The Sign and Magnitude of the ^{77}Se–^{195}Pt Coupling Constant

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There is evidence that reduced spin-spin coupling constants between directly bound nuclei are positive unless an electronegative element is involved. Thus the C–H, Si–H, and P–H coupling constants are positive, whereas the corresponding ones involving fluorine instead of hydrogen are negative.[1] The P–C coupling constant may have either sign according to the valence of phosphorus,[2] and the Se–H and Se–C ones are positive and negative respectively.[3] Since selenium is intermediate in electronegativity between phosphorus and fluorine it is important to know the sign and magnitude of its coupling constant with other nuclei, and platinum is useful in this respect since its electronegativity lies between those of hydrogen and carbon.

The ^{1}H n.m.r. spectra of saturated solutions of *cis*- and *trans*-$(\text{Me}_2\text{Se})_2\text{PtCl}_2$ in methylene dichloride have satellite lines due to the isotopes ^{77}Se ($I = \frac{1}{2}$, abundance 7·5%) and ^{195}Pt ($I = \frac{1}{2}$, abundance 33·7%), and it was also possible to observe some of the lines from the doubly substituted species $(\text{Me}_2\text{Se}^{195}\text{Pt}^{77}\text{SeMe}_2)\text{Cl}_2$. Observation of these, and simultaneous irradiation at either the ^{77}Se or the ^{195}Pt resonant frequency, gave the magnitude of $^{1}J(^{77}\text{Se}-^{195}\text{Pt})$ and its sign relative to $^{3}J(^{195}\text{Pt}\cdots\text{H})$ and $^{2}J(^{77}\text{Se}\cdots\text{H})$. Since $^{3}J(^{195}\text{Pt}\cdots\text{H})$ is of similar size and has been shown to be positive[4] in analogous phosphine complexes of platinum(II) we assume this is also true in the selenium compounds. This is then consistent with a positive value for $^{2}J(^{77}\text{Se}\cdots\text{H})$, as is found[3] in Me_2Se and Me_3Se^+.

The chemical shifts given in the Table were obtained by observation of the singly isotopically substituted species, and are quoted in the form Ξ = the resonant frequency appropriate to a polarizing magnetic field of strength such that tetramethylsilane would give an ^{1}H resonance at 100 Mc./sec. The results for the *trans*-isomer are more precise than for the *cis*-isomer because of the lower solubility of the latter.

TABLE. *N.m.r. parameters for* $(\text{Me}_2\text{Se})_2\text{PtCl}_2$ *in c./sec.*

	cis	*trans*
$^{1}J(^{195}\text{Pt}-^{77}\text{Se})$	$+480 \pm 20$	$+365 \pm 4$
$^{1}K(\text{Pt}-\text{Se})$	$+959 \times 10^{-20}$ cm.$^{-3}$	$+745 \times 10^{-20}$ cm.$^{-3}$
$^{2}J(^{77}\text{Se}\cdots\text{H})$	$+10{\cdot}0 \pm 0{\cdot}2$	$+9{\cdot}5 \pm 0{\cdot}2$
$^{3}J(^{195}\text{Pt}\cdots\text{H})$	$+41{\cdot}8 \pm 0{\cdot}2$	$+36{\cdot}6 \pm 0{\cdot}2$
$\Xi(^{195}\text{Pt})$	$21{,}417{,}185 \pm 10$	$21{,}422{,}128 \pm 3$
$\Xi(^{77}\text{Se})$	$19{,}073{,}818 \pm 3$	$19{,}074{,}102 \pm 1$

The Se–Pt reduced coupling constant is thus positive, but is rather small by comparison with the analogous P–Pt reduced coupling constants (*ca.* $+3400$ and $+2300 \times 10^{-20}$ cm.$^{-3}$ in *cis*- and *trans*-isomers). Selenium is a third row element, so use of the expression developed[5] for the Fermi contact contribution to Pt–P coupling constants would lead to a larger value for K(Pt–Se). However, it is doubtful whether the use of a mean excitation energy can be justified in either case, and the error will be greatest for selenium. The Fermi contact contribution can be negative in extreme cases.[6] The ratio $K_{cis}:K_{trans}$ is about 1·3 for the selenium compounds and 1·5 for analogous phosphorus ones. This is probably due to variations in α^2_{Pt}, since $^{2}J(^{77}\text{Se}\cdots\text{H})$ and $^{2}J(^{31}\text{P}\cdots\text{H})$ differ little between the *cis*- and *trans*-isomers.

An alternative explanation of the smaller *cis*:*trans* coupling constant ratio is that there is less $d\pi-d\pi$ bonding in the selenium compounds, but this concept has been questioned recently.[5,7] It has been demonstrated however, that if bonding is important its contribution is positive,[4] so the change is in the expected direction. The chemical shifts do not conflict with this interpretation.

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