Short Communication

The Se–Se Coupling in Bis(cyclopentadienyl)titanium Pentaselenide [Ti(C₅H₅)₂Se₅]

Pentti Pekonen, a Yrjö Hiltunen b and Risto S. Laitinen a, *

aDepartment of Chemistry and bDepartment of Physics, University of Oulu, Linnanmäki, SF-90570 Oulu, Finland


Bis(cyclopentadienyl)titanium sulfides and selenides of the types [Ti(C₅H₅)₂E₂] and [Ti(C₅H₅)₂(E–E)] (E = S or Se) have turned out to be attractive starting materials in the synthesis of pure stoichiometric selenium sulfides, which by most methods are produced only as complicated mixtures. (For a recent review, see Ref. 5.) The identification of the molecular species in these mixtures has been rather problematic. It is only with the advent of ⁷⁷Se NMR spectroscopy that the characterization of their molecular composition has been achieved. The spectral analysis is based on the combined information obtained from the samples containing natural-abundance selenium and from those containing selenium enriched in the ⁷⁷Se isotope. The natural-abundance selenium NMR spectra of Se₅S₁, 1,2-Se₅S₂, ¹ 1,2-Se₅S₂, ¹ 1,2,5,6-Se₅S₄ have also been reported.

The present study forms part of a systematic ⁷⁷Se NMR spectroscopic investigation of cyclic selenium compounds using ⁷⁷Se-enriched selenium. Since [Ti(C₅H₅)₂Se₅] contains a six-atom chelate ring in a chair conformation, the structure of which is similar to those of Se₅S₂ and Se₅S₄, the Se–Se coupling constants obtained for this complex should give more information on the coupling pattern to be expected for the six-membered heterocyclic selenium sulfides, the characterization of which is presently in progress.

Experimental

Natural-abundance [Ti(C₅H₅)₂Se₅] was prepared by treating [Ti(C₅H₅)₂Cl₂] (Fluka Chemie AG) with Li₂Se, in a hot solution of tetrahydrofuran (J. T. Baker Chemicals), as described by Shaver and McCall. Li₂Se was prepared by reducing elemental selenium (E. Merck GmbH) with LiH-BE₃ (“superhydride”, Aldrich). The synthesis of the ⁷⁷Se-enriched [Ti(C₅H₅)₂Se₅] was carried out in an analogous manner, except that ⁷⁷Se-enriched selenium powder (94 % enrichment in the ⁷⁷Se isotope, Techsnabexport) was used in the preparation of Li₂Se.

Results and discussion

The ⁷⁷Se NMR spectra of both the natural-abundance and ⁷⁷Se-enriched [Ti(C₅H₅)₂Se₅] were recorded at 300 K with a Jeol JNM-GX400 spectrometer operating at 76.317 MHz. The spectral width was 65.790 kHz and the resolution 0.5 Hz per data point. The pulse length was 9.0 μs, corresponding to a nuclide tip angle of 45°. The pulse delay was 2.0 s. The accumulations contained 5000 and 2248 transients for the natural-abundance and enriched pentaselenides, respectively. Deuterium oxide was used as an external ²H lock, and a saturated solution of SeO₂ formed an external reference. The chemical shifts (ppm) are reported relative to neat Me₂Se [δ(Me₂Se) = δ(SeO₂) + 1302.6]. The spectral analysis was carried out using the program MAOCON.

In the enriched [Ti(C₅H₅)₂Se₅] all three signals appear unexpectedly as complicated second-order multiplets (Fig. 1). The simulation of the spectrum yielded all ⁷⁷Se–⁷⁷Se coupling constants. They are shown in Table 1, together with the corresponding coupling constants of ¹ 1,2,3,4,5-Se₅S₄.
The coupling constants in these two molecules are relatively similar. The coupling over one bond is negative with respect to the positive $J_{SeSe}$ and $J_{SeSe}$ coupling constants. Our recent calculations\textsuperscript{9} utilising the program REX\textsuperscript{17} indicate that the signs chosen for the coupling constants also represent their absolute values.

The trends in the coupling constants of the two species are analogous. The $J_{SeSe}$ coupling constant of the bond adjacent to a heteroatom in the ring shows a larger absolute value than those of the bonds which are surrounded by SeSe bonds. It can be seen that the presence of titanium has a more pronounced effect on the coupling constants than that of sulfur.

It is evident from both spectra in Fig. 1 that the signal due to the two selenium atoms bound to titanium shows additional splitting because of coupling to the $C_2H_4$ protons. As far as the NMR timescale is concerned, the inversion of the TiSe$_2$ ring is slow at ambient temperatures\textsuperscript{11,18} but the rotation of the cyclopentadienyl rings about the ring-to-metal-bond is fast.\textsuperscript{18} Thus at room temperature all protons within the Cp-fragments are equiv-

![Fig. 2.](image)

**Fig. 2.** The numbering of selenium atoms in (a) $[\text{Ti}(C_2H_4)_2\text{Se}_2]$ and (b) $1,2,3,4,5\text{-Se}_5\text{S}_5$.  

**Table 1.** The $^{77}\text{Se}–^{77}\text{Se}$ Coupling Constants (in Hz) of $[\text{Ti}(C_2H_4)_2\text{Se}_2]$ and $1,2,3,4,5\text{-Se}_5\text{S}_5$.

<table>
<thead>
<tr>
<th>$J_{SeSe}$</th>
<th>$[\text{Ti}(C_2H_4)_2\text{Se}_2]$</th>
<th>$1,2,3,4,5\text{-Se}_5\text{S}_5$</th>
</tr>
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<tbody>
<tr>
<td>$J_{SeSe}$</td>
<td>$-64$</td>
<td>$-40$</td>
</tr>
<tr>
<td>$J_{SeSe}$</td>
<td>$-17$</td>
<td>$-23$</td>
</tr>
<tr>
<td>$J_{SeSe}$</td>
<td>$72$</td>
<td>$110$</td>
</tr>
<tr>
<td>$J_{SeSe}$</td>
<td>$118$</td>
<td>$108$</td>
</tr>
<tr>
<td>$J_{SeSe}$</td>
<td>$-7$</td>
<td>$5$</td>
</tr>
<tr>
<td>$J_{SeSe}$</td>
<td>$0$</td>
<td>$-3$</td>
</tr>
</tbody>
</table>

\textsuperscript{a}For the numbering of the selenium atoms, see Fig. 2. \textsuperscript{b}See Ref. 7.
alent, but the two cyclopentadienyl ligands are inequivalent. Therefore the spin system is best described as \([\text{AX}_3\text{Y}_3]\), which should yield a complicated splitting pattern in the signal due to Se(1) and Se(5) (see Fig. 2). The \(^{13}J_{\text{SeSe}}\) coupling constants, however, are expected to be less than 1 Hz. Therefore the present spectral resolution does not warrant complete assignment of all transitions. Because of the strong temperature dependence of the selenium chemical shifts, attempts to record proton-decoupled spectra resulted in a severe line-broadening of all signals, with a loss of meaningful information.

It can be concluded that the main differences in the corresponding coupling constants in \([\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_2]\) and \(1,2,3,4,5-\text{Se}_5\text{S}_3\) arise only from the different natures of the heteroatoms in the ring, and not from the different ring sizes. Indeed, coupling constants involving selenium atoms far removed from the heteroatoms (i.e. \(J_{23}, J_{45}\) and \(J_{34}\)) are practically identical (see Table 1). Therefore the values obtained for the \(\text{Se}_5\text{S}_{6-n}\) species serve as a reasonable starting model for the interpretation of the spectra of \(75\text{Se}\)-enriched \(\text{Se}_n\text{S}_{6-n}\) molecules.

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References


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