^{77}Se N.M.R. Study of the Sulphur–Selenium Binary System

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^{77}Se N.m.r. spectroscopy provides attractive possibilities in the characterization of selenium and selenium sulphide ring molecules.

The characterization of the sulphur–selenium binary system has turned out to be problematic. Whereas cyclic selenium sulphides of different ring sizes have been produced from molten mixtures of the elements or by use of various synthetic routes, it is generally not possible to obtain pure stoicheiometric compounds, because different Se_mS_n species of a given ring size tend to crystallize together forming mixed phases of complex molecular composition. (For two recent reviews, see ref. 1.) Thus far, most reliable information on selenium sulphides has been obtained from Raman and h.p.l.c. investigations.[2]

A technique overlooked in the study of selenium sulphides is ^{77}Se n.m.r. spectroscopy which has been applied successfully in the characterization of organic polyselenides,[3] as well as selenium containing cations[4a—d] and Zintl-anions.[4e] The ^{77}Se isotope has a nuclear spin of 1/2 and a natural abundance of 7.58%. The sensitivity of ^{77}Se relative to ^{13}C is 2.98 rendering spectroscopic measurements with modern spectrometers straightforward, the limiting factor being the decreasing solubility of the selenium sulphides as the selenium content increases.

Sulphur and selenium were mixed together in a molar ratio of 9 : 1, heated for four hours in a sealed ampoule under reduced pressure at 770 K, and cooled rapidly to room temperature, and the resulting amorphous mass was extracted with CS_2. The ^{77}Se n.m.r. spectrum was recorded from the solution thus obtained. The natural abundance of ^{77}Se isotope is low enough to give uncoupled homonuclear ^{77}Se spectra. Coupled spectra are conveniently obtained using elemental selenium enriched with ^{77}Se (96%, Techsnabexport, Moscow). A sample of pure enriched selenium was also treated as described above in order to obtain information on the homocyclic selenium molecules.

All n.m.r. spectra were recorded with a Bruker AM-250 multinuclear spectrometer at 47.705 MHz. The data were accumulated in 64 K of memory using a spectral width of 10.638 kHz yielding a resolution of 0.325 Hz/data point. The pulse width was 25 µs and the relaxation delay 10.0 s. D_2O was used as an external ^2H lock and a saturated aqueous solution of SeO_2 as an external reference. The chemical shifts (p.p.m.) are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$].

The spectrum of the solution enriched in ^{77}Se is shown in Figure 1. According to a recent h.p.l.c. study the equilibrium solution of monoclinic selenium in CS_2 contains Se_8, Se_7, and Se_6.[5] The n.m.r. spectrum shows two singlets, that at 614.6 p.p.m. being assigned to Se_8 and that at 685.1 p.p.m. to Se_6, as both contain only chemically equivalent selenium atoms. The intensity ratio of the two signals is 1 : 0.13 implying that the molar ratio of Se_8 to Se_6 is *ca.* 1 : 0.17 which is in qualitative agreement with the h.p.l.c. studies.[5] No signals are observed in the spectrum which could be attributed to Se_7. This can be explained as follows.

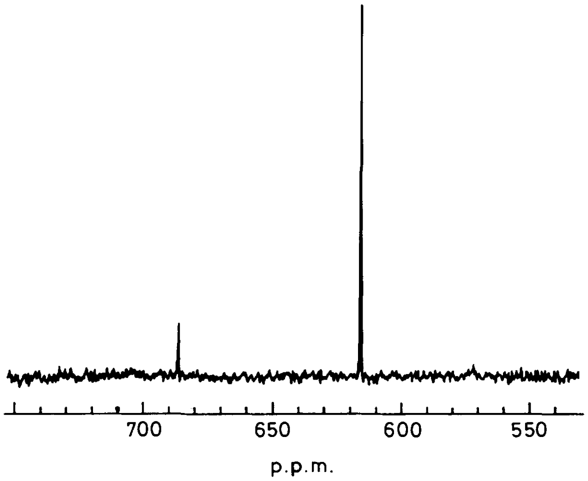

Figure 1. The ^{77}Se n.m.r. spectrum of an equilibrium solution in CS_2 of homocyclic selenium molecules, prepared using selenium enriched in ^{77}Se.

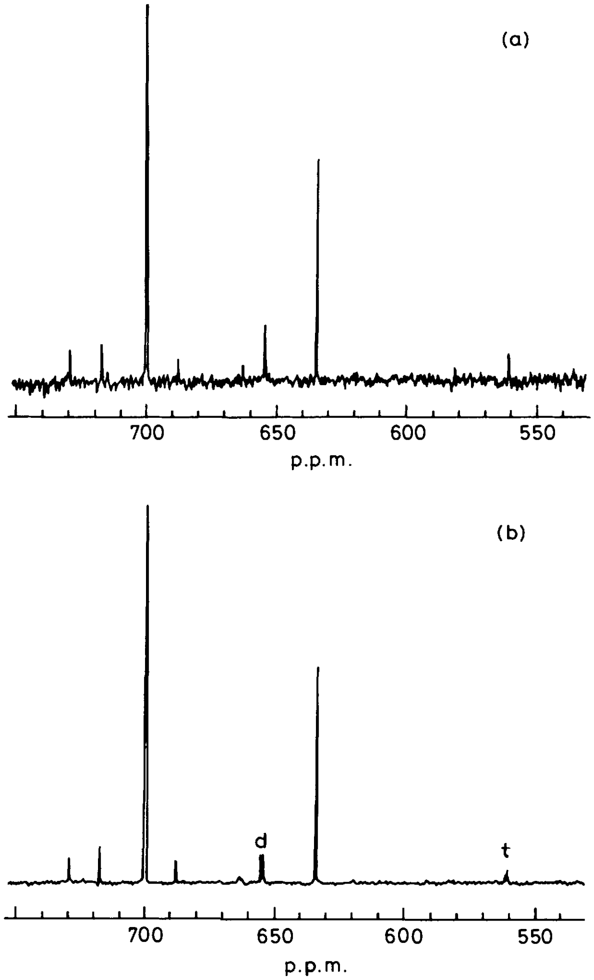

Figure 2. The ^{77}Se n.m.r. spectrum of a selenium sulphide solution in CS_2 prepared from sulphur and selenium in a molar ratio of 9 : 1: (a), natural abundance selenium; (b), selenium enriched with ^{77}Se.

In the solid state the approximate molecular symmetry of cycloheptasulphur, S_7, is C_s with four chemically inequivalent sulphur atoms.[6] A recent *X*-ray study of a seven-membered selenium sulphide ring molecule, 1,2-Se_5S_2, has shown that its conformation is similar to that of S_7 and therefore the geometry of Se_7 is also assumed to be analogous.[2g] If the conformation of Se_7 is preserved in solution the n.m.r. spectrum of the enriched Se_7 sample should show four signals with complicated coupling patterns. The relative intensities of these signals compared to the singlets of Se_6 and Se_8 are expected to be much lower and are thus probably not observed. Furthermore, according to recent theoretical considerations[7] the molecule has low barriers to internal rotation. The resulting pseudorotation in solution may also render the n.m.r. signals unobservable.

The ^{77}Se n.m.r. spectra of the sulphur-rich selenium sulphide solutions are shown in Figure 2. The spectrum in Figure 2(a) obtained from a sample with a natural abundance of selenium shows seven signals ranging from 730 to 560 p.p.m. With enriched selenium five of the signals remain singlets while the signals at 654.2 and 560.6 p.p.m. are split [see Figure 2(b)]. The former is split into a doublet and the latter into a triplet. Both signals show an identical Se–Se coupling constant of 34 Hz. In the uncoupled spectrum shown in Figure 2(a) the intensity ratio of the signals at 654.2 and 560.6 p.p.m. is 2 : 1. It seems evident that these two signals can be assigned to a selenium sulphide molecule having three selenium atoms of which two are equivalent. Since it has been shown that CS_2 solutions of selenium sulphides contain mainly eight-membered crown-shaped ring molecules[1] the n.m.r. evidence indicates the presence of an Se_3S_5 molecule. Even though some cyclic selenium-rich six- and seven-membered species are surprisingly stable,[2g] it is unlikely that the analogous sulphur-rich species survive in the CS_2 solution at room temperature.[2f]

Se_3S_5 has five possible isomers. Of these 1,2,3-Se_3S_5, 1,3,5-Se_3S_5, and 1,4,6-Se_3S_5 have the necessary selenium atom configuration. In a very recent ^{77}Se n.m.r. study on organic polyselenides, Eggert *et al.*[3] have shown that the Se–Se coupling constants between directly bonded selenium atoms range from 4.4 to 47.3 Hz. Therefore the coupling constant of 34 Hz measured for the signals at 654.2 and 560.6 p.p.m. indicates the presence of 1,2,3-Se_3S_5. A further confirmation is obtained from the uncoupled ^{77}Se n.m.r. spectrum of a product in a reaction between bis(cyclopentadienyl)titanium pentasulphide, $[Ti(C_5H_5)_2S_5]$, and dichlorodiselane, Se_2Cl_2, which has been shown to contain mainly 1,2,3-Se_3S_5 by Raman spectroscopic and h.p.l.c. evidence.[2d] Also in this case only two signals at 654.2 and 560.6 p.p.m. with an intensity ratio of 2 : 1 are observed.

The five singlets at 729.1, 716.9, 699.7, 687.3, and 633.9 p.p.m. in the spectrum of Figure 2(b) indicate molecules with only equivalent selenium atoms. There are seven such possibilities for the eight-membered selenium sulphide ring molecules: SeS_7, Se_2S_6 (1,2-, 1,3-, 1,4-, and 1,5-isomers), and Se_4S_4 (1,2,5,6- and 1,3,5,7-isomers).

Thus, ^{77}Se n.m.r. spectroscopy provides attractive possibilities for the characterization of the complicated sulphur–selenium binary system, but more work is needed for the reliable assignment of the signals observed in the spectra. Work on the influence of selenium content on the ^{77}Se-n.m.r. spectra of the selenium sulphide solutions is presently in progress.

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