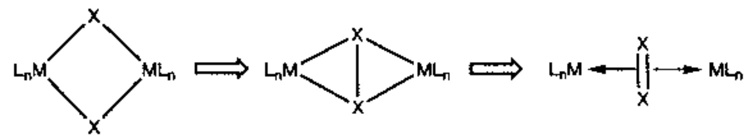


Fig. 4. Simplified orbital correlation diagram for an M_2X_2 ring in its two isomeric forms without and with through-ring X–X bond. Adapted from Ref. [46].



FEC =	8	6	4
Metal configuration	d^n	d^{n+1}	d^{n+2}
Bridge	X^{x-}	$(X_2)^{2-x}$	$(X_2)^{4-x}$

3h

On one hand, there is an increase by two in the number of electrons that can be formally attributed to the d orbitals of each metal atom. On the other hand, given the σ(X–X) and π(X–X) nature of $\varphi(a_g)$ and $\varphi(b_{1u})$, respectively, the X–X interaction can formally be described as a double bond. In that case, the only donor-acceptor interactions left between the $R_mX{=}XR_m$ group and the ML_n fragments are those corresponding to the $\varphi(a_g)$ and $\varphi(b_{1u})$ orbitals. This means that each metal atom is now accepting only one electron pair, and the bonding is best described as an μ-η^2:η^2 coordination of the double bond to the two metal atoms, a result that is crucial for the understanding of the structural aspects to be discussed below. Of course, one can imagine an intermediate situation in which $\varphi(b_{2g})$ still retains a significant part of its delocalization, resulting in an electron configuration $\varphi(a_g)^2\varphi(b_{2g})^2\varphi(b_{1u})^2(d_{xy}-d'_{xy})^2$, with a formal transfer of two electrons from the framework to the metal atoms. In the other direction, extrapolation to the extreme case in which a double X=X bond is formed and the ring dissociates would result in an $R_mX{=}XR_m$ molecule and two reduced ML_n fragments (**3h**).

3.4. Chalcogen–chalcogen bonds in palladium and platinum complexes

Let us now apply such concepts to the specific system $[M_2(\mu\text{-}X)_2L_4]$, with M = Pd or Pt; X = S, Se, Te. In these compounds, the d^8 transition metal ions have approximately square planar coordination. We will focus on two structural parameters, the L–M–L bond angle and the difference between the through-ring X–X distance and twice the atomic radius of X, represented by Δ_{XX}. Although this is so far a small family, there are known examples of compounds with two independent X^{2-} bridges and with one X_2 bridge (which can in principle be considered either as X_2 or X_2^{2-}) coordinated in a μ-η^2:η^2 mode (Table 2). According to the orbital picture discussed above, two extreme bonding situations can be envisaged for such compounds (**3h**). On one hand, the long X–X distances would be consistent with a d^8 metal configuration and a square planar coordination sphere, for which L–M–L bond angles close to 90° should be expected. On the other hand, the other extreme would correspond to a d^{10} metal configuration and a planar trigonal coordination

Table 2
Structural data for compounds of the type [$L_2M(\mu\text{-}X)_2ML_2$], with M = Pd, Pt; X = S, Se or Te[a]

M	X	L_2	β	Δ_{XX}	Ref.
Experimental data					
Pd	Te	$(PEt_3)_2$	108	0.07	[47]
Pt	S	$(PpyPh_2)_2$	103	0.96	[49]
Pt	S	dppe	86	1.10	[50]
Pt	Se	$(PPh_3)_2$	100	0.70	[51]
Pt	Te	$(PEt_3)_2$	106	0.32	[48]
Pt	Te	$(PPh_3)_2$	100	0.32	[52]
Pt	Te	dppe	86	0.53	[53]
Au	Se	$(Se_4)^{2-}$	100	0.81	[54]
Theoretical Results					
Pd	S	$(PH_3)_2$	112	0.17	[55]
Pd	S	$(PH_3)_2$	106	1.09	"
Pt	S	$(PH_3)_2$	103	1.18	"
Pd	Te	$(PH_3)_2$	102	0.22	"
Pd	S	dpe	88	1.18	"
Pd	S	dpe	88	0.20	"
Pt	S	dpe	88	1.22	"

[a] β is the LML bond angle, Δ_{XX} is the difference between the X–X distance and the atomic radii sum.

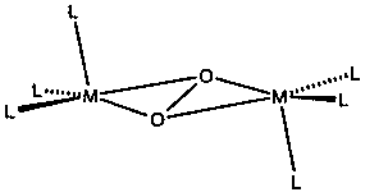
sphere for which larger L–M–L bond angles (close to 120°) should be expected. Although this is a naïve description and one should not expect to find bond angles in agreement with the numerical values quoted, the qualitative aspect of such picture should still be valid. Thus, other things being equal, a larger L–M–L bond angle should appear for the molecule with an X–X bond than for that with isolated X^{2-} ions.

Although there are not many structurally characterized compounds of this family, one can find examples of both situations, as shown in Table 2. For the Te-bridged palladium compounds, for instance, one finds relatively large bond angles associated with Te–Te distances within a 11% of the atomic radii sum. Apparently, the geometric preferences change from Pd to Pt, since a smaller LML bond angle in the analogous platinum compound yields a similar Te–Te bond distance. The fact that a similar Se-bridged compound of platinum shows a long Se–Se distance with the same L–M–L angle is probably also due to the different effect of that angle on different bridging atoms. This can be seen by comparing the series of analogous platinum compounds with S, Se or Te as bridging atoms, although further structural data would be desirable before having definitive conclusions. Finally, it is worthy of note that the chelating phosphine dppe that imposes a small bond angle results in the only known compound with a Te–Te distance in clear excess (more than 20%) of the atomic radii sum.

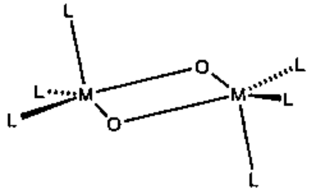
Theoretical studies [55] confirm the trends suggested by the small set of experimental data. Thus, one can see that the energy minimum found for the sulfur-bridged Pd model complex with a large P–Pd–P angle presents a S–S bond, whereas another minimum was found with a smaller bond angle and a long S–S distance. Although in the latter structure the molecule was found to be bent around the S–S hinge, this distortion does not affect the bonding within the Pd_2S_2 framework, and a discussion on the factors that affect bending can be found elsewhere [56,57]. For the analogous Pt complex, the only minimum found in the potential energy surface is similar to that for Pd with the smaller angle. In the analogous model complex with the dpe ligand, the bond angle is imposed by the chelating nature of the ligand. Although two energy minima were found with the same P–Pd–P bond angle, one with a short and one with a long S–S distance, the former is found to be about 11 kcal mol^{-1} less stable, in agreement with the prediction that smaller angles should favor the square planar coordination provided by two independent bridges. This trend becomes clearer for Pt, for which only one minimum with a long S–S distance was found with the dpe ligand.

3.5. Oxygen–oxygen and sulfur–sulfur bonds in copper complexes

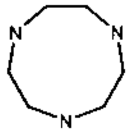
Another interesting family of compounds for which isomers with or without through-ring bonds can be found is that of the synthetic analogues of oxyhemocyanin (**3i** and **3j**), in which the peripheral coordination positions are occupied by the donor atoms of tridentate ligands such as tris(3,5-dialkylpyrazolyl)borate(1-), ^{R}TPB, or 1,4,7-trialkyl-1,4,7-triazacyclononane, ^{R}TACN.



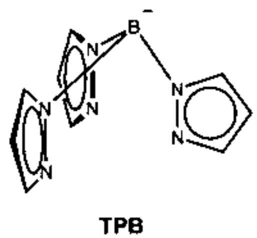
3i



3j



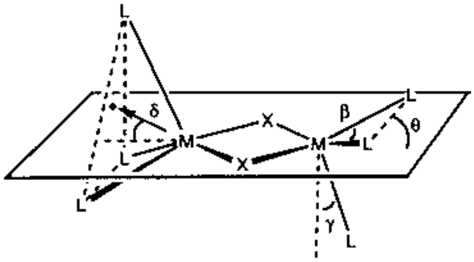
TACN



TPB

The interested reader may find more information on structural aspects and on the chemical and spectroscopic properties of the copper–oxygen systems in excellent recent reviews [58–61]. For the present discussion let us just stress that when the terminal ligand is $^{i\text{-}Pr}$TPB, only the peroxo isomer **3i** is identified [62], whereas for $L_3 = {}^{Bz}$TACN the two isomers exist in equilibrium [63,64].

To understand the different behavior of the systems with these two ligands one has to define in a simplified way the spatial distribution of the terminal donor atoms. Several structural parameters vary from one structure to another, such as the Cu–N distances, or the bond angles defined in **3k** as β, θ and γ.



3k

However, we choose to summarize the overall structural differences by the orientation of the axis of the CuN_3 pyramid relative to the M_2X_2 plane, defined by the angle δ, and by the sum of the three N–Cu–N bond angles, Σ. We consider three ideal situations summarized at the top of Table 3. For an ideal vacant octahedral coordination geometry around each metal atom, the L–M–L bond angles should be close to 90°, δ is expected to be 35° (if the three M–L bond distances are the

Table 3
Structural data for compounds of the type $[L_3M(\mu\text{-}X)_2ML_3]$, with M = Cu, Ni; X = O, S, Se or Te[a]

M	X	L_3[b]	β	δ	Σ	Δ_{XX}	Ref.
Ideal geometries							
Tetrahedral			109.5	0	328	Small	
Vacant octahedron			90	>35	270	Large	
Square planar			90	90		Large	
Experimental data							
Cu		Hc			352		
Cu	O	oxy-Hc	96	12	319	0.0	[65]
Cu	O	$^{i\text{-}Pr}$TPB	93	17	268	0.05	[62]
Cu	O	^{Bz}TACN	89	27	257	0.93	[63,64]
Cu	S	$^{i\text{-}Pr}$TPB	93	19	273	0.03	[66]
Ni	S	TPPE	92	3	279	0.17	[67]
Ni	Te	TPPE	94	2	287	0.36	[68]
Theoretical results							
Cu	O	$(NH_3)_3$	104	19	313	0.16	[46]
Cu	O	$(NH_3)_3$	99	29	289	0.93	“
Cu	S	$(NH_3)_3$	102	16	289	0.29	“

[a] For the definition of β and δ see **3k**. Δ_{XX} is the difference between the X–X distance and the atomic radii sum.

[b] Hc, hemocyanin; $^{i\text{-}Pr}$TPB, tris(3,5-diisopropylpyrazolyl)borate; ^{Bz}TACN, 1,4,7-tribenzyl-1,4,7-triazacyclononane; TPPE, 1,1,1-tris(diphenyl-phosphinomethyl)-ethane.

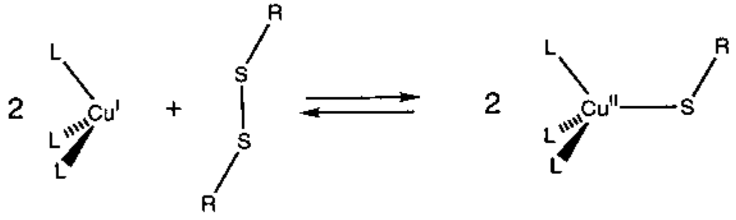
same) or larger (when the axial M–L distance is longer than the basal ones), and Σ should be around 270°. For that coordination geometry, one needs the two X bridges to act as independent donors (i.e. Δ_{XX} must be large). A square planar coordination would correspond to a distorted vacant octahedral geometry with the axial ligand at a very long distance, and the expected parameters are given in Table 3. Alternatively, for a tetrahedral coordination around each metal atom, and considering the X_2 group as an η^2 ligand, the bond angles should be expected to be close to 109°, the axis of the CuN_3 pyramid should be colinear with the M–M vector (i.e. $\delta = 0°$), and the sum of the N–Cu–N bond angles (Σ) should be around 328°. In such case, the X–X distance is expected to be close to the sum of the atomic radii, hence Δ_{XX} must have a small value.

The analysis of the experimental structural data for the copper–oxygen systems (Table 3) clearly shows the expected qualitative trend, with the oxo-bridged isomer **3j** (large Δ_{XX} values) being favored for the smaller values of β, relatively large values of δ, and Σ smaller than 260°. The theoretical data for the two minima of a model copper oxygen system [46] in which $L = NH_3$, show the same trends, even if the actual values of the structural parameters β and Σ differ from the experimental ones. Other theoretical studies have been devoted to the copper–oxygen systems [69–71] but structural data needed for the calculation of δ are not available and have not been included in Table 3. A structural database study carried out with the help of the Cambridge Structural Database [72] has shown that the TACN ligands are stiffer than the TPB ones, explaining why the latter adapt best to the larger bond angles required by the peroxo-bridged form. As an example, the values of Σ for Cu complexes with TACN ligands appear in the range 242–262°, with a mean of 251°, whereas with TPB ligands the same parameter is found in the range 255–289°, with a mean of 271°.

The same type of behavior can be found in *S*-bridged complexes. For the case of Cu, our model theoretical study [46] predicted an S–S bond ($\Delta_{SS} = 0.29$ Å) associated with angular parameters $\beta = 102°$, $\delta = 16°$ and $\Sigma = 289°$. Although in a Cu compound with the TPB ligand the experimental β angle is 93°, its geometry is still close to a pseudotetrahedral one with an apical η^2 diatomic bridging ligand, as indicated by a δ angle of 19°, $\Sigma = 273°$ and a short S–S distance ($\Delta_{SS} = 0.03$ Å). Similar behavior can be found in the related Ni complexes with a tridentate phosphine and S or Te as bridges, in which small δ values are associated with short S–S or Te–Te distances. In brief, both the experimental and theoretical data consistently show that the coordination sphere around each metal atom can be described as tetrahedral when there is a short X–X distance (considering X_2 as an η^2 ligand), and as vacant octahedral when there is no through ring X–X bond.

Recently, Tolman et al. [73] have obtained similar compounds with 1,4,7-trialkyl-1,4,7-triazacyclodecane ligands, ^{R}TACD. The different geometrical constraints imposed by the $^{i\text{-}Pr}$TACD ligand as compared to ^{Bz}TACN results in the existence of only the peroxo isomer **3h** in the former case. Moreover, the ^{Me}TACN ligand results in the formation of the two isomers, suggesting that steric effects also have a say on the relative stabilities of the two isomeric forms.

Along the same line, Lledós et al. [74] have carried out a theoretical study of the relative stability of the Cu(II) thiolato complexes and the formation of a disulfide and Cu(I) by performing density functional calculations on [CuL_3SMe] ($L_3 =$ $(NH_3)_3$, TPB or TACN). The decomposition of the Cu(II) derivatives was found to be strongly ligand-dependent. Hence for the three ligand sets studied, the enthalpy of formation of the Cu(II) thiolate (**3m**) was found to be large and positive (103 kcal mol^{-1}) for $L = NH_3$, but negative for $L_3 =$ TPB or TACN (-9 and -21 kcal mol^{-1}, respectively), associated with an increasing degree of pyramidalization of the CuN_3 fragment in the thiolato complex ($\Sigma = 315$, 271 and 250° for NH_3, TPB and TACN, respectively).



3m

Most interesting is the result reported by these authors that ammonia ligands are able to stabilize the Cu(II) thiolato complex, provided they are forced to occupy the same position as the donor atoms in the TPB (-4 kcal mol^{-1}) or TACN (-14 kcal mol^{-1}) ligands. This result clearly indicates that a large part of the stability of the Cu(II) thiolato complex is associated to ligand orientation effects, and explains why the TPB compound reported by Kitajima et al. [75] is the only such stable compound with non-planar coordination geometry.

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