NMR Magnetic Shielding in Transition Metal Compounds Containing Cadmium, Platinum, and Mercury

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In this document we shall present:

- The perturbative Hamiltonians used in the LRESC model within the SI system of units.
- Contributions of the different relativistic corrections to the shielding in some of the studied systems.
- Cartesian coordinates of the molecules studied.

We adopted a nomenclature in which blue and red colors indicate shielding and deshielding effects, respectively.

1. Perturbative Hamiltonians used in the LRESC model

The paramagnetic relativistic corrections that depend of the nuclear spin, μ_k, are the following[1–3]

$$H^{PSO} = \frac{e}{m}\frac{\mu_0}{4\pi}\left(\frac{\mu_k L_k}{r_k^3}\right) \tag{S1}$$

$$H^{FC} = \frac{e}{2m}\frac{8\pi}{3}\frac{\mu_0}{4\pi}\left(\mu_k \sigma \delta(r_k)\right) \tag{S2}$$

$$H^{SD} = \frac{e}{2m}\frac{\mu_0}{4\pi}\left(\frac{3(\mu_k r_k)r_k - r_k^2\mu_k}{r_k^5}\right) \tag{S3}$$

$$\tag{S4}$$

while those depending on the external magnetic field, *B*, are written as

$$H^{OZ} = \frac{e}{2m}(BL_0) \tag{S5}$$

$$H^{SZ-K} = -\frac{e}{8m^2c^2}[3(\sigma B)p^2 - (\sigma p)(pB)] \tag{S6}$$

$$H^{BSO} = \frac{e}{4m^2c^2}(\nabla V_c \times [B \times r_0]) \tag{S7}$$

The perturbative Hamiltonian corresponding to the one–body spin–orbit coupling and those scalar relativistic corrections known as Mass-velocity (Mv) and Darwin (Dw) are written as

$$H^{SO(1)} = \frac{1}{4m^2c^2}\sigma(\nabla V_C \times p) \tag{S8}$$

$$H^{Mv} = -\frac{1}{8m^3c^2}p^4 \tag{S9}$$

$$H^{Dw} = \frac{1}{4m^2c^2}\nabla^2 V_c \tag{S10}$$

The expressions of the diamagnetic Hamiltonians that contribute to the LRESC model are

$$H^{Dia} = \frac{e}{2mc}\frac{\mu_0}{4\pi}\left[(\mu_k B)\left(\frac{r_k r_0}{r_k^3}\right) - (\mu_k r_0)\left(\frac{r_k B}{r_k^3}\right)\right] \tag{S11}$$

$$H^{Dia-K} = -\frac{1}{4m^3c^4}\left[2\left(\frac{\mu_M L_M}{r_M^3}\right)(BL_M) + BB_M + 2(A_M A_B)p^2 + 2\pi(\mu_M B)\delta(r_M)\right] \tag{S12}$$

where σ are the Pauli matrices, μ_0 is the vacuum permeability, c is the velocity of light in vacuum, r_k and r_0 are the positions with respect to the nuclear position $(r - R_k)$ and the gauge origin $(r - R_0)$, respectively. L_k and L_0 are the corresponding angular momenta. $p = -i\bar{\nabla}$ is the linear momentum operator and e and m are the charge and mass of the electron. Furthermore, A_{μ_k} and A_B are the potential vector operators associated with the nuclear spin and the external magnetic field given in Equations S13 and S14, respectively.

$$A_{\mu_k} = \frac{\mu_k \times r_k}{r_k^3} \tag{S13}$$

$$A_B = \frac{B \times r_0}{2} \tag{S14}$$

2. Relativistic corrections to the shieldings of the molecules of interest

2.1. PtX_i^{-2}

Table S1. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Pt in the $PtCl_4^{-2}$. The theory level is HF/cv3z and the gauge is on Pt. All values are reported in ppm.

	Core(Pt)	4xCore(Cl)	4xPt–Cl	4xLP$_\sigma$Cl	8xLP$_\pi$Cl	Σ
σ_d^{NL}	-3034.6	-0.4	0.0	0.6	0.0	-3034.5
σ_d^{NR}	9378.2	162.6	27.9	47.8	62.4	9678.8
σ^{OZ-K}	533.6	0.0	0.2	0.6	-1.0	533.5
σ^{PSO-K}	511.4	0.5	38.7	344.6	10.0	905.1
σ_p^{Mv+Dw}	-1872.2	3.7	-104.8	-861.8	71.7	-2763.4
$\sigma^{SO(1)}$	2005.2	-2.6	-8.9	-164.3	-71.6	1757.8
σ^{ligand}	1177.9	1.7	-74.7	-680.9	9.0	433.0
σ_p^{core}	6574.9	0.0	0.1	0.4	0.0	6575.4
σ_p^{NR}	-14195.5	-326.3	116.5	807.3	582.7	-13015.3

Table S2. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Pt in the $PtBr_4^{-2}$. The theory level is HF/cv3z and the gauge is on Pt. All values are reported in ppm.

	Core(Pt)	4xCore(Br)	4xPt–Br	4xLP$_\sigma$Br	8xLP$_\pi$Br	$\sum$
σ_d^{NL}	-3034.4	-2.3	0.3	0.0	0.0	-3036.5
σ_d^{NR}	9377.6	432.7	47.0	27.2	58.7	9943.2
σ^{OZ-K}	533.2	3.6	0.8	0.6	-3.5	534.7
σ^{PSO-K}	439.9	1.5	387.4	24.6	15.7	869.1
σ_p^{Mv+Dw}	-2179.1	11.2	-1030.0	-54.5	-1.0	-3253.3
$\sigma^{SO(1)}$	1634.3	-26.0	-169.7	15.0	61.1	1514.6
σ^{ligand}	428.4	-9.7	-811.5	-14.4	72.2	-335.0
σ_p^{core}	6575.0	0.0	0.7	0.0	0.0	6575.7
σ_p^{NR}	-12309.4	-367.3	903.6	75.4	396.0	-11301.7

Table S3. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Pt in the $PtCl_6^{-2}$. The theory level is HF/cv3z and the gauge is on Pt. All values are reported in ppm.

	Core(Pt)	6xCore(Cl)	6xPt–Cl	6xLP$_\sigma$Cl	12xLP$_\pi$Cl	$\sum$
σ_d^{NL}	-3033.8	-0.6	-0.3	-0.2	0.0	-3035.0
σ_d^{NR}	9353.1	238.8	78.8	42.7	92.3	9805.7
σ^{OZ-K}	535.2	0.2	1.6	0.5	-2.1	535.3
σ^{PSO-K}	682.4	-0.7	327.3	10.8	-42.6	977.1
σ_p^{Mv+Dw}	-2912.5	-14.1	-1248.0	-118.2	-78.6	-4371.5
$\sigma^{SO(1)}$	1151.7	-0.5	3.0	23.1	-7.7	1169.6
σ^{ligand}	-543.3	-15.2	-916.2	-83.8	-131.0	-1689.5
σ_p^{core}	6574.0	0.0	0.1	-0.1	0.0	6574.0
σ_p^{NR}	-18363.7	-252.9	2130.8	99.3	2042.7	-14343.9

Table S4. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Pt in the $PtBr_6^{-2}$. The theory level is HF/cv3z and the gauge is on Pt. All values are reported in ppm.

	Core(Pt)	6xCore(Br)	6xPt–Br	6xLP$_\sigma$Br	12xLP$_\pi$Br	$\sum$
σ_d^{NL}	-3033.7	-3.3	-0.7	0.0	0.0	-3037.7
σ_d^{NR}	9352.0	626.3	78.7	41.3	86.4	10184.7
σ^{OZ-K}	533.9	5.2	1.8	1.1	-5.9	536.0
σ^{PSO-K}	549.5	2.8	325.8	6.7	-39.2	845.6
σ_p^{Mv+Dw}	-2770.0	15.0	-1257.7	-29.3	-172.3	-4214.4
$\sigma^{SO(1)}$	1108.1	-21.9	86.7	15.9	173.0	1361.8
σ^{ligand}	-578.5	1.1	-843.5	-5.6	-44.4	-1470.9
σ_p^{core}	6573.8	0.0	1.0	-0.4	0.0	6574.4
σ_p^{NR}	-14849.8	-576.1	2164.6	47.9	1853.0	-11360.3

2.2. $Cl_2XTe_2Y_2H_6$

Table S5. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Te_1 in the $Cl_2CdTe_2N_2H_6$. The theory level is HF/cv3z and the gauge is on Te_1. All values are reported in ppm.

	Core(Te_1)	Cd-Te_1	$LP_\pi Te_1$	others[1]	$\sum$
σ_d^{NL}	-892.7	0.5	1.9	-1.8	-892.1
σ_d^{NR}	5306.3	16.7	37.4	380.3	5740.8
σ^{OZ-K}	132.5	0.6	1.4	2.7	137.2
σ^{PSO-K}	-0.2	231.6	514.9	-48.3	698.0
σ_p^{Mv+Dw}	-108.8	-407.6	-868.2	-13.5	-1398.1
$\sigma^{SO(1)}$	-74.5	548.9	687.4	31.5	1193.3
σ^{ligand}	-51.0	373.6	335.6	-27.7	630.5
σ_p^{core}	1925.6	1.5	8.6	-0.1	1935.5
σ_p^{NR}	1.4	-1645.4	-3645.7	-40.9	-5330.7

[1] Contribution from others LMOs.

Table S6. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Te_1 in the $Cl_2CdTe_2P_2H_6$. The theory level is HF/cv3z and the gauge is on Te_1. All values are reported in ppm.

	Core(Te_1)	Cd-Te_1	$LP_\pi Te_1$	others[1]	$\sum$
σ_d^{NL}	-889.7	0.4	-1.2	-1.8	-892.2
σ_d^{NR}	5122.9	16.2	220.5	417.8	5777.3
σ^{OZ-K}	125.2	0.7	8.4	3.1	137.4
σ^{PSO-K}	11.1	108.4	149.6	-46.1	223.1
σ_p^{Mv+Dw}	-64.7	-198.3	-274.3	11.0	-526.3
$\sigma^{SO(1)}$	16.9	129.2	113.4	-0.7	258.7
σ^{ligand}	88.5	40.0	-2.8	-32.8	92.9
σ_p^{core}	1929.0	0.7	3.3	-0.1	1933.0
σ_p^{NR}	0.7	-768.4	-1133.9	-82.5	-1984.1

[1] Contribution from others LMOs.

Table S7. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Te_1 in the $Cl_2HgTe_2N_2H_6$. The theory level is HF/cv3z and the gauge is on Te_1. All values are reported in ppm.

	Core(Te_1)	Hg-Te_1	$LP_\pi Te_1$	others[1]	$\sum$
σ_d^{NL}	-892.6	0.3	1.8	-4.1	-894.5
σ_d^{NR}	5305.8	16.8	37.9	482.3	5842.8
σ^{OZ-K}	132.3	0.6	1.5	6.2	140.7
σ^{PSO-K}	-0.6	253.5	536.4	-47.8	741.5
σ_p^{Mv+Dw}	636.2	-851.6	-1101.4	-166.5	-1483.3
$\sigma^{SO(1)}$	-37.7	357.3	463.3	556.8	1339.8
σ^{ligand}	730.2	-240.0	-100.2	348.6	738.6
σ_p^{core}	1924.6	1.1	9.4	0.2	1935.4
σ_p^{NR}	3.9	-1800.6	-3798.1	-117.7	-5712.5

[1] Contribution from others LMOs.

Table S8. Isotropic values of the LRESC mechanisms with localized molecular orbital over the Te_1 in the $Cl_2HgTe_2N_2H_6$. The theory level is HF/cv3z and the gauge is on Te_1. All values are reported in ppm.

	Core(Te_1)	Hg-Te_1	$LP_\pi Te_1$	others[1]	$\sum$
σ_d^{NL}	-892.6	0.3	1.9	-4.1	-894.6
σ_d^{NR}	5306.4	16.2	37.0	520.3	5879.8
σ^{OZ-K}	129.4	0.8	4.2	6.7	141.0
σ^{PSO-K}	-0.1	109.2	154.5	-44.7	218.9
σ_p^{Mv+Dw}	197.4	-281.6	-468.1	7.3	-545.0
$\sigma^{SO(1)}$	-8.7	67.5	99.1	71.4	229.3
σ^{ligand}	317.9	-104.1	-210.3	40.7	44.3
σ_p^{core}	1925.2	0.4	7.2	0.4	1933.2
σ_p^{NR}	0.6	-774.0	-1090.1	-168.9	-2032.4

[1] Contribution from others LMOs.

3. Cartesian coordinates

CdCl$_2$Te$_2$N$_2$H$_6$

Cd	0.0000000000	0.0000000000	0.0000000000
Cl	-1.4436897967	-1.0531752215	1.7310650646
Cl	1.410619733	2.0014815406	0.4363485975
Te	2.2461715236	-1.6755329392	-1.0555009416
Te	-2.1971106183	0.3318355078	-2.0046565929
N	3.6590609411	-0.0769988314	-0.5697595829
N	-3.6405714491	-0.4105653106	-0.5376980956
H	-3.1388535503	-0.7021542837	0.2927560169
H	-4.2907170372	0.3052626227	-0.2841429069
H	-4.1485352983	-1.1918636258	-0.8990890286
H	4.2920140767	-0.3671062227	0.1475975744
H	3.1388384122	0.7264655311	-0.2379064631
H	4.1875242686	0.1904924048	-1.3748880582

CdCl$_2$Te$_2$P$_2$H$_6$

Cd	0.0000000000	0.0000000000	0.0000000000
Cl	-1.4021917857	-0.7913567967	1.8564329319
Cl	1.3915059543	2.0213393273	-0.1075551982
Te	2.1681679841	-2.0019355257	-0.7503327647
Te	-2.1526969141	-0.0437463701	-2.1532432566
P	3.8142695452	-0.2472629372	-0.8113866603
P	-3.8065796800	-0.7018964634	-0.5336339933
H	-3.6279167004	-1.9370551237	0.0631028479
H	-4.0063103317	0.1669255700	0.5240648462
H	-5.0624672552	-0.8006169533	-1.1188842223
H	4.0003123986	0.4577790600	0.3640914658
H	3.6391065603	0.7290863936	-1.7754644697
H	5.0751964936	-0.759037519	-1.0898252126

$HgCl_2Te_2N_2H_6$

Hg	0.000000000	0.000000000	0.000000000
Cl	-1.666937928	-1.690332677	-0.690746315
Cl	1.416251124	0.041209794	2.053079192
Te	2.210390976	0.758601769	-1.860770373
Te	-2.052867560	2.283607231	-0.039289475
N	3.590637509	0.859413663	-0.151689453
N	-3.659310267	0.843554076	-0.467267824
H	-4.561871260	1.265581697	-0.365614816
H	-3.579867675	0.490950507	-1.397744569
H	-3.598099956	0.050921260	0.141439734
H	4.534219265	0.952097947	-0.465973561
H	3.493613244	0.034244833	0.420522597
H	3.341355162	1.632350029	0.444805492

$HgCl_2Te_2P_2H_6$

Hg	0.000000000	0.000000000	0.000000000
Cl	-1.558571551	-1.805418959	-0.574873680
Cl	1.357318126	0.265499219	2.066867328
Te	2.184712546	0.503209542	-1.999065442
Te	-2.004892489	2.338962096	-0.263788701
P	3.814209115	0.744023333	-0.249320435
P	-3.839380873	0.797706350	-0.534629011
H	-5.052862312	1.471047280	-0.607546033
H	-3.823515527	0.036694997	-1.695571184
H	-4.029677369	-0.123842608	0.488059995
H	5.075374992	0.962502590	-0.789452536
H	3.982101229	-0.343077350	0.585011530
H	3.634988844	1.816343371	0.609805083

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