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O–H···Pt^{II}: Hydrogen Bond with a Strong Dispersion Component[**]

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In the past decade, crystallographic and spectroscopic evidence has accumulated showing that d^8 metal ions such as platinum(II) are capable of acting as hydrogen-bond acceptors.[1, 2] One may ask whether water could undergo similar hydrogen bond like interactions with solvated platinum complexes. We report here an ab initio study, at the Møller-Plesset second-order perturbation (MP2) level, of the interaction between a water molecule and two platinum(II) complexes $[Pt(NH_3)_4]^{2+}$ (**1**) and *trans*-$[Pt(OH)_2(NH_3)_2]$ (**2**). Our calculations indicate that a linear HO–H···Pt interaction is stabilized by a strong dispersion component. In the case of the HO–H···$Pt(NH_3)_4{}^{2+}$ interaction, the dispersion component considerably reduces the electrostatic repulsion, while for the HO–H···$Pt(OH)_2(NH_3)_2$ approach, it adds to the electrostatic attraction, giving rise to a hydrogen bond like interaction with a dissociation energy of about 4 kcal mol^{-1}. It is suggested for the previously reported complex *cis*-$[PtBr_2(gly\text{-}N)_2]\cdot H_2O$ (gly = NH_2CH_2COOH) that a similar hydrogen bond between a water molecule and an uncharged platinum central atom occurs in the solid state. Therefore, not only in anionic but also in electrically neutral platinum(II) complexes can the platinum atom act as a hydrogen-bond acceptor.

Two approaches of a water molecule to **1** or **2** along the *z* axis (defined as the normal to the platinum coordination plane through the Pt atom) were considered: approach I with the O atom oriented toward Pt and approach II with the O–H vector directed toward Pt, as shown for complex **2** in Figure 1.

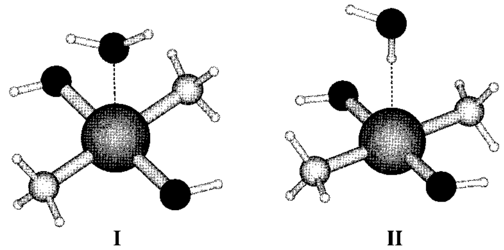

Figure 1. Approaches of H_2O, using complex **2** as an example. Approach I: O atom directed toward Pt; approach II with O–H vector directed toward Pt.

The interaction energies at the Hartree–Fock (E_{HF}) and at the MP2 (E_{MP2}) levels were evaluated as the difference between the total energy of the two interacting species and the sum of the total energies of the individual molecules, corrected for the basis set superposition error. In addition, an estimate of the electrostatic component (E_{ES}) was obtained as the sum of Coulomb terms q_iq_j/r_{ij} between atomic charges determined by optimizing the fit to the MP2 electrostatic potential of the isolated molecules. To an approximation, the interaction energy E_{MP2} can be considered to be the sum of the electrostatic (E_{ES}), exchange-repulsion (E_{EX}), polarization (E_{POL}), and charge-transfer (E_{CT}) components, plus the contribution of electron correlation effects E_{CORR}[4–6] (Eq. 1).

$$E_{MP2} = E_{ES}+E_{EX}+E_{POL}+E_{CT}+E_{CORR} \qquad (1)$$

It is common practice to associate the interaction energy determined at the Hartree–Fock level E_{HF} with the sum $E_{ES}+E_{EX}+E_{POL}+E_{CT}$.[5] The difference $E_{MP2}-E_{HF}$ can be therefore used as an estimate for E_{CORR}. In Figure 2, the interaction energies E_{MP2}, E_{HF}, and E_{ES} are plotted against the Pt···O separation, together with the differences $E_{MP2}-E_{HF}$ and $E_{HF}-E_{ES}$.

Approach I (Figure 2a, b): In approach I, both E_{HF} and E_{MP2} curves quite closely follow the E_{ES} curve at long and intermediate distances, indicating that the interaction is mainly determined by electrostatic (long-range) and exchange-repulsion (short-range) energy. For the approach I/**1** the electrostatic energy is negative, giving rise to a profound (−11 kcal mol^{-1}) energy minimum at a Pt···O distance of about 3.3 Å, whereas approach I/**2** is purely repulsive. Agreement with the deep minimum for approach I/**1** is found in the Cambridge Crystallographic Data Centre (CCDC), which contains several entries of dicationic platinum(II) tetraamine complexes with axial water ligands at distances between 3 and 3.5 Å. The structure of $[Pt(py)_4]Cl_2\cdot 3H_2O$ (py = pyridine), determined by neutron diffraction,[7] (Figure 3) for example, features a square-planar PtN_4 coordination, which is extended

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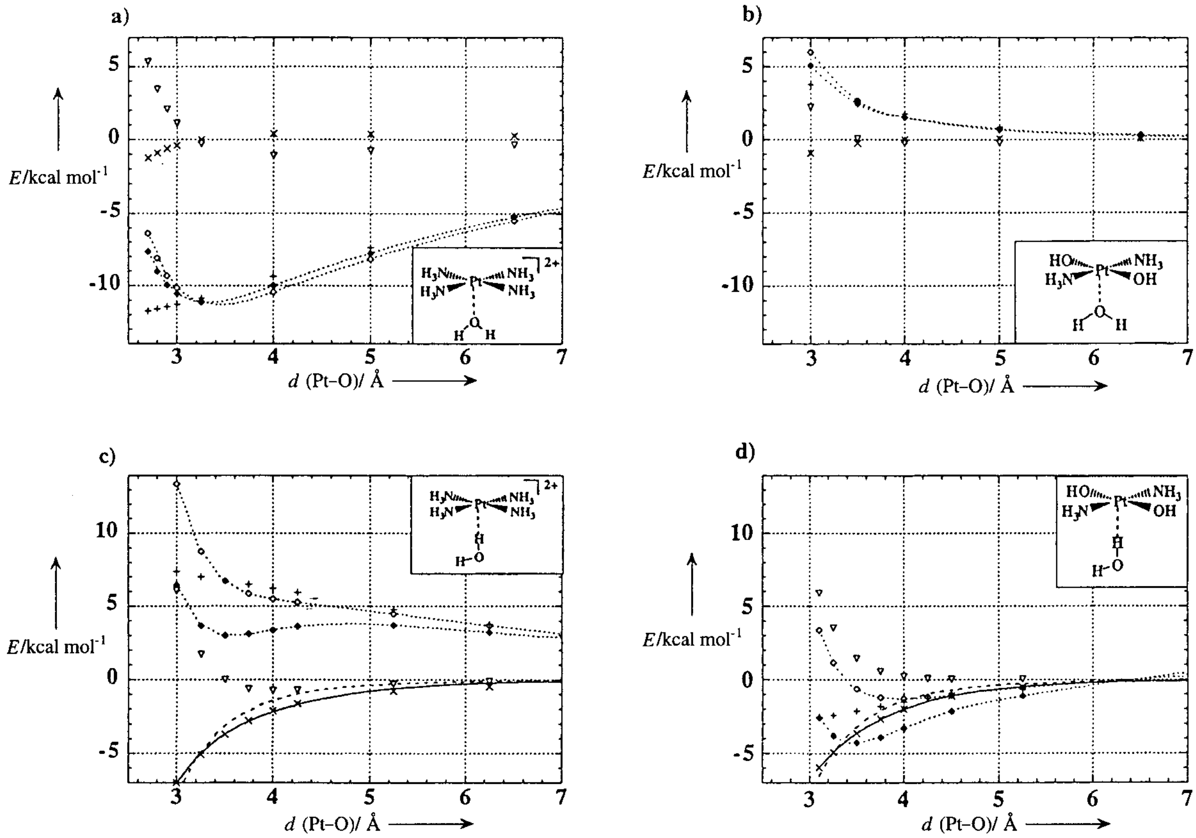

Figure 2. Plots of the interaction energy and its components E_{HF} (----◇----), E_{MP2} (----◆----), E_{ES} (+), $E_{\mathrm{HF}}-E_{\mathrm{ES}}$ (▽), $E_{\mathrm{MP2}}-E_{\mathrm{HF}}$ (×), and fits to the $E_{\mathrm{MP2}}-E_{\mathrm{HF}}$ curves using a single $-C_6d^{-6}$ term (----) and a Buckingham function $Ce^{-\alpha(d-d_0)}$ with $d_0=3.5$ Å (——). Approaches: a) I/**1**; b) I/**2**; c) II/**1**; d) II/**2**.

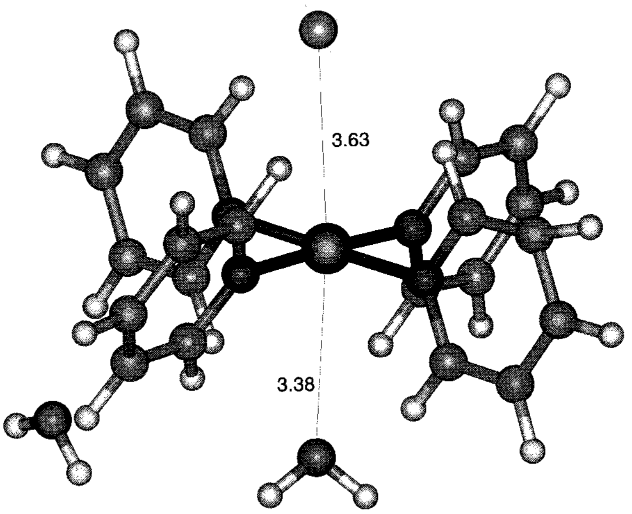

Figure 3. Crystal structure of $[\mathrm{Pt(py)_4}]\mathrm{Cl_2}\cdot 3\,\mathrm{H_2O}$ (CCDC entry CIWKEY01).[7, 28] Distances are in Å.

to a pseudo-octahedron by axial chloride and water ligands. Water is coordinated to platinum through the oxygen lone pairs with a Pt ··· O distance of 3.38 Å, close to the optimum distance of 3.3 Å that we calculated for the $\mathrm{H_2O}\cdots\mathrm{Pt(NH_3)_4}^{2+}$ (I/**1**) interaction.

Approach II (Figure 2c, d): In contrast to approach I, the E_{HF} and E_{MP2} curves differ considerably in approach II, indicating that E_{CORR} is much more important. The E_{MP2} curves show pronounced minima at a Pt ··· O distance of about 3.5 Å, which were not observed in the E_{HF} curves. The electrostatic components of the approaches II/**1** and II/**2** have inverted signs with respect to the approaches I/**1** and I/**2**. Thus, for approach II/**1** the E_{MP2} energy is positive throughout, in spite of the local minimum at about 3.5 Å. In contrast, for approach II/**2**, this minimum corresponds to a bound state with a dissociation energy of about 4 kcal mol^{-1}. Importantly, the $E_{\mathrm{MP2}}-E_{\mathrm{HF}}$ curves, which provide an estimate for E_{CORR}, are almost superimposable for II/**1** and II/**2**. This indicates that E_{CORR} is independent of the charge on the platinum complex and suggests that dispersion energy is the main contributor to E_{CORR}. Ionic contributions to E_{CORR}, which have been shown to be significant, for example, in the case of water clusters,[8] and second-order induction terms would be expected to be different for II/**1** and II/**2**, and can therefore play only a minor role. Figures 2c, d show that the $E_{\mathrm{MP2}}-E_{\mathrm{HF}}$ curves fit poorly to a $-C_6d^{-6}$ function, but they fit perfectly to a Buckingham function $Ce^{-\alpha(d-d_0)}-C_6d^{-6}$ ($d_0=3.5$ Å). The need for a *positive* exponential term suggests that apart from the pure dispersion energy E_{DISP} proportional to d^{-6}, we have a significant dispersion-exchange cross-term $E_{\mathrm{DISP\text{-}EX}}$. A similar partial compensation of E_{DISP} by an $E_{\mathrm{DISP\text{-}EX}}$ term has been found in other weakly bound systems such as hydrogen-bonded clusters of $\mathrm{H_2O}$, $\mathrm{NH_3}$, and HF molecules,[9] as well as clusters of gold(I) complexes displaying aurophilic attraction.[10] Higher order terms to E_{DISP}, proportional to d^{-8}, d^{-10}, and so forth, whose minor contributions cannot be a priori excluded, have a *negative* sign.

The observation of a bound state at a Pt···O distance of about 3.5 Å for approach II/**2** is particularly interesting, since it indicates that not only anionic but even uncharged platinum(II) complexes should undergo hydrogen bonding like associations. The CCDC lists a large number of uncharged and anionic platinum complexes with water of crystallization, and we searched for examples that showed indications of HO–H···Pt hydrogen bonding. This search revealed that water in platinum complex crystals overwhelmingly prefers hydrogen-bonding contacts with ligand atoms to those with the platinum central atom.[11] Nevertheless, Figure 4 shows the crystal structure of the complex *cis*-[$PtBr_2$(gly-*N*)$_2$]·H_2O[12] in which we believe HO–H···Pt hydrogen bonding does occur. In this structure, the oxygen atom of water lies 3.32 Å above the platinum atom, the Pt···O vector subtending an angle of 82° with the mean $PtBr_2N_2$ plane. Apart from the short contact to platinum, the oxygen atom of the water molecule forms a hydrogen bond with a glycine hydroxy group of a second complex molecule (O···O 2.52 Å), and one with a carbonyl oxygen atom of a third molecule (O···O 2.76 Å). The carbonyl and hydroxy groups of the uncoordinated carboxylates are clearly distinguished in the crystal structure. Since the hydrogen atoms could not be localized the use of crystal structure analysis alone does not allow one to conclude that the second hydrogen atom of the water molecule points towards the platinum center. However, our calculations for the approach between the electrically neutral complex **2** and water strongly suggest that such is the case, since the coordination of platinum by hydrogen (approach II) is attractive, whereas that by the lone pair of electrons of oxygen (approach I) is repulsive.

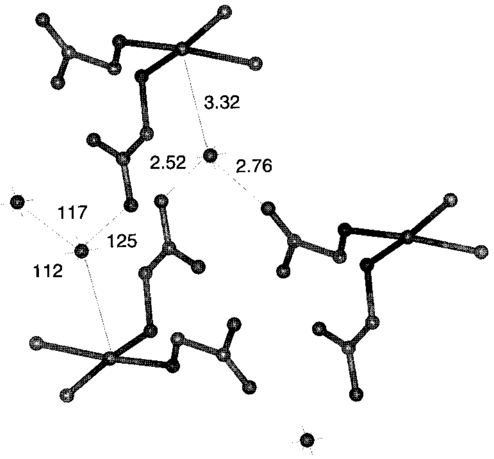

Figure 4. Crystal packing of *cis*-[$PtBr_2$(gly-*N*)$_2$]·H_2O (CCDC entry BGLYPT[12, 28]). Distances are in Å, angles in degrees.

Although no Morokuma analysis[13] of the HF energy was performed, some qualitative statements about the size of E_{POL} and E_{CT} can be made from the differential $E_{HF} - E_{ES}$ curves. The polarization energy is expected to be considerably stronger for the cationic complex **1** than for the uncharged species **2**. In fact, the $E_{HF} - E_{ES}$ curves, which represent the sum $E_{EX}+E_{POL}+E_{CT}$, show shallow minima (ca. -1 kcal mol^{-1}) at a Pt···O distance of about 4 Å for both approaches of water to complex **1** (Figure 2a, c), whereas the analogous curves for complex **2** (Figure 2b, d) show virtually no minima at all. This suggests that the contributions of E_{POL} to the water interaction of complex **1** are rather small, and those of species **2** are negligible. Furthermore, the absence of minima in the $E_{HF} - E_{ES}$ curves in Figure 2b, d indicates that the E_{CT} component is insignificant throughout.

Some of the best characterized H···Pt hydrogen bonds reported so far are N–H···Pt bonds from a quaternary ammonium group to a formally monoanionic platinum atom.[1, 2] In these complexes the strong electrostatic attraction enhances the binding interaction. Calculations on the model system $NH_4^+\cdots[PdCl(CH_3)_2(NH_3)]^-$ at the CAS-SCF level did not reveal any significant orbital interactions,[14] in agreement with our results for the HO–H···Pt interaction, which suggest that stabilization due to electron transfer is small. (However, the orbital interaction is sufficient to give rise to ^{195}Pt–^{1}H spin–spin coupling which was detected in some cases.[2, 3, 15]) Intramolecular O–H···Pt hydrogen bonding has been reported for the anions $[Pt(C_6F_5)_3L]^-$ (L = 8-hydroxyquinoline, 8-hydroxyquinaldine).[3] Our calculations presented in this work suggest that the O–H···Pt interaction has a non-negligible dispersion component. This dispersion component significantly contributes to the energetics of interactions between water and platinum(II) and should therefore be taken into account in force-field studies of solvated platinum(II) complexes.

One referee pointed out that the value of about 4 kcal mol^{-1} determined for E_{CORR} of the HO–H···Pt interaction at the energy minimum may be exaggerated because MP2 calculations are known to overestimate the correlation contributions, and suggested a single-point CCSD or CCSD(T) calculation as a check. While it is correct that MP2 calculations generally yield too high estimates for E_{CORR}, we wish to emphasize that CCSD(T) and especially CCSD calculations may *underestimate* the correlation energy. For instance, supermolecular MP2 calculations on Xe_2 by Runeberg and Pyykkö overestimated the dissociation energy much less heavily (thanks to compensation of errors) than CCSD and CCSD(T) calculations underestimated it.[16] A refinement of our value for E_{CORR} could consist in a series of correlated calculations, such as MP2, MP3, MP4, CCSD, and CCSD(T), as applied by Pyykkö et al to the model system $[\{HAu(PH_3)\}_2]$.[17] Such a series would hopefully converge towards the correct value of E_{CORR}. Such a project was clearly out of the scope of the present paper.

Computational Methods

MP2 calculations[18] were performed using GAUSSIAN 94[19] on a Cray C98 computer. The Dolg–Pélissier pseudopotential/pseudoorbital basis set including two polarization f orbitals[20, 21] was used for Pt, whereas the N, O, and H atoms were represented by the 6-311++G(2p,2d) all-electron basis. The geometries of **1**, **2**, and H_2O were optimized at the MP2 level using the same orbital bases, except that the f orbitals of Pt were excluded. D_{2h} symmetry was imposed to **1**, C_{2h} to **2**, and C_{2v} to H_2O. For the water interaction calculations with **1** and **2**, H_2O was oriented to lie in the bisector of the N-Pt-N and N-Pt-O angles for approaches I and II, respectively, as shown for **2** in Figure 1. To assess the effect of nuclear relaxation, we re-optimized the geometry of **2** during H_2O approach II at the E_{MP2} minimum (Pt···O 3.5 Å). The energy gain from nuclear relaxation amounted to -0.05 kcal mol^{-1} and was considered negligible. The geometry of the systems was therefore not re-optimized. The basis set superposition error (BSSE) was evaluated using the counterpoise method[22, 23] for the approaches I/**2** and II/**2**. For the interactions of **1**, the BSSE was assumed to be the same as for the corresponding approach of **2** at the same Pt···O distance. The atomic charges used for the estimation of E_{ES} were determined from fits to the MP2 electrostatic potential for the isolated species using the Merz–Kollman routine[24] implemented in GAUSSIAN 94, with a van der Waals radius of 2.3 Å for Pt. A check calculation using the CHELPG routine[25] yielded only slightly different E_{ES} curves. The CCDC crystal structures (Figures 3, 4) were drawn using the program Insight II.[26]

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Investigations of Thin Films with Amphiphilic Dendrimers Bearing Peripheral Fullerene Subunits**

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Dedicated to Dr. Antoine Skoulios
on the occasion of his 65th birthday

The preparation and study of fullerene derivatives are being intensively pursued, with the aim of generating new supramolecular assemblies and advanced materials.[1] Incorporation of fullerenes into thin ordered films appears as an important issue in the applications of this carbon allotrope.[2] However, monolayers of fullerene itself at the air–water interface are difficult to achieve due to strong fullerene–fullerene interactions and three-dimensional aggregation, and all attempts to create defined Langmuir–Blodgett (LB) multilayers of fullerenes have failed.[3, 4] Whereas functionalization of the fullerene sphere with hydrophilic addends leads to significant improvements,[4, 5] fullerene derivatives with good spreading characteristics and reversible compression/expansion behavior are quite rare.[6, 7] In a collaborative work among the research groups of Diederich, Stoddart, Echegoyen, and Leblanc, dendrimers with a fullerene core and peripheral acylated glucose units have been investigated.[6] These derivatives show reversible behavior of fullerene monolayers in successive compression/decompression cycles, the dendritic portion preventing the irreversible aggregation

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