

The Se–Se Coupling in Bis(cyclopentadienyl)titanium Pentaselenide $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$

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Bis(cyclopentadienyl)titanium sulfides and selenides of the types $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{E}_5]$ and $[\text{Ti}(\text{C}_5\text{H}_5)_2(\mu\text{-E}_2)_2\text{Ti}(\text{C}_5\text{H}_5)_2]$ (E = S or Se) have turned out to be attractive starting materials in the synthesis of pure stoichiometric selenium sulfides,^{1–4} 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.^{6–8} 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 SeS_5 , 1,2- Se_2S_3 ,⁹ 1,2- Se_5S_2 ,¹⁰ and 1,2,5,6- Se_4S_4 ⁴ 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 $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ contains a six-atom chelate ring in a chair conformation,¹¹ the structure of which is similar to those of Se_6 ¹² and $\text{Se}_n\text{S}_{6-n}$,³ 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 $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ was prepared by treating $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2]$ (Fluka Chemie AG) with Li_2Se_x in a hot solution of tetrahydrofuran (J. T. Baker Chemicals), as described by Shaver and McCall.¹³ Li_2Se_x was prepared by reducing elemental selenium (E. Merck GmbH) with LiH-BEt_3 ("superhydride", Aldrich).¹⁴ The synthesis of the ⁷⁷Se-enriched $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ was carried out in an analogous manner, except that ⁷⁷Se-enriched selenium powder (94 % enrichment in the ⁷⁷Se isotope, Techsabexport) was used in the preparation of Li_2Se_x .

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The ⁷⁷Se NMR spectra of both the natural-abundance and ⁷⁷Se-enriched $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ 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 SeO_2 formed an external reference. The chemical shifts (ppm) are reported relative to neat Me_2Se [$\delta(\text{Me}_2\text{Se}) = \delta(\text{SeO}_2) + 1302.6$]. The spectral analysis was carried out using the program MAOCON.¹⁵

Results and discussion

The ⁷⁷Se NMR spectra of both the natural-abundance and the ⁷⁷Se-enriched $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ are shown in Fig. 1. They consist of three signals in an intensity ratio of 2:2:1, which is consistent with a six-membered TiSe_5 chelate ring of site symmetry C_s (Fig. 2). The chemical shifts (1237.9, 728.3, and 654.0 ppm) agree closely with those observed in the natural-abundance spectrum of a closely related pentaselenide $[\text{Ti}(i\text{-PrC}_5\text{H}_4)_2\text{Se}_5]$.⁴ It is interesting to compare these chemical shifts with those observed in 1,2,3,4,5- Se_5S_3 (657.9, 598.2 and 591.2 ppm, with a respective intensity ratio 2:1:2),⁷ since both compounds have a similar spin system. The presence of the $(\text{C}_5\text{H}_5)_2\text{Ti}$ fragment shifts all three signals downfield from those of 1,2,3,4,5- Se_5S_3 . The chemical shift due to the two symmetry-related selenium atoms Se(1) and Se(5) which are bound to titanium is especially large when compared with those of selenium atoms bound to sulfur in the $\text{Se}_n\text{S}_{8-n}$ species.

In the enriched $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ all three signals appear expectedly 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 1,2,3,4,5- Se_5S_3 .

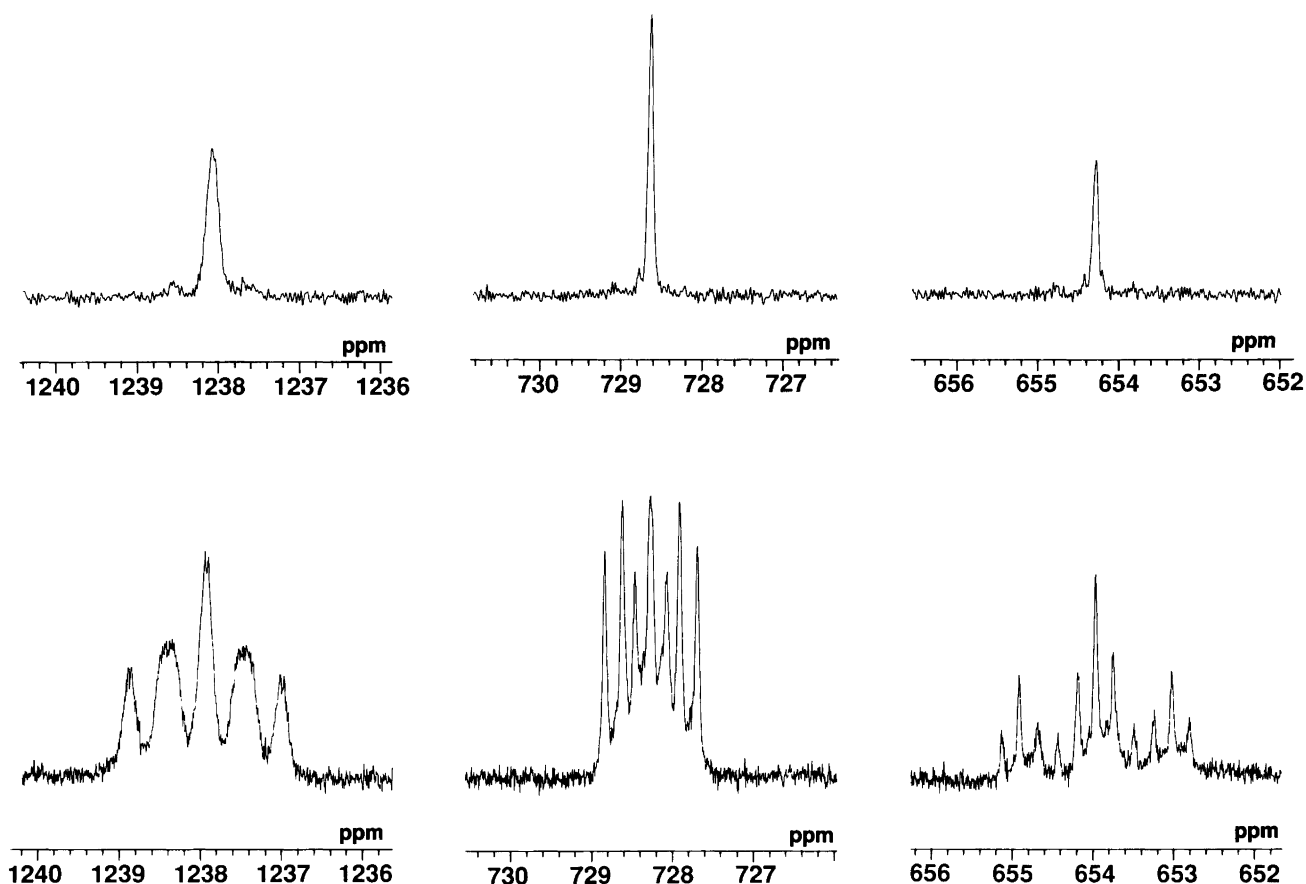


Fig. 1. The ^{77}Se NMR spectrum of the natural-abundance $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ (top) and the ^{77}Se -enriched $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ (94% enrichment; bottom). The signal at 1237.9 ppm is due to the symmetry-related atoms Se(1) and Se(5), the signal at 728.3 ppm is due to atoms Se(2) and Se(4), and the signal at 654.0 ppm is due to Se(3). [For the numbering of atoms see Fig. 2(a).]

The coupling constants in these two molecules are relatively similar. The coupling over one bond is negative with respect to the positive $^2J_{\text{SeSe}}$ and $^3J_{\text{SeSe}}$ coupling constants. Our recent calculations¹⁶ utilising the program REX¹⁷ 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 $^1J_{\text{SeSe}}$ 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_5H_5 protons. As far as the NMR timescale is concerned, the inversion of the TiSe_5 ring is slow at ambient temperatures,^{11,18} but the rotation of the cyclopentadienyl rings about the ring-to-metal-bond is fast.¹⁸ Thus at room temperature all protons within the Cp-fragments are equiv-

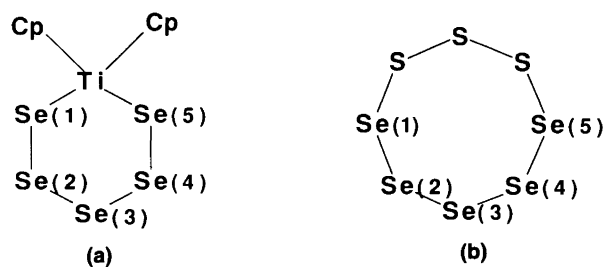


Fig. 2. The numbering of selenium atoms in (a) $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ and (b) 1,2,3,4,5- Se_5S_3 .

Table 1. The ^{77}Se - ^{77}Se Coupling Constants (in Hz) of $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ and 1,2,3,4,5- Se_5S_3 .

J_{SeSe}^a	$[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$	1,2,3,4,5- Se_5S_3^b
$^1J_{12}, ^1J_{45}$	-64	-40
$^1J_{23}, ^1J_{34}$	-17	-23
$^2J_{13}, ^2J_{35}$	72	110
$^2J_{24}$	118	108
$^3J_{14}, ^3J_{25}$	-7	5
$^4J_{15}$	0	-3

^aFor the numbering of the selenium atoms, see Fig. 2. ^bSee Ref. 7.

alent, but the two cyclopentadienyl ligands are inequivalent. Therefore the spin system is best described as $[AX_5Y_5]$, which should yield a complicated splitting pattern in the signal due to Se(1) and Se(5) (see Fig. 2). The $^3J_{\text{SeH}}$ coupling constants, however, are expected to be less than 1 Hz.¹⁹ Therefore the present spectral resolution does not warrant complete assignment of all transitions. Because of the strong temperature dependence of the selenium chemical shifts,²⁰ 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 $[\text{Ti}(\text{C}_5\text{H}_5)_2\text{Se}_5]$ and 1,2,3,4,5- Se_5S_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. $^1J_{23}$, $^1J_{34}$ and $^2J_{24}$) are practically identical (see Table 1). Therefore the values obtained for the $\text{Se}_n\text{S}_{8-n}$ species serve as a reasonable starting model for the interpretation of the spectra of ^{77}Se -enriched $\text{Se}_n\text{S}_{6-n}$ molecules.

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