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Toward an Accurate Determination of ^{195}Pt Chemical Shifts by Density Functional Computations: The Importance of Unspecific Solvent Effects and the Dependence of Pt Magnetic Shielding Constants on Structural Parameters

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Density functional theory using the zero-order regular approximate two-component relativistic Hamiltonian has been applied to calculate the ^{195}Pt chemical shifts for the complexes $[PtCl_6]^{2-}$, $[PtCl_4]^{2-}$, and $[Pt_2(NH_3)_2Cl_2((CH_3)_3CCONH)_2(CH_2COCH_3)]Cl$. It is demonstrated that, in contrast to recent findings by other authors, platinum chemical shift calculations require not only a basis set beyond polarized triple-ζ quality for the metal atom but also, in principle, the consideration of explicit solvent molecules in addition to a continuum model for the first two complexes. We find that the inclusion of direct solvent–solute interactions at the quantum mechanical level is important for obtaining reasonable results despite that fact that these solvent effects are rather nonspecific. The importance of solvent effects has also implications on how experimental data should be interpreted. Further, in contrast to several previous studies of heavy-metal NMR parameters, functionals beyond the local density approximation were required both in the geometry optimization and the NMR calculations to obtain reasonable agreement between the computed and experimental NMR data. This comes with the disadvantage, however, of increased Pt–ligand bond distances leading to less good agreement with experiment for structural data. A detailed analysis of the results for the two chloroplatinate complexes is presented. The same computational procedure has then been applied to the dinuclear Pt(III) complex. Chemical shifts have been calculated with respect to both $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ chosen as the NMR reference, yielding good agreement with experiment. The determination of preferred solvent locations around the complexes studied turned out to be important for reproducing experimental data.

1. Introduction

Despite the first ^{195}Pt NMR experiments being performed already in the early 1950s,[1] the first platinum chemical shift was determined only almost 20 years later.[2] Since then, the ^{195}Pt isotope with nuclear spin $I = 1/2$ has become a very powerful probe to study platinum chemistry by NMR.[3,4] The first theoretical predictions of ^{195}Pt NMR chemical shifts date back to the 1960s, when Pidcock et al.[5] and Dean and Grean[6] applied Ramsey's equation for paramagnetic shielding to square-planar Pt(II) complexes. However, the results were in poor agreement with the experimental data. Reasonably accurate computations of NMR parameters for heavy transition metal complexes based on first principles theory were not feasible. The large number of electrons contributed by the heavy atom has been one of the main obstacles preventing routine NMR calculations for heavy nuclei even in small metal complexes. During the next two decades following the work of Pidcock et al. and Dean and Grean, extended Hückel theory was mainly used for analysis purposes (see refs 7 and 8 for examples of applications to Pt complexes). For early work on metal complex NMR using Hartree−Fock (HF) theory, we refer to an article by Nakatsuji.[9] It was later concluded that the HF method is not adequate for metal NMR

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calculations.[10] The situation changed during the 1990s because of the rapid development of density functional theory (DFT) methods. Malkin et al.[11] computed NMR chemical shifts with DFT within the independent gauge for localized orbitals (IGLO) scheme. Further development in chemical shift calculations came from the works of Schreckenbach and Ziegler,[12] which were based on London's[13] recipe for applying gauge-including (or -independent) atomic orbitals (GIAOs)[14] within the DFT framework. Other implementations followed soon after.[15,16] Still, another hurdle to be taken because the determination of a heavy nucleus chemical shift requires the use of a relativistic method. A general-purpose variationally stable relativistic analytic-derivative DFT NMR code for molecules that includes both scalar relativistic effects as well as spin−orbit coupling was been developed by Wolff et al.[17] The method is based on the "zeroth-order regular approximate" (ZORA) two-component relativistic Hamiltonian.[18] In recent years, relativistic GIAO NMR chemical shift calculations have been successfully applied to a variety of molecules containing transition metal atoms and have become a routine tool for understanding their chemistry (see, for example, refs 19−24 for overviews).

The success of the GIAO-DFT method in general notwithstanding, the modeling of ^{195}Pt chemical shifts with DFT has met with some difficulties. A study by Gilbert and Ziegler in 1999[25] reported problems obtaining good agreement with experimental values for a series of chemically rather closely related systems despite the fact that one of the compounds, *cis*-$PtCl_2(SMe_2)_2$, was used as the reference for the computations (i.e., chemical shifts were calculated with respect to this "internal" standard and the experimental chemical shift of that reference was added to obtain calculated chemical shifts with respect to a standard experimental reference). Autschbach and Le Guennic[26] have also studied platinum chemical shifts using DFT, with a focus on solvent effects. Again, these authors found it difficult to determine accurate chemical shifts and further showed that even with a suitable internal reference, in many cases, calculations require consideration of explicit solvation shells in addition to an implicit solvation model to describe the bulk solvation effects. As an alternative to such static calculations, Bühl and co-workers have applied molecular dynamics (MD) simulations extensively. They were able to successfully determine the chemical shifts for metal complexes. Calculations of the metal chemical shifts for a number of Fe,[27,28] Mn,[29] V,[30] and recently, Co[31] complexes, to list a few representative studies, showed sizable solvent effects. However, nuclei as heavy as Pt, Hg, etc., were not studied with such a dynamical approach. Consideration of solvent effects is also important for other frequently measured NMR parameters such as the indirect spin−spin coupling constants (*J* couplings). For instance, Autschbach et al. have demonstrated that the inclusion of solvent effects is a key ingredient for proper determination of NMR parameters for a series of mercury, platinum, and Pt−Tl-bonded complexes.[32−34] For *J* couplings, sometimes even an "inert" solvent, such as chloroform, cannot be neglected.[32] Still, even with a solvent model that turned out to yield very good agreement between theory and experiment for metal−metal and metal−ligand *J* couplings, Pt chemical shifts were not obtained with reasonable accuracy unless a compound very similar to the investigated ones was employed as an internal reference for the calculations. In this case, the similarity of the chemical environment of the probe and the reference nucleus allows for a certain degree of error cancellation. A portion of these errors result from the usual approximations made in the computations such as basis set truncation, the approximation of electron correlation by the density functional, and self-interaction errors. The body of data now available for NMR parameters of heavy metal nuclei indicates that approximations in the computational model for the solvated complexes might be even more critical. From the unexpected difficulties with modeling Pt chemical shifts, it appears that error cancellation is obtained for the "usual" approximations but not necessarily for solvent and counterion effects. As we have previously pointed out,[26] the fact that both the probe and the reference complex have to be modeled in solution for chemical shift calculations adds a layer of complexity to

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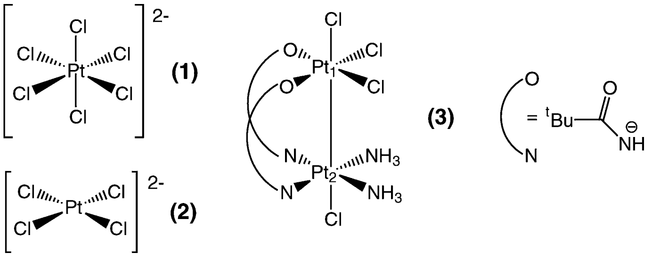

Figure 1. Chemical structure of hexachloroplatinate(IV) **1**, tetrachloroplatinate(II) **2**, and Matsumoto's Pt(III)−Pt(III) bridged complex **3**.

the computational problem if error cancellation cannot be relied upon.

A recent study by Fowe et al.[35] reported very accurate results for the ^{195}Pt chemical shifts for the series of complexes $[PtCl_XBr_{6-X}]^{2-}$ ($X = 1-6$) calculated with the aforementioned ZORA method of Wolff and Ziegler. However, it needs to be emphasized that the experimental Pt NMR reference $[PtCl_6]^{2-}$ is a member of this series of very similar complexes, and therefore a maximum amount of error cancellation might be expected for the calculated chemical shifts not only for basis set, electron correlation, etc., but also in the modeling of the chemical environment of the complexes. The authors of ref 35 pointed out a strong sensitivity of the Pt NMR to structural parameters and found the inclusion of solvent effects at the continuum model level to be beneficial.

The aim of this work is to show that the theoretical determination of ^{195}Pt NMR parameters remains a challenge. We believe that the strong structural dependence of the chemical shifts and the significant solvent effects reported here (both direct electronic influence and indirect solvent effects via structural changes) also have implications on how the experimental data is interpreted. For example, they should be taken into consideration as a potentially significant influence when comparing systems with different coordination or oxidation states. In contrast to Fowe et al. (ref 35), who studied systematic chemical shift trends for a class of very similar complexes, we have adopted a different strategy. To gain experience with the modeling of Pt shifts, we decided to study three very different molecules: hexachloroplatinate $[PtCl_6]^{2-}$ (**1**), tetrachloroplatinate $[PtCl_4]^{2-}$ (**2**), and a Pt−Pt complex (**3**) recently synthesized by Matsumoto et al.[36] The complexes are depicted in Figure 1.

This choice represents a stringent test for the computational model because of the three different platinum oxidation states, namely, Pt^{IV}, Pt^{II}, and Pt^{III}, and because of the very different structures of the solvent (H_2O) can be expected around these three systems. Different oxidation states means different behavior chemically and in solution, which will prevent some of the error cancellations often found in chemical shift calculations. The chosen molecules are still relatively small (although the two metals in dinuclear complex **3** do indeed cause significant computational cost), and we were able to perform a large number of different calculations. Further, **1** and **2** are commonly used as reference compounds in ^{195}Pt NMR spectroscopy. The calculation of the $[PtCl_4]^{2-}$ chemical shift with respect to $[PtCl_6]^{2-}$ as a reference turned out to be rather challenging and might serve as a typical to worst-case estimate of the errors of Pt chemical shift calculations based on the relativistic nonhybrid DFT GIAO approach. In agreement with the findings from our previous studies of heavy-metal NMR parameters, we will demonstrate here that choosing an appropriate solvent model is one of the key ingredients for successful modeling of Pt NMR.

This work is organized as follows. In the next section we give a brief description of the computational procedures applied to the problem. Then we present the geometrical and NMR parameters computed for the complexes shown in Figure 1. The geometries will be discussed in detail because of the strong influence of structure on the NMR parameters. The final section contains some concluding remarks.

2. Computational Details.

Density functional computations have been carried out with the Amsterdam Density Functional (ADF)[37] program suite using locally modified 2004 and 2005 versions. In most of our computations, we have applied the Vosko−Wilk−Nusair (VWN)[38] local density approximation (LDA) and revised PBE (revPBE)[39] gradient corrections (GGA = generalized gradient approximation). The PBE is a family of GGA functionals which does not make heavy use of empirical parameters and yields quite accurate energies, structures, and properties of molecules. Previous experience with computations of metal NMR parameters indicated that in transition metal complexes most GGA functionals yield similar results and no overall "best" functional could yet be identified.[20] The revPBE functional serves here as a typical example for results obtained at the GGA level. For most of the 3d and 4d metal shifts that were calculated with DFT so far, hybrid functionals have turned out to be beneficial,[20,22,24] in particular, as may be expected, for 3d metals. For 5d metals, this issue has not been as thoroughly investigated. The programs employed in this work for calculating heavy atom NMR shifts make use of non-hybrid functionals. Differences between LDA and GGA results might indicate how severely approximations in the density functional affect the Pt NMR parameters. Obviously, we are not able to ascertain that our results would not be improved further by applying a hybrid density functional; however previous work on the chemical shifts of 5d metals, other than Pt, has so far indicated a satisfactory performance of the GGA functionals.[20]

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For geometry optimization, we have applied the spin-free (scalar) ZORA (zeroth-order regular approximation)[40,41] relativistic Hamiltonian and the frozen core Slater-type basis sets, which included 4f, 5spd, and 6sp and 3s, 3p, and 3d as valence shells for Pt and Cl, respectively. The 1s shell has been kept frozen for O, N, C atoms. A polarized valence triple-ζ basis set (TZP) from the ADF database has been employed. Additionally, some of the geometry optimizations employed bigger basis sets of valence triple-ζ plus two polarizations (TZ2P) and valence quadruple-ζ with four polarization functions (QZ4P). Local minima were confirmed by numerical frequency calculations except where we carried out optimizations including a number of explicit solvent molecules. These optimizations were based on starting geometries where a number of solvent molecules were added to a confirmed local minimum structure of the metal complex. In the case of the $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ complexes, we have taken advantage of their high symmetries to estimate the affects of spin−orbit coupling on the bond length, which turned out to be negligible. The spin−orbit potential energy minima were determined graphically by calculating the binding energy of the complex for a series of geometries where all of the Pt−Cl bond distances were varied simultaneously in steps of 0.0001 Å around the scalar ZORA minimum and by subsequent cubic spline fitting with the GnuPlot software.

Shielding tensor calculations have been performed using the all-electron analogues of the basis sets and spin−orbit coupling included variationally in the calculations. Spin−other-orbit effects were neglected. They are small for truly heavy atoms compared to the one-electron spin−orbit effects;[42−45] therefore we do not regard this approximation a major source of error in our computations. The effect of the ZORA approximation on the calculation of atomic hyperfine integrals has been evaluated in ref 46 where it was shown that for valence shells in heavy atoms the ZORA is an excellent approximation. Since the chemical shift (not the nuclear magnetic shielding) can be regarded as a valence shell property, the approximate relativistic treatment based on the ZORA Hamiltonian is also not considered a major source of error in the present computations.

The experimental NMR parameters were determined in aqueous solution; therefore, solvent effects were taken into account in most calculations. Mainly, we used COSMO (conductorlike screening model)[47,48] as implemented in ADF[49] to treat the solvent as a polarizable continuum. We have used the same atomic radii to construct the solvent cavity as that in ref 26. The metal NMR shifts for a set of Pt−Tl-bonded complexes were previously found to not depend strongly on the COSMO radii as long as they were chosen within reasonable limits.[26] In addition to the COSMO model, we have studied the complexes with varying numbers of explicit water molecules. Further, for $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$, we have performed molecular dynamics (MD) simulations.

For the free (gas phase) dianions $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$, we obtained positive frontier molecular orbitial (MO) energies (e.g., +0.133 au for the HOMO of $[PtCl_4]^{2-}$). As one might expect, the COSMO model stabilizes these orbitals significantly, with and without additional explicit solvent molecules, leading to consistently negative frontier MO energies (e.g., −0.186 au for the HOMO of $[PtCl_4]^{2-}$). Throughout the rest of this paper, we report results obtained with the COSMO solvent model.

A developer's version of the "frog" program from TURBOMOLE[50] has been used for the Born−Oppenheimer (B−O) MD simulations which we report results here. For this purpose, we have developed an interface between the frog and ADF programs so that the forces necessary for the MD were provided by the ADF code at the spin-free ZORA DFT level. Our aim was to employ the same approach (ZORA relativistic corrections, Slater-type basis, and revPBE gradient correlated density functional) throughout all of our calculations, including the MD, to systematically investigate the influence of the solvent on the structure and NMR parameters of the Pt complexes. We have included 12 water molecules in the MD simulations. For the solvent molecules, a basis set of double-ζ quality (DZ) has been used to keep the computational effort manageable. Each sample has been equilibrated at 300 K for about 4 ps with a default time step (80 au) which is typical for a B−O type MD.[48] Afterward, a 2 ps production run was performed. The temperature fluctuated around 300 K, and the total energy was well conserved. The final chemical shift calculation has been done for each 50th geometry to obtain an average over 65 snapshots along the MD trajectory. To keep the solvent from evaporating, we have applied an ellipsoidal barrier potential around the complexes. Such a simple MD affords comparatively large temperature fluctuations with accompanying fluctuations in the Pt nuclear shielding constants. The main purpose of these simulations was to determine if static calculations with or without some explicit solvent molecules and the COSMO model can potentially yield qualitatively similar results to an explicit dynamic water coordination for both $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ and to study the influence of the MD versus static calculations on the complexes' structures. These computational results should be regarded as preliminary in the sense that the frog program does not support a thermostat. We have further applied a locally modified version of a program developed by Prof. T. Woo,[52] which is based on the velocity version of the Verlet[53] algorithm and includes the Andersen thermostat.[54] Our local modifications included an interface with the ADF code as well as the implementation of a barrier potential. However, the results obtained within the short simulation times were very similar to the ones obtained with the frog code. In longer simulations with 12 waters, we observed a significant clustering of the water molecules when the thermostat was used, indicating that a much larger solvent shell would be needed for a reasonable isotropic sampling in these simulations. Because of the high basis set requirements for MD,

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Table 1. Selected Calculated and Experimental Pt−Cl Bond Lengths (all values in Å) for the Complexes Studied Here[a]

	$[PtCl_6]^{2-}$		$[PtCl_4]^{2-}$		Pt−Pt complex **3**		
	LDA	GGA	LDA	GGA	LDA	GGA	
TZP	2.3288	2.3946	2.3007	2.3682	2.4352	2.5331	ax
					2.3075	2.3674	eq
TZ2P(Pt)	2.3163	2.3824	2.2913	2.3585	2.4196	2.5170	
					2.2916	2.3512	
QZ4P(Pt)	2.3175	2.3842	2.2920	2.3595	2.4215	2.5164	
					2.2929	2.3526	
QZ4P(all)	2.3084	2.3748	2.2812	2.3485	2.4128	2.5058	
					2.2848	2.3452	
B−O MD[b]		2.4126		2.3959			
S−O TZP	2.3259	2.3945	2.2974	2.3691			
experiment	2.315		2.307		2.4013		ax
					2.2985		eq

[a] Letters in parentheses indicate for which element a given basis set replaced the TZP basis used by default. The COSMO solvation model was used in all calculations except for the B−O MD. [b] Average distance as determined from the 65 geometries used for the NMR averaging.

as determined during the course of this study (see section 3.2), and the expected formidable computational effort, we decided not to make the MD results the main focus of the present paper but rather to use the data obtained with the frog program to support our conclusions regarding the performance of the static COSMO calculations with the QZ4P basis set. One might expect that the computational effort for the MD can be reduced somewhat by employing a pseudopotential (commonly used in Turbomole and other DFT codes that employ Gaussian-type basis sets) instead of the frozen-core basis sets used in the ADF calculations. We performed some MD calculations with the Turbomole code for comparison. The computation time savings were not significant (because there was only one Pt atom to be considered), and the results obtained at the GGA level were similar to the ones obtained from the ADF gradients. As already mentioned, for this work, we decided to uses an approach as consitent as possible (apart from the choice of the basis set) for the MD and NMR calculations. For future benchmark studues, we plan to determine if applying a hybrid functional in the MD is beneficial. Ideally this would also involve a comparison with an MD averaging of hybrid-DFT NMR results for which, however, at present, no sufficiently fast spin−orbit relativistic DFT code is available.

3. Results and Discussion

3.1. Geometries. Selected computed geometry parameters along with experimental single-crystal X-ray structural data for our complexes are collected in Table 1. The symmetries of the unsolvated molecules were O_h, D_{4h}, and C_s (or C_1 depending on the conformation of the *tert*-butyl groups) for complexes **1**, **2**, and **3**, respectively. Geometries for all three molecules were calculated at the ZORA scalar relativistic level. ZORA spin−orbit gradients were not available, but it was possible to determine the Pt−Cl bond lengths of hexachloro- and tetrachloroplatinate at the ZORA spin−orbit level because of their high symmetry. The optimized bond lengths are collected in Table 1 and show that spin−orbit coupling has little impact on the geometry of these two systems and just slightly shortens the metal−ligand distances. This is true for both the LDA and revPBE functionals. The small geometry change was expected because the spin−orbit operator contributes only in order c^{-4} to the energy of a closed-shell molecule, whereas the scalar effects contribute in order c^{-2} (c is the speed of light, 137.036 atomic units). Nonetheless, because the Pt nuclear shielding of both complexes depends very sensitively on the metal−ligand distances it is important to rule out any potential influence on the geometry from spin−orbit coupling. Finally, to gain further insight into the solvent−solute interactions, we have performed molecular dynamics (MD) simulations.

Our data in Table 1 confirm well-known general rules about the performance of the LDA and GGA functionals. The LDA functional reproduces the X-ray crystal structure metal−ligand distances very well, whereas the revPBE GGA functional tends to yield larger Pt−Cl distances. An increase of the basis set from TZP to TZ2P to QZ4P tends to shorten the length of the Pt−Cl bonds and thus improves the agreement with experiment. In case of LDA, very good agreement between the theoretical and experimental values is obtained with the TZ2P(Pt) basis set. For more flexible basis sets, the Pt−ligand distances tend to be calculated slightly too short. The shortening of the bond length with increasing flexibility of the metal basis set is also found in the revPBE calculations. However, even with a the difference between the TZP and QZ4P optimized bond lengths of 0.02 Å, the Pt−Cl bond distance obtained at the QZ4P/revPBE level is still larger than the experimental one.

For the Pt^{III} complex, the LDA computations also yield very good agreement with experimental structural data. The Pt−Pt bond length of 2.5997 Å obtained with VWN agrees better with the experimental value of 2.6178 Å than the value obtained with revPBE (2.6723 Å). A reduction of computational effort by imposing symmetry restrictions or by replacing the *tert*-butyl groups with methyl does not lead to significant changes in the metal−metal bond length. A similar situation can be observed for the Pt−Cl distances (Table 1). Increased basis set flexibility tends to result in decreased the bond lengths for both the LDA and revPBE geometries (as is the case for hexachloro- and tetrachloroplatinate). Again, however, the best revPBE bond lengths are still somewhat too long, compared to the crystal structure measurements. It is interesting to note that all calculations with the COSMO model gave almost equal axial Pt−Cl bond distances. In contrast, the crystal structure shows a Pt_2−Cl bond 0.04 Å longer than the Pt_1−Cl bond, demonstrating a significant influence from crystal packing. This further suggests that a pronounced solvent coordination might also have a strong influence on the complex's structure in solution. There is no experimental data available for the preferred solvent locations around complex **3**. However, the inclusion of only one explicit water molecule in addition to the COSMO model in the vicinity of the axial Cl atom increases the Pt_2−Cl bond lengths to 2.4501 and 2.5394 Å for LDA and GGA, respectively, which are much closer to the experimental value of 2.4453 Å. Other locations chosen for the water molecule tended to favor coordination of the NH_3 groups instead (i.e., migration of the solvent toward the amine groups during the course of the optimization) which had no further effect on the on the axial Pt−Cl bond distance. We tested this with one and two explicit water

Table 2. Experimental and Selected Calculated Chemical Shifts for Examined Complexes with Respect to (wrt) $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-a}$

	$[PtCl_4]^{2-}$		Pt−Pt complex							
	wrt $[PtCl_6]^{2-}$		wrt $[PtCl_6]^{2-}$				wrt $[PtCl_4]^{2-}$			
			Pt$_1$		Pt$_2$		Pt$_1$		Pt$_2$	
	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
TZP//TZP	−934	−1291	746	595	−575	−1010	50	256	−1271	−1249
TZ2P(Pt)//TZP	−1078	−1439	623	487	−788	−1222	80	296	−1340	−1413
TZ2P(Pt)//TZ2P(Pt)	−986	−1370	609	466	−731	−1180	−37	205	−1387	−1442
QZ4P(Pt)//TZP	−1109	−1528	644	458	−758	−1225	123	356	−1279	−1327
QZ4P(Pt)//QZ4P(Pt)	−1020	−1466	610	409	−719	−1208	−2	243	−1331	−1374
QZ4P//QZ4P	−752	−1389	320	392	−1066	−1594	−556	−176	−1716	−2163
QZ4P(Pt)//TZP^b				475		−1216		372^c		−1318
QZ4P(Pt)//B−O MD^d		−1369								
experiment	−1630		535		−1023		535		−1023	

[a] Results for complex **3** with respect to **2** have been shifted by −1630 ppm for direct comparison to the results where the reference is $[PtCl_6]^{2-}$. All calculations were performed using the COSMO model. [b] Calculations with one water molecule at "bottom side" of **3** (see Figure 1). [c] The same as for *b* but with respect to $[PtCl_4]^{2-}$ with six solvent molecules. [d] Preliminary results obtained without a thermostat.

molecules in the calculations. Our results suggest that given a large enough solvent shell the axial Cl will be coordinated by a water molecule with the concomitant change of the Pt−Cl bond distance. Therefore, for complex **3**, the explicit coordination by water molecules might be crucial in obtaining correct calculated structural data, which is important for obtaining correct NMR parameters.

The inclusion of explicit solvent molecules, and simultaneously the COSMO model to approximate the remaining bulk effects, in the geometry optimization further leads to changes of the Pt−Cl bond length in the $[PtCl_4]^{2-}$ complex. Because of experimental evidence for a pseudooctahedral symmetry[55] with two water molecules located at a distance of approximately 2.8 Å and strong hydrogen bonds between the water and chlorine atoms, we have studied the geometry of this complex with different numbers of solvent molecules. It was found that the inclusion of just two water molecules (above and below the molecule's plane) favors the creation of chlorine−water hydrogen bonds (i.e., during the course of the optimization, both water molecules leave the initial axial positions and migrate into the plane of the molecule to coordinate the Cl ligand). Geometry optimizations with different orientations of six solvent molecules, for example, preserves the pseudooctahedral symmetry of the complex. This result provides further evidence of the need for a large enough solvation shell, as was pointed out in the discussion of complex **3** above. The Pt−water distance changes in the range from 2.2 to 3.5 Å for LDA and from 2.6 to 3.4 Å for the GGA density functional.

Unfortunately there is no experimental data available for the arrangement of solvent molecules around the $[PtCl_6]^{2-}$ complex so we could not make a similar comparison. From previous force-field MD simulations,[56] it was concluded that the first coordination sphere consists of about eight water molecules on average. Because it is less intuitive to estimate which positions eight solvent molecules should prefer around this complex, we have performed MD simulations with 12 water molecules. As a result we obtained a first coordination sphere consisting of seven solvent molecules on average which is in reasonable agreement with the computational results obtained by the authors of ref 56. Similar simulations have been performed for the present work on the $[PtCl_4]^{2-}$ complex. The average Pt−Cl bond distance is about 0.02 Å larger than the bond length from static calculations without explicit water. This can be explained by interactions between solvent and solute (i.e., hydrogen-bonding between the solvent and the solute's ligands weakens the metal−ligand bonds). In fact, inclusion of explicit solvation in a static geometry optimization also leads to an increase of the Pt−Cl bond length. As a final test of the MD, we have roughly estimated an average wavenumber for the Pt−Cl stretching vibrations over a 2 ps MD production run from the frequency of the oscillations in a plot of the Pt−Cl bond distances. The value of 316 cm^{-1} for $[PtCl_6]^{2-}$ is somewhat lower than the range of the experimental IR Pt−Cl stretching frequencies reported at 346 and 325 cm^{-1} (see ref 56; the bending modes are found between 183 and 147 cm^{-1}). For comparison, in ref 56, harmonic frequencies were calculated at the LDA level and found to be approximately 27 cm^{-1} below the experimental values.

3.2. Chemical Shifts. Both $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ are widely used as a reference in ^{195}Pt NMR measurements. It turns out to be difficult to obtain the correct chemical shift for the latter with respect to $[PtCl_6]^{2-}$ in the computations. All the static calculations performed for all considered models do not reach the experimental value of −1630 ppm but always stay above (i.e., they are smaller in magnitude). Our results are collected in Table 2.

Before we discuss the results, a general remark about the importance of relativistic effects for NMR chemical shifts is appropriate. As long as relativistic effects do not change the chemical environment in the valence shell of a heavy atom, the large relativistic effects in the shielding tensor found, for instance, for 3d and 4d metals often almost completely cancel when the chemical shift is evaluated. However, this is no longer the case for 5d metals where relativistic effects have a direct and sometimes very strong influence on the metal's chemistry.Generally, it appears that

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(unlike for structure and energy) for the chemical shift of 5d metals and heavy main group atoms both spin-free and spin−orbit relativistic effects can play an equally important role.[19−21] Spin-free relativistic calculations were performed as part of this study but led to consistently weaker agreement with the experiment. We therefore do not report NMR results here that were obtained with a spin-free relativistic method.

As one can see from Table 2, the spin−orbit result which is in best agreement with the experiment is −1528 ppm. It was obtained with the revPBE density functional and the QZ4P basis set centered on the Pt atom (nicknamed QZ4P(Pt) which implies the TZP basis for all other atoms) for both the geometry optimization and the NMR calculation. Results with the same QZ4P(Pt) basis at the TZ2P(Pt) and QZ4P(Pt) geometries are 62 and 148 ppm, respectively, smaller in magnitude. In contrast to findings reported recently[35] which suggested that a polarized triple-ζ basis might be sufficient for calculating Pt chemical shifts, one can see that significant improvement of the $[PtCl_4]^{2-}$ chemical shift with the increase of basis set flexibility is obtained both at the LDA and GGA levels when based on the same geometry. The difference of about 230 ppm between the TZP and QZ4P(Pt) calculations cannot be neglected. Finally, static calculations with the COSMO model performed at the full QZ4P level (i.e., for all atoms for both optimization and spin−orbit NMR) yield a chemical shift of −1389 ppm for $[PtCl_4]^{2-}$ with respect to $[PtCl_6]^{2-}$. The lesser agreement with the experiment compared to the QZ4P(Pt)//TZP level is somewhat unfortunate but can be rationalized by considering our preliminary MD results.

The NMR calculations at the QZ4P(Pt) level based on geometries from the MD trajectories performed with the TZP basis did not lead to further improvement of the $[PtCl_4]^{2-}$ chemical shift with respect to $[PtCl_6]^{2-}$ when compared to the static COSMO calculations at the QZ4P(Pt) level. This is mainly the result of an increase of the average Pt−Cl bond lengths for both complexes in the MD, compared to the static calculations, that leads to very similar changes in the shielding constants (see discussion below and Figure 2). Unfortunately, we could not computationally afford to perform the MD with the full QZ4P basis. However, from an extrapolation of the trends observed for the different basis sets, we would expect a shortening of the Pt−ligand bonds if the MD were performed with the full QZ4P basis instead of TZP. From an alternative viewpoint, a lengthening of these bonds at the full QZ4P level would be obtained in the MD calculations when compared to the static QZ4P calculations discussed in the previous paragraph. In both cases, we may expect a more negative chemical shift of $[PtCl_4]^{2-}$ with respect to $[PtCl_6]^{2-}$ and closer agreement with the experimental values. It appears that the QZ4P(Pt) basis set effectively balances the approximations from the static calculations as compared to the more realistic dynamic picture. In light of this argument is is not surprising that the static QZ4P(Pt) results are closest to experiment.

One needs to be careful not to consider the agreement with experiment as the only criterion for assessing the computations unless calculatation on a large set of diverse complexes are performed. The main point here is that the chemical shifts are sensitive to changes in the basis set and the structural parameters. They do not seem to be sufficiently well described with a basis set of TZP quality.

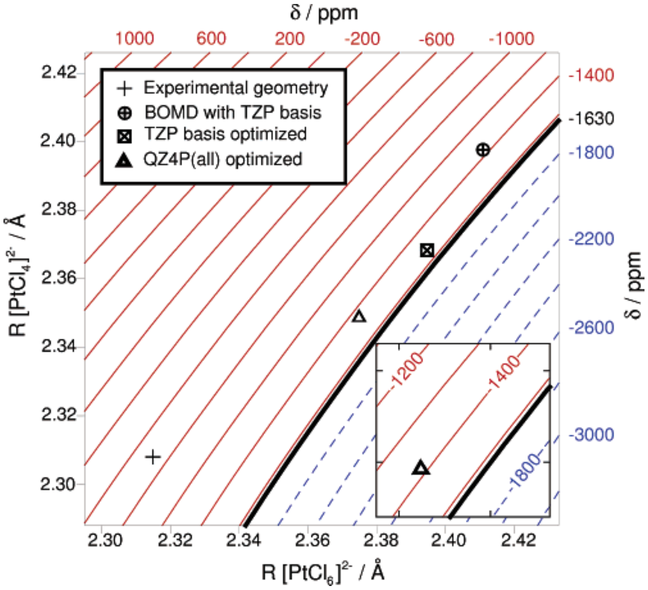

Figure 2. Dependence of the $[PtCl_4]^{2-}$ chemical shift ($[PtCl_6]^{2-}$ reference) on the Pt−Cl bond distances in the probe and the reference complex. Chemical shift surface calculated with the QZ4P basis set on Pt and a TZP basis on the remaining atoms (labeled QZ4P(Pt) in the text). Inset: Surface calculated with QZ4P on all atoms. Solid thin lines indicate where the calculated shift is more positive and dashed thin lines show where the shift is more negative than the experimental value of −1630 ppm (solid thick line). The markers indicate the optimized/average geometries obtained with the method listed in the key and the resulting QZ4P(Pt) chemical shift (inset: QZ4P).

As already mentioned, the Pt−Cl bond lengths calculated with revPBE are somewhat larger than those from the experimental crystal structure and solvent data. To gain further insight into the consequences of these geometry changes, we have calculated the shielding constants of both the $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ complexes as a function of the platinum−chlorine bond distance (Figure 2). The structure of the complexes obviously has severe consequences for the calculated chemical shift of one complex with respect to the other. It should be noted that the difference between neighboring contour lines is large, viz. 200 ppm. This rationalizes the huge difference between the value of the chemical shift obtained for experimental and calculated geometries. Further, it is important to note that the slope of the contours is different from 45° and that the contours also have a noticeable curvature. This means that even if the calculations would make similar errors for the structural parameters, the nuclear shielding constants might yield different errors which will not cancel completely when the chemical shift is evaluated. The Pt−Cl bond distances of **1** and **2** must be overestimated differently to obtain the correct chemical shift. This shows that by necessity some approximate methods yield “better” NMR properties than others. Our findings are in line with those reported by Bühl et al. who reported that for a number of negatively charged complexes the chemical shift of the metal is particularly sensitive to geometry parameters. As examples, we refer to the molecular dynamics studies of Fe[27,28] and Co[31] NMR shifts. As already mentioned, part of the reason the QZ4P(Pt) basis leads to results which are in good agreement with experimental values in the static calculations is that it apparently mimics the solvent effects on the structures in a rather balanced way. However the lengthening of the bonds resulting from explicit solvent−ligand interactions seems to be somewhat overestimated by the GGA calculations. Just employing the experimental X-ray crystal structure bond lengths leads to very bad results. However, the strong sensitivity of the Pt chemical shift to geometric distortions in conjunction with the necessity to model solvent−solute interactions accurately shows that gas phase calculations on Pt complexes lead to good agreement with experiment only by fortuitous error cancellation. By extrapolating our calculated results, one may expect that NMR calculations based on MD performed with the full QZ4P basis and a large number of solvent molecules will yield good agreement with experiment without having to rely on fortuitous error cancellation. However, such computations will be quite expensive.

Now we are in a position to discuss our results for the Pt−Pt bonded complex **3**. In Table 2, one can see that the LDA results are far from the experimental ones for almost every computational model. At the LDA level the complex is not even suitable as a "reference for itself" because the difference between the shielding constants of the Pt_1 and Pt_2 nuclei is poorly reproduced. Thus, we will focus our discussion on the revPBE results only.

The best agreement between theory and experiment (see Table 2) is for the TZP basis set with the $[PtCl_6]^{2-}$ complex as a reference: 595/−1010 versus 535/−1023 ppm. However if we compare the chemical shift with respect to $[PtCl_4]^{2-}$ (after adding −1630 ppm to account for the experimental chemical shift between $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$), the result is off by almost 300 ppm for both nuclei compared to the experimental data. Obviously, chemical shifts should not be so strongly reference dependent in the calculations. Therefore, we cannot accept the model with the TZP basis set as one that yields a "reasonably good answer for acceptable reasons". The agreement between the calculated and experimentally measured chemical shift is a bit worse for the QZ4P(Pt)//TZP model. However, the agreement between the calculated chemical shift with respect to $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$ (offset by −1630 ppm) is much better, with a difference of only about 100 ppm. If we improve our model by inclusion of four explicit solvent molecules around the $[PtCl_4]^{2-}$ complex in the static calculations and let them create hydrogen bonds with the chlorine atoms, the chemical shifts for the Pt−Pt complex **3** will be lower by about 30 ppm. Inclusion of even more solvent molecules around $[PtCl_4]^{2-}$ leads to large number of local minimum structures. Some of them improve the chemical shifts, and some of them do not. The chemical shift of **3** with respect to tertrachloroplatinate (obtained with six water molecules for the reference in static calculations) closest to the experimental value is 557/1126; it is only 100 ppm too large, compared with the experimental value for the Pt_2 nucleus. This difference is approximately within the error bars of the calculations if we consider the deviations between theory and experiment for the $[PtCl_4]^{2-}$ chemical shift with respect to $[PtCl_6]^{2-}$ as a reference. The TZP result is still off by approximately 200 ppm. This behavior of the chemical shift gives us some insight into the solvent structure of $[PtCl_4]^{2-}$. Its proper determination is obviously crucial for calculations of ^{195}Pt chemical shifts with respect to this complex and should ideally be determined from an MD with a highly flexible basis for all atoms of the complex. Finally we want to point out that the inclusion of one explicit solvent molecule coordinated to the axial Cl ligand of Pt_2 (i.e., trans to the Pr−Pt bond) in complex **3** increases the axial Pt_2−Cl bond length in agreement with experiment. The Pt chemical shifts do not change very much but at least they are slightly improved.

4. Conclusion

From our results it becomes clear why almost all DFT studies of Pt chemical shifts so far have reported difficulties with the choice of reference, comparatively poor agreement with experimental values, or both. Potentially, our findings are transferable to other heavy metal systems where the metal shift is equally strongly influenced by geometric and electronic factors. The previously cited work by Bühl et al. on the NMR of lighter metal nuclei supports this hypothesis. The results obtained in ref 35 for Pt chemical shifts are likely to be in such excellent agreement with the experimental values because of a significant degree of error cancellation. The molecules studied in ref 35 are chemically very similar (Cl/Br substitution in $[PtCl_XBr_{6-X}]^{2-}$, $X = 1-6$), and one of the complexes is the experimental reference. Because chemical shift calculations involve the subtraction of two shielding constants that often have similar errors for similar compounds most of the errors were canceled. One might also expect similar solvent shell structures for this set of complexes. It appears that a basis of triple-ζ-polarized quality for the metal is not flexible enough to capture important differences between the electronic structure around the Pt nucleus because of different Pt coordinations and oxidation states.

We have shown in this work that for different platinum compounds ^{195}Pt NMR remains a challenge for computational chemistry and that routine calculations cannot yet be performed easily with a well-defined computational model. In particular, it is necessary to perform a comparatively high-level modeling of the solvent effects on both the probe and reference compound unless the complexes are chemically very similar. These solvent effects influence the Pt chemical shift both via structural parameters as well as via direct electronic solvent−solute interactions. The latter cannot be properly modeled with a continuum model alone, although such a continuum model turns out to be instrumental for describing the remaining bulk solvent effects. This finding is in agreement with similar studies performed by us on Pt−Tl bonded systems.[26,34,58] We have shown in this paper that Pt chemical shifts might be obtained within reasonable agreement with experimental values if the solvent−solute interactions are modeled at a high level. The comparison for complex **3** using two different references (with all three complexes calculated at the same level of theory) provides some evidence that our computational model is an improvment over previous models for good reasons. At the same time, there could still be a certain degree of error compensation present that might show up when more complexes are considered simultaneously. The expected computational expense for a reliable modeling of Pt and other heavy metal complexes in solution is high because, ideally, the solvent–solute interaction should be described in a dynamic framework. Further, there is the necessity for large-basis all-electron spin–orbit NMR calculations of the metal complex which should include at least one explicit solvation shell and, in for the MD simulations, need to be performed for a representative set of MD configurations (perhaps the solvent shell can be modeled using a smaller basis set). Such a study on a large set of complexes has not been possible but will be attempted by us in the future now that some of the underlying problematic issues have been identified. It not clear yet, for instance, in which way approximations made in the GGA functional do or do not balance approximations made in the solvent model or the basis set. Another issue that should be investigated is the zero-point vibrational correction of the calculated nuclear shielding constants. The strong sensitivity of the calculated chemical shifts with respect to the structural parameters indicates that anharmonicity and property-curvature corrections may not be negligible. The results obtained for complex **3**, however, are encouraging.

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