

Solvent Effects on ^{195}Pt and ^{205}Tl NMR Chemical Shifts of the Complexes $[(\text{NC})_5\text{Pt-Tl}(\text{CN})_n]^{n-}$ ($n=0-3$), and $[(\text{NC})_5\text{Pt-Tl-Pt}(\text{CN})_5]^{3-}$ Studied by Relativistic Density Functional Theory

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Abstract: The ^{195}Pt and ^{205}Tl NMR chemical shifts of the complexes $[(\text{NC})_5\text{Pt-Tl}(\text{CN})_n]^{n-}$ ($n=0-3$), and of the related system $[(\text{NC})_5\text{Pt-Tl-Pt}(\text{CN})_5]^{3-}$ have been computationally investigated. It is demonstrated that based on relativistically optimized geometries, by applying an explicit first solvation shell, an additional implicit solvation model to represent the bulk solvent effects (COSMO model), and a DFT exchange-correlation potential that was specifically designed for the treatment of response properties, that the experi-

mentally observed metal chemical shifts can be calculated with satisfactory accuracy. The metal chemical shifts have been computed by means of a two-component relativistic density functional approach. The effects of electronic spin-orbit coupling were included in all NMR computations. The impact of the choice of the reference, which ideally should not affect the ac-

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curacy of the computed chemical shifts, is also demonstrated. Together with recent calculations by us of the Pt and Tl spin-spin coupling constants, all measured metal NMR parameters of these complexes are now computationally determined with sufficient accuracy in order to allow a detailed analysis of the experimental results. In particular, we show that interaction of the complexes with the solvent (water) must be an integral part of such an analysis.

Introduction

The complexes $[(\text{NC})_5\text{Pt-Tl}(\text{CN})_n]^{n-}$, $n=0-3$, (**I**, **II**, **III**, and **IV**) and $[(\text{NC})_5\text{Pt-Tl-Pt}(\text{CN})_5]^{3-}$ (**V**) (see Figure 1) belong to a fascinating class of inorganic compounds that are stable in aqueous solution and afford direct, nonbridged, Pt-Tl bonds. Complex **II** was first synthesized by Glaser et al. in 1995, and characterized by multinuclear NMR spectroscopy.^[1] The experimental studies were subsequently extended to include the other complexes **I** and **III-V**, and related compounds. The structures were extensively investigated by NMR spectroscopy, vibrational spectroscopy, X-ray diffraction of single crystal samples, and EXAFS (extended X-ray absorption fine structure analysis) studies of the complexes in solution.^[2-6] A number of computational studies on the title compounds have so far been carried out by several

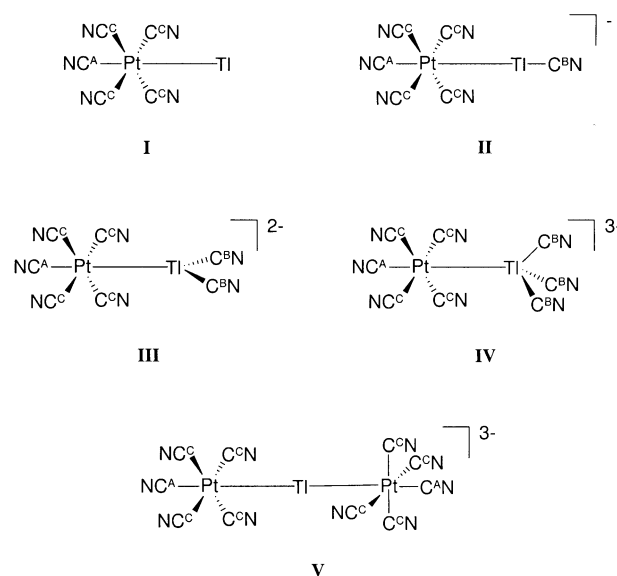


Figure 1. Proposed (see Ref. [2]) structures for the complexes **I-V**.

groups.^[7-9] Russo and Kaltsoyannis have performed relativistic density functional theory (DFT) calculations.^[7] By computing harmonic vibrational frequencies they confirmed that the proposed structures of complexes **I-IV** (Figure 1) are

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compatible with the experimentally observed infrared spectra. Pyykkö and Patzschke have recently investigated the structural features of complexes **I–IV** with a variety of methods.^[8,9] They have focused in particular on the reasons for the occurrence of the rather short Pt–Tl internuclear distances (around 2.6 Å), and on an analysis of the pronounced multicenter character of the metal–metal bond, and on the question of the oxidation state of the metal atoms. The multicenter bond has also been analyzed in Ref. [10] for complex **II**. The nuclear spin–spin coupling constants of complex **II** were first calculated by Autschbach and Ziegler with relativistic DFT.^[10] It was shown that the curious fact of ${}^2J_{\text{Tl-C}}^{\text{A}}$ being about four times larger than ${}^1J_{\text{Tl-C}}^{\text{B}}$ is also compatible with the proposed structure, and a nonbridged Pt–Tl bond, provided that coordination of the Tl center by four water molecules is taken into account in the computations. The large magnitude of the experimental $J_{\text{Pt-Tl}}$ of 57 kHz could not quantitatively be reproduced in the computations (calculated value: ~40 kHz). However, the results already indicated that 50% or more of the magnitude of $J_{\text{Pt-Tl}}$ must be attributed to solvent coordination of the Tl center.

Recently, we have computationally investigated the nuclear spin–spin coupling constants of the whole series of complexes **I–V**.^[11] We could demonstrate that based on accurate relativistically optimized geometries, by applying an explicit first solvation shell, an additional implicit solvation model to represent the bulk solvent effects, and a DFT exchange–correlation (XC) potential that was specifically designed for the treatment of response properties, that the experimentally observed spin–spin coupling constants can be calculated with satisfactory accuracy (typically within about 15% deviation from experimental values). Thereby, remarkably large effects from the bulk solvent, and from the influence of the XC potential were found. In particular $J_{\text{Pt-Tl}}$ is a very sensitive indicator for the quality of the computational model. We showed that the experimentally observed trend of decreasing $J_{\text{Pt-Tl}}$ along the series **I–V** can only be understood by taking direct solvent coordination of Tl and bulk solvent effects into consideration. The other coupling constants are also very strongly affected.

So far, no attempts have been made to compute the metal chemical shifts for the title compounds. NMR observables are very sensitive to experimental probes, and therefore not easy to reproduce in computations. The NMR properties of complexes **I–V** are especially sensitive to the quality of the computational model. Thus, they serve as an ideal benchmark to simultaneously test a variety of parameters that define the quality of a model for the description of heavy atomic main group and transition-metal complexes in general, and compounds with directly bonded heavy main group and transition-metal elements in particular. The NMR observables probe, for instance, the geometry, the quality of the calculated electronic structure, the quality of the relativistic approach, and the extent to which the environment must be treated, and so on. It is the purpose of the present paper to demonstrate that the same computational model that yields the best agreement with experimental data for the spin–spin coupling constants performs also best for the metal chemical shifts. As already mentioned, this model in-

volves an explicit treatment of the Tl–solvent coordination, implicit bulk solvent effects, and the use of the aforementioned improved XC potential, employed in relativistic DFT calculations. Both ${}^{195}\text{Pt}$ and ${}^{205}\text{Tl}$ chemical shifts are investigated. The effects of the electronic spin–orbit coupling, known to be of high importance for a correct description of heavy nucleus magnetic shieldings and chemical shifts, are included in all NMR computations.^[12–14] Taking the large effects from various competing influences (relativity, solvents, the quality of the description of the electronic structure, geometries, etc.) into consideration, the final results can be regarded as quite satisfactory when compared to experimental data (remaining errors are typically within ~15%, depending on the reference). The choice of the reference nucleus for the evaluation of the chemical shift is extensively discussed, since it imposes an additional layer of complexity for the present study relative to spin–spin coupling calculations, but also allows us to choose a presentation of the results with a maximum cancellation of systematic errors.

In Computational Details, we describe the computational details and the computational models that have been applied in this study. The Results and Discussion is devoted to the presentation of the results and their analysis, as well as a discussion of the various possible reference compounds. Some concluding remarks are given in the Conclusion.

Computational Details

Density functional computations have been carried out by using the Amsterdam Density Functional (ADF) program package.^[15–17] It incorporates a modified version^[18] of the code developed by Wolff et al.^[19] for the two-component relativistic computation of nuclear shielding constants, based on the zeroth-order regular approximation (ZORA) Hamiltonian.^[20,21] The modifications that have been made do not affect the results obtained with the program, but implement a significantly better scaling of the computational time with increasing system size. It has recently been demonstrated that the ZORA yields very accurate hyperfine integrals for the valence orbitals of heavy atoms, relative to a fully relativistic treatment.^[22] See also Ref. [23]. The chemical shifts can therefore be expected to be close to not yet available fully relativistic DFT NMR results, which would otherwise be equivalent in terms of basis functions, XC potential, and other parameters, which affect the quality of the computation.

The shielding constant σ_A for a nucleus A within the relativistic ZORA formalism consists of four terms as shown in Equation (1) below.

$$\sigma_A = \sigma_A^{\text{D}} + \sigma_A^{\text{P}} + \sigma_A^{\text{SO}} + \sigma_A^{\text{GC}} \quad (1)$$

Here, σ_A^{D} is the diamagnetic shielding, and σ_A^{P} the paramagnetic one. These two terms are also present in a nonrelativistic or a scalar (i.e., “one-component relativistic”) ZORA calculation. σ_A^{SO} denotes the spin–orbit induced terms due to the ZORA analogues of the Fermi–contact (FC) and the spin–dipole (SD) operators.^[12] It is important to note that, due to the different shapes of the orbitals obtained from a variational two-component calculation, σ_A^{D} and σ_A^{P} are also somewhat different compared with scalar relativistic calculations. Finally, σ_A^{GC} denotes gauge correction terms obtained from the implemented GIAO (gauge including atomic orbitals) formalism in a finite basis^[24–26] (it should be noted that σ^{GC} is supposed to include all GIAO related terms. This is different from the “gauge terms” that are printed by the ADF NMR program). Chemical shifts with respect to a reference nucleus (ref) are calculated as shown below in Equation (2).

$$\delta_A = \sigma_A^{\text{ref}} - \sigma_A^{\text{probe}} \quad (2)$$

The Vosko-Wilk-Nusair (VWN) local density approximation (LDA) functional has been used in all geometry optimizations, and a subset of the NMR computations.^[27] It provides a reasonable accuracy for structures, and often of NMR properties, of heavy metal complexes.^[10,12,18,28–32] In addition, the NMR chemical shifts have also been computed by using the Perdew-Wang (PW91)^[33] generalized gradient correction (GGA) density functional in order to demonstrate that the results are not very sensitive to the particular choice of the approximate (nonhybrid) density functional for the ground-state computation. The “statistical average of orbital-dependent model potentials” (SAOP) Kohn-Sham potential has been previously designed for, and successfully applied to, excitation energies and frequency-dependent response properties.^[34–38] Poater et al. have recently reported that SAOP results show considerable improvement with respect to other potentials, such as VWN or Becke-Perdew (BP),^[39,40] for a range of light-nuclei chemical shifts.^[41] In our previous study, its influence on the calculation of spin-spin coupling constants has been described.^[11] Its association with a continuum solvation model (see below) has resulted in good agreement between computed and experimental nuclear spin-spin coupling constants for **I–V**.

The optimized geometries of the complexes **I–V** have already been discussed in a previous paper.^[11] The frozen core Slater-type basis sets used for geometry optimizations include 4f, 5spd and 6s, or 6sp, as valence shells for Pt, and for Tl, respectively. The 1s shell has been kept frozen for C, N, and O. For reasons of consistency with Ref. [11], all-electron Slater-type basis sets augmented with steep 1s and 2p functions in the case of Pt and Tl have been used for the computations of NMR chemical shifts. All basis sets are of triple- ζ quality augmented with two polarization functions for the metal's valence shells, one polarization function for C, N, and O, and of double- ζ quality for the core shells in the case of all-electron computations.

Solvent effects have been taken into account by using two different approaches. In solution, complexes **I**, **II**, **III**, and **V** are moderately strongly coordinated by water molecules.^[3,10] This first (solvation or coordination) water shell is represented in the computation by explicitly adding water molecules to surround the Tl atom. We have also used the COSMO (conductor-like screening model) as implemented in ADF^[45] in order to implicitly treat the remaining bulk solvent effects.^[46,47] (The radii of the atomic spheres used in the COSMO calculations are 1.39, 1.7, 2.2, 1.4, 1.3, and 1.16 Å for Pt, Tl, C, N, O, and H, respectively. The metal radii are not optimized. However, a modification of the metal radii should not change the computational results by a significant amount).^[42–44] It has previously been demonstrated that usually the innermost solvent shell has to be included explicitly^[48] when computed nuclear shieldings are to be directly compared to experimental data. In Ref. [11], we showed that for the present samples the nuclear spin-spin coupling constants are very strongly affected both by direct H₂O coordination, and bulk solvent effects.

There is no real perturbation of the electron density by a static external magnetic field. Consequently, at the level of “uncoupled” DFT response theory that is employed in our NMR calculations, no perturbation of the effective Kohn-Sham potential, and also the COSMO potential is considered in the expression of the shielding tensor. The unperturbed Kohn-Sham potential directly enters the shielding tensor first, in principle, through the ZORA operators,^[19] and secondly through σ_A^{GC} .^[49,50] We have considered the COSMO potential in the latter terms, and should note that its effect on the results is not at all negligible. Its indirect effects on the chemical shifts, through an alteration of the unperturbed orbitals and their energies, are very important as well, as will be shown in the Results and Discussion. The ZORA operators are built from a model potential (sum of atomic potentials) instead of the self-consistently determined Kohn-Sham potential of the molecules.^[20,21] Consequently, the COSMO potential has no direct influence on these operators, which we would expect to be negligible anyway.^[51]

For the anionic species, the counterion effects have not been simulated. It has previously been demonstrated that solvent effects can be similar to counterion effects in the computation of NMR properties.^[32]

Results

Choice of references for the determination of the chemical shifts: By definition [Eq. (2)], chemical shifts are reported with respect to a reference nucleus. This is not the case for a number of other magnetic resonance properties that are currently accessible to computation, for instance, nuclear spin-spin coupling constants. Usually, the presence of a reference in the calculation is helpful, because of systematic error cancellation. However, in this work the heavy-nucleus reference choice adds a layer of complexity, because of the need to accurately describe the reference shielding.

All measurements were carried out in aqueous solution. For the present samples, experimental data have been reported with respect to Tl⁺ or Tl(CN)₃ for Tl chemical shifts, and with respect to [Pt(CN)₆]²⁻ for Pt chemical shifts.^[2] Accordingly, these references have been used in our calculations. However, Tl chemical shifts computed with respect to the rather problematic Tl⁺ reference will be omitted from the discussion, because of the considerably large error obtained from these calculations. In order to take into account the solvent effects on the reference, Tl chemical shifts have also been computed with respect to Tl(CN)₃·2H₂O with the two additional water molecules situated on both sides of the Tl(CN)₃ plane. The significance of the reference choice will also be demonstrated for the Pt chemical shift calculations by comparing the two dianionic complexes [Pt(CN)₆]²⁻ and [Pt(Cl)₆]²⁻ as references.

Calculated chemical shifts are often reported with respect to references that are closely related to the studied complexes in order to take advantage of a maximum amount of error cancellation. Consequently, for the present work, Pt and Tl chemical shifts were additionally evaluated with respect to complex **IV**. For this system, no first (explicit) metal coordination shell by water molecules needs to be considered, because of the high number of cyanide ligands on the Tl atom and its pseudotetrahedral coordination.^[11]

¹⁹⁵Pt and ²⁰⁵Tl NMR chemical shifts: As in our previous work about the nuclear spin-spin coupling constants of the same complexes,^[11] different computational methods applied to several structural arrangements have been used with the aim of well reproducing the experimental Pt and Tl chemical shifts, and to understand the various electronic and structural influences. The solvent effects due to the water molecules coordinated to the Tl atom strongly shift the Pt-Tl coupling constants. Consequently, in the present work, we have also applied this approach of adding an explicit solvation shell to those of the studied complexes with open coordination spheres around Tl (“model A”, excluding complex **IV**, and the Pt references [Pt(CN)₆]²⁻ and [Pt(Cl)₆]²⁻. For these systems, model A, and the not explicitly solvated systems are considered to be equivalent). Instead of calling this a solvent shell, it is also possible to view this model as treating the aquo-complexes of **I**, **II**, **III**, and **V**. It was previously shown that regarding heavy metal spin-spin coupling constants, even “inert” solvents such as chloroform can cause very sizeable solvent shifts, compared with the free systems.^[30] The stronger nucleophilic the solvent, the larger is

the effect. With the present samples, we believe that is somewhat a matter of taste to view the first solvation shell as regular ligands.

Recent studies have demonstrated that treating the solvent implicitly as a polarizable continuum may yield important contributions to the NMR parameters.^[52–55] This was, to an unexpected extent, confirmed by our work on the present sample's coupling constants.^[11] Such an approach, available in form of the COSMO model in the ADF code,^[45] has been applied here first on the free molecules ("model B"), and secondly on the previously described water complexes "model A", in order to simultaneously take into account the explicit first solvation shell, and implicit bulk solvent effects. This combined treatment of solvent effects will be termed "model C". This model might give a good representation of the effects on the Pt and Tl chemical shifts of both the direct coordination of the Tl atom by solvent molecules, and the electrostatic interaction with the bulk solvent. We should point out that "model B" and "model C" are not the same as those defined in our previous paper.^[11]

The experimentally observed and computed Pt and Tl chemical shifts for complexes I–V are collected in Table 1 and 2, and graphically displayed in Figure 2 and 3, respectively. Although a certain amount of redundancy is introduced in the tables, for the convenience of the reader we

have tabulated the chemical shifts with respect to the various references instead of the calculated shielding constants. In order to allow the interested reader to obtain the individual shielding constants, the absolute shieldings for complex IV in the various models are listed in Table 3.

The first observation concerns the comparison between the results obtained with established standard LDA and GGA functionals (by using the PW91 functional as a typical representative for the latter). For this series of complexes, the chemical shifts are not particularly sensitive to the choice of the approximate density functional, though differences are, of course, observed. For instance, Pt chemical shifts are systematically lowered by 100 ppm, at the most, when the GGA functional is applied. The influence of the GGA functional is even less noticeable in the case of the Tl chemical shifts. We do not expect any significant changes of the results upon switching to a different nonhybrid GGA. It has previously been demonstrated that for heavy atomic molecules, for which the NMR results are not too delicately balanced by different contribution of varying sign, the heavy atom chemical shifts tend to be rather insensitive to the particular choice of the approximate nonhybrid density functional. To compare, please see Refs. [19], [56], and [12].

In the following, we will thus focus on the results computed with the LDA and SAOP functionals. We should already

Table 1. Calculated NMR chemical shifts [ppm] of ¹⁹⁵Pt in the complexes I–V with respect to [Pt(CN)₆]²⁻, [Pt(Cl)₆]²⁻, and complex IV.^[a]

Reference	[Pt(CN) ₆] ²⁻			[Pt(Cl) ₆] ²⁻			complex IV		
	LDA	GGA	SAOP	LDA	GGA	SAOP	LDA	GGA	SAOP
complex I									
unsolvated	1150	973	937	-943	-1002	-70	2446	2337	2078
model A (3 H ₂ O) ^[b]	-337	-434	-325	-2430	-2409	-1332	959	930	816
model A (4 H ₂ O) ^[b]	-529	-620	-494	-2622	-2595	-1501	767	744	647
model A (5 H ₂ O) ^[b]	-655	-745	-600	-2748	-2720	-1607	641	619	541
model B ^[c]	989	899	1017	-1898	-1918	-967	1362	1298	1335
model C (3 H ₂ O) ^[d]	73	32	118	-2814	-2785	-1866	446	431	436
model C (4 H ₂ O) ^[d]	109	56	126	-2778	-2761	-1858	482	455	444
model C (5 H ₂ O) ^[d]	99	50	116	-2788	-2767	-1868	472	449	434
exptl ^[e]	-182	-182	-182	473	473	473	405	405	405
complex II									
unsolvated	-546	-649	-528	-2639	-2624	-1535	750	715	613
model A (4 H ₂ O) ^[b]	-1145	-1227	-1016	-3238	-3202	-2023	151	137	125
model B ^[c]	198	141	211	-2689	-2676	-1773	571	540	529
model C (4 H ₂ O) ^[d]	-68	-112	-37	-2955	-2929	-2021	305	287	281
exptl ^[e]	-272	-272	-272	383	383	383	315	315	315
complex III									
unsolvated	-942	-1031	-840	-3035	-3006	-1847	354	333	301
model A (2 H ₂ O) ^[b]	-1042	-1127	-919	-3135	-3102	-1926	254	237	222
model B ^[c]	-49	-99	-25	-2936	-2916	-2009	324	300	293
model C (2 H ₂ O) ^[b]	-229	-266	-184	-3116	-3083	-2168	144	133	134
exptl ^[e]	-471	-471	-471	184	184	184	116	116	116
complex IV									
unsolvated	-1296	-1364	-1141	-3389	-3339	-2148	0	0	0
model B ^[c]	-373	-399	-318	-3260	-3216	-2302	0	0	0
exptl ^[e]	-587	-587	-587	68	68	68	0	0	0
complex V									
unsolvated	-192	-324	-103	-2285	-2299	-1110	1104	1040	1038
model A (4 H ₂ O) ^[b]	-753	-857	-647	-2846	-2832	-1654	543	507	494
model B ^[c]	887	794	855	-2000	-2023	-1129	1260	1193	1136
model C (4 H ₂ O) ^[d]	231	168	238	-2656	-2649	-1746	604	567	556
exptl ^[e]	-56	-56	-56	599	599	599	531	531	531

[a] Spin-orbit relativistic chemical shifts from scalar relativistically optimized geometry. [b] Model A: scalar relativistically optimized geometry, which includes explicit first solvation shell. [c] Model B: scalar relativistically optimized geometry by using the COSMO model for all solvent effects. No explicit first solvation shell. [d] Model C: model A+COSMO for the bulk solvent effects. [e] References [2] and [3].

Table 2. Calculated NMR chemical shifts [ppm] of ^{205}Tl in the complexes **I–V** with respect to $\text{Tl}(\text{CN})_3$, $\text{Tl}(\text{CN})_3+2\text{H}_2\text{O}$, and complex **IV**.^[a]

Reference	$\text{Tl}(\text{CN})_3$			$\text{Tl}(\text{CN})_3+2\text{H}_2\text{O}$			complex IV		
	LDA	GGA	SAOP	LDA	GGA	SAOP	LDA	GGA	SAOP
complex I									
unsolvated	–3890	–3777	–4079	–3140	–3085	–3295	–2266	–2259	–2480
model A (3 H_2O) ^[b]	–2368	–2342	–2687	–1618	–1650	–1903	–744	–824	–1088
model A (4 H_2O) ^[b]	–2357	–2347	–2715	–1607	–1655	–1931	–733	–829	–1116
model A (5 H_2O) ^[b]	–2308	–2291	–2635	–1558	–1599	–1851	–684	–773	–1036
model B ^[c]	–6566	–6277	–6334	–6198	–6250	–5907	–5839	–5662	–5611
model C (3 H_2O) ^[d]	–1631	–1609	–1909	–1263	–1300	–1482	–904	–994	–1186
model C (4 H_2O) ^[d]	–1657	–1657	–2027	–1289	–1348	–1600	–930	–1042	–1304
model C (5 H_2O) ^[d]	–1629	–1621	–2022	–1261	–1312	–1595	–902	–1006	–1299
exptl ^[e]	–2056	–2056	–2056	–2056	–2056	–2056	–1438	–1438	–1438
complex II									
unsolvated	–663	–685	–513	87	7	271	961	833	1086
model A (4 H_2O) ^[b]	–1650	–1615	–1851	–900	–923	–1067	–26	–97	–252
model B ^[c]	–1064	–1069	–923	–696	–760	–496	–337	–454	–200
model C (4 H_2O) ^[d]	–1244	–1222	–1520	–876	–913	–1093	–517	–607	–797
exptl ^[e]	–1471	–1471	–1471	–1471	–1471	–1471	–853	–853	–853
complex III									
unsolvated	–109	–139	–78	641	553	706	1515	1379	1521
model A (2 HO) ^[b]	–1745	–1659	–1678	–995	–967	–894	–121	–141	–79
model B ^[c]	53	27	26	421	336	453	780	642	749
model C (2 HO) ^[d]	–790	–716	–850	–422	–407	–423	–63	–101	–127
exptl ^[e]	–867	–867	–867	–867	–867	–867	–249	–249	–249
complex IV									
unsolvated	–1624	–1518	–1599	–874	–826	–815	0	0	0
model B ^[c]	–727	–615	–723	–359	–306	–296	0	0	0
exptl ^[e]	–618	–618	–618	–618	–618	–618	0	0	0
complex V									
unsolvated	931	910	1235	1681	1602	2019	2555	2428	2834
model A (4 H_2O) ^[b]	–2319	–2251	–2379	–1569	–1559	–1595	–695	–733	–780
model B ^[c]	1045	995	1202	1413	1304	1629	1772	1610	1925
model C (4 H_2O) ^[d]	–1664	–1597	–1754	–1296	–1288	–1327	–937	–982	–1031
exptl ^[e]	–1605	–1605	–1605	–1605	–1605	–1605	–987	–987	–987

[a] Spin–orbit relativistic chemical shifts from scalar relativistically optimized geometry. [b] Model A: scalar relativistically optimized geometry including explicit first solvation shell. [c] Model B: scalar relativistically optimized geometry using the COSMO model for all solvent effects. No explicit first solvation shell. [d] Model C: model A+COSMO for the bulk solvent effects. [e] Reference [2] and [3].

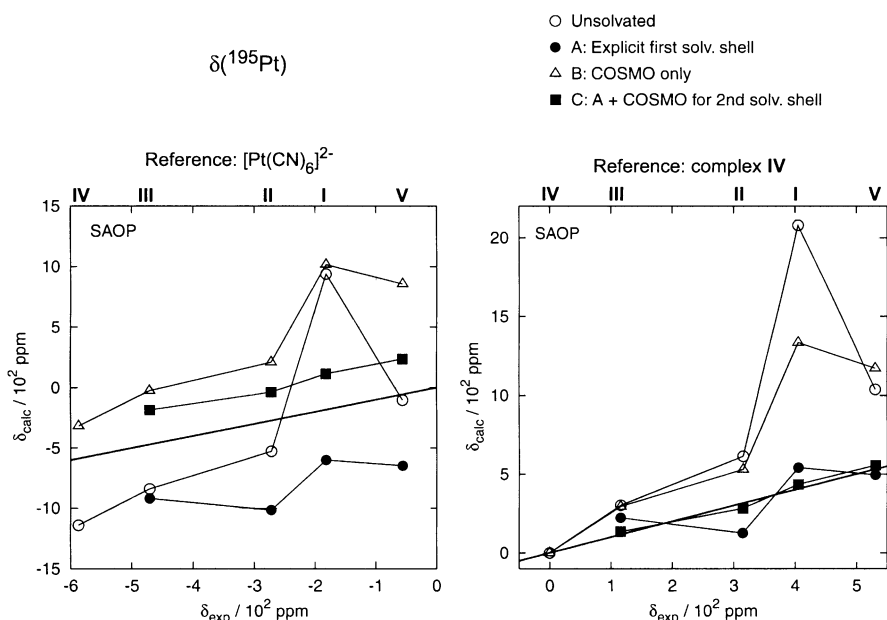


Figure 2. Comparison of calculated and experimental ^{195}Pt NMR chemical shifts for different computational approaches and references (given above the graphics). See footnotes of Table 1 for an explanation of the computational models. The experimental values are labeled on the top of the graphics. The straight thick line indicates where $\delta_{\text{calc}} = \delta_{\text{exp}}$. The lines connecting the points do not represent fits to the data points, but were added to guide the eye. LDA and GGA results are not shown because of their similarity to the SAOP values.

mention here that “model C” yields good agreement between computed and experimental chemical shifts, whereas the other models sometimes afford huge errors. A detailed discussion of the different models follows below.

We shall begin with the discussion of the Pt chemical shifts calculated with respect to the $[\text{Pt}(\text{CN})_6]^{2-}$ reference. There is poor agreement between computed and experimental Pt chemical shifts for the free molecules. In particular, for complex **I**, the experimental chemical shift is overestimated by more than 1300 ppm. For the other complexes, we find an underestimation of $\delta(\text{Pt})$ between 136 and 701 ppm. This unsolvated “model” has also been used as a benchmark in order to estimate the importance of elec-

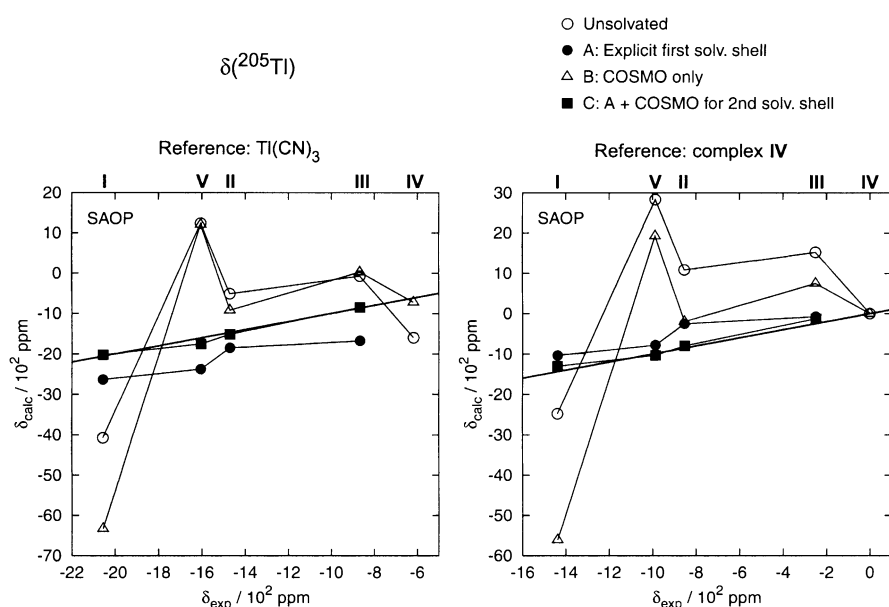


Figure 3. Comparison of calculated and experimental ^{205}Tl NMR chemical shifts for different computational approaches, and references (given above the graphics). See footnotes of Table 2 for an explanation of the computational models, and details about the graphics.

Table 3. Calculated absolute NMR $\sigma(^{195}\text{Pt})$ and $\sigma(^{205}\text{Tl})$ shielding constants [ppm] for the reference complex **IV**.^[a]

Reference	LDA	GGA	SAOP
		$\sigma(^{195}\text{Pt})$	
unsolvated	6237	6118	6197
model B ^[b,c]	6478	6358	6425
model B ^[b,d]	–	6368	6421
model B ^[b,e]	–	6354	6434
		$\sigma(^{205}\text{Tl})$	
unsolvated	10034	10154	10209
model B ^[b,c]	9664	9781	9860
model B ^[b,d]	–	9796	9867
model B ^[b,e]	–	9791	9881

[a] Spin–orbit relativistic chemical shifts from scalar relativistically optimized geometry. [b] Model B: scalar relativistically optimized geometry by using the COSMO model for all solvent effects. No explicit first solvation shell. [c] The radii of the atomic spheres used in the COSMO calculations are 1.39, 1.7, 2.2, 1.4, 1.3, and 1.16 Å for Pt, Tl, C, N, O, and H, respectively. [d] The radii of the atomic spheres of the ligand atoms are 20% smaller than used usually, that is, 1.76 and 1.12 Å for C and N, respectively. [e] The radii of the atomic spheres of the ligand atoms are 20% larger than used usually, that is, 2.64 and 1.68 Å for C and N, respectively.

tronic spin–orbit coupling in the calculations. For instance, the scalar relativistic ^{195}Pt chemical shifts for the complexes **I**, **II** and **III** with respect to $[\text{Pt}(\text{CN})_6]^{2-}$ deviate from experiment by 2132, 682, and 493 ppm, respectively, whereas the errors are reduced to 1332, 274, and 471 ppm when spin–orbit coupling is considered.

The explicit inclusion of the solvent molecules (“model A”) negatively shifts all the calculated Pt chemical shifts. The effect of this explicit solvation is comparatively small for complexes **II**, **III**, and **V**, but increases the differences with the experimental values. As expected, and similar to the coupling constants,^[11] the higher the coordination of the Tl by the cyano ligands, the smaller the effect of coordi-

nation of additional solvent molecules on the Pt chemical shifts. For complex **I**, it can be seen that the solvent effect is also increasing with increasing number of coordinated water molecules.

A next step to improve the computational model is the implicit addition of bulk solvent effects. However, without the explicit first solvation shell (“model B”), no agreement is observed between calculated (COSMO) and experimental Pt chemical shifts. For instance, for complexes **I** and **V**, for which no cyano ligand is coordinated to the Tl atom, a huge error of more than 900 ppm is obtained. Similar to our “model A”, the higher the $(\text{CN})^-$ coordination is around the Tl atom, the closer the computed chemical shift is to the experimental one.

The presence of both explicit first solvation shell, and implicit bulk solvent effects (“model C”) clearly increases the quality of the calculated Pt chemical shifts. The maximum error is 287 ppm for complex **V**. The application of a standard GGA functional (PW91) slightly improves the agreement between computed and experimental Pt chemical shifts.

Regarding the spin–spin coupling constants, we could show that the simultaneous application of explicit solvation, the COSMO model, and the SAOP potential allowed to obtain a very good agreement between computed and experimental coupling constants.^[11] Here, we do not obtain a substantial improvement from the SAOP potential for the Pt chemical shift calculated with respect to $[\text{Pt}(\text{CN})_6]^{2-}$ at the level of “model C”. Moreover in this particular case, it seems that the PW91 functional is slightly more accurate than the SAOP potential. For all complexes, the difference between calculated and experimental data is still about 200 ppm. However, it must be noted that by applying the different models, changes of $\delta(\text{Pt})$ in the order of thousand ppm are obtained, with the final results being balanced by various competing effects. Thus, the errors of 200 ppm with respect to the experiment data are not particularly large.

In order to investigate the influence of the reference choice, Pt chemical shifts have been further calculated with respect to $[\text{Pt}(\text{Cl})_6]^{2-}$, and complex **IV**. The more similar to the studied complexes the reference is, the more accurate the agreement between computed and experimental values can be expected, because of a better compensation of systematic errors. This is demonstrated by the results obtained with respect to complex **IV**. The same trends with $[\text{Pt}(\text{CN})_6]^{2-}$ are obtained, of course, but the agreement with the experiment values is much better for the best computa-

tional model with complex **IV** as the reference. For instance, by using the solvated “model A”, the LDA calculations qualitatively reproduce the experimental data. Only the Pt chemical shift for the complex **I** is overestimated by about 500 ppm. The inclusion of both explicit and bulk solvent effects in the SAOP calculations (“model C”) finally allows a very good agreement between calculated and measured values to be obtained. In that case, the largest error is of about 30 ppm for complexes **I** and **II**, which corresponds to a deviation of the experimental values by 7% and 10%, respectively. Results of a similar quality have also been obtained with the standard LDA and GGA functionals.

With respect to the reference $[\text{Pt}(\text{Cl})_6]^{2-}$, the differences between computed and experimental Pt chemical shifts are huge. It can be seen that when applying the SAOP potential in the shielding calculations for $[\text{Pt}(\text{Cl})_6]^{2-}$, the errors decrease significantly, but remain unacceptably large. For instance, at the level of “model C” (SAOP) the Pt chemical shift of complex **I** is in error by 2341 ppm when taken with respect to $[\text{Pt}(\text{Cl})_6]^{2-}$, but only by 29 ppm with respect to complex **IV**. Unlike the other references, $\sigma(\text{Pt})$ in $[\text{Pt}(\text{Cl})_6]^{2-}$ appears to be very sensitive to the choice of the potential. In comparison to $[\text{Pt}(\text{CN})_6]^{2-}$, σ^{SO} and σ^{D} are of the same magnitude in $[\text{PtCl}_6]^{2-}$, but σ^{P} is much larger, and most likely the source of the errors. This might be indicated by, and partially attributed to, the significantly smaller HOMO–LUMO gap computed for this reference. It could be the cause of an overestimation of the negative σ^{P} contribution by about 2000 to 3000 ppm, depending on the functional, with the positive σ^{SO} being less sensitive to deficiencies in the electronic structure. We believe that the huge disagreements with the experimental values are due to a particularly poor description of the reference $[\text{PtCl}_6]^{2-}$, not the complexes **I–V**.

The conclusions previously drawn for the computed Pt chemical shifts of complexes **I–V**, are also valid for the Tl chemical shift calculations. The best agreement is obtained by using the solvated “model C”. Although the standard LDA and GGA functionals yield acceptable results, in contrast to the Pt chemical shifts a significant improvement is obtained for the Tl shifts of complexes **I–III** when using the SAOP potential. Considering solvent effects on the reference shielding by using $\text{Tl}(\text{CN})_3 + 2\text{H}_2\text{O}$ instead does not enhance the agreement with experimental values. The addition of the water molecules in both sides of the $\text{Tl}(\text{CN})_3$ plane only results in a small increase of all Tl chemical shifts. With complex **IV** as the reference, the agreement with the experimental data is best, with an error of about 10% for the complexes **I**, **II**, and **V**. The percentage error is somewhat larger for complex **III** due to the small magnitude of the experimental value.

In order to study the reliability of the final results obtained with the COSMO model, NMR $\sigma(^{195}\text{Pt})$ and $\sigma(^{205}\text{Tl})$ shielding constants have been calculated for the reference complex **IV** (“model B”) with different COSMO radii for the atomic spheres of the ligand atoms. In other terms, how sensitive are the computed shieldings to the cavity size? The results are collected in Table 3. Changing the radii of the atomic spheres for C and N by $\pm 20\%$ changes the Pt and

Tl shielding constants far less than the calculated magnitude of the total COSMO contributions. This indicates that the calculated shieldings, at least at the level of “model C”, are not particularly sensitive towards the choice of the COSMO radii.

We have previously seen a very pronounced dependence of $J_{\text{Pt–Tl}}$ on $R(\text{Pt–Tl})$.^[11] It is thus important to investigate the sensitivity of the shielding constants with respect to the structural parameters. Additional data have therefore been obtained for complex **I** (“model C”) with varying fixed values of $R(\text{Pt–Tl})$, and all other geometrical variables optimized. It appears that around the equilibrium Pt–Tl distance, the shielding constants are not extremely sensitive to the modification of the structural parameters. For example, a decrease of as much as 0.13 Å of the Pt–Tl distance, affects the Pt and Tl shielding constants by 9 and 429 ppm, respectively. However, the Tl chemical shifts are obviously more sensitive to the Pt–Tl distance than the Pt shifts.

Discussion

When comparing chemical shifts to experimental data it is very important to consider solvent effects. Sizeable solvent effects on ^{199}Hg chemical shifts were already known experimentally for many years.^[57] This specific case has been computationally investigated for the first time by Wolff et al. (linear ^{199}Hg complexes).^[19] Solvent-induced changes of δ_{Hg} were experimentally reported to be of the order of 10^3 ppm for HgI_2 , and found to be of similar magnitude in the computations in Ref. [19]. These are cases in which the solvent strongly coordinates to the heavy atom, and it is obvious that it must be considered explicitly to some extent. In some cases this coordination causes large geometry changes,^[19] which are partially responsible for the effects on the chemical shift. Unfortunately, the inclusion of solvent molecules usually causes the systems to be rather large for relativistic computations. This might be the reason why, to the best of our knowledge, no further detailed computational study regarding solvent effects on heavy “relativistic” transition-metal nuclear shieldings has so far appeared. Treating the solvent as a polarizable continuum may also have important effects on the NMR parameters.^[52–54] We are not aware of previous applications to heavy transition-metal complexes. To remind the reader, “model C” takes into account both explicit and implicit solvent effects, whereas “model A” and “model B” are only concerned with either one of them.

Our previous study on the same heavy metal complexes has revealed that all calculated spin–spin coupling constants are systematically improved upon introducing more realistic computational models for the treatment of the solvent.^[11] This conclusion can not be directly transferred to the calculation of the Pt and Tl NMR chemical shifts. In particular, though “model B” might be thought of as an improved model of the solvated systems, the chemical shifts are not much improved. However, its use in addition to the explicit first solvation shell (“model C”) noticeably enhances the agreement between computed and experimental Pt chemical shifts, even if the SAOP potential is not applied at the same

time. Including the SAOP potential, this most realistic computational model yields the best agreement between computed and experimental data for the Tl chemical shifts. For the Pt chemical shifts, the results are of similar quality with all functionals. The results are close to the experimental data when $[\text{Pt}(\text{CN})_6]^{2-}$ or complex **IV** are chosen as the reference.

In exact theory, chemical shift calculations should not depend on the choice of reference. However, the comparison between the approximate calculated results obtained with respect to Tl^+ , $\text{Tl}(\text{CN})_3$, $\text{Tl}(\text{CN})_3+2\text{H}_2\text{O}$, and complex **IV** for the Tl chemical shifts, and with respect to $[\text{Pt}(\text{CN})_6]^{2-}$, $[\text{Pt}(\text{Cl})_6]^{2-}$ and complex **IV** for the Pt chemical shifts, reveals the inherent errors of the computations. It can be seen that with the most reasonable computational model, acceptable though not uniformly accurate, results are obtained with all references, excluding $[\text{Pt}(\text{Cl})_6]^{2-}$. Obviously, the closer the reference is to the geometry and electronic structure (structural arrangement, ligands, charge and so on) of the samples, the better the agreement is with the experimental values.

Conclusion

A large variety of parameters, including geometries, basis sets, solvents, references, and so on, can drastically influence the quality of NMR chemical shift computations. Many studies on small and light atomic molecules have already been published which were concerned with the effects related to each of them.^[49,50] In comparison, little is known about transition metal nuclei, in particular for the heavier ones, since the usage of a relativistic theoretical formalism is imperative. The past years have seen a strongly increasing interest in the relativistic computation of nuclear shieldings in molecules, which contain heavy atoms.^[12,13] However, most of them have so far focused on novel relativistic methodology, a comparison to nonrelativistic data, and interpretations of relativistic effects. Some of these methods have by now been established as useful computational tools to study NMR spectroscopy of transition metals, and the computationally more efficient among those can be applied to larger and/or more complicated systems.

In the present work, we have focused on the importance of modeling the electronic structure, and the chemical environment of complexes **I–V**, and for the first time computed their metal chemical shifts. Together with Ref. [11], all experimentally determined NMR parameters of the heavy nuclei have now been computed with sufficient accuracy (typically within about 15% deviation from experimental data) in order to allow a detailed analysis of the observed trends. We believe that in order to achieve a much better agreement with experimental data, significantly more involved computations in which a number of remaining sources of errors are simultaneously eliminated, are required. This is likely to demand the dynamical calculation of time-averaged nuclear shieldings of the solvated systems at finite temperature,^[58] and include the counter ions, along with a more accurate treatment of electron correlation. Perhaps ex-

plicit interaction of the solvent with the ligands is also needed, and its neglect could be partially responsible for the drastic failure of the $[\text{PtCl}_6]^{2-}$ reference.

The effects of the solvent (H_2O) on the NMR observables have turned out to be remarkably large, and in some cases account for most of their magnitudes. The best computational models uniformly agree with the experimental data, which gives some confidence both in that the results recover the experimental trends for the right reason, and that the originally proposed structures (Figure 1) of the complexes^[1,2] are correct, despite some unintuitive details of the NMR spectra, for instance for complex **II**.

Generally, for transition-metal complexes with a possibility of direct metal–solvent interaction we believe that a model of comparable quality as our “model C”, perhaps in conjunction with the SAOP potential or one with similar characteristics regarding response properties, is necessary to cover most of the environmental effects, and to obtain a reasonably good electronic structure. This model represents a good compromise at affordable computational cost.

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