On the Existence of a Pyramidality Effect in $d^8\cdots d^8$ Contacts. Theoretical Study and Structural Correlation

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A qualitative molecular orbital study of $d^8\cdots d^8$ contacts, using as models the dimers of [RhCl(CO)$_3$] and *cis*-[PtCl$_2$(CO)$_2$], is presented, focusing on the effect of the pyramidalization of the metal atom on the strength of the metal−metal interaction. The existence of a pyramidality effect in dimers of d^8-ML$_4$ complexes is supported also by the results of ab initio MP2 calculations on the dimer of *cis*-[PtCl$_2$(CO)$_2$]. A structural database analysis shows that a correlation between the pyramidality and the M···M distance exists for several families of dimers, oligomers, and polymers of square planar complexes of Ni(II), Pd(II), Pt(II), and Au(III). The importance of the pyramidality effect in those compounds is discussed in comparison with similar effects in binuclear complexes with metal−metal bonds of different multiplicities.

Introduction

An important geometrical parameter of a chemical bond is its pyramidality. Imagine a chemical bond between atoms A and B in an X_mA-BY_n molecule. The degree of pyramidalization of atom A relative to the A−B bond is given by the average of the BAX bond angles (α_A), and similarly, the degree of pyramidalization of B is the average of the ABY angles (α_B). The pyramidality associated with the A−B bond (α) is simply the average of the degrees of pyramidalization of the two atoms involved in that bond; i.e., $\alpha = (\alpha_A + \alpha_B)/2$. Such a structural parameter, which is too often overlooked in the discussion of chemical bonding in molecules or crystals, has an important effect on the A−B bond distances in coordination or organometallic complexes with metal−metal multiple[1,2] or single[3] bonds in organic[4,5] molecules and probably also in extended structures with M−M bonds.[6] In general, as the pyramidality increases, the A−B distance becomes shorter, with a practically linear dependence, although the trend might be reversed for large angles.

Square planar complexes of Pt(II) or other d^8 metal ions form dimers[7−12] or chains[13−20] with intermolecular M···M contacts in their crystal structures within the range 2.7 Å < d < 3.5 Å. The weakly bonding nature of the $d^8\cdots d^8$ interactions proposed originally by Gray *et al.*[21] is supported by spectroscopic evidence of the presence of intermolecular association in solution[22,23] and by EXAFS data acquired both in solution and in the solid state[24] and was recently confirmed through ab initio molecular orbital calculations.[25] However, these are formally nonbonded systems.

The obvious question that arises is whether the pyramidality effect, which is so important for metal−metal bonds with varying bond orders, is also present in the nonbonded M···M contacts found for dimers and chains of d^8-ML$_4$ complexes. In the present paper, we report our theoretical analysis of the influence of the pyramidality on the intermolecular M···M distances, whose results are corroborated by the structural correlations found for other d^8 transition metal ions.

Computational Results

For the subsequent orbital analysis of the pyramidality effect, it is convenient to briefly summarize here the physical basis of such an effect in the case of M−M single bonds. Although the explanations given in this section are based on the qualitative concepts of molecular orbital theory, results of extended Hückel

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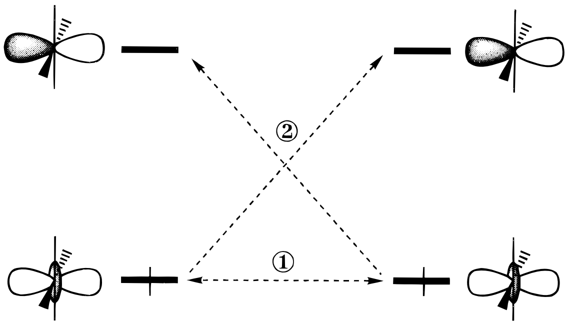
calculations for model complexes are presented in some cases to illustrate the discusion (see Appendix for computational details).

A simplified orbital interaction diagram for the formation of a single M−M bond between two d^7-ML_4 fragments[3] is represented in **1**. The interaction labeled ① between d_{z^2} orbitals accounts for the formation of a single bond. Additionally, interactions of type ② between d_{z^2} and p_z orbitals are one-electron donor−acceptor interactions reinforcing the bonding. Alternatively, one may describe interactions ② as a hybridization **2**, which favors the overlap between the semioccupied orbitals (formally d_{z^2}) of the two ML_4 fragments. Such hybridization is favored by a large pyramidality; hence, the interactions of type ② are responsible for the pyramidality effect in d^7−d^7 single bonds.



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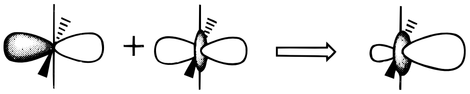

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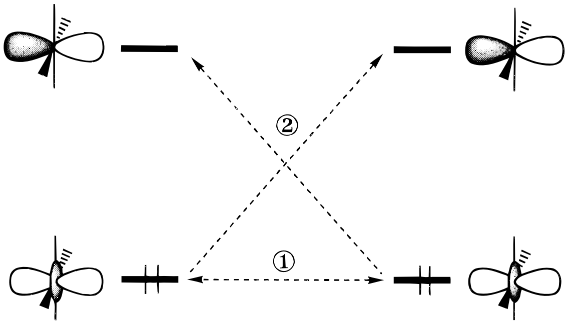
Schematically, the orbital explanation of the $d^8 \cdots d^8$ interactions is similar to that for the bonding d^7−d^7 interactions and can be summarized as in **3**. The two atomic orbitals of a metal atom oriented along the metal−metal vector are d_{z^2} and p_z and can interact with the same AO's of the other metal atom. The interaction ① between z^2 orbitals is a four-electron repulsion, acting against the approximation of the two metal atoms. The interactions ②, between z^2 and p_z orbitals, on the other hand, are bonding donor−acceptor interactions. Finally, interaction between the empty p_z orbitals has no effect. Hence, the combination of interactions ① and ② accounts for the weakly bonding $d^8 \cdots d^8$ interactions. Consistently, the calculated overlap populations for Rh(I)···Rh(I) contacts in a model dimer have positive values, if much smaller than for the Rh(II)−Rh(II) single bonds.



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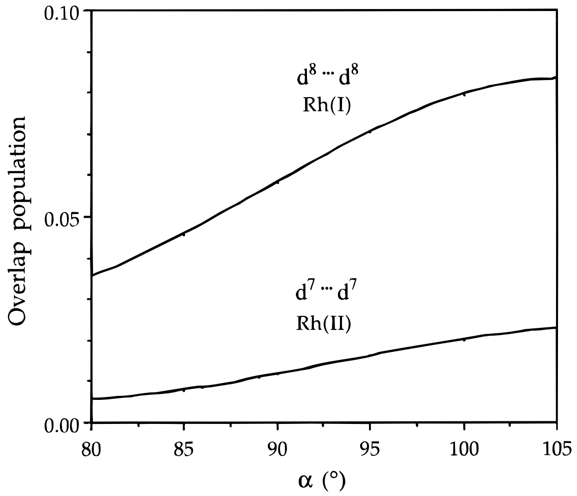

Figure 1. Contribution of interaction ② (see **1** and **3**) to the Rh−Rh overlap population for Rh(II)−Rh(II) single bonds and Rh(I)−Rh(I) contacts as a function of the pyramidality α, calculated for model compounds $[Rh_2O_8]^{n-}$.

Two-electron interactions of type ② are in this case much stronger than the corresponding one-electron interactions in d^7−d^7 bonds. Consequently, the variation of the strength of the M−M interaction with α is expected to be more important for the $d^8 \cdots d^8$ contacts than it is for the metal−metal single bonds. In Figure 1 we show the overlap population arising from only interactions of type ② for the two cases (d^7−d^7 and $d^8 \cdots d^8$ dimers with Rh_2O_8 cores) as a function of the pyramidality α. This figure confirms our qualitative prescription that in the $d^8 \cdots d^8$ dimer such interaction is stronger and has a larger susceptibility to pyramidalization (similar results are obtained using chloride ions as ligands).

As was previously found for formally bonded dimers, the addition of axial ligands results in a decrease of the pyramidality. In this case, the optimum angle for the dimer $[RhCl_4{}^{3-}]_2$ ($\alpha = 97.7°$) decreases to 94.7 or 94.3° upon addition of two axial chloride or CO ligands, respectively. Hence, the axial ligands indirectly favor weaker M···M interactions by decreasing the pyramidalization around the metal atoms, in much the same way as in the M−M-bonded dimers.[1,2]

The addition of a Lewis acid to one of the metal atoms in the $d^8 \cdots d^8$ dimers has been shown to slightly reinforce the M···M contact, and a handful of examples of such adducts have been reported in the literature.[25] However, at difference with the addition of a Lewis base, the pyramidality is slightly decreased by the incorporation of an acid to an axial position:[26] the optimized angles for two models of such adducts, $[Rh_2Cl_8(H)_2]^{4-}$ and $[Rh_2Cl_8(AuCl)_2]^{6-}$, are 96.5 and 96.9°, respectively, to be compared with that for the bare dimer, 97.7°. The different effects of a base and an acid on the degree of pyramidalization of the metal atom are best seen in the results of a calculation for the model complex $[Rh_2Cl_8(AuCl)(CO)]^{6-}$, for which the optimized angles are $\alpha_A = 85.7°$ and $\alpha_B = 103.7°$, to be compared with $\alpha = 97.7°$ for the parent complex $[Rh_2Cl_8]^{6-}$. Such a dramatic difference is in good qualitative agreement with experimental data, as discussed below.

The qualitative ideas discussed above, validated within the simplifying approximations of the extended Hückel method, are based on the topology of the molecular orbitals of square planar transition metal complexes and should apply equally well to similar complexes of other transition metal ions. Nevertheless, we have verified our qualitative conclusions by performing ab

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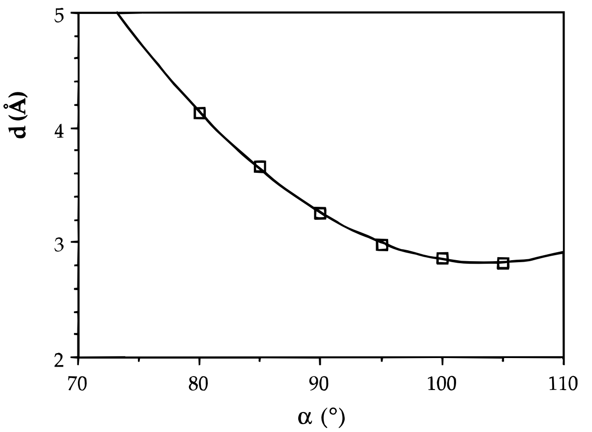

Figure 2. Calculated (MP2) Pt$\cdots$Pt distance (*d*) in the dimer of *cis*-[$PtCl_2(CO)_2$] as a function of the pyramidality α.

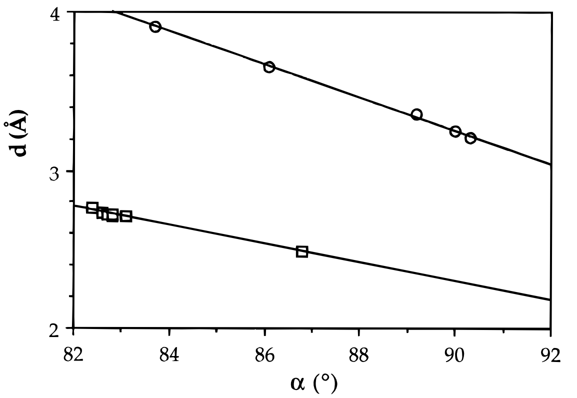

Figure 3. Experimental Ni$\cdots$Ni distances as a function of the pyramidality for the dimethylglyoximato (circles; see Table 1) and bridged (squares; Table 2) binuclear complexes of Ni(II).

initio MP2 calculations on the dimer of *cis*-[$PtCl_2(CO)_2$]. Starting from the geometry optimized for the monomer,[25] we have reoptimized the bond distances and the Pt$\cdots$Pt distance in the dimer at different Pt−Pt−L angles (α) while keeping the rest of the structural parameters frozen. The results are presented in Figure 2. The minimum in energy is found at $\alpha = 91.3°$. Thus, a small degree of pyramidalization is expected around the metal atoms in an unsupported binuclear compound, even if no formal metal−metal bond can be invoked. Furthermore, from Figure 2 it can be seen that a correlation must exist between the pyramidality and the M$\cdots$M distance, in much the same way as found for compounds with quadruple M−M bonds,[1,2] summarized by the least-squares equation (1). Note

$$d(\mathrm{Pt}\cdots\mathrm{Pt}) = 28.09 - 0.4876\alpha + 0.00235\alpha^2 \qquad (1)$$

that in the region of small values of α (between 80 and 95°) the dependence is practically linear, but curvature appears at larger angles, with a minimum at 103.7°. Therefore, a fine tuning of the pyramidality, achieved through a careful choice of the ligands, should allow one to modify at will the M$\cdots$M contact distance.

Although the scatterplot of *d* as a function of α is a direct and clear representation of the correlation between the two parameters, it is often useful to represent *d* as a linear function of cos α because the fitting parameters are best suited for comparison with experimental geometrical parameters[3] (see below). Since for small ranges of an angle, cos α and α are linearly related, one can choose either of the two representations, and we will continue to use the angle for graphical display but cos α for the least-squares equations. Hence, eq 1 can be replaced by eq 2.

Table 1. Structural Data for Dimeric and Chain Compounds of Ni(II) with Dimethylglyoximato ($Hdmg^-$) and Related Ligands

compound	Ni$\cdots$Ni (Å)	α (deg)	$Ni-L_{ax}$ (Å)	ref
$[Ni(dmgBF_2)_2]_2$	3.208	90.3		28
$[Ni(Hdmg)_2]_n$	3.245	90.0		29
$[Ni(dmgBF_2)_2(benzimidazole)]_2$	3.358	89.2		30
$[Ni(dmgBF_2)_2(PhNH_2)]_2$	3.654	86.1	2.601, 2.723	31
$[Ni(dmgBF_2)_2(4,4'\text{-bipy})]_n$	3.909	83.7	2.348	32

$$d(\mathrm{Pt}\cdots\mathrm{Pt}) = 3.254 + 3.705 \cos\alpha + 7.802 \cos^2\alpha \qquad (2)$$

If one disregards the largest angles, the data in Figure 2 can be represented by a linear equation, which will be useful for later comparison with experimental data:

$$d(\mathrm{Pt}\cdots\mathrm{Pt}) = 3.308 + 4.428 \cos\alpha \qquad (3)$$

In equations of the general form

$$d(\mathrm{M}\cdots\mathrm{M}) = b + c \cos\alpha \qquad (4)$$

the parameter *b* gives an *intrinsic* distance, i.e., the M−M distance at the standard angle $\alpha = 90°$, and *c* represents the *susceptibility* to pyramidalization of the particular family of compounds.[2]

Structural Correlations

The theoretical results presented above prompted us to carry out a structural database study, in order to check to what extent the experimental data conform to the theoretical predictions. In this section, we present an analysis of the structural correlation between the pyramidality α and the M$\cdots$M distance (*d*) in dimers of d^8-ML_4 complexes, obtained through a systematic search of the Cambridge Structural Database[27] for families of complexes with the same metal atom and analogous ligands.

Two families of Ni(II) compounds have been identified, and their Ni$\cdots$Ni distances are plotted as a function of α in Figure 3. The values of α for the family of bis(dimethylglyoximato)nickel(II) derivatives (Table 1) vary within the range $83° < \alpha < 91°$, and a very good linear correlation is found between *d* and cos α, as represented by the least-squares fitting of eq 5

$$d(\mathrm{Ni}\cdots\mathrm{Ni}) = 3.252 + 5.993 \cos\alpha \qquad (5)$$

(regression coefficient $r = 0.999$). Notice that the values of the pyramidality are smaller for those cases in which axial ligands are present and also that the smaller angles correspond to the stronger metal−axial ligand interactions (i.e., shorter $M-L_{ax}$ distances), in excellent agreement with the theoretical predictions. It is also noteworthy that the regular chain of [$Ni(dmgH)_2$] with its angle of 90° nicely fits into the general picture and can be considered as a particular case of dimers in which the axially coordinated groups are just additional molecules of the complex. Although the data set is relatively small, the extremely good correlation is remarkable, since it covers variations of up to 0.7 Å in the Ni$\cdots$Ni distances for changes of less than 7° in the pyramidality.

The second family studied is that of the Ni(II) carboxylates and analogous complexes, in which the bidentate ligands act as bridges between the two Ni atoms and additional ligands

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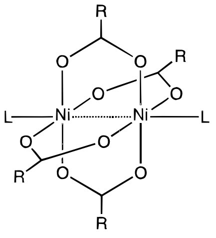
Table 2. Structural Data for Tetrakis(carboxylato)dinickel(II) and Analogous Complexes

compound	Ni···Ni (Å)	α (deg)	ref
$[Ni_2(HC\{NTol\}_2)_4]$	2.485	86.8	35, 36
$[Ni_2(7\text{-azaindolato})_4]$	2.594	87.0	33
$[Ni_2(MePh_2SiCO_2)_4(PPh_3)_2]$	2.708	83.1	37
$[Ni_2(Me_3CCO_2)_4(2,4\text{-}Me_2py)_2]$	2.708	82.8	38
$[Ni_2(Me_3CCO_2)_4(2\text{-picoline})_2]$	2.717	82.8	37
$[Ni_2(Me_3CCO_2)_4(2,5\text{-}Me_2py)_2]$	2.720	82.8	37
$[Ni_2(Me_3CCO_2)_4(2\text{-Etpy})_2]$	2.723	82.7	37
$[Ni_2(Me_2PhSiCO_2)_4(quinoline)_2]$	2.734	82.6	37
$[Ni_2(MePh_2SiCO_2)_4(quinoline)_2]$	2.765	82.4	37

Table 3. Structural Data for Tetrakis(bridge)dipalladium(II) Complexes

compound	Pd···Pd (Å)	α (deg)	ref
$[Pd_2(mhp)_4]$	2.543	86.8	39
	2.551	87.0	
	2.560	86.5	
$[Pd_2(mhp)_4]$	2.545	86.9	40
$[Pd_2(chp)_4]$	2.562	86.5	39
$[Pd_2(Ph_2N_3)_4]$	2.563	84.9	34
$[Pd_2(chp)_4]$	2.565	86.4	39
	2.571	86.5	
$[Pd_2(chp)_4]$	2.570	86.6	39
$[Pd_2(PhC\{NPh\}_2)_4]$	2.576	85.7	41
$[Pd_2(PhC\{NTol\}_2)_4]$	2.622	85.0	35, 36

can be found in the axial coordination positions (**4**; Table 2).



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We have disregarded the 7-azaindolato complex,[33] since compounds with this ligand are known to deviate from the general trend because of the misalignment of its lone pairs,[2] and also $[Ni_2(Ph_2N_3)_4]$, because of the low value of the refinement parameter ($R = 0.13$).[34] The rest of the structural data conform to eq 6 (regression coefficient $r = 0.995$ for eight data sets).

$$d(\mathrm{Ni}\cdots\mathrm{Ni}) = 2.291 + 3.437 \cos \alpha \qquad (6)$$

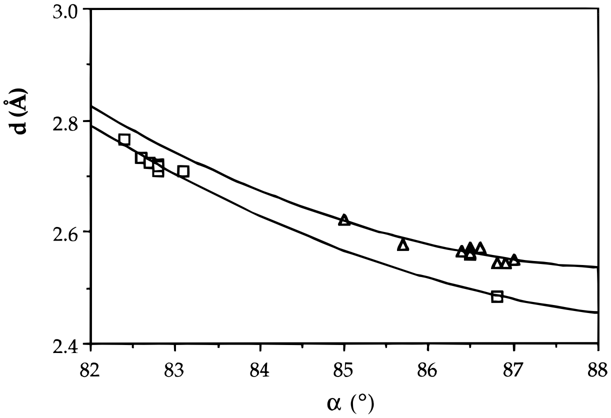

Figure 4. Experimental M···M distances as a function of the pyramidality for the bridged binuclear complexes of Ni(II) (squares) and Pd(II) (triangles; Table 3).

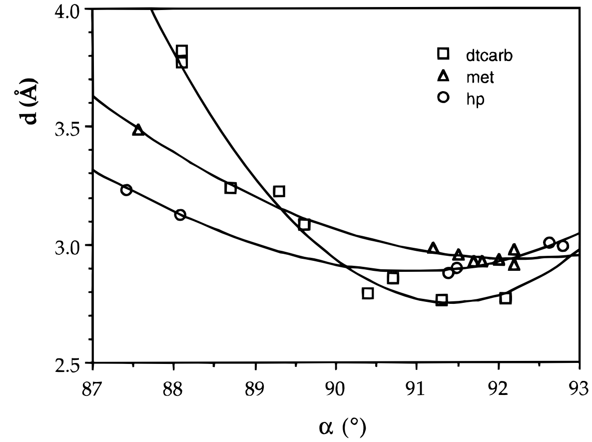

Figure 5. Experimental Pt···Pt distances as a function of the pyramidality for the binuclear complexes of Pt(II) with dithiocarboxylato (**6**; squares), hydroxopyridinato (circles), and methyluracil or related ligands (**5**; triangles).

Closely related to the family of the Ni carboxylates is a group of Pd complexes with bridging ligands (Table 3), from which one of the reported structures for $[Pd_2(HC\{NTol\}_2)_4]$ is discarded in the structural analysis, given the low refinement of its structure[35] ($R = 0.13$). The remaining structural data can be fitted to a second-order polynomial equation (Figure 4; regression coefficient $r = 0.939$), but a reasonable description of the pyramidality effect can be obtained through a linear equation:

$$d(\mathrm{Pd}\cdots\mathrm{Pd}) = 2.444 + 1.948 \cos \alpha \qquad (7)$$

Three different families of Pt(II) complexes can be analyzed: the dithiocarboxylato complexes (dtcarb), the hydroxy-

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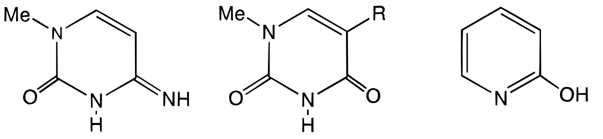
Table 4. Structural Data for Tetrakis(dtcarb)-, Bis(hp)-, and Bis(meL)-diplatinum(II) Complexes (meL = mec, met, or meu)[a]

	intramolecular		intermolecular		
complex	Pt···Pt (Å)	α (deg)	Pt···Pt (Å)	α (deg)	ref
$[Pt_2(PhCH_2CS_2)_4]$	2.765	91.3	3.238	88.7	42
$[Pt_2(MeCS_2)_4]$	2.767	92.1	3.776	88.1	43
			3.819	88.1	
$[Pt_2(Me_2CHCS_2)_4]$	2.795	90.4	3.081	89.6	44
$[Pt_2(HexCS_2)_4]$	2.855	90.7	3.224	89.3	45
$[Pt_2(p\text{-}^iPrC_6H_4CS_2)_4]$	2.862	92.2			46
$[Pt_4(hp)_4(NH_3)_8]^{4+}$	2.877	91.4	3.129	88.1	47
$[Pt_2(hp)_2(NH_3)_4]^{2+}$	2.898	91.5			47
$[Pt_4(hp)_4(en)_4]^{4+}$	2.991	92.8	3.235	87.4	48
$[Pt_2(\mu\text{-}NHCOPh)_2(C,N)_2]$	3.005	92.6			49
$[Pt_2(met)_2(NH_3)_4]^{2+}$	2.927	91.8			50, 51
$[Pt_2(met)_2(NH_3)_4]^{2+}$	2.923	91.7			52
	2.915	92.2			
$[Pt_2(met)_2(NH_3)_4]^{2+}$	2.974	92.2			53
$[Pt_4(meu)_4(NH_3)_4(bipy)_2]^{4+}$	2.929	91.7	3.489	87.6	54
$[Pt_2(meu)_2(NH_3)_4]^{2+}$	2.937	92.0			55
$[Pt_2(meu)_2(NH_3)_4]^{2+}$	2.953	91.5			56
$[Pt_2(mec)_2(NH_3)_4]^{2+}$	2.981	91.2			57

[a] dtcarb = dithiocarboxylato; hp = hydroxopyridinato; mec = methylcytosinato; met = methylthyminato; meu = methyluracilato; (C,N) = $C_6H_4CH_2(NMe_2)_2$.

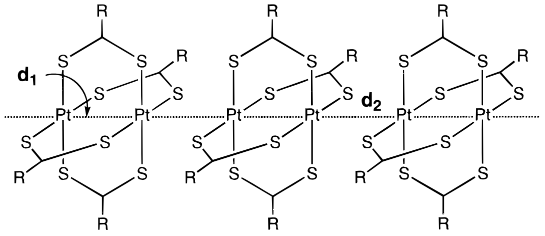
pyridinato (hp$^-$) derivatives, and the complexes of methylcytosinato (mec$^-$), methylthyminato (met$^-$), and methyluracilato (meu$^-$), referred to in general in this paper as meL (**5**). The structural data for these compounds are plotted in Figure 5. The platinum dithiocarboxylato complexes form chains of bridged dimers (**6**), whose structural parameters are gathered in Table 4. For this group of compounds, due to the presence of bidentate bridging ligands, the intramolecular Pt···Pt distances (d_1) vary very little within the family. If the intermolecular Pt···Pt contacts (d_2) are taken into account, together with the intramolecular ones, a clear trend appears, even if there is some dispersion of the experimental values around the least-squares curve (eq 5) due probably to the differences in the ligands under consideration. According to the least-squares equation (8), the



mecH (methylcytosine) metH (methyltymine, R = CH_3) hpH (hydroxopyridine)

meuH (methyluracil, R = H)

5



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$$d(\text{Pt}\cdots\text{Pt}) = 2.928 + 14.159 \cos\alpha + 301.57 \cos^2\alpha \qquad (8)$$

minimum possible distance in this family of compounds corresponds to $\alpha = 91.3°$ and $d = 2.762$ Å. If only the intermolecular contacts are considered, the behavior can be approximately represented by a linear equation:

$$d(\text{Pt}\cdots\text{Pt})_{\text{inter}} = 2.846 + 26.88 \cos\alpha \qquad (9)$$

Table 5. Structural Data for Au(III) Ylides of General Formula $[Au_2(Ph_2P\{CH_2\}_2)_2X_4]$

compound	Au···Au (Å)	α (deg)	ref
$[Au_2(Ph_2P\{CH_2\}_2)_2Br_4]$	3.069	97.1	59
$[Au_2(Ph_2P\{CH_2\}_2)_2Br_4]$	3.076	93.9	60
$[Au_2(Ph_2P\{CH_2\}_2)_2Cl_4]$	3.088	92.8	61
$[Au_2(Ph_2P\{CH_2\}_2)_2Cl_4]$	3.091	90.3	60
$[Au_2(Ph_2P\{CH_2\}_2)_2Br_2Cl(CH_2Cl)]$	3.070	92.6	62
$[Au_2(Ph_2P\{CH_2\}_2)_2Cl_3(CCl_3)]$	3.089	92.1	63
$[Au_2(Ph_2P\{CH_2\}_2)_2Br_3(CH_2CF_3)]$	3.102	90.9	62

A similar behavior is found for the hydroxopyridinato-bridged complexes and a compound with the topologically equivalent ligand NHCOPh, identified as the hp family, as well as for the compounds of methyluracil and analogous ligands (**5**), as seen in Figure 5, although the susceptibility of the intermolecular contacts to pyramidalization is smaller for these two families than it is for the dithiocarboxylates.

Two Pt(II) compounds with the tridentate terpyridine ligand have been found in our literature search. Although these do not contribute statistical significance to the structural data, the trend appears clear: $[Pt(terpy)Cl]^+$ forms stacks[58] with the shortest Pt···Pt contacts at 3.328 Å and a pyramidality of 90.3°, whereas the analogous compound $[Pt_2(terpy)_2(guanidinato)]^{3+}$ presents dimers with $\alpha = 93.4°$ and Pt···Pt contacts at 3.090 Å.

Finally, there is a family of Au(III) ylides, of general formula $[Au_2(Ph_2P\{CH_2\}_2)_2X_4]$, where X is a halide or a halogenated organic group (Table 5). As previously found for families of metal−metal-bonded dimers,[2,3] compounds with M−C bonds and analogous compounds with M−X bonds (X = halogen) must be grouped separately. Although the resulting families are rather small, they also seem to follow the expected pyramidaliy trend, given by eq 10 for those compounds with

$$d(\text{Au}\cdots\text{Au}) = 3.093 + 0.196 \cos\alpha \qquad (10)$$

X = halogen and by eq 11 for those in which X is a C-bonded

$$d(\text{Au}\cdots\text{Au}) = 3.119 + 0.976 \cos\alpha \qquad (11)$$

organic group. In these equations, a relatively small susceptibility to pyramidalization in the case of the nonorganometallic compounds can be seen.

Given the scarcity of known structures, we cannot compare the experimental data for analogous dimers with and without axial groups. However, in dimers, all the metal atoms axially bonded to a Lewis base (M_B) show a degree of pyramidalization relative to the M···M contact smaller than 90° ($82.4° < \alpha_B < 89.6°$; see Table 6 and also Tables 1 and 2), and those metal

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Table 6. Selected Structural Data for Dimers of d^8-ML_4 Complexes with Lewis Bases (B) and/or Acids (A) in Axial Coordination Sites[a]

complex	M	M···M, Å	degree of pyramidalization (deg) α_A	α_B	ref
B−ML_4−ML_4					
$[Ni_2(PhCOS)_4(EtOH)]$	Ni	2.503		89.6	64
$[Ni_2(tzt)_4Cl]^-$	Ni[b]	2.649		85.4	65
B−ML_4−ML_4−B					
$[PtCl_2(HNC\{OH\}CMe_3)_3]_2$	Pt	3.399		89.6	8
A−ML_4−ML_4					
$[\{Pt(meu)_2(NH_3)_4\}_2Ag]^{5+}$	Pt	2.886	89.8		66
$[Pt_2Ag(meu)_2(NH_3)_4(NO_3)_2]^+$	Pt	2.950	91.1		67
A−ML_4−ML_4−A					
$[Pt_2Ag_2(meu)_2(NH_3)_4(NO_3)_2]^{2+}$	Pt	2.892	91.2		68
A−ML_4−ML_4−B					
$[Os_2W(Me_3CNC)_2(CO)_{12}]$	Os	2.907	94.4	83.9	69
$[Os_2W(MeC\{CH_2O\}_3P)_2(CO)_{12}]$	Os	2.940	96.5	85.3	70
$[Ir_2(dimen)_4(AuPPh_3)(PPh_3)]^{3+}$	Ir[b]	2.986	93.8	88.2	71

[a] For Ni(II) complexes of type B−ML_4−ML_4−B, see also Tables 1 and 2. [b] dimen = 1,8-diisocyano-*p*-menthane; Htzt = thiazole-2-thiol.

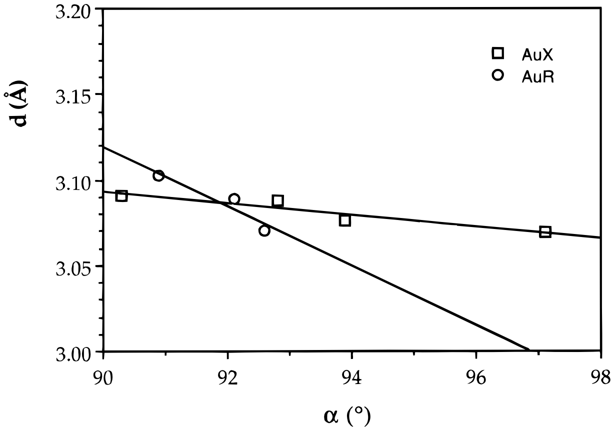

Figure 6. Experimental Au···Au distances as a function of the pyramidality for the binuclear complexes of Au(III) with halo (squares) and organometallic (circles) ylides.

atoms bearing a Lewis acid in an axial position (M_A) have larger degrees of pyramidalization (89.8° < α_A < 96.5°; Table 6). Such difference in the degree of pyramidalization is best appreciated in those compounds having both a base and an acid attached to the two axial positions (Table 6, bottom) and is in good qualitative agreement with the results reported above for $[Rh_2Cl_8(AuCl)(CO)]^{6-}$.

Discussion

Our theoretical results and the structural analysis presented above show that the $d^8 \cdots d^8$ contacts behave qualitatively in the same way as M−M bonds of different multiplicities as far as their response to pyramidalization is concerned. The families of compounds studied show a good correlation between the M···M distance and the pyramidality α (eqs 5−11). In this section we discuss first the similarities and differences among the families of d^8 dimers and present also a comparison with the M−M-bonded dimers.

The M···M distance can be expressed in most cases as a linear function of the pyramidality (Figures 1−6), and the pyramidality effect can be represented by eqs 5−7 and 9−11. In those cases in which the two metal atoms are supported by a bridging ligand, there is a purely geometrical relationship between *d* and α given by eq 12, where X···X is the bite of the bridging ligand and

$$d(\mathrm{M\cdots M}) = (\mathrm{X\cdots X}) + 2(\mathrm{M-X})\cos\alpha \qquad (12)$$

M−X is the metal−ligand bond distance. Hence, important differences between the least-squares parameters *b* and *c* and the experimental values of X···X and 2(M−X) provide an indication that the pyramidality effect is not merely geometric but also electronic.

Table 7. Summary of Pyramidality Parameters for Different Families of Binuclear Complexes with M−M Bonds or M···M Contacts[a]

M/ligands	bond order	*b*	*c*	*N*	(X···X)	2(M−X)	N
Cr(II)/bridged	4	2.241	3.740	52	2.24(3)	4.04(2)	43
Cr(II)/unsupported	4	3.138	3.847	5			
Mo(II)/bridged	4	2.158	1.774	62	2.24(2)	4.24(1)	64
Mo(II)/carbox+phos	4	2.131	0.189	7			
Mo(II)/halo+phos	4	2.191	0.197	13			
W(II)/bridged	4	2.222	1.873	21	2.27(3)	4.20(2)	21
Re(III)/halo	4	2.337	0.455	34			
Re(III)/bis(bridged)	4	2.361	1.158	15			
Re(III)/tetrakis(bridged)	4	2.232	1.509	5	2.23(2)	4.04(1)	5
Os(III)/carboxylates	3	2.329	0.256	18	2.27(3)	4.00(2)	8
Os(III)/chloride (calcd)	3	2.494	1.396				
Re(II)/ diphosphines	3	2.379	0.562	8			
Co(II)/bridged	1	2.141	4.604	6	2.23(4)	3.98(5)	6
Rh(II)/bridged	1	2.299	2.934	101	2.26(2)	4.08(1)	101
Ni(II)/dmgH	0	3.252	5.993	5			
Ni(II)/bridged	0	2.291	3.437	8	2.24(4)	3.98(5)	8
Pd(II)/bridged	0	2.444	1.948	10	2.33(3)	4.06(2)	12
Pt(II)/Cl(CO) (calcd)	0	3.308	4.428				
Pt(II)/RCS_2 (intermol)	0	2.846	26.88	5			
Au(III)/ylide+halo	0	3.093	0.196	4			
Au(III)/ylide+R	0	3.119	0.976	3			

[a] *b* is the *intrinsic* metal−metal distance, *c* the *susceptibility to pyramidalization* for each family (distances in Å, angles in deg), and *N* the number of structures in each data set. carbox = carboxylates; phos = phosphines; dmgH = dimethylglyoximato derivatives.

The nonlinearity of the *d*(α) function in some cases is in keeping with the theoretical results presented above and is also consistent with what has been found both theoretically and experimentally for several families of dimeric compounds with multiple metal−metal bonds.[2] The fact that a linear correlation is found in many of the families analyzed here is probably due to the small values of the experimental angles (close to 90°), in the linear part of the *d*(α) curves.

We have collected in Table 7 the parameters *b* and *c* of a wide variety of compounds for the sake of comparison. The value of *b* is the *intrinsic* metal−metal bond distance for a particular family of compounds which should be used when comparing different families. On the other hand, the slope of the linear equation (*c*) is a measure of the *susceptibility to pyramidalization* of a given family of compounds. The following observations can be made:

(a) The bridged compounds present shorter M···M distances than the unsupported ones, as found also for complexes of other metal ions with metal−metal bonds.[2,3] This can be clearly seen by looking at the data for bridged and unsupported (Hdmg and $dmgBF_2$) Ni(II) complexes, which present similar curves (Figure 3) but much longer Ni···Ni distances for the unsupported dimers, and also for the families of bridged and unsupported Cr(II) compounds. One can conclude that the bridging ligands impose shorter contacts than those due solely to the electronic Ni···Ni interaction.

(b) The susceptibility to pyramidalization is always greater for the first- than for second- or third-row transition metals,

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whereas the intrinsic metal−metal distance is practically the same for the different metals in the same group of the periodic table if compounds with similar ligands and different metal atoms are compared (Table 7). This can be illustrated by Ni(II) and Pd(II) compounds with analogous bridges, which show a somewhat larger susceptibility for Ni (Figure 4). The difference in the intrinsic distance of these two metals is significantly smaller than expected on the basis of their atomic radii (2.75 and 2.49 Å in metallic Pd and Ni, respectively).

(c) The correlation between pyramidality and metal−metal distance cannot be ascribed only to the geometrical constraint imposed by the bridging ligands. The fact that, e.g., the unsupported Ni(II) dimethylglyoximato derivatives show a clear pyramidality effect (see Figure 2), together with the important differences between c and 2(M−X), cannot be explained solely on the basis of the geometrical constraints of the bridging ligands (compare eqs 4 and 12) and suggest the existence of an electronic effect.

(d) The intermolecular Pt···Pt distances in the dithiocarboxylato complexes of Pt(II) present a sensibly larger susceptibility to pyramidalization (see Figure 5 and parameter c in Table 7) than compounds with carboxylato or analogous bridges with smaller bites. The experimental values of α differ by less of 2° within every set of contacts (intra- or intermolecular), yet the intermolecular distances change by up to 0.7 Å. It is not clear at this point whether this enhanced effect is due to the larger bite of the bridging ligand, to stronger ligand···ligand repulsions, or to the softer character of the sulfur donor atoms, and the explanation of this enhanced pyramidality effect remains an interesting theoretical challenge. However, since the number of such compounds is not large, the synthesis and structural characterization of new members of this family should be useful to confirm or rule out the apparent correlation shown in Figure 2.

(e) Comparison of the pyramidality parameters for the $d^8 \cdots d^8$ contacts with those for M−M bonds (Table 7) presents a surprising aspect, since the intrinsic metal−metal distance for bridged compounds with single M−M bonds (e.g., Co(II) and Rh(II)/bridged) are only marginally shorter than those for analogous compounds with no formal M−M bond (i.e., Ni(II) and Pd(II)/bridged). This suggests that the short M−M distances in these types of compounds are imposed by the bridging ligands, as can be confirmed by the longer distances found for the unsupported Ni(II) dioximates and Au(III) ylides and that calculated for the Pt(II) chloro−carbonyl model dimer. On the other hand, the susceptibility to pyramidalization of the $d^8 \cdots d^8$ contacts is variable but similar to that of other families of complexes with M−M bonds, with the exception of the enhanced pyramidality effect of the Pt(II) dithiocarboxylates discussed in the previous paragraph.

Concluding Remarks

Semiempirical theoretical studies on dimers of Rh(I) square planar complexes and ab initio calculations on analogous Pt(II) compounds are reported in this paper. The theoretical results predict that a correlation must exist between the length of the M···M contacts between square planar ML_4 complexes of d^8 metal ions and the degree of pyramidalization (i.e., out-of-plane displacement) of the metal atoms: the larger M···M−L angles are associated with shorter M···M distances. Consequently, addition of an axial ligand, producing a decrease in the degree of pyramidalization, produces weaker (longer) M···M contacts. In contrast, bonding of a Lewis acid in an axial position affects the pyramidality only slightly but strengthens the M···M contacts.

A structural database search has shown several families of Ni(II), Pd(II), Pt(II), and Au(III) to follow the expected trends, with 48 data pairs for the bond angle−bond length relationship. Although less structural information is available for complexes with axially bonded groups, 12 sets of structural data agree well with the predicted trends, comprising Ni(II), Pt(II), Os(0), and Ir(I) compounds.

Since the binding energy associated with the formation of M···M contacts has been reported to be relatively small (probably a few kcal/mol), it is just natural that the intermolecular M···M distance and the associated M···M−L angles are modified by other intermolecular forces. Hence, besides the different electronic effects of ligands with different σ-donor and π-donor/acceptor properties, other factors that may influence the pyramidality angle include the steric demands of the different ligands, their unidentate or bridging nature, ionic bonding between the ligands and counterions, and hydrogen bonding with solvation molecules in the crystal. In summary, the main conclusion is that, for a particular family of compounds, once the pyramidality angle is fixed, it determines the intermolecular M···M distance or vice versa.

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Appendix: Computational Details

Extended Hückel calculations of molecular orbitals[72] were carried out using the modified Wolfsberg−Helmholz formula[73] and standard atomic parameters.[72,74−76] The bond distances used for the EH calculations were Rh−O = 2.04 Å and Rh−Rh = 2.39 Å for the model complex $[Rh_2O_8]^{n-}$ (n = 12, 14) and Rh−Cl = 2.40 Å, Rh−Rh = 2.90 Å, Rh−Au = 2.70 Å, Au-Cl = 2.28 Å, Rh−H = 1.59 Å, Rh−C = 1.80 Å, and C−O = 1.15 Å for the model complex $[Rh_2Cl_8]^{6-}$ and its adducts with AuCl, H^+, Cl^-, and CO. Ab initio MP2 calculations were carried out with the GAUSSIAN92 program[77] using effective core pseudopotentials and the LANL2DZ basis set.[78−80] The bond distances used for $[PtCl_2(CO)_2]$ were those of $[PtCl_4]^{2-}$ (Pt−Cl = 2.323 Å) and of $[Pt_2(CO)_2(CH_3)_2(\mu\text{-dppm})_2]^{2+}$ (Pt−C = 1.960, C−O = 1.101 Å).[81]

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