Electronic supplementary materials *Mendeleev Commun.*, 2019, **29**, 315–317

Geometries and NMR properties of cisplatin and transplatin revisited at the four-component relativistic level

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Table S1 Bond lengths (Å) and bond angles (deg) of cis- and transplatin optimized using different DFT functionals.

Compound	Functional	DFT	4DFT	DFT	4DFT	DFT	4DFT	DFT	4DFT
Cisplatin		Pt-N		Pt-Cl		N-Pt-N		Cl-Pt-Cl	
	X-ray	2.036		2.311		91.90		92.63	
	B3LYP	2.197	2.110	2.378	2.324	99.22	99.43	97.68	96.63
	BHLYP	2.500	2.382	2.620	2.574	96.76	94.33	97.57	94.31
	B60LYP	2.500	2.415	2.634	2.559	98.09	94.86	99.79	96.48
	B70LYP	2.421	2.413	2.656	2.577	98.37	95.24	97.86	96.00
	OLYP	2.198	2.111	2.373	2.319	98.74	102.66	97.35	100.31
	PBE	2.189	2.090	2.355	2.297	99.99	98.86	96.20	95.49
	PBE0	2.169	2.093	2.341	2.305	98.82	98.76	96.47	95.96
	PBE38	2.164	2.088	2.334	2.301	98.34	98.28	96.15	95.63
Transplatin		Pt-N		Pt-Cl		N-Pt-Cl(1)		N-Pt-Cl(2)	
	X-ray	2.050		2.320		88.50		91.50	
	PBE38	2.111	2.030	2.352	2.298	89.41	88.98	90.59	91.02

Computational details

Geometry optimizations of all compounds were performed using the DIRAC code at the DFT/dyall.ae2z level with and without taking into account relativistic effects within the formalism of the four-component fully relativistic Dirac equation. Calculations of zero-point vibrational corrections were perfomed using DALTON code at the PBE38/ADZP level. All calculations of ^{1}H, ^{15}N and ^{195}Pt NMR isotropic magnetic shielding constants were carried out with DIRAC package at the DFT level using PBE, PBE38 and KT2 functionals within the LDBS scheme implying Dyall's basis set dyall.ae2z for platinum and Jensen's basis set aug-pcS-2 for

all atoms of the rest of molecule. Conversion of calculated ^{15}N NMR shielding constants into chemical shifts scale was performed *via* secondary standards scheme using trimethylamine as a secondary standard to minimize the error associated with the presence of a highly conjugated π-system of nitromethane. To transform calculated ^{1}H and ^{195}Pt NMR shielding constants into chemical shifts scale, tetramethysilane and sodium hexachloroplatinate were used throughout with respect to proton and platinum shielding constants calculated at exactly the same levels of theory.