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General cooperative effects of single atom ligands on the metal: [195]Pt NMR chemical shift as a function of the coordinated halido ligands' ionic radii overall sum

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An inverse linear relation between experimentally observed [195]Pt NMR signals and the overall sum of coordinated halido ligands' ionic radii was discovered in Pt(II) and Pt(IV) complexes. The reduction of [195]Pt NMR frequencies parallels the increase of coordinated halido ligands' ionic radii sum, suggesting that each halido ligand may acts as a conducting ring which induced electric current shields the [195]Pt NMR signals proportionally to the ionic radius of the coordinated halido ligand.
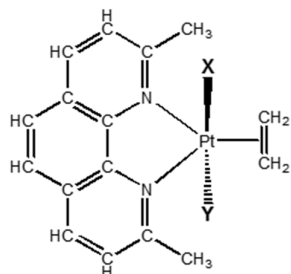
Figure 1. Schematic representation of the structure of pentacoordinate complexes of the type [PtXY(η^2-CH$_2$=CH$_2$)(Me$_2$phen)], (X,Y = Cl, Br, I; Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline).

In previous works we analyzed the NMR properties of pentacoordinate complexes, formed by interaction of the Zeise's anion, [PtCl$_3$(η^2-CH$_2$=CH$_2$)]$^-$, with *N,N*-chelate ligands.[1-14] These specific complexes are generally considered interesting since platinum bonded unsaturated ligands are useful models in the study of the
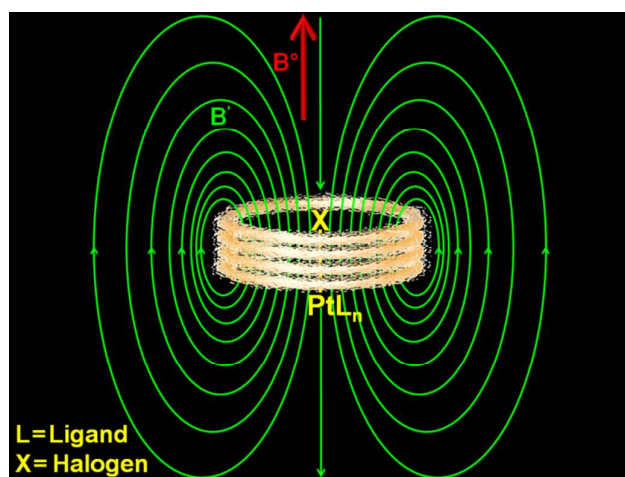
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Figure 2. Schematic representation of hypothesized pseudoring currents induced by an applied external magnetic field (**B°**) on a platinum coordinated X$^-$ halido ligand, explaining the reduction of [195]Pt NMR frequency, observed in platinum complexes, which parallels the increase of ionic radius of a coordinated halido ligand.

interaction of alkenes and alkynes with metals.[14-22] In particular, in the study of the single crystal X-ray structures and NMR signals of the symmetric [PtX$_2$(η^2-CH$_2$=CH$_2$)(Me$_2$phen)] (X = Cl, Br, I; Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline) pentacoordinate complexes, we described the evidence of *pseudo*-ring currents circulating around the Pt−X axes, Figures 1-2. These currents seemed modulated by the ionic radius of the halido ligands coordinated in *trans* positions, above and below the trigonal equatorial plane. Indeed, in these complexes, characterized by negligible Pt−η^2-ethene and Pt−N bond lengths variations in the trigonal plane, the two *trans*-axial halido ligands clearly influence the observed ^{1}H, ^{13}C, ^{15}N and [195]Pt NMR chemical shifts of neighbour atoms.[20] Platinum chemical shifts correlations with other parameters such as coordinated halido ligands electronegativity were previously reported.[23,24] Nevertheless we could evidence recently the existence of a linear relation between the ionic radii of coordinated halido ligands and the [195]Pt NMR chemical shifts.[20]
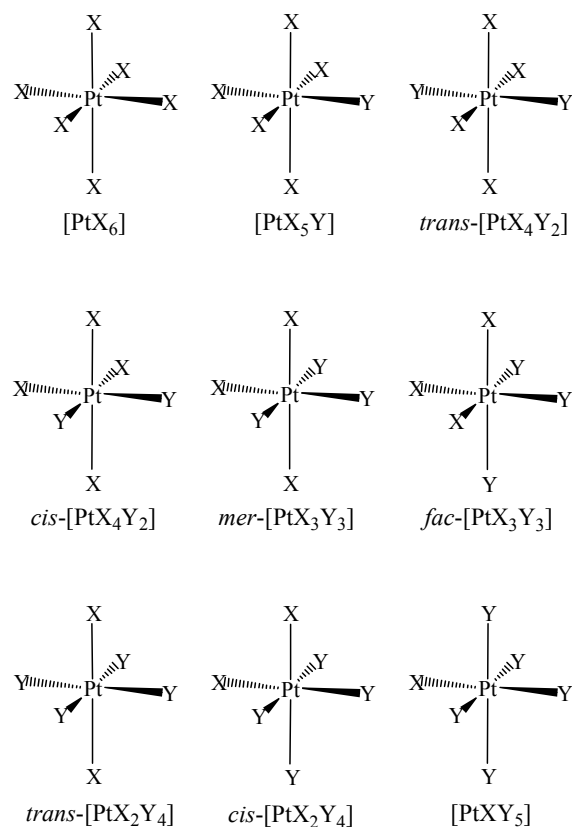
Figure 3. Representation of the general structures of $[PtX_nY_{6-n}]^{2-}$ ($0 \leq n \leq 6$; X,Y = F, Cl, Br, I) octahedral complexes.

The problem of understanding the phenomena influencing the NMR signals frequencies, which can be also related to the physical properties of a molecule, has deserved a particular attention in the recent literature.[23-28] In this work, we evaluated the NMR shielding properties of coordinated halido ligands in Pt(II) trigonal-bipyramidal and Pt(IV) octahedral complexes (Figures 1 and 3). [195]Pt NMR data for Pt(II) pentacoordinate complexes of the type $[PtXY(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$ (X≠Y = Cl, Br, I), where two not equivalent axial halido ligands are bonded to the metal (Figure 1), have been collected together with those of the previously reported symmetrical analogues (X = Y = Cl, Br, I), Table 1.[20] In a further step, octahedral Pt(IV) complexes of the type $[PtX_4Y_{6-n}]^{2-}$ (X,Y = F, Cl, Br, I) were also studied by [195]Pt NMR spectroscopy, in order to analyse the effect of changing the oxidation state and the coordination

Table 1. Experimental [195]Pt NMR chemical shifts of pentacoordinate platinum(II) complexes of the type $[PtXY(Me_2phen)(\eta^2\text{-}ethene)]$ (X,Y = Cl, Br, I).

Complex	[195]Pt δ (ppm)	Ref.
$[PtCl_2(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$	−2169	20
$[PtBrCl(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$	−2456	*a*
$[PtBr_2(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$	−2886	20
$[PtClI(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$	−3087	*a*
$[PtBrI(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$	−3426	*a*
$[PtI_2(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$	−4041	20

(*a*) This work.

Table 2. Experimental [195]Pt NMR chemical shifts of octahedral platinum(IV) complexes of the type $[PtX_nY_{6-n}]^{2-}$ (X,Y = F, Cl, Br, I).

Complex	[195]Pt δ (ppm)	Ref.
$[PtF_6]^{2-}$	7090	25
$[PtClF_5]^{2-}$	5856	25
$[PtBrF_5]^{2-}$	5669	25
trans-$[PtCl_2F_4]^{2-}$	4887	25
trans-$[PtBr_2F_4]^{2-}$	4551	25
cis-$[PtCl_2F_4]^{2-}$	4547	25
cis-$[PtBr_2F_4]^{2-}$	4136	25
mer-$[PtCl_3F_3]^{2-}$	3551	25
fac-$[PtCl_3F_3]^{2-}$	3191	25
mer-$[PtBr_3F_3]^{2-}$	2907	25
trans-$[PtCl_4F_2]^{2-}$	2534	25
fac-$[PtBr_3F_3]^{2-}$	2487	25
cis-$[PtCl_4F_2]^{2-}$	2171	25
trans-$[PtBr_4F_2]^{2-}$	1157	25
cis-$[PtBr_4F_2]^{2-}$	1142	25
$[PtCl_5F]^{2-}$	1111	25
$[PtCl_6]^{2-}$	0	23
$[PtCl_5Br]^{2-}$	−286	23
$[PtBr_5F]^{2-}$	−311	25
cis-$[PtCl_4Br_2]^{2-}$	−583	23
trans-$[PtCl_4Br_2]^{2-}$	−585	23
$[PtCl_5I]^{2-}$	−854	23
fac-$[PtCl_3Br_3]^{2-}$	−892	23
mer-$[PtCl_3Br_3]^{2-}$	−894	23
cis-$[PtCl_2Br_4]^{2-}$	−1213	23
trans-$[PtCl_2Br_4]^{2-}$	−1216	23
$[PtClBr_5]^{2-}$	−1547	23
cis-$[PtCl_4I_2]^{2-}$	−1806	23
trans-$[PtCl_4I_2]^{2-}$	−1884	23
$[PtBr_6]^{2-}$	−1891	23
$[PtBr_5I]^{2-}$	−2545	23
fac-$[PtCl_3I_3]^{2-}$	−2849	23
mer-$[PtCl_3I_3]^{2-}$	−2849	23
trans-$[PtBr_4I_2]^{2-}$	−3132	23
cis-$[PtBr_4I_2]^{2-}$	−3252	23
mer-$[PtBr_3I_3]^{2-}$	−3898	23
cis-$[PtCl_2I_4]^{2-}$	−3932	23
trans-$[PtCl_2I_4]^{2-}$	−3932	23
fac-$[PtBr_3I_3]^{2-}$	−4014	23
trans-$[PtBr_2I_4]^{2-}$	−4603	23
cis-$[PtBr_2I_4]^{2-}$	−4719	23
$[PtClI_5]^{2-}$	−5081	23
$[PtBrI_5]^{2-}$	−5483	23
$[PtI_6]^{2-}$	−6293	23
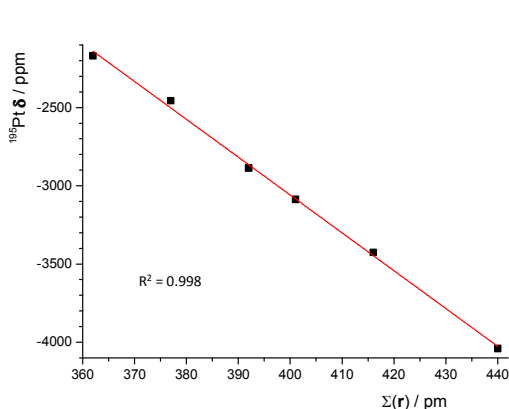
Figure 4. [195]Pt NMR chemical shifts (**δ**) of pentacoordinate [PtXY(η^2-CH$_2$=CH$_2$)(Me$_2$phen)] (Me$_2$phen = 2,9-dimethyl-1,10-phenanthroline; X,Y = Cl, Br, I) complexes, as a function of the sum of coordinated halido ligands' ionic radii, $\Sigma(\mathbf{r})$. The interpolating line is also shown in red.

number and geometry of the metal which also includes *cis*, *trans*, *fac* and *mer* isomers, Table 2.

The general structure of the considered pentacoordinate complexes is reported in Figure 1. The [195]Pt NMR chemical shifts of these pentacoordinate species are reported in Table 1. A clear inverse linear relationship between [195]Pt NMR frequencies and the overall sum of coordinated halido ligands' ionic radii (R^2 = 0.998) can be observed in the plot of [195]Pt NMR data (Table 1) as a function of the coordinated halido ligands' ionic radii sum (Figure 4). This means that in [PtXY(η^2-CH$_2$=CH$_2$)(Me$_2$phen)] complexes the shielding produced by each halido ligand on the observed [195]Pt NMR signal frequency, depends in first approximation only on its ionic radius, as previously stated for the symmetric [PtX$_2$(η^2-CH$_2$=CH$_2$)(Me$_2$phen)] species.[20] On the other hand, it appears that the [195]Pt NMR shielding is not directly related to the mutual *trans* influence of the axial X$^-$ ligands, potentially able to affect the Pt–X(Y) bond lengths in [PtXY(η^2-CH$_2$=CH$_2$)(Me$_2$phen)] complexes.
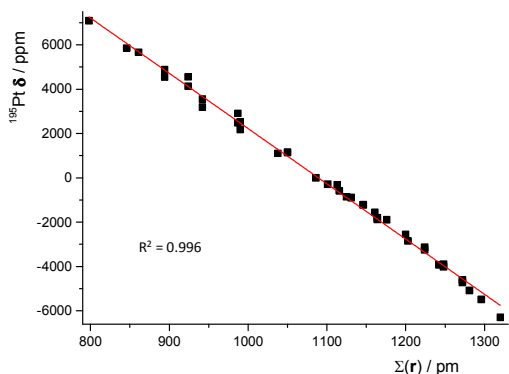
Figure 5. [195]Pt NMR chemical shifts (**δ**) of [PtX$_n$Y$_{6-n}$]$^{2-}$ ($0 \leq n \leq 6$; X,Y = F, Cl, Br, I) octahedral complexes, as a function of the sum of coordinated halido ligands' ionic radii, $\Sigma(\mathbf{r})$. The interpolating line is also shown in red.
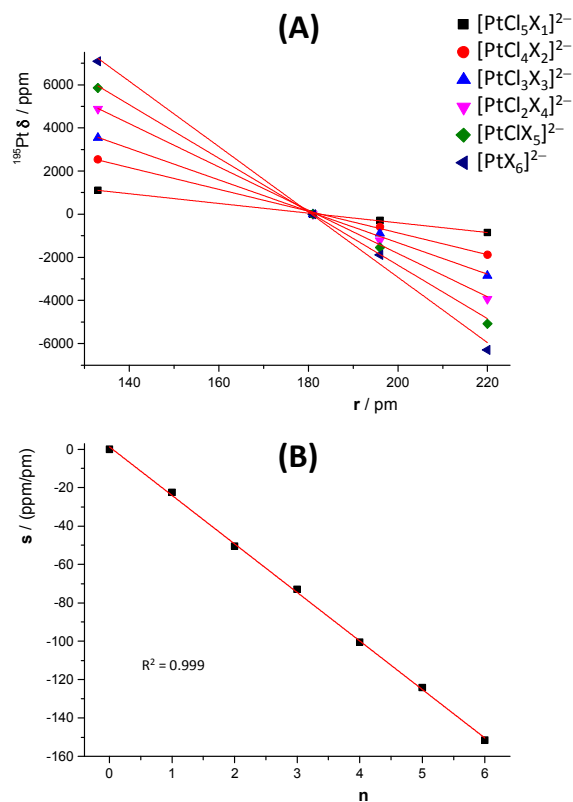

Figure 6. **(A)** [195]Pt NMR chemical shifts (**δ**) of octahedral [PtCl$_n$X$_{6-n}$]$^{2-}$ ($1 \leq n \leq 6$; X = F, Cl, Br, I) complexes, as a function of the variable ionic radius of the coordinated X$^-$ halido ligands, **r**. **(B)** Slopes (**s**) of the interpolating lines reported in Figure 6A, represented as a function of the number of variable X$^-$ halido ligands, **n**. In **(A)** and **(B)** the interpolating lines are also shown in red.

The correlation of [195]Pt NMR frequencies, with the overall sum of coordinated halido ligands' ionic radii, also in platinum complexes with a different oxidation state, coordination number and geometry were therefore investigated. We studied with a similar approach the [195]Pt NMR frequency variation observed in octahedral Pt(IV) complexes of the type [PtX$_n$Y$_{6-n}$]$^{2-}$, $0 \leq n \leq 6$, X,Y = F, Cl, Br, I, Figure 3. The [195]Pt NMR signals of the investigated Pt(IV) model complexes are reported in Table 2. Also for [PtX$_n$Y$_{6-n}$]$^{2-}$ octahedral Pt(IV) complexes a clear inverse linear relationship between [195]Pt NMR frequencies and the overall sum of coordinated halido ligands' ionic radii was found. This is evident in the linear plot (R^2 = 0.996) of [195]Pt NMR data, as a function of the coordinated halido ligands' ionic radii sum, reported in Figure 5. The pure additional effect of halido ligands' ionic radii on [195]Pt NMR frequencies, in the studied Pt(IV) species, is further evidenced in Figure 6, where the [195]Pt chemical shifts are reported as a function of the X$^-$ halido ligand ionic radius, for six different groups of complexes of the type [PtCl$_n$X$_{6-n}$]$^{2-}$. In each group, the platinum complexes bear a specific number (n; $0 \leq n \leq 5$) of chlorido ligands and a variable X$^-$ halido ligand for the remaining 6-n coordination sites. Six different lines interpolating the [195]Pt NMR chemical shifts,

as a function of the remaining specific X^- ionic radius, in $[PtCl_nX_{6-n}]^{2-}$ complexes, are reported in Figure 6A. Interestingly, each unit increase of the chlorido ligands number (n), results in a nearly constant increase of the slope of the specific interpolating line. The linear relation between the slopes of the six lines in Figure 6A and the chlorido ligands number (n) ($R^2 = 0.999$) is reported in Figure 6B. It is also noteworthy that all the six interpolating lines of Figure 6A pass exactly trough the data point representing in the graph the ^{195}Pt NMR chemical shift of the $[PtCl_6]^{2-}$ complex, the only one that belongs to all the six groups of model complexes. These results further confirm the regular trend of the observed correlation. Consistently, similar trends are observed in the analogue $[PtF_nX_{6-n}]^{2-}$, $[PtBr_nX_{6-n}]^{2-}$ and $[PtI_nX_{6-n}]^{2-}$ series of complexes.

Our hypothesis on the ^{195}Pt NMR chemical shift linear dependence from the overall halido ligands' ionic radius sum therefore holds not only for Pt(II) trigonal-bipyramidal $[PtXY(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$ but also for Pt(IV) octahedral $[PtX_nY_{6-n}]^{2-}$ (X,Y = halido ligand) complexes. As a further confirm of the simply additional effect of the overall halido ligands' ionic radius sum, only slight variations of the ^{195}Pt NMR frequency are here observed on passing from *cis* to *trans* and from *fac* to *mer* geometric isomers. Therefore, at least for the studied model complexes, it is also possible, based on the ^{195}Pt NMR data for some complexes within a series, to easily predict the ^{195}Pt NMR shifts for analogue complexes bearing a different combination of coordinated halido ligands.

Notes and references

§ Experimental. All solvents and reagents, except otherwise stated, were purchased from Aldrich Chemical Company and used as received. The symmetric $[PtX_2(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$ (X = Cl, Br, I) pentacoordinate complexes were prepared with previously reported methods.[29] $[PtXY(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$ (X≠Y = Cl, Br, I). These complexes were obtained in equilibrium mixtures with symmetric $[PtX_2(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$ (X = Cl, Br, I) species, following previously reported procedures.[29] Alternatively, similar mixtures of complexes could be also obtained by direct reaction of symmetric $[PtX_2(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$ (X = Cl, Br) derivatives with KBr or KI. The asymmetric $[PtXY(\eta^2\text{-}CH_2=CH_2)(Me_2phen)]$ species, with mixed halido ligands, could be identified by ^{1}H and ^{195}Pt NMR spectroscopy. NMR (CDCl$_3$, 600 MHz (^{1}H), 130 MHz (^{195}Pt), 300 K): [PtClBr(η^2-CH$_2$=CH$_2$)(Me$_2$phen)]. δ(^{1}H) 3.48 (s, 6H, CH$_3$); 3.68 (m, 2H, CH, η^2-ethene, $^2J_{\text{Pt-H}}$ = 70 Hz); 3.78 (m, 2H, CH, η^2-ethene, $^2J_{\text{Pt-H}}$ = 70 Hz); 7.79 (d, 2H, CH, $^3J_{\text{H-H}}$ = 8 Hz); 7.85 ppm (s, 2H, CH); 8.31 (d, 2H, CH, $^3J_{\text{H-H}}$ = 8 Hz). δ(^{195}Pt) −2456 ppm. [PtClI(η^2-CH$_2$=CH$_2$)(Me$_2$phen)]. δ(^{1}H) 3.47 (s, 6H, CH$_3$); 3.68 (m, 2H, CH, η^2-ethene, $^2J_{\text{Pt-H}}$ = 70 Hz); 3.90 (m, 2H, CH, η^2-ethene, $^2J_{\text{Pt-H}}$ = 70 Hz); 7.79 (d, 2H, CH, $^3J_{\text{H-H}}$ = 8 Hz); 7.85 ppm (s, 2H, CH); 8.29 (d, 2H, CH, $^3J_{\text{H-H}}$ = 8 Hz). δ(^{195}Pt) −3087 ppm. [PtBrI(η^2-CH$_2$=CH$_2$)(Me$_2$phen)]. δ(^{1}H) 3.46 (s, 6H, CH$_3$); 3.68 (m, 2H, CH, η^2-ethene, $^2J_{\text{Pt-H}}$ = 70 Hz); 3.90 (m, 2H, CH, η^2-ethene, $^2J_{\text{Pt-H}}$ = 70 Hz);

7.79 (d, 2H, CH, $^3J_{\text{H-H}}$ = 8 Hz); 7.85 ppm (s, 2H, CH); 8.27 (d, 2H, CH, $^3J_{\text{H-H}}$ = 8 Hz). δ(^{195}Pt) −3426 ppm.

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General cooperative effects of single atom ligands on the metal: ^{195}Pt NMR chemical shift as a function of the coordinated halido ligands' ionic radii overall sum

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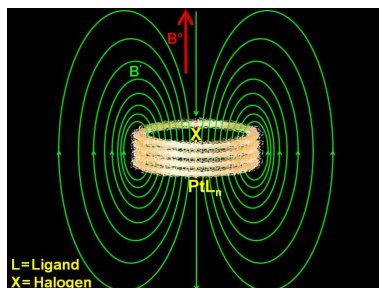
An inverse linear relation between experimentally observed ^{195}Pt NMR signals and the overall sum of coordinated halido X ligands' ionic radii was discovered in Pt(II) and Pt(IV) complexes.