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Optimizing the Structure of Tetracyanoplatinate (II): A Comparison of Relativistic Density Functional Theory Methods

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Abstract: The geometry of tetracyanoplatinate(II) (TCP) has been optimized with density functional theory (DFT) calculations in order to compare different computational strategies. Two approximate scalar relativistic methods, i.e. the scalar zeroth-order regular approximation (ZORA) and non-relativistic calculations with relativistic effective core potentials (ECPs), were benchmarked against the four-component fully relativistic approach using the Dirac-Coulomb Hamiltonian and all-electron non-relativistic calculations. We find that the 5% contraction of the platinum-carbon bond due to relativistic effects is almost quantitatively reproduced in the ZORA and ECP calculations. In addition, the effect of the exchange-correlation functional and one-electron basis set was studied by employing the two generalized gradient approximation (GGA) functionals, BLYP and PBE, as well as their hybrid version B3LYP and PBE0 in combination with both correlation consistent and Ahlrichs type basis sets. The platinum-carbon bond length (relativistic or non-relativistic) is approximately 1% shorter on using the PBE exchange-correlation functional compared to the BLYP functional but including exact exchange has no significant effect. For the C-N bond these trends are reversed and an order of magnitude smaller. With respect to the basis set dependence we observed that a triple zeta basis set with polarization functions gives in general sufficiently converged results, but while for the Pt-C bond it is advantageous to include extra diffuse functions, this did not turn out to be important for the C-N bond.

Keywords: 4-Component calculations, DFT, geometry optimization, relativistic effects, transition metal complexes, ZORA.

1. INTRODUCTION

Transition metals are important in almost every field of chemistry, from organometallic chemistry to biochemistry, where transition metals are found in active sites of metalloproteins. Platinum complexes such as cis-diamminedichloroplatinum(II) [1], also known as cisplatin, have been known for a very long time and are used for example in certain types of cancer treatment. New platinum complexes are thus still synthesized in search of enhanced efficiency of the drugs [2, 3]. Furthermore, platinum is renowned for its catalytic abilities, from platinum surfaces [4] to more advanced systems of platinum nanoparticles in nanoporous arrays, which possess enhanced activity of oxygen reduction as used in fuel cell technology [5].

A particularly well-studied platinum complex is $[\text{Pt}(\text{CN})_4]^{2-}$, called tetracyanoplatinate(II) (TCP), Fig. (1). This compound has been known since early in the 19th century [6], and is capable of forming oligomeric chains of TCP units. The compound can be modeled as a quasi one-dimensional metal-metal bonded chain, exhibiting extremely anisotropic conductivity [7], making it interesting for transport studies and molecular electronics. Furthermore, the Pt-Pt distance in the crystal chains strongly influences the corresponding electronic transition energies [8], indicating that excitation of the complex will also affect the Pt-Pt distance. An excellent method for studying this phenomenon

is Time-Resolved X-ray Scattering (TRXRS). This approach has already been used successfully in solution, using systems with similar properties [9, 10]. These studies impart unprecedented insight into the structure of transient molecular species, information consequential to understanding reaction pathways and dynamics of these systems. Obtaining a deeper understanding of these phenomena is necessary for the advance of better catalysts and functionalised biomolecules. Electronic structure calculations, such as geometry optimization of the complexes in the ground and excited states [11], are essential for the interpretation of the experimental TRXRS data.

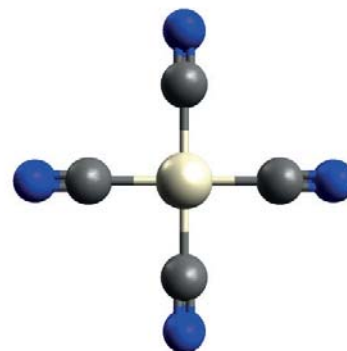


Fig. (1). Illustration of the tetracyanoplatinate complex $[\text{Pt}(\text{CN})_4]^{2-}$.

In this article, we therefore discuss the importance of relativistic effects, exchange-correlation functional and one-electron basis set on the platinum-carbon and carbon-nitrogen bond lengths in TCP in its electronic ground state.

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For that purpose we compare the results of geometry optimizations carried out as four-component relativistic density functional theory (DFT) calculations using the Dirac-Coulomb Hamiltonian with the results of DFT calculations using a scalar implementation of the zeroth-order regular approximation (ZORA) Hamiltonian, [12-15], as well as with non-relativistic DFT calculations with two types of relativistic effective core potentials (ECPs), and with the results of standard non-relativistic all-electron DFT calculations. Moreover, we investigate the effect of the exchange-correlation functional on the optimized bond lengths by employing two generalized gradient approximation (GGA) functionals, BLYP [16] and PBE [17, 18] as well as their hybrid version B3LYP [19-21] and PBE0 [22] in combination with correlation consistent and Ahlrichs type basis sets.

Previous calculations on TCP include non-relativistic and two-component relativistic DFT calculations [23] as well as two-component ZORA TDDFT calculations [24] of its electronic absorption spectrum. In a recent computational study [25] on the related cisplatin it was investigated how the quantum chemical method, Hartree-Fock, second order Møller-Plesset perturbation theory and DFT with various exchange-correlation functionals, and the one-electron basis set, both all electron and ECP basis sets, influence the structure and reactivity of cisplatin. Furthermore fully relativistic four-component Dirac-Fock Coulomb geometry optimizations have been presented for the cationic platinum carbene complex PtCH_2^+ [26]. However, we are not aware of any previous fully relativistic four-component calculations of the geometry of TCP or a comparison between four-component, two-component and non-relativistic calculations.

2. COMPUTATIONAL DETAILS

The fully four-component relativistic calculations with the Dirac-Coulomb Hamiltonian were carried out using the DIRAC v.08 program [30]. In these calculations the dyall.v2z (large component: 22s19p12d9f) and dyall.v3z (29s24p15d11f2g) basis sets by Dyall [31, 32] were used on the Pt atom, while for the carbon and nitrogen atoms Dunning's correlation consistent (aug)-cc-pVDZ (3s2p1d plus 1s1p1d in the augmented version) and (aug)-cc-pVTZ (4s3p2d1f plus 1s1p1d1f in the augmented version) basis sets [33] were employed. The basis sets for the small components were automatically generated using the kinetic balance condition [34].

The ZORA- and all-electron, non-relativistic calculations were carried out with the ORCA [35] program using the largest grid for the numerical integration. To confirm that the optimizations have converged to a minimum, numerical frequency calculations were conducted. The RI (Resolution of the Identity) approximation was turned off in all calculations with the ORCA program. In the ZORA calculations, we tested both the Ahlrichs SVP / TZVP / QZVP [36], the newer, corresponding Ahlrichs-def2-type [37] basis set, and the Dyall/Dunning combination used for the 4-component calculations. It should be noted that the basis for Pt is the same in the TZVP and QZVP sets (17s11p8d3f) and only slightly smaller in the SVP (17s11p8d2f), while it differs in the newer def2-type basis sets (17s11p8d3f1g vs 17s11p8d3f2g). The basis sets for

carbon and nitrogen in the SVP, TZVP, QZVP, def2-TZVP and def2-QZVP are 3s2p1d, 6s3p1d, 8s4p3d2f1g, 6s3p2d1f and 15s8p3d2f1g. In the all-electron non-relativistic calculations the large component basis sets of the four-component relativistic calculations were employed, i.e. the dyall.v2z and dyall.v3z basis sets on Pt and (aug)-cc-pVXZ (X = D, T) on carbon and nitrogen.

The calculations using relativistic effective core potentials were carried out in the Turbomole program package [38-42], with the finest possible grid. Two different types of ECPs were used for Pt: 1) the Stuttgart-Dresden-Bonn energy-adjusted ECPs ECP60MWB [43] with the associated Ahlrichs TZVP valence electron basis set and the Ahlrichs def2-type basis sets for carbon and nitrogen in order to be as comparable as possible to the ZORA calculations; 2) the new relativistic energy-consistent pseudopotentials ECP60MDF and associated correlation consistent basis sets cc-pVXZ-PP (X = D, T, Q) for the valence electrons of Pt [44] and the corresponding correlation consistent basis.

3. RESULTS AND DISCUSSION

3.1. Dependence on the Basis Set

The results of the four-component DFT geometry optimizations with the Dirac-Coulomb Hamiltonian and various combinations of exchange-correlation functionals and basis sets are shown in Table 1. All changes in the Pt-C bond length due to the basis set are smaller than 0.5 pm or 0.15% independent of the exchange-correlation functional indicating that it is sufficiently converged with the Dyall.v3z/aug-cc-pVTZ or even Dyall.v3z/cc-pVTZ basis set. The carbon-nitrogen bond distance, on the other hand, is reduced by 1% or ~ 1 pm on going from the double to the triple zeta basis sets for all exchange-correlation functionals, while addition of diffuse functions on the carbon and nitrogen atoms in the aug-cc-pVDZ or aug-cc-pVTZ basis has no significant effect.

In Table 2 the results of the ZORA geometry optimizations using the Ahlrichs basis sets, SVP, TZVP, QZVP, def2-TZVP and def2-QZVP, and the largest basis set from the four-component calculations, Dyall.v3z/aug-cc-pVTZ basis sets, using the four functionals are shown. The basis set dependence of the Pt-C bond length turns out to be slightly larger than in the four-component calculations, as the changes on going from TZVP to QZVP are still larger than the change on going from Dyall.v2z/cc-pVDZ to Dyall.v3z/cc-pVTZ in the four-component calculations, i.e. in the order of 0.3 pm or 0.15% which is thus solely due to the significantly larger carbon and nitrogen basis set in the QZVP basis set while the extra one or two g-functions on Pt in the def2-TZVP or def2-QZVP basis sets lead to smaller changes. The maximal changes in the C-N bond length are of the same order of magnitude and thus somewhat smaller than in the four-component calculations, which probably reflects the fact that we go up to the QZV level in contrast to those calculations. Consequently, the results obtained with the Dyall.v3z/aug-cc-pVTZ basis set lie for both bond lengths between the TZVP and QZVP results.

Table 1. Optimized Pt-C and C-N Bond Lengths of $[\text{Pt}(\text{CN})_4]^{2-}$ in pm Obtained with Four-Component Dirac-Coulomb DFT Calculations for Various Basis Sets and Exchange-Correlation Functionals.

Distance	Basis Set	BLYP	B3LYP	PBE	PBE0
<i>R</i> (Pt-C)	Dyall.v2z/cc-pVDZ	202.64	201.79	200.28	199.80
	Dyall.v2z/aug-cc-pVDZ	202.51	201.68	200.11	199.63
	Dyall.v3z/cc-pVTZ	202.60	201.67	200.13	199.57
	Dyall.v3z/aug-cc-pVTZ	202.54	201.66	--- ^a	199.53
<i>R</i> (C-N)	Dyall.v2z/cc-pVDZ	118.62	117.36	118.65	117.22
	Dyall.v2z/aug-cc-pVDZ	118.60	117.36	118.64	117.22
	Dyall.v3z/cc-pVTZ	117.38	116.20	117.50	116.15
	Dyall.v3z/aug-cc-pVTZ	117.44	116.24	--- ^a	116.18

^aconvergence problems**Table 2. Optimized Pt-C and C-N Bond Lengths of $[\text{Pt}(\text{CN})_4]^{2-}$ in pm Obtained with ZORA DFT Calculations for Various Basis Sets and Exchange-Correlation Functionals.**

Distance	Basis Set	BLYP	B3LYP	PBE	PBE0
<i>R</i> (Pt-C)	SVP	197.34	202.15	200.84	200.31
	TZVP	202.98	202.00	200.68	200.06
	QZVP	202.63	201.66	200.34	199.75
	def2-TZVP	202.66	201.67	200.34	199.72
	def2-QZVP	202.53	201.57	200.24	199.64
	Dyall.v3z/aug-cc-pVTZ	202.87	201.93	200.58	200.00
<i>R</i> (C-N)	SVP	117.70	117.07	118.37	116.93
	TZVP	117.55	116.32	117.62	116.23
	QZVP	117.33	116.12	117.45	116.07
	def2-TZVP	117.41	116.20	117.51	116.14
	def2-QZVP	117.33	116.13	117.45	116.06
	Dyall.v3z/aug-cc-pVTZ	117.43	116.23	117.55	116.18

The same holds in general also for the non-relativistic calculations using the ECP60MWB effective core potentials in combination with the def2-type basis sets for carbon and nitrogen or the ECP60MDF effective core potentials in combination with correlation consistent basis sets on carbon and nitrogen, presented in Table 3 and for the latter also shown in Fig. (2). The geometries obtained using the Dunning basis set series exhibit steady convergence towards shorter length for the Pt-C bond and C-N bond, as seen in Fig. (2). However, the addition of diffuse functions greatly helps to speed up the convergence for the Pt-C bond. Concerning the Ahlrichs basis sets we note that for the C-N bond there is not significant difference between the corresponding ECP60MWB/def2-XZVP and ECP60MDF_VXZ/cc-pVXZ results for both X = T and Q, which both differ clearly from the ECP60MDF_VDZ/(aug-cc-pVDZ) values, whereas for the Pt-C bond the ECP60MWB/def2-

XZVP results lie between the ECP60MDF_VDZ/cc-pVDZ and ECP60MDF_VDZ/aug-cc-pVDZ results.

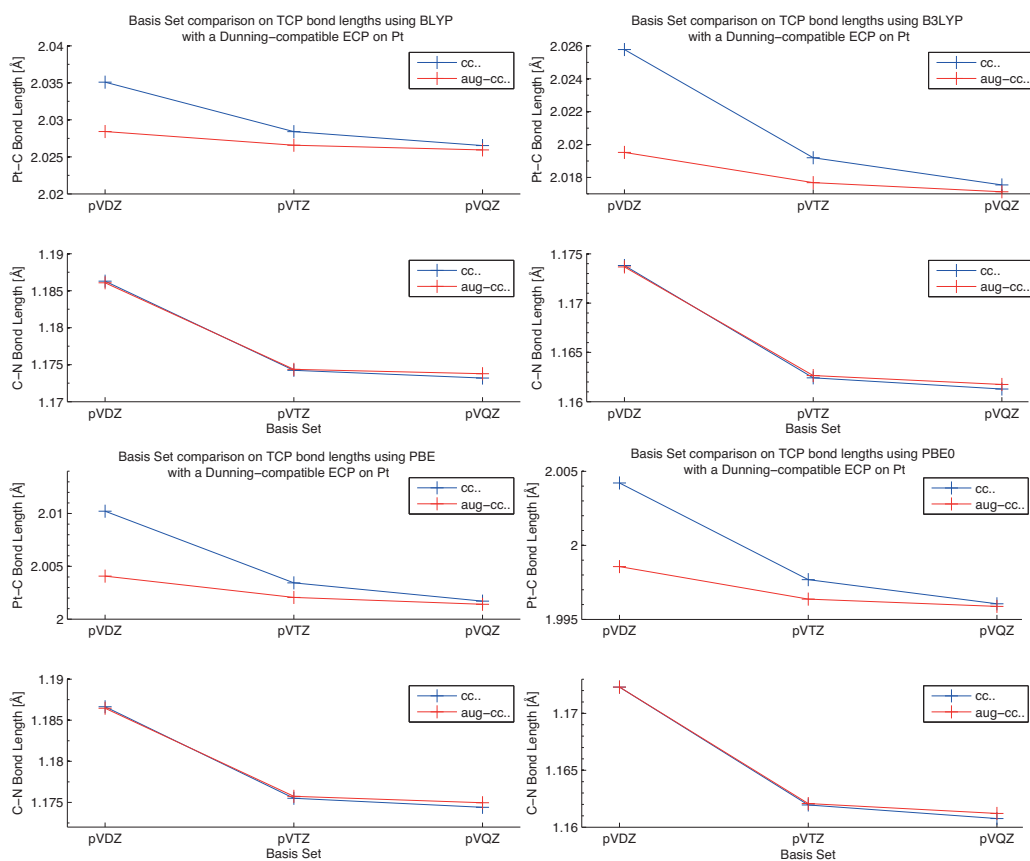
Concluding we can say, that with the largest basis sets employed in the different approaches, sufficient basis set convergence has been reached - in particular in the light of the much larger variations with the exchange-correlation functionals, as discussed in the following section.

3.2. Dependence on the Exchange-Correlation Functional

Different studies on similar transition metal compounds reported satisfactory results using various exchange-correlation functionals, such as B3LYP [25, 26] and PBE0 [25, 45] Both are hybrid functionals, but the PBE0 exchange-correlation functional includes 5% more exact Hartree-Fock exchange than B3LYP, in the standard setup. Here, we compare their performance with their two

Table 3. Optimized Pt-C and C-N Bond Lengths of $[\text{Pt}(\text{CN})_4]^{2-}$ in pm Obtained with Non-Relativistic Calculations using the ECP60MWB with the Ahlrichs def2-Types Basis Sets for Carbon and Nitrogen and the ECP60MDF Pseudopotentials with the Correlation Consistent Basis Sets for Carbon and Nitrogen.

Distance	Basis Set	BLYP	B3LYP	PBE	PBE0
$R(\text{Pt-C})$	ECP60MWB/def2-TZVP	203.44	202.49	200.92	200.03
	ECP60MWB/def2-QZVP	203.29	202.35	200.79	200.19
	ECP60MDF_VDZ/cc-pVDZ	203.51	202.58	201.02	200.42
	ECP60MDF_VDZ/aug-cc-pVDZ	202.84	201.95	200.41	199.87
	ECP60MDF_VTZ/cc-pVTZ	202.84	201.92	200.34	199.77
	ECP60MDF_VTZ/aug-cc-pVTZ	202.66	201.77	200.20	199.64
	ECP60MDF_VQZ/cc-pVQZ	202.65	201.75	200.17	199.61
	ECP60MDF_VQZ/aug-cc-pVQZ	202.59	201.71	200.14	199.59
$R(\text{C-N})$	ECP60MWB/def2-TZVP	117.41	116.21	117.51	116.21
	ECP60MWB/def2-QZVP	117.33	116.13	117.45	116.07
	ECP60MDF_VDZ/cc-pVDZ	118.63	117.37	118.66	117.23
	ECP60MDF_VDZ/aug-cc-pVDZ	118.61	117.38	118.65	117.23
	ECP60MDF_VTZ/cc-pVTZ	117.42	116.24	117.55	116.20
	ECP60MDF_VTZ/aug-cc-pVTZ	117.44	116.26	117.57	116.21
	ECP60MDF_VQZ/cc-pVQZ	117.32	116.13	117.44	116.08
	ECP60MDF_VQZ/aug-cc-pVQZ	117.38	116.18	117.50	116.12

**Fig. (2).** Dependence of the calculated bond lengths in $[\text{Pt}(\text{CN})_4]^{2-}$ on the basis sets in non-relativistic calculations using the ECP60MDF effective core potentials on platinum and correlation consistent basis sets on carbon and nitrogen.

corresponding non-hybrid functionals BLYP and PBE. Fig. (3) compares the results for the four functionals and the largest basis sets with all relativistic methods.

One can observe a significant difference between the platinum-carbon and carbon-nitrogen bond. For the C-N bond length, the crucial factor is whether the functional includes exact Hartree-Fock exchange or not. The Pt-C bond, on the other hand, is in general more sensitive, and in particular the choice of correlation functional has larger impact. Employing the hybrid functionals shortens the C-N bond length by 1.2 to 1.4 pm or approximately 1% for all methods, while the differences between the exchange-correlation functionals BLYP and PBE or B3LYP and PBE0 amounts to at most 0.1 pm or 0.1%. For the Pt-C carbon bond employing a hybrid functional shortens the bond length by less than 1 pm or 0.5%, whereas using PBE or PBE0 instead of BLYP or B3LYP shortens the bond length by 2.0 to 2.5 pm or 1%.

3.3. Treatment of Relativistic Effects

Table 4 and Fig. (3) show the comparison of the calculated bond lengths obtained using various approximations to the fully relativistic 4-component treatment using the Dirac-Colomb Hamiltonian. The Pt-C bond contracts almost 10 pm or about 5% when adding relativistic effects, and becomes shortest when using the Dirac-Colomb Hamiltonian, for all the functionals in agreement with the previous study on the cationic platinum carbene complex PtCH_2^+ [26] and the general rule-of-thumb that the effect of relativity on chemical bonds from a heavy atom is in most cases a contraction. This might seem counter-intuitive due to the fact that it is the 5d atomic orbitals from Pt that contributes to the Pt-CN bond, orbitals that are known to expand when treated relativistically [27]. However, it has been known for a long time that bond-length

contractions are *not* caused by orbital contractions, but rather due to the relaxation of the kinetic repulsion [28, 29]. If a bond is contracted, the electrons will have to occupy a smaller volume, which will result in a rise of kinetic energy, due to the uncertainty principle. However, the relativistic mass-velocity correction becomes more negative with increasing non-relativistic kinetic energy, thus diminishing the relativistic kinetic repulsion term, effectively shifting the minimum of the total binding potential. As such, our results are in accordance with the expected effects of a relativistic treatment.

This contraction is very well reproduced with maximum errors less than 1 pm in the ZORA and relativistic effective core potential calculations. In the ECP60MDF_VTZ/aug-cc-pVTZ or ZORA/def2-TZVP calculations an accuracy of 0.02 pm is even achieved, whereas the deviations are slightly larger in the ZORA/Dyall.v3z/aug-cc-pVTZ and even more in the ECP60MWB/def2-TZVP calculations. However, these differences are significantly smaller than the variation observed when changing the exchange-correlation functional. For the C-N bond the relativistic effects elongate the bond length, but the effect is an order of magnitude smaller than for the Pt-C bond. Here, all relativistic methods give very similar results.

We can compare our theoretical predictions of bond lengths with one experimental x-ray and neutron scattering study [46] on $[\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}\cdot 3.2\text{H}_2\text{O}]$ crystals. The x-ray and neutron scattering C-N bond lengths are 117.0 pm and 116.4 pm, respectively, which are in excellent agreement with our calculated results, even though the bromine and crystal water is likely to perturb the bond lengths. The same study also reports Pt-C bond lengths of 200.7 pm and 200.1 pm, measured using x-rays and neutrons, respectively. These differ by at most only 2 pm from our 4-component results.

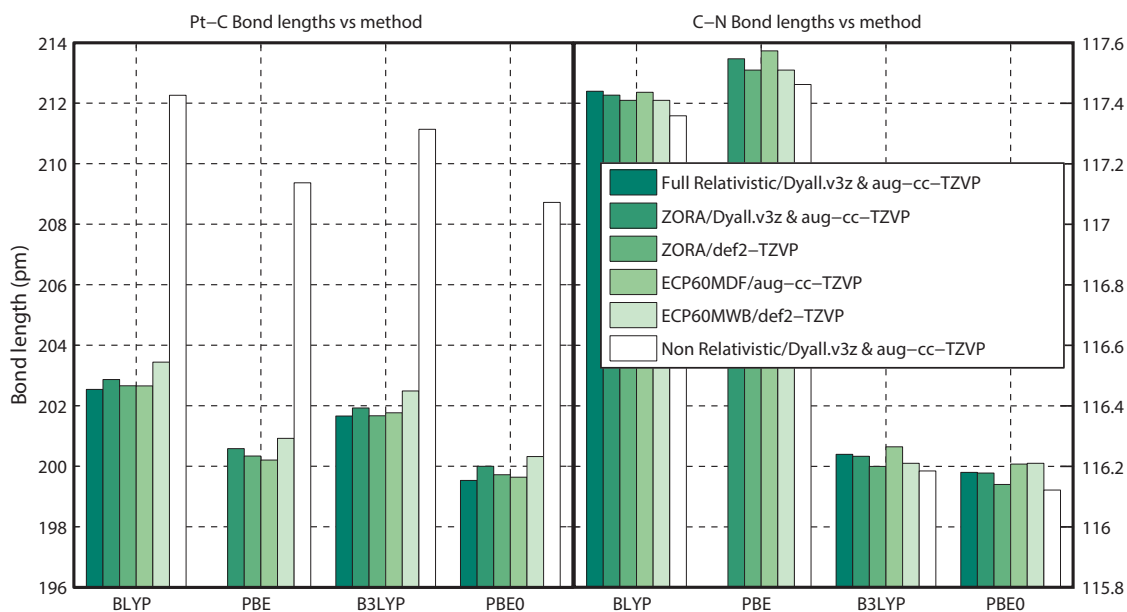


Fig. (3). Effect of the exchange-correlation functional on the calculated bond lengths in $[\text{Pt}(\text{CN})_4]^{2-}$ obtained in the following ways: Four-component and nonrelativistic calculations, both with the Dyall.v3z/aug-cc-pVTZ basis set, ZORA and ECP60MWB calculations with the def2-TZVP basis set and ECP60MDF_VTZ calculations with the aug-cc-pVTZ basis set. The reader should note that the ordinate axis is truncated, and that the distance in the left plot ordinate is 10 times longer than in the right plot.

Table 4. Deviations from the 4-Component Results for the Optimized Pt-C and C-N Bond Lengths of $[\text{Pt}(\text{CN})_4]^{2-}$ in pm. Four-Component and Non-Relativistic Calculations, Both with the Dyall.v3z/aug-cc-pVTZ Basis Set (with the Exception of the PBE 4-Component Calculation Which was Carried Out with the Dyall.v3z/cc-pVTZ Basis Set), ZORA Calculations with the def2-TZVP Basis Set and ECP60MDF_VTZ Calculations with the aug-cc-pVTZ Basis Set.

Approximate Method	Δr (Pt-C)				Δr (C-N)			
	BLYP	B3LYP	PBE	PBE0	BLYP	B3LYP	PBE	PBE0
ZORA/Dyall.v3z/aug-cc-TZVP	0.33	0.27	0.45	0.47	-0.01	-0.01	0.05	0.00
ZORA/def2-TZVP	0.12	0.01	0.21	0.19	-0.03	-0.04	0.01	-0.04
ECP60MDF/aug-cc-TZVP	0.12	0.11	0.07	0.11	0.00	0.02	0.07	0.03
ECP60MWB/def2-TZVP	0.90	0.83	0.79	0.50	-0.03	-0.03	0.01	0.03
None	9.72	10.60	--- ^a	9.19	-0.08	1.12	--- ^a	-0.06

^aconvergence problems

4. CONCLUSION

We have carried out geometry optimizations of tetracyanoplatinate(II) at the DFT level using the four-component formalism based on the Dirac-Coulomb Hamiltonian, the scalar zeroth-order regular approximation (ZORA) formalism, the non-relativistic formalism calculations with relativistic effective core potentials and with standard non-relativistic all-electron basis sets.

We find, as expected, that relativistic effects contract the Pt-C bond, making it approx 4.6-4.8% shorter (depending on the functional used), when comparing the full relativistic calculation to the nonrelativistic, while the C-N bond is not affected (as) much. This relativistic bond contraction is almost perfectly reproduced in scalar ZORA calculations and also in calculations with relativistic effective core potentials. Our predicted bond lengths are in good agreement with experimental x-ray and neutron scattering values for $[\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}\cdot 3.2\text{H}_2\text{O}]$ crystals.

We observe that addition of exact HF exchange in the hybrid functionals plays a large role for the C-N bond lengths, but only a small role for the Pt-C bond lengths, whereas it is the choice of correlation functional, PBE(0) or B(3)LYP, which has a large effect on the Pt-C bond lengths with PBE and its hybrid version generally producing shorter Pt-C bond lengths than B(3)LYP. Furthermore we note that the choice of DFT functional has a larger effect on the bond lengths than the level of relativistic treatment. Finally, we observe that an adequate description of the distance from the heavy Pt atom to the C atom, as expected, requires *some* method of relativistic treatment, but the different levels of approximations used in this work all show good performance.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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