

## Selenium Sulphur Dihalides, $\text{SeSX}_2$ ( $\text{X} = \text{Br}, \text{Cl}$ ); a Raman and $^{77}\text{Se}$ NMR Spectroscopic Study

John Milne

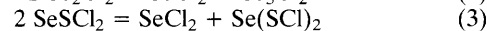
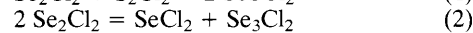
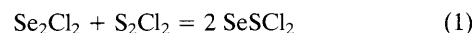
Department of Chemistry, University of Ottawa, Ottawa K1N 6N5, Canada

Mixtures of  $\text{S}_2\text{Cl}_2$  with  $\text{Se}_2\text{X}_2$  ( $\text{X} = \text{Br}, \text{Cl}$ ) yield dichalcogen dihalides with mixed chalcogens,  $\text{ClSeSCl}$ ,  $\text{BrSeSCl}$ ,  $\text{ClSeSBr}$  and  $\text{BrSeSBr}$ , which have been shown by  $^{77}\text{Se}$  NMR and Raman spectroscopy to have chain structures.

The structural chemistry of the catenated forms of sulphur and selenium constitutes a rich and varied field of study.<sup>1</sup> Amongst the simplest chains are the dichalcogen dihalides,  $\text{Ch}_2\text{X}_2$  ( $\text{Ch} = \text{S}, \text{Se}$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ). While mixed halide members of this class of compound have been studied previously,<sup>2,3</sup> the mixed chalcogen compounds, although reported<sup>4,5</sup> have not been studied by physical methods. The stereochemistry of selenium sulphur dichloride,  $\text{SeSCl}_2$ , presents some interesting structural questions, since three isomers may exist for this compound, the trigonal pyramidal form, which is the structure of  $\text{SeOCl}_2$ <sup>6</sup> and which may have a central S or Se,<sup>4,5</sup> and the chain form,  $\text{ClSeSCl}$ , like that of  $\text{Se}_2\text{Cl}_2$ .<sup>7</sup> Both types of isomer exist for  $\text{S}_2\text{F}_2$ <sup>8</sup> and  $\text{Se}_2\text{F}_2$ .<sup>9</sup> Although their electronegativities are very close (which is the most electronegative depends upon the scale used<sup>10</sup>), the structure of  $\text{SeSCl}_2$  might be expected to be like that of  $\text{SeOCl}_2$  with the selenium in a central position.

Selenium sulphur dichloride may be prepared by mixing  $\text{S}_2\text{Cl}_2$  and  $\text{Se}_2\text{Cl}_2$ , which are miscible in all proportions. The Raman spectrum of a 1 : 1 molar mixture of  $\text{S}_2\text{Cl}_2$  and  $\text{Se}_2\text{Cl}_2$  cannot be accounted for by the sum of the spectra of the separate liquids. In addition to peaks due to the reactants, the spectrum exhibits peaks at  $449\text{ cm}^{-1}$ , coincident with  $\nu_{\text{S-Cl}}$  of  $\text{S}_2\text{Cl}_2$ <sup>11</sup> and  $414\text{ cm}^{-1}$ , which are the expected frequencies for  $\nu_{\text{S-Cl}}$  and  $\nu_{\text{Se-S}}$  of the chain isomer of  $\text{SeSCl}_2$ . For the pyramidal structure with a central Se, no SCl stretching band is expected and a band corresponding to  $\nu_{\text{Se-S}}$  should arise at  $\sim 560\text{ cm}^{-1}$  or higher (estimated from the mean of the SeO and SeSe diatomic stretching frequencies<sup>12</sup>). The  $^{77}\text{Se}$  NMR spectrum of this mixture shows a strong signal at  $\delta -16.3 (\pm 0.2)$ ,<sup>†</sup> due

to  $\text{Se}_2\text{Cl}_2$ ,<sup>2</sup> a weaker signal at  $\delta -3.6 (\pm 0.2)$ , assigned to  $\text{SeSCl}_2$  and three very weak signals at  $\delta 438.7 (\pm 0.7)$ ,  $8.3 (\pm 0.2)$  and  $-21.7 (\pm 0.7)$ , arising from  $\text{SeCl}_2$  and  $\text{Se}_3\text{Cl}_2$ <sup>2</sup> and  $\text{Se}(\text{SCl})_2$ ,<sup>13</sup> respectively. The equilibria taking place in the mixture are shown in eqns. (1)–(3).



The  $^{77}\text{Se}$  chemical shift of  $\text{SeSCl}_2$  is consistent with a chain structure,  $\text{ClSeSCl}$ , and not the trigonal pyramidal structure for which a chemical shift, corresponding to that of  $\text{Se}^{\text{IV}}$  would be expected ( $\text{SeOCl}_2$ ,  $\delta -196.6$ ;<sup>14</sup>  $\text{SeCl}_4$ ,  $\delta -153.7$ ).

When  $\text{Se}_2\text{Br}_2$  is used instead of  $\text{Se}_2\text{Cl}_2$ , in a 1 : 1 molar mixture with  $\text{S}_2\text{Cl}_2$ , seven different Se containing linear  $\text{Ch}_2\text{X}_2$  compounds, every combination possible including mixed

**Table 1** Chemical shifts ( $\delta$ ) and areas for  $^{77}\text{Se}$  NMR signals in the spectrum of a 1 : 1 molar mixture of  $\text{Se}_2\text{Br}_2$  and  $\text{S}_2\text{Cl}_2$

$\delta^a$	Area <sup>b</sup>	Assignment
-123.1	945	BrSeSeCl
-116.8	1509	BrSeSeBr
-97.6	141	BrSeSCl
-80.7	131	BrSeSBr
-18.1	624	ClSeSeCl
-12.6	959	ClSeSeBr
-5.4	142	ClSeSCl
9.3	100	ClSeSBr

<sup>a</sup> Relative areas normalized to 100 for ClSeSBr. <sup>b</sup> The uncertainty on these shifts is  $\pm 1.5$  ppm;  $\delta = 0$  for saturated aqueous selenious acid at 21 °C.

<sup>†</sup> Referenced to saturated aqueous selenious acid at 21 °C;  $\delta(\text{Me}_2\text{Se}) = [\delta(\text{H}_2\text{SeO}_3) + 1282]$ .

chalcogen (a mixed halogen species), are formed. The  $^{77}\text{Se}$  NMR spectrum shows eight strong signals and these are listed with corresponding peak areas and assignment in Table 1. Weak peaks, due to  $\text{Se}_3\text{X}_2$  and other minor species, accounted for <1% of the total area intensity of the spectrum. The signals may be divided into two groups with four signals each, the more shielded part of the spectrum due to Se/Br species and the less shielded part, due to Se/Cl species. The two signals expected for  $\text{Se}_2\text{BrCl}$ , one each for Se bound to Br and Se bound to Cl, are easily assigned as the peaks with equivalent areas at  $\delta -12.6$  (Se on Cl) and  $-123.1$  (Se on Br). The other two strong signals at  $\delta -18.1$  and  $-116.8$ , lying close to the  $\text{Se}_2\text{BrCl}$  peaks, belong to  $\text{Se}_2\text{Cl}_2$  and  $\text{Se}_2\text{Br}_2$ , respectively. There is slightly greater screening of Se in this solution than in the pure liquids ( $\text{Se}_2\text{Cl}_2$ ,  $\delta -8.5$ ;  $\text{Se}_2\text{Br}_2$ ,  $\delta -110.9^2$ ). The signal at  $\delta -5.4$  lies close to that of  $\text{ClSeSCl}$  in the  $\text{S}_2\text{Cl}_2/\text{Se}_2\text{Cl}_2$  mixtures ( $\delta -3.6$ ) and the remaining peak in the Se bound to Cl region is assigned to  $\text{ClSeSBr}$ . The two signals at  $\delta -80.7$  and  $-97.6$  are assigned to  $\text{BrSeSBr}$  and  $\text{BrSeSCl}$ , respectively based on the intensity and shift relationship, which parallels that of the  $\text{ClSeSBr}$  and  $\text{ClSeSCl}$  pair of peaks.

In general, it is found that, for the same oxidation state,  $^{77}\text{Se}$  signals shift to higher frequencies when the atoms attached to selenium have greater electronegativity.<sup>15,16</sup> This is true, for the most part, with the signals reported here. The Se atoms bound to Br are shielded to a greater extent than Se bound to Cl and, for the same pair of halogens in the molecule, Se bound to Se is shielded more than Se bound to S. However, the dependence on electronegativity is the opposite of that expected if the next nearest atom to the Se, undergoing resonance, is considered. For the same halogen bound directly to Se, the signal shifts to higher frequency for  $-\text{ChBr}$  bound to Se than for  $-\text{ChCl}$ . Thus, for the more electronegative  $\text{ChX}$  group, the Se, undergoing resonance, is more shielded.

Finally, it is interesting to note that, except for the  $\text{BrSeSeCl}$  signals, the Se/Br region of the spectrum is more intense than the Se/Cl region and that the concentration of  $\text{BrSeSCl}$  is greater than that of  $\text{ClSeSBr}$ , reflecting the preferred tendency for Se-Br and S-Cl bond formation as opposed to S-Br and Se-Cl.

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