van der Waals Radii of Pt(II) and Pd(II) in Molecular Mechanics Models and an Analysis of Their Relevance to the Description of Axial M···H(−C), M···H(−N), M···S, and M···M (M = Pd(II) or Pt(II)) Interactions

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Parameters have been developed for the molecular mechanics modeling of nonbonded interactions involving Pt(II) and Pd(II). The value obtained for the van der Waals radius—about 1.7 Å—accords well with the value proposed by Bondi (*J. Chem. Phys.* **1964**, *68*, 441−451). This model has been used to investigate close M···H(−C), M···H(−N), M···H(−O), M···S, and M···M (M = Pd(II) or Pt(II)) contacts that have previously been described as weak or agostic bonds. It is argued that the M···H(−C) interactions are best described as van der Waals interactions that are in the repulsive region but the results are in accord with the description of M···H(−N) and M···H(−O) contacts as weak hydrogen bonds. M···S and M···M separations in systems without π-acceptor ligands were accurately reproduced by using the same van der Waals parameters.

Introduction

The metal atoms in the d^8 square-planar Pt(II) and Pd(II) complexes frequently make close contacts with atoms lying above or below the coordination plane, and M···H, M···S, and M···M contacts have variously been described as weak bonding interactions, weak agostic bonds, or hydrogen bonds.[1−11] For example, Pt···H contacts in [$PtCl_2$(7,8-benzo[*h*]quinoline)(PEt_3)] and [$PtCl_2$(quinoline-8-carbaldehyde)(PEt_3)] of 2.53(8) and 2.6(1) Å, respectively,[3,4] have been described as weak (though not agostic) Pt←H−C interactions and NMR evidence provides support for the hypothesis that there is some interaction. However, close inspection of the crystal structures of these complexes reveals that the aromatic ligands are highly distorted in a manner that is only consistent with an attempt to at least partially relieve the Pt···H interactions. Thus, if there are attractive forces between the Pt and H atom, they are in balance with significant repulsive forces.

We have recently observed a number of close M···H(ligand) interactions in complexes with aliphatic ligands. These range from 2.58 to 2.83 Å for the complexes [$PdCl_2$(ahaz)] (ahaz = 3-aminohexahydroazepine), [$PtCl_2$(ahaz)], [$PtCl_2$(meahaz)] (meahaz = *N*-methyl-3-aminohexahydroazepine), [$PtCl_2$(dimeahaz)] (dimeahaz = *N*,*N*-dimethyl-3-aminohexahydroazepine), [$PtCl_2$(tmdz)] (tmdz = 5,5,7-trimethyl-1,4-diazacycloheptane), and [$PtCl_2$(1,3-dach)] (1,3-dach = 1,3-cyclohexanediamine) (Figure 1).[12−16] In these cases the ligands are more flexible than the aromatic ligands referred to above so it is not immediately apparent whether the geometries they have adopted result in shorter or longer M···H interactions than would be the case if the ligand was fully “relaxed”. In other words, it is not clear whether the M···H interactions are predominantly attractive or repulsive. One way of determining how the ligands have reacted to these short contacts is through the use of molecular mechanics modeling.

Nonbonded interactions involving the metal atom have usually been omitted from molecular mechanics models of metal complexes.[17−20] That this has not led to obvious problems is probably because the metal center itself makes few close contacts, other than those with atoms connected to the metal by only two or three intervening bonds. However, as we have just noted, this is not the case for square-planar complexes and we and others have recently encountered problems when modeling Pt binding to nucleobases or DNA if nonbonded interactions involving the metal are omitted because these close

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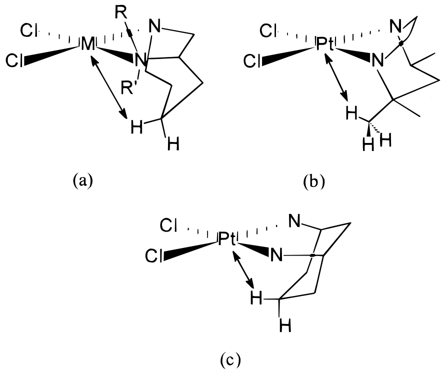

Figure 1. Schematic representations showing close contacts in (a) $[MCl_2(R,R'\text{-ahaz})]$ (M = Pd or Pt, R = H or CH_3, R′ = H or CH_3), (b) $[PtCl_2(tmdz)]$, and (c) $[PtCl_2(1,3\text{-dach})]$.

approaches to the square-planar metal do occur.[19,21] To include these nonbonded interactions in the models, the extent and deformability of the Pt atom (van der Waals radius and ϵ value) are required. Appropriate values of the van der Waals radius and ϵ are not well established for any of the transition metals, and where such interactions have been have included, the values used for the van der Waals radii have varied enormously. For example, a value of 0.69 Å has been used for Co(II) and a value of 2.60 Å for Pd(II).[22,23] In a recently reported force field for modeling Pt−guanine interactions, a van der Waals radius of 2.44 Å was adopted for Pt(II).[21] Part of the reason for this uncertainty is the aforementioned rarity of close contacts which makes parametrization difficult.

There have been a few estimates of van der Waals radii of transition metals based on crystallographic and other experimental data. For example, Bondi obtained estimates of 1.63 and 1.72 for the radii of Pd and Pt, respectively.[24] It is not clear whether these values are appropriate for use in molecular mechanics models. Therefore, we undertook a molecular modeling study of the aforementioned molecules and others that exhibit close M···X contacts in order to develop van der Waals parameters for Pd and Pt suitable for molecule mechanics models and at the same time contribute to an understanding of the nature of the close contacts with these metal atoms.

Methods

Starting models were generated and final models were viewed and analyzed with HyperChem version 4.5.[25] Strain energies were minimized by using MOMECPC.[26] Refinement was continued until all shifts were less than 0.001 Å. The starting points for the force field were taken from the parameter sets reported previously for modeling Pt complexes of amine ligands, thioether ligands, nucleobases, and nucleotides.[27−29] Extensions to and modification of the force field are detailed below and the full parameter set is available as an accessory publication.

Results and Discussion

M···H(−C) Contacts in Complexes with Aliphatic Ligands. The complexes of the ahaz, meahaz, dimeahaz, tmdz, and 1,3-dach ligands (Figure 1) are ideal for the development of nonbonded parameters for the metal atoms because, in all cases, the H atoms making the close contacts are many bonds removed from the metal atom, the ligands are flexible, and there are thoroughly tested force field parameters available for complexes of the aliphatic amine ligands involved. As a first step, the structures were minimized by using the force field described previously[28,30] without van der Waals terms for the metal atoms. This resulted in complex geometries in which the ligand had relaxed toward the metal atom with, in all cases, substantially shorter M···H contacts (Table 1, $\epsilon = 0$) than those observed in the crystal structures. Thus, it is immediately apparent that something is distorting the ligand from its "relaxed" state in such a way that it moves away from the metal atom. This is a general observation that applies to all other complexes discussed below and leads to the conclusion that the interaction between the metal and the ligand, although it may contain an attractive component, is in the repulsive region in these compounds. The next step was to derive van der Waals parameters in order to establish whether these could reliably reproduce the observed ligand distortions.

If we assume that the Pt and Pd atoms have the same van der Waals radius (r_{vdW}) and deformability (ϵ), then there are two parameters to be established. The energy arising from a separation between atoms i and j of r_{ij} (Å) is calculated by using the Buckingham and Hill equations (1−4).

$$E_{nb} = ae^{-br_{ij}} - cr_{ij}^{-6} \qquad (1)$$

$$a = 2014(\epsilon_i\epsilon_j)^{1/2} \qquad (2)$$

$$b = 12.50/(\mathrm{rvd}W_i + \mathrm{rvd}W_j) \qquad (3)$$

$$c = (2.25(\epsilon_i\epsilon_j)^{1/2}(\mathrm{rvd}W_i + \mathrm{rvd}W_j)^6)/144 \qquad (4)$$

The Buckingham equation has attractive and repulsive components; $\mathrm{rvd}W_i + \mathrm{rvd}W_j$ is the separation when these are in balance and the energy is a minimum and ϵ can be considered as describing the steepness of the curve or deformability of the atom. Determining two parameters from a limited set of experimental data will not yield reliable estimates of both parameters. Our initial approach then was to set ϵ to 0.2 and to adjust the van der Waals radius to best reproduce the nonbonded contacts involving the metal atoms in the structures listed in Table 1. In each crystal structure the H atoms were fixed at calculated or observed sites and therefore it was the M···C distances that were used to guide the choice of van der Waals radius. Using the same force field as above and a value of 1.7 Å for the van der Waals radius of the metal atoms resulted in errors in the range 0.01 to 0.05 Å in the M···C distances (Table 1). Given the flexibility of the ligands and the potential for crystal packing effects to influence these distances (note the +0.06 Å range in the two independent molecules in $[PdCl_2(ahaz)]$ and the 0.09 Å range in the two determinations of the $[PtCl_2(tmdz)]$ structure), such deviations are considered to be satisfactory. Setting ϵ to higher values (0.3 or 0.4) necessitated the use of smaller values for the van der Waals radius (1.6−1.65 Å) and marginally worsened the fit of any one van der Waals radius to all structures. Using the parameters proposed

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Table 1. Metal Atom to Ligand Atom Distances for the Complexes Used To Derive the van der Waals Radius

complex	exptl		$\epsilon = 0$		$\epsilon = 0.2$, $r_{\mathrm{vdW}} = 1.70$ Å		$\epsilon = 0.4$, $r_{\mathrm{vdW}} = 2.44$ Å	
	M···C	M···H[a]	M···C	M···H	M···C	M···H	M···C	M···H
[PtCl$_2$(ahaz)]	3.40[12]	2.72	3.19	2.50	3.39	2.75	3.79	3.26
[PdCl$_2$(ahaz)]	3.30[14]	2.60	3.19	2.50	3.39	2.75	3.79	3.26
	3.36	2.70						
[PtCl$_2$(meahaz)]	3.39[13]	2.71	3.16	2.47	3.36	2.72	3.77	3.25
[PtCl$_2$(dimeahaz)]	3.35[13]	2.83	3.26	2.59	3.39	2.76	3.73	3.20
[PtCl$_2$(tmdz)]	3.10[15]	2.58	2.97	2.40	3.15	2.66	3.45	3.11
	3.19	2.73						
[PtCl$_2$(1,3-dach)]	3.33[16]	2.66	2.80	1.99	3.31	2.60	3.97	3.16

[a] Determined from calculated H atom positions.

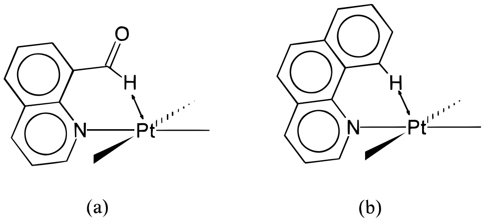

Figure 2. Schematic representations showing close contacts in (a) [PtX$_3$(quinoline-8-carbaldehyde)] and (b) [PtX$_3$(benzoquinoline)].

by Yao *et al.*[21] leads to M···C and M···H separations substantially longer than those observed in the test structures.

From the foregoing, it is clear that inclusion of a repulsive component between the metal center and the ligand is needed for the crystallographically observed geometry to be reproduced. Also, a single set of values for the van der Waals parameters is able to reproduce the geometries of a range of complexes consistent with this being a valid approach to modeling these interactions. We return later to the question as to whether there is also an attractive component to the Pt···H interaction. However, it should be noted here that the ahaz ligand can and regularly does adopt an alternative conformation in which the C−H group disposed toward the metal atom in the conformation under consideration here is disposed away from the metal atom. The strain energies of these two conformations are similar, in accord with their being observed equally often.[12,13] On the basis of these observations no case can be made for there being any significant attractive interaction between the metal atom and the C−H group disposed toward it because this would be expected to lead to exclusive population of the conformation with the shortest M···H contact.

A van der Waals radius of about 1.7 Å is in accord with the values proposed by Bondi[24] but it should be noted that the value is dependent on the entire force field. Therefore, the reliability of this radius depends on how “realistic” the force field is, particularly in terms of the energy required to distort the ligand conformations in the ways observed in these complexes.

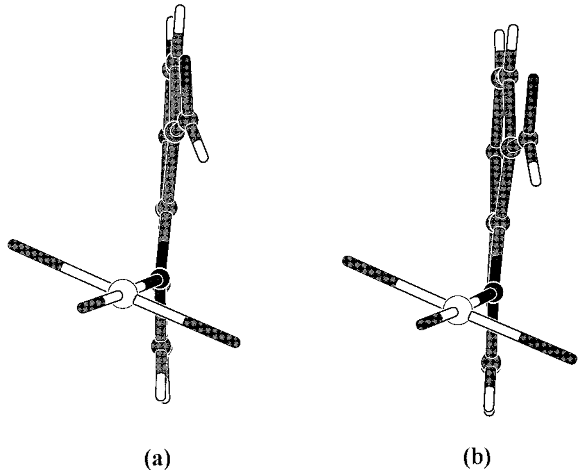

Figure 3. Crystal structure (a) and energy minimized (b) views of [PtX$_3$(quinoline-8-carbaldehyde)].

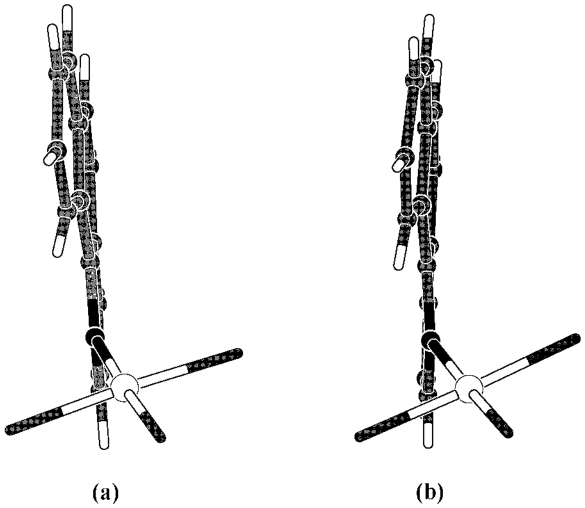

Figure 4. Crystal structure (a) and energy minimized (b) views of [PtX$_3$(benzoquinoline)].

M···H(−C) Contacts in Complexes with Aromatic Ligands. The complexes with the some of the shortest Pt···H contacts are those with aromatic ring systems that result in the disposition of a H atom into an axial position with respect to the Pt atom (Figure 2). Albinati, Pregosin, and colleagues have reported on a number of these complexes[3,4,31] and have discussed the nature of the Pt···H interaction at length. These complexes do reveal short Pt···H contacts but close inspection of the structures reveals that they have undergone extraordinary distortion, evidently in order to relieve these very interactions. For example Pt−N−C angles are distorted by more than 10° from expected values and the aromatic systems are grossly distorted from planarity.[3,4,31] The extent of this distortion is shown in Figures 3a and 4a for *trans*-[PtCl$_2$(quinal)(PEt)$_3$] (quinal = quinoline-8-carbaldehyde) and *trans*-[PtCl$_2$(7,8-benzo[*h*]quinoline)(PEt)$_3$], respectively. These systems are potentially better candidates for defining the van der Waals interaction parameters for the Pt atom because the contacts are shorter. However, the force field parameters for the interaction of metal atoms with aromatic ligands are less well developed than those for aliphatic ligands and in order to model these complexes substantial changes to existing force fields were required. In particular, we found that the molecular mechanics parameters defining the energy cost associated with distortion of the Pt atom out of the plane of the aromatic ligand were deficient. The values we had

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Table 2. Metal Atom to Ligand Atom Distances (Å) for the Complexes of Aromatic Ligands

	exptl		$\epsilon = 0$		$\epsilon = 0.2$, $r_{vdW} = 1.70$ Å		$\epsilon = 0.4$, $r_{vdW} = 2.44$ Å	
complex	M···C	M···H	M···C	M···H	M···C	M···H	M···C	M···H
[PtX$_3$(quinal)]	3.12[3]	2.56 (2.37[a])	2.66	1.76	3.11	2.41	3.50	3.08
[PtX$_3$(benzoquin)]	3.19[4]	2.53 (2.31[a])	2.66	1.75	3.13	2.36	3.45	3.05
[PtX$_3$(8-mequin)]	3.17[10]		2.68	1.74	3.16	2.40	3.56	3.05

[a] Determined from calculated H atom positions.

been using were estimates because it is difficult to extract the appropriate energy terms from vibrational spectra and, until now, these estimates had not been rigorously tested because we had not modeled complexes in which the Pt was significantly distorted from the ligand plane.

These complexes of the aromatic ligands were initially modeled by using the van der Waals parameters derived above and a force field derived from the AMBER force field as described previously.[28] Simplified models with three chloro ligands were employed to reduce the number of new force field parameters required. The out of plane energy term was then adjusted to give the best fit for [PtX$_3$(quinal)] and was tested on the other aromatic ligands in Table 2. Energy minimized views of trans-[PtX$_3$(quinal)] and *trans*-[PtX$_3$(7,8-benzo[*h*]-quinoline)] are shown in Figures 3b and 4b alongside the crystallographically determined structures. As can be seen, the out of plane deviations and the geometry of the complex are well reproduced in both cases as are the Pt−N−C angles in these and the other structures in Table 2. Energy minimization with the van der Waals parameters of the metal atom omitted from the model resulted in Pt···H and Pt···C separations that are approximately 0.5 Å shorter than those observed experimentally. Thus, a van der Waals repulsion not only provides a rationalization for the observed distortion of the aromatic groups but is also essential to reproduce the observed Pt···H and Pt···C separations.

We have also found[32] that the out-of-plane distortion term developed in this way accurately reproduces the deviations of the Pt from the planes of the guanine bases observed in the recently reported crystal structure of a cisplatin/DNA complex.[33]

M···H(−N) Contacts. M···H(−N) contacts are potentially different from M···H(−C) contacts because there is the possibility of the more acidic amine proton hydrogen bonding with the electron pair occupying the axially oriented d$_{z^2}$ orbital. Yao *et al.*[11] have recently reported an analysis of a wide range of Pt···H(−N) and Pt···H(−C) contacts and concluded that the former are best described as four-electron, three-center hydrogen bonds, noting in particular that the low field NMR shift of the H atom associated with the Pt atom is more consistent with a hydrogen bond than an agostic interaction. Perhaps the most compelling evidence for an attractive interaction is the intermolecular Pt···H(−N) interaction described by Brammer et al.[5] The H atom in this example was located by using neutron diffraction, and Pt···H and Pt···N separations of 2.262(11) and 3.275(5) Å were found.

We have investigated complexes from both categories described above: those with flexible ligands that are able to reorganize and relieve the M···H(−N) interaction and those with aromatic ligands where the H atom is forced to lie close to the Pt atom. In the case of the tacnH$^+$ ligand (tacn = 1,4,7-triazacyclononane) the N−H group can be oriented toward the Pt atom or away from it. Crystal structures of [Pt(Br,Cl)$_2$-(tacnH)]$^+$, [PdCl$_2$(tacnH)]$^+$, and [Pd(tacn)(tacnH)]$^{3+}$ all have the tacnH$^+$ ligand with conformations that result in the protonated amine being disposed toward the Pt or Pd atoms.[34−36] In the latter case this is due, at least in part, to a hydrogen-bonding interaction between the tacn and tacnH$^+$ (N···N 2.95(1) Å).[34] The two conformations of the tacn ligand have almost identical strain energies, thus which is adopted may reflect the nature of the Pt···H or Pd···H interaction.

In the case of [Pt(Br,Cl)$_2$(tacnH)]$^+$ and [PdCl$_2$(tacnH)]$^+$ complexes the axial Pt···N and Pd···N distances are 3.11 and 3.11−22 Å, respectively, with calculated Pt···H and Pd···H distances of 2.31 and 2.30−2.40 Å.[35,36] These distances are similar to those reported by Brammer et al.[5] If the van der Waals parameters for the Pt atom are omitted and the strain energy of [PtCl$_2$(tacnH)]$^+$ is minimized, Pt···N and Pt···H distances of 2.85 and 1.97 Å result. If the van der Waals parameters derived above (1.7 Å, 0.2) are used the separations become 3.24 and 2.58 Å. The former values show that the tacnH$^+$ ligand in these complexes is not fully relaxed but is repelled significantly by the metal atom. The latter values are a little longer than the crystallographically determined separations and we found that in order to reproduce these separations it was necessary to reduce the van der Waals radius to 1.40 Å. Thus, these results are consistent with there being a weak attraction between the Pt or Pd atom and the protonated amine group. Using constraints to set the Pt···N and Pt···H separations to those observed in the crystal structures, within the framework of the force field used above, results in an energy cost of about 3 kJ, suggesting that the energy cost derived from the putative hydrogen bond is probably at the lower end of the range for hydrogen bonds.

We have shown elsewhere that in [PtCl(trenH)]$^+$ (tren = 2,2,2-triaminotriethylammonium), where an intramolecular Pt···H(−N) hydrogen bond could form at the cost of only a few kilojoules, it does not, and instead an intermolecular Cl···H-(−N) hydrogen bond is observed.[36] It is also worth noting that intermolecular Pt···H(−N) hydrogen bonds such as the one described by Brammer et al.[5] are frequently not observed in [PtCl$_4$]$^{2-}$ salts of protonated amines that have been structurally characterized. Thus, if there is a Pt···H(−N) hydrogen bond, then it is unlikely that it contributes more than a few kilojoules in accord with the calculations described above. In the complexes [M(tacn)$_2$]$^{2+}$ (M = Pd or Pt) the noncoordinated amine groups are disposed away from the metal atom.[37,38] These amine groups do have one H atom and it is clear from the structures of the [MX$_2$(tacnH)] structures that this could be oriented toward the metal. Thus, it seems likely that the lack

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Table 3. Metal Atom to Ligand Atom Distances (Å) for the Complexes with M···H−N Interactions

complex	exptl		$\epsilon = 0$		$\epsilon = 0.2$, $r_{vdW} = 1.70$ Å		$\epsilon = 0.4$, $r_{vdW} = 2.44$ Å	
	M···N	M···H	M···N	M···H	M···N	M···H	M···N	M···H
$[PtX_2(tacnH)]^+$	3.11[36]	2.31	2.85	1.97	3.24	2.58	3.67	3.14
$[PtX_3$(8-dmamnapth)]	2.98[39]	2.11	2.60	1.70	3.07	2.27	3.42	2.79
$[PtX_3$(acetamquin)]	3.08[6]	2.24	2.66	1.80	3.08	2.40	3.45	3.05

of a positive charge on the noncoordinated amine reduces the tendency for it to associate with the metal center. This is in accord with the description of these contacts as weak hydrogen bonds since electrostatic interactions make a substantial contribution to the energy of hydrogen bonds. We have not attempted to include an electrostatic component in our models, because it is not obvious what negative charge should be associated with the d_{z^2} orbital or at what distance from the metal it should be located. However, even a modest electrostatic attraction could account for the 3−4 kJ mol^{-1} that we have estimated to arise from these interactions.

There are few examples of aromatic ligands that result in short and largely unavoidable Pt···H(−N) contacts. However, one example [PtBr(8-dmamnaphth)(8-dmamnaphthH)] (8-dmamnaphth = *N*,*N*-dimethyl-8-naphthaleneamine) is remarkably different from the closely related aromatic ligands described above that generate short Pt···H(−C) contacts. Where the latter ligands have undergone gross distortion and twisting in an apparent attempt to relieve the interaction, the 8-dmamnaphthH ligand is not significantly distorted from planarity and a Pt···H contact of 2.11(5) Å is observed with a Pt···N separation of 2.982(4) Å.[39,40] Energy minimization in the absence of a van der Waals parameters for the Pt atom results in Pt···H and Pt···N distances of 1.70 and 2.60 Å, respectively. Thus, it is clear that the 8-dmamnaphthH ligand is not fully relaxed but has undergone some distortion to partially relieve the Pt···H interaction. This can be seen in the Pt−C−C angles, which are 126.9 and 117.4°, with the larger angle being located on the side adjacent to the dimethylamine substituent[39,40] and apparently being opened as a consequence of an interaction between the substituent and the Pt atom. When the van der Waals parameters (1.70 Å, 0.2) are introduced, the distances become 2.27 and 3.07 Å, significantly longer than the distances in the crystal structure. Minimization with Pt···H constrained to 2.11 Å results in an increase of only 3.2 kJ mol^{-1} in the strain energy. Thus, the results are again consistent with there being a small attractive component to the Pt···H(−N) interaction. Similar results are observed for the complex of acetamquin (acetamquin = *N*-acetyl-8-aminoquinoline) (Table 3).[6]

A similar situation is observed in $[Pt(C_6F_5)_3$(8-hydroxyquinaldine)] where the ligand is not distorted from planarity and a Pt···H(−O) contact of 2.19 Å is observed.[10] Here too, the relatively acidic phenol group leads to a reasonable expectation of a hydrogen bond and the results are consistent with this description of the Pt···H(−O) interaction. If no van der Waals parameters are included for the Pt atom, then a Pt···H distance of 1.88 Å is predicted and with the parameters derived above this becomes 2.38 Å. Constraining the Pt···H distance to 2.19 Å incurs an energy cost of 4.8 kJ mol^{-1}, similar to the energy difference calculated for the Pt···H(−N) interaction. What is most revealing about this structure in particular is that the hydroxyl H atom is directed toward the Pt atom, which it could easily avoid.[10] Thus, in this case, it is difficult to avoid the conclusion that there is an attractive interaction between the H atom and the Pt atom.[10]

In all cases involving short Pt···H(−N) and Pt···H(−O) distances, where the H atom donor group is relatively acidic, the distances calculated from the van der Waals parameters derived by using Pt···H(−C) interactions are larger than the crystallographic values. These results are consistent with there being a weak Pt···H hydrogen bond as suggested by Brammer et al. and Yao et al.[5,11] There is ample evidence of Pt(II) being able to act as a Lewis base by donation of the electrons occupying the d^8 orbital in the "T over square" complexes described by Randaccio, Lippert, and colleagues.[41−43] Wehman-Ooyevaar et al have concluded from theoretical calculations that the Pt···H(−N) interaction is primarily electrostatic.[44] Inclusion of electrostatic interactions between the amine groups and the d_{z^2} orbital might account for the additional attraction but this would not be inconsistent with the description of the interactions as weak hydrogen bonds.

M···S Contacts. Short M···S contacts have been observed in a variety of complexes with macrocyclic ligands such as [9]ane-S_3 (=1,4,7-trithiacyclononane), [9]ane-NS_2 (=1,4-dithia-7-azacyclononane), and [9]ane-N_2S (=1-thia-4,7-diazacyclononane). In all cases it is a long M···S contact that occupies the axial position or positions and the distances have generally been in the range 2.9−3.3 Å,[1,2,34,45−50] though recently a series of shorter contacts have been reported.[9] We have modeled the complexes $[MCl_2([9]ane-S_3)]$, $[MCl_2([10]ane-S_3)]$, $[M([9]ane-S_3)_2]^{2+}$ and $[M([10]ane-S_3)_2]^{2+}$, using the force field parameters derived previously for Pt/thioether interactions[29] and the nonbonded parameters derived above for the Pt atom. The Pt···S separations returned by these models are 3.06, 3.09, 3.02, and 3.07 Å, respectively, which are in reasonable agreement with the crystal structure values for these complexes (Table 4). Clearly, there is substantial variability in these M···S separations and even more notable is the observation that in some apparently unpredictable cases the noncoordinated thioether is oriented away from the metal atom. For example, in $[Pt([9]ane-S_3)_2]^{2+}$ one of the noncoordinated thioethers is oriented away from the

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Table 4. Metal Atom to Ligand S Atom Distances (Å)

complex	exptl M···S	$\epsilon = 0$ M···S	$\epsilon = 0.2$, $r_{\mathrm{vdW}} = 1.70$ Å M···S
$[MX_2([9]ane\text{-}S_3)]$	3.12−3.14[1,34]	2.69	3.06
$[MX_2([10]ane\text{-}S_3)]$	3.07[50]	2.72	3.09
$[M([9]ane\text{-}S_3)_2]^{2+}$	2.88−3.01[1,46]	2.59	3.02
$[M([10]ane\text{-}S_3)_2]^{2+}$	3.03−3.23[47,48]	2.69	3.07

metal[46] and in $[Pt([9]ane\text{-}N_2S)_2]^{2+}$ both are.[2] Thus, any attraction between the metal and the S atom is weak at best. Minimization with nonbonded parameters for the metal removed results in M···S separations of 2.59 to 2.72 Å, up to 0.5 Å shorter than any of the separations observed experimentally. Thus, as before, there is clear evidence that repulsion between the metal and the ligand results in distortion of the ligand away from the metal compared to what would be observed if the ligand were fully relaxed.

These results are in accord with the Pt···S separations being in the repulsive range and contributing little if anything to the stability of the complexes. Also, the van der Waals radius derived for Pt from Pt···H contacts is evidently applicable to these interactions. However, Schröder and colleagues have recently reported on a new series of $[Pt([9]ane\text{-}S_3)(L)_2]$ complexes and have found a range of Pt···S separations with the shortest being 2.698(3) Å.[9] The additional ligands (L) in this case are π acceptors and the authors argue that this will result in a decrease in the electron density on the Pt atom allowing for a shorter Pt···S interaction. It may be then, that a single van der Waals radius will not adequately reproduce these separations in all types of complexes and that the value we have derived should be viewed as being appropriate only for the classes of complexes used in its derivation.

M···M Contacts. There are numerous examples of dimeric complexes with Pt···Pt contacts in the range 2.7−3.4 Å and distances at the longer end of this range have frequently been observed in the solid state. For example, there are many complexes with acetate, pyrimidine, or hydroxopyridinato bridging ligands giving rise to close contacts.[8,51−54] There has been extensive discussion on whether these contacts are weakly bonding in nature[7,8,55−58] and a semiquantitative study indicates a bonding energy of about 12 kJ mol^{-1}.[56] Also, it is clear that the spectroscopic properties of the complexes are influenced by the M···M separations.[59] Applying the van der Waals parameters derived above has the potential to shed further light on this question but, unfortunately, a molecular mechanics analysis of most of these molecules is not likely to be informative at this time because reliable force field parameters for the M−O−C and M−N−C angles involved have not yet been developed and these will be critical in determining the M···M distances. We have therefore identified two candidate systems with simple aliphatic amine ligands and short M···M contacts.

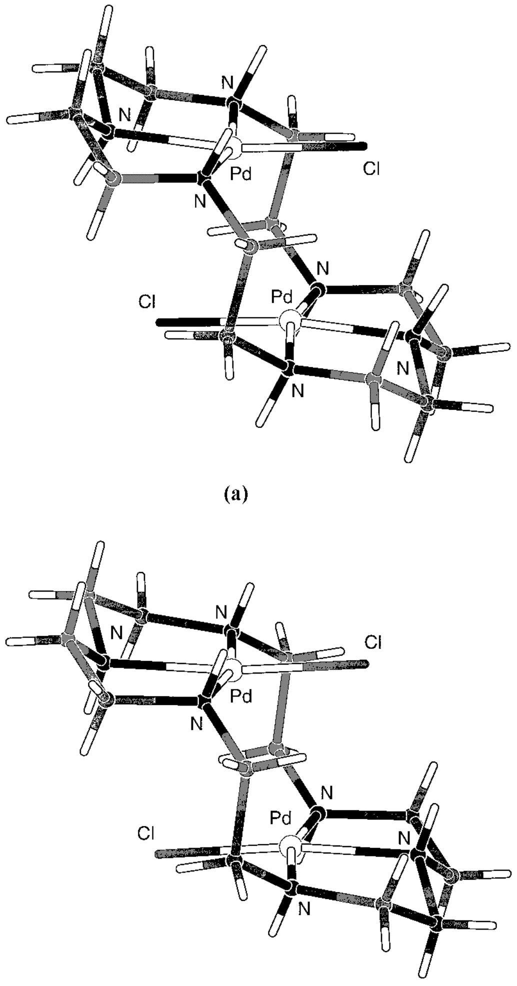

Figure 5. Crystal structure (a) and energy minimized (b) views of $[Pd_2Cl_2(18ane\text{-}N_6)]^+$.

In $[Pd_2X_2(18ane\text{-}N_6)]^{2+}$, X = Cl^-, Br^-, the Pd···Pd contacts are 3.04 and 3.02 Å, respectively (Figure 5a).[60,61] Energy minimization of chloro complex using no van der Waals parameters for the metal yielded a Pd···Pd separation of 3.009 Å and with the parameters described above the separation becomes 3.045 Å. The latter value is in excellent agreement with the crystal structures and therefore it is not necessary to invoke a weak bonding interaction. There are some interesting features to this structure that warrant further comment. The Pd atoms deviate toward each other from the planes defined by the coordinating atoms and similar pyramidalizations have led to the suggestion that there is a bonding interaction between the metals.[55] However, the molecular mechanics calculations clearly reveal that this aspect of the geometry is determined more by the interaction between the chloro ligands and the amine group that lies trans to the chloro ligand bound to the other Pd atom. The Cl···H separation in the crystal structure

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is 2.57 Å and is probably a weak hydrogen bond. Indeed, to reproduce this geometry is was necessary to include in our molecular mechanics model the very weak hydrogen bonding term that we have used previously for chloro/amine interactions.[62] The out-of-plane deviation of the Pd atom is accurately reproduced by the model and arises not from an attraction between the metals but from a repulsion between the chloro ligand and the amine group (Figure 5b). It is possible that other instances of pyramidalisation are also due to factors other than M···M attractions.

In $[Pd_2Cl_2(heptam)_3]^{2+}$ (heptam = (2*S*,3*S*)-2,3-diaminobicyclo[2.2.1]heptane) the Pd···Pd contacts average at 3.31 Å.[63] Energy minimization with and without van der Waals terms for Pd gave separations of 3.46 and 3.49 Å, respectively, both greater than the van der Waals radius sum. Minimization with the separation constrained at 3.31 Å increased the strain energy by only 1.9 kJ mol^{-1}. Thus, this is a highly flexible system in which the Pd···Pd separation is evidently determined more by external forces such as crystal packing than by any interaction between the metal atoms. There is little barrier to further contraction of the Pd···Pd separation and contraction to 3.05 Å, for example, increases the strain energy by only 12.8 kJ mol^{-1}, most of this being due to Cl···Cl repulsion. Thus, if there was a substantial attraction it should give rise to significantly shorter Pd···Pd separations.

On the basis of these two studies it would be inappropriate to conclude that there is no attractive force between the metal atoms. However, it is possible to deduce, using the van der Waals parameters we have derived for the metal, that a separation of the order of 3.0 Å can be readily induced by a relatively flexible ligand, viz., 18-aneN$_6$. Also, it must be emphasized that, in the systems modeled, none of the ligands are π-acceptors and Gray et al. have argued that the presence of such ligands promotes Pt···Pt bonding interactions.[58] This also accords with the observations for the M···S interactions as discussed above. Thus, the van der Waals parameters derived here probably cannot be expected to reproduce M···M or M···S separations in systems with π-acceptor ligands but can be used to factor out steric components and so shed light on those situations when a genuine bonding interaction does exist or some other factor allows for closer than normal contacts.

Conclusions

Using molecular mechanics modeling we have developed a van der Waals radius for Pt and Pd of about 1.7 Å. This value is clearly dependent on the force field and therefore must be considered within this constraint. However, a van der Waals radius in the range 1.6−1.7 Å does accord well with the values proposed for transition metals by Bondi.[24] Additional support for such a van der Waals radius comes from M···M separations in the solid state. In $K_2[Pt(CN)_4]$ the Pt···Pt separation is 3.48 Å and in the structures of both $[PdCl_2(ahaz)]$ and $[PdCl_2(tacnH)]_4(PF_6)_2Cl_2$ “dimers” with Pd···Pd separations of 3.36 and 3.31 Å, respectively, are seen.[14,35] Schroder et al. have represented the latter Pd···Pd interaction as a bond;[35] however, $K_2[Pt(CN)_4]$ has a similar M···M separation but is a nonconductor and as pointed out by Cotton and Wilkinson “the Pt···Pt distances are so long that no significant M−M bonding would be expected”.[64] The forces holding these Pd···Pd “dimers” together are more likely to be the H-bonding interactions between the H(amine) atoms and the chloro ligands.[14]

We have assumed here that the van der Waals radii of Pt(II) and Pd(II) are the same. Bondi deduced values of 1.63 and 1.72 Å for Pd and Pt, respectively, and there is some evidence from the foregoing to support the notion that the radius of Pd is smaller than that for Pt. For instance Pd···H contacts are generally marginally shorter than Pt···H contacts in otherwise isostructural complexes. Also, for some of the complexes where a close Pd···S contact is observed, the analogous Pt complex has one or both of the noncoordinated S atoms oriented away from the metal. However, the differences are too small to reliably distinguish with the limited amount of experimental data currently available.

We return now to the question as to whether the close M···H contacts are weakly attractive (agostic) interactions. If they are, then the van der Waals radius we have arrived at might be an underestimate. Our principal justification for arguing that these are not favorable interactions is that omission of nonbonded interactions involving the metal or omission of just the M···H interaction from the models results in shorter M···C and M···N separations than those observed in the crystal structures (Tables 1 and 2). In other words, the ligand geometries in the solid state are evidently strained as a consequence of the M···H interaction and removal of this interaction results in relaxation of the ligand toward the metal and even shorter contacts. It is clear that in other cases where short intramolecular Pd···H or Pt···H contacts are observed, considerable deformation of the molecule consistent with attempts to increase these Pt···H separations has occurred (Figures 3 and 4).[3,4,31] This is most evident in the Pt−N−C angles, which are opened in the direction of the Pt···H contact by 4.5−10°.[3,4,31] Thus, if there is an attractive component to the interaction, as may be indicated by NMR coupling constants,[3,4,31] then when it is combined with the repulsive component, the overall interaction has a minimum at distances longer than the separations observed in these structures.

Much of the evidence for an attractive Pt···H interaction derives from the ^{1}H NMR shifts for the H atom in the vicinity of the Pt atom. Agostic interactions are typified by large upfield shifts.[65] Albinati and Pregosin report weak downfield shifts for the complexes referred to above.[3,4,31] Such a shift is more consistent with the description of the interaction as a hydrogen bond. In addition, ^{195}Pt−^{1}H coupling constants were taken to indicate an interaction. These coupling constants possibly reflect the separation between the Pt and the H rather than the nature of the interaction, and in the complex [PtBr(8-dmamnaphth)(8-dmamnaphthH)] there is a very strong coupling constant observed for a Pt···H interaction that is probably best described as a hydrogen bond.[39,40] Our observation that a single van der Waals radius for Pt reproduces separations from H, S, and Pt is also consistent with these interactions being in the repulsive region because some of these atoms are electron donors and others are electron acceptors and it would be most unlikely that similar types of bonding interactions would be expected for all of them.

Our calculations provide support for the description of Pt···H(−N) interactions as weak four-electron, three-center hydrogen bonds proposed previously by Brammer et al. and Yao et

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al.[5,11] Aliphatic and aromatic H atoms have been known to make still weaker hydrogen bonds and, therefore, we do not rule out the possibility of such an interaction making a minor attractive contribution to M•••H(−C) interactions. If this is the case, our value of the van der Waals radii of Pt(II) and Pd(II) will be slightly underestimated. However, it would remain a valid value for use in molecular mechanics models involving such interactions.

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Supporting Information Available: Complete force field parameter list (7 pages). See any current masthead page for ordering and Internet access information.

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