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On the Bonding Nature of the M···M Interactions in Dimers of Square-Planar Pt(II) and Rh(I) Complexes

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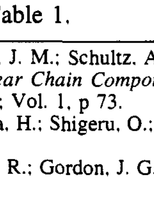
Abstract: A qualitative and semiquantitative study of the weakly bonding nature of M···M contacts between square-planar d^8-ML$_4$ molecules is presented. The results of ab initio calculations on the model dimers *cis*-[PtCl$_2$(CO)$_2$]$_2$ (in two different conformations), [PtCl$_2${HNCH(OH)}$_2$], and [RhCl(CO)$_3$]$_2$ are reported. These are predicted to be stable toward dissociation into two monomers, with bonding energies in excess of 3 kcal/mol and M···M distances well in the range of the experimental values for dimers and chains. The effect of adding axial groups to the ML$_4$ dimers on the strength of the M···M interaction has been explored by means of ab initio calculations on several adducts of [PtCl$_2$(CO)$_2$] as well as by extended Hückel calculations on the model adducts [Cl$_4$YRh···RhZCl$_4$]$^{n-}$ (Y, Z = Cl$^-$, CO, H$^+$, or AuCl). A qualitative ordering for the M···M *bond* strengths is proposed, which is consistent with the available experimental data.

The existence of intermolecular M···M contacts in the range 2.7 Å < *d* < 3.5 Å, shorter than the van der Waals sum, in the crystal structures of square-planar complexes of Pt(II) or other d^8 metal ions is well-known, both in dimers[1–6] and in chains.[7–13] Clear evidence also exists for the presence of intermolecular association in solution.[14,15] The d^8···d^8 contacts are not canonical bonds, in the sense that they cannot be represented as Lewis structures. Furthermore, in most of the known Pd(II) and Pt(II) dimers, the two metal atoms are held together by bridging ligands,[1,16] making it unclear whether there is metal–metal bonding or the two metals are held together by the chelating ligands. Probably the best characterized unsupported dimers are that of a chloro-amidato Pt(II) complex reported recently by Natile *et al.*[2] and a Rh(I) isonitrile derivative,[3] although intermolecular hydrogen bonding might play a significant role in holding the metal atoms together in the former case.

The prototypic family of chain compounds is formed by the salts of the tetracyanoplatinate anion, [Pt(CN)$_4$]$^{2-}$, for which the Pt···Pt distances are quite long (3.3–3.7 Å)[7,9] but become shorter when subject to partial oxidation.[17] In K$_2$[PtCl$_4$], the Pt···Pt distance within the stacks of [PtCl$_4$]$^{2-}$ ions is quite long (4.105 Å),[18] and the neighboring anions appear to be held together by ionic Cl···K···Cl interactions. Hence, it is not clear whether there is an electronic reason for the short contacts or these are imposed by the geometry of the molecule or the crystal.

A qualitative orbital model for the d^8···d^8 interactions, based on the hybridization of the metal d_{z^2} orbitals through mixing with s and p_z, was proposed by Gray *et al.*,[19] who also provided spectroscopic evidence of the weakly bonding nature of such interactions.[14,15] However, we are not aware of any detailed theoretical study of the M···M bonding in square-planar d^8 dimers. For these reasons, we have carried out a theoretical study of the d^8···d^8 interactions in Pt(II) and Rh(I) square-planar complexes. Our calculations aimed at evaluating the stability of the dimers toward dissociation and at finding some hints on how to enhance the stability through the addition of axial groups.

To evaluate the M···M interaction, ab initio Hartree–Fock (HF) calculations were carried out for the neutral dimers *cis*-[PtCl$_2$(CO)$_2$]$_2$ (in two conformations: eclipsed, **1**, or rotated, **2**), [PtCl$_2${HNCH(OH)}$_2$], and [RhCl(CO)$_3$]$_2$ (with the chloro ligands in a trans orientation),[20] including the electron correlation at the MP2 level.[21] The main results of these calculations are presented in Table 1.



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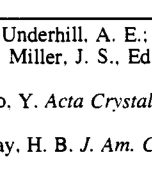

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Table 1. MP2 Optimized M···M Distances (Å) and Interaction Energies (E_i) for the [d^8-ML$_4$]$_2$ Dimers and Their Adducts[a]

compd	M···M single-ζ[b]	M···M double-ζ	E_i,[c] kcal/mol
$[PtCl_2(CO)_2]_2$ (rotated, **2**)		3.319(5)	−9.9 [+7.4]
$[PtCl_2(CO)_2]_2$ (eclipsed, **1**)	3.420	3.249(11)	−27.5 [−9.1]
$[RhCl(CO)_3]_2$	3.551*		−18.07 [−3.3]
$[PtCl_2\{HNCH(OH)\}_2]_2$	3.218*		−39.1 [−19.9]
$H[PtCl_2(CO)_2]_2Cl$	3.203	2.869(3)	−47.1[d]
$OC[PtCl_2(CO)_2]_2AuCl$	3.341		
$[PtCl_2(CO)_2]_2CO$	3.480		
$OC[PtCl_2(CO)_2]_2CO$	3.570		

[a] The eclipsed conformation (**1**) was used for all Pt dimers, except when otherwise specified. [b] The single-ζ LANL1MB basis set was used except for those compounds marked with an asterisk, for which the single-ζ LANL2MB basis set was employed. [c] For those cases in which different basis sets were used, the reported interaction energy corresponds to the double-ζ basis set. Given in brackets are the values corrected for the basis set superposition error. [d] Calculated for the interaction between $[HPtCl_2(CO)_2]$ and $[ClPtCl_2(CO)_2]$ fragments, found to be more stable than $[HPtCl_2(CO)_2]^+$ and $[ClPtCl_2(CO)_2]^-$. The mononuclear fragments were optimized within the C_s symmetry point group. The Pt···Pt distance was optimized for the dimer, keeping all bond angles at 90° and other bond distances as in the optimized fragments.

Table 2. Experimental M···M Distances in Dimers and Chains of d^8-ML$_4$ Complexes of Pt(II) and Rh(I)

compd	M···M, Å	ref
dimers		
$[Pt(Me_2CHCS_2)_2]_2$	2.760	28, 29
$[Pt(PhCH_2CS_2)_2]_2$	2.765	29
$[Pt(MeCS_2)_2]_2$	2.767	30
$[Pt(Me_2CHCS_2)]_2$	2.795	28
$[Pt(C_6H_{13}CS_2)_2]_2$	2.855	31
$[Pt(H_2C_2S_2)_2]_2$	2.749	32
$[Pt_2(p\text{-}Me_2CHC_6H_4CS_2)_4]$	2.862	33
$[Pt_2(terpy)_2(\mu\text{-}gu)]^{3+}$[a]	3.090	6
$[PtCl_2\{HNCBu^t(OH)\}_2]_2$	3.165	2
$[RhCl(CO)_2(Imidazole)]_2$	3.519	34
chains		
$[Pt(dmgH)_2]$	3.256	35
$[RhCl(CO)_2(pzH)]$	3.452	36

[a] guH = $(H_2N)_2CNH$.

Table 3. M···M Distances (Å) for Dimers of d^8-ML$_4$ Complexes and for Their Derived Adducts [Y−ML$_4$−ML$_4$−Z] (**3**)

M	Y	Z	M···M (dimer)	M···M (adduct)	ref
Ir	PPh_3	$AuPPh_3$		2.986(2)	40
Os	CO	$W(CO)_5$		2.907(2)	41
Os	CO	$W(CO)_5$		2.940(1)	42
Pt[a]	Ag(I)	Ag(I)	2.90−2.98	2.892(1)	43
Pt	ROH	ROH	3.165(1)	3.399(1)	2
Ni	aniline	aniline	3.208(1)	3.654(2)	44, 45
Ni	4,4′-bpy	4,4′-bpy	3.208(1)	3.909(3)	46, 45
Rh	$AuPPh_3$	$AuPPh_3$		3.262(1)	47

[a] Data for the bare dimer comes from six Pt compounds found in a structural database search.[48]

The model dimeric complexes are predicted to be stable toward dissociation into two mononuclear complexes, with bonding energies in excess of 3 kcal/mol, Pt···Pt distances between 3.25 and 3.32 Å, and a Rh···Rh distance of 3.55 Å, in agreement with the observed values experimentally reported for unsupported dimers and chains (Tables 2 and 3). The binding energies are probably overestimated due to the basis set superposition error (BSSE). If the results are corrected for the BSSE by applying the counterpoise method, the interaction energies are less stabilizing but still clearly bonding except for $[PtCl_2(CO)_2]_2$ in its rotated conformation.

One might think that the stability of the eclipsed $[PtCl_2(CO)_2]_2$ dimer is associated to ligand···ligand interactions. In fact, the interaction energy between a CO molecule and a chloride ion is calculated to be −5.3 kcal/mol (−1.7 kcal/mol after BSSE correction) in the geometry corresponding to the eclipsed dimer **1**,[27] in which there are four such contacts. A similar interaction is found between CO and Cl$^-$ at the rotated geometry **2**, with E_i = −4.8 kcal/mol for each of the two contacts (−2.4 kcal/mol after BSSE correction). These results suggest that both the ligand···ligand interactions and a weak M···M bond are important in determining the stability of the studied dimers.

Although our data suggest that the platinum amido dimer is in part stabilized by interligand hydrogen bonding, the stability of the remaining model compounds is undoubtedly associated with weak M···M bonding interactions. The intermolecular interaction of an amido ligand with a chloro ligand has been found to be −1.6 kcal/mol (−1.0 kcal/mol with BSSE correction) for the HNCH(OH)···Cl$^-$ bimolecular complex torn apart from the optimized geometry of the dimer.

We have also explored the effect of adding axial groups to the ML$_4$ dimers on the strength of the M···M interaction.

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(20) The bond distances for the monomeric complexes were optimized keeping the coordination spheres of the metals planar and L−M−L angles of 90°. The optimized values for $[PtCl_2(CO)_2]$ are Pt−C = 1.924 Å, Pt−Cl = 2.400 Å, and C−O = 1.186 Å in fair agreement with the experimental values in $[PtCl_4]^{2-}$ (Pt−Cl = 2.323 Å) and in $[Pt_2(CO)_2(CH_3)_2(\mu\text{-}dppm)_2]^{2+}$ (Pt−C = 1.960 Å, C−O = 1.101 Å).[26] For $[RhCl(CO)_3]$, the optimized distances are the following: Rh−Cl = 2.462 Å, Rh−C = 1.994 Å, and C−O = 1.203 Å. Such distances were used without change in the dimeric complexes and only the distance between monomers and their relative orientation were varied. A reoptimization of the dimers $[PtCl_2(CO)_2]_2$ and $[RhCl(CO)_3]_2$ was carried out as a check (MP2, single-ζ), in which the intramonomer bond distances were found to remain practically constant relative to the monomer (within 0.03 Å) at the same level of calculation, and the variations of the Pt−Pt−L bond angles were smaller than 3° (other angles were kept constant), with small changes in the total energy (e.g., 0.0005 au for the dimer of Pt).

(21) Ab initio MP2 calculations were carried out with the GAUSSIAN92 program[22] using effective core potentials (ECP) and single-ζ or double-ζ basis sets.[23−25] For the smaller systems, double-ζ (LANL2DZ and LANL1DZ[22]) basis sets were used. The number in the acronyms indicates the nature of the ECP used: LANL1 stands for the Los Alamos large core ECP and LANL2 for the Los Alamos small core ECP.[23,24] For the largest systems, single-ζ (LANL1MB and LANL2MB) basis sets were used. The Moeller−Plesset perturbation treatment was carried out to fourth order (MP4SDTQ) in the case of eclipsed $[PtCl_2(CO)_2]_2$ and the calculated interaction energy differs from the MP2 value by only a 7%.

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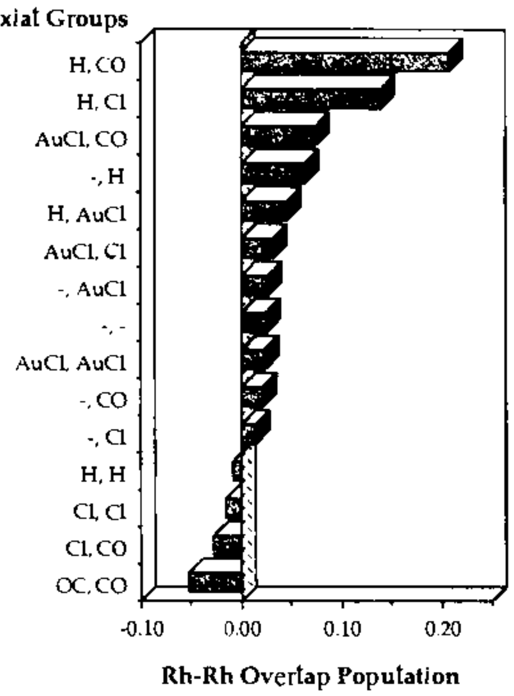
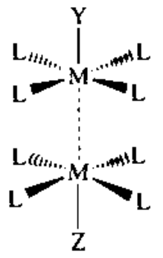


Figure 1. Calculated Rh−Rh overlap population (EH) for the dimer of square-planar $[RhCl_4]^{3-}$ and its adducts of the type $[YRhCl_4\cdots RhZCl_4]^{n-}$ (**3**), where Y, Z = H^+, AuCl, Cl^-, or CO.

Preliminary extended Hückel calculations on the corresponding model adducts $[Cl_4YRh\cdots RhZCl_4]^{n-}$ (**3**; Y, Z = Cl^-, CO, H^+ or AuCl) yield the Rh(I)··Rh(I) overlap populations shown in the histogram of Figure 1, suggesting that binding of Lewis acids (A) and/or bases (B) to the metal atoms at the axial positions has an increasing effect on the M··M bond strength according to the following series: $L_4BM-MBL_4 < L_4BM-ML_4 \approx L_4AM-MAL_4 \approx L_4M-ML_4 < L_4M-MAL_4 < L_4BM-MAL_4$.



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These qualitative predictions are in agreement with the experimental data for several Ni and Pt compounds (Table 3) and also have been checked through MP2 calculations on several adducts of $[PtCl_2(CO)_2\cdots PtCl_2(CO)_2]$. These computationally demanding systems were calculated with a single-ζ basis set, but the correctness of the trends in the calculated Pt··Pt distances is assessed by the calculation of $[H-PtCl_2(CO)_2\cdots PtCl_2(CO)_2-Cl]$ with a double-ζ basis set (Table 1). The calculated binding energies and optimized Pt··Pt distances are in excellent agreement with the above qualitative predictions. Indeed, these adducts are found to present Pt··Pt distances much shorter than in the bare dimer and, for the latter, in fair agreement with the experimental value found for the product of oxidative addition with, e.g., methyl iodide (2.78 Å). Such contacts are at the long end of the typical Pt(III)−Pt(III) bond distances (2.45−2.78 Å),[16] although it must be kept in mind that the experimental values correspond to complexes with bridging ligands.

Although metal−metal bond formation upon oxidative addition has been experimentally realized by several authors for d^8 and d^{10} dimers,[37−39] the present results have a wider scope and indicate that significant strengthening of the $d^8\cdots d^8$ contacts may be obtained by the simultaneous association of a base and an acid, even without change in the formal oxidation state.

A simple model to account for the bonding in acid−base adducts of d^8-ML_4 dimers considers that each metal center contributes two d_{z^2} electrons to bonding along the z direction. Hence, in the bare dimers there is an excess of electron density along the z direction (four electrons for only one M··M contact). The proposed chemical strategies to strengthen the M··M interaction imply the formation of two-electron bonds in the z direction. For instance, adding a Lewis acid to a metal atom in an axial position allows the formation of two bonds (M−M and M−A) with the four d_{z^2} electrons. Alternatively, one can add two radicals (or a Lewis acid and a Lewis base) to the axial positions, thus forming three bonds with a total of six electrons. On the other hand, the addition of one or two Lewis bases to the metal atoms results in an excess of z electron density and less stable systems.

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