Low Temperature Raman Spectra of Dichlorosulfane (SCl₂), Tetrachlorosulfuranne (SCl₄), Dichlorodisulfane (S₂Cl₂) and Dichlorodiselenane (Se₂Cl₂) [1]

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The Raman spectrum of commercial “sulfur dichloride” shows strong lines due to SCl₂ and S₂Cl₂ and weak Cl₂ lines at 25 °C, but strong SCl₂ and SCl₄ signals at −100 °C (the latter are superimposed on the S₂Cl₂ lines). Thus, the intense Raman effect of SCl₂ can be used to detect small amounts of chlorine in SCl₂. Mixtures of SCl₂ and Cl₂ (1:15) yield the Raman spectrum of SCl₂ at −140 °C, while at 25 °C not trace of this compound can be detected. The spectra of SCl₂ and α-SeCl₂ are quite different, indicating different molecular and/or crystal structures, although ECl₃⁺ ions (E = S, Se) are present in both cases. While Se₂Cl₄ dimerizes reversibly below −50 °C, S₂Cl₂ neither dimerizes nor isomerizes on cooling. The S₂Cl₂ dimer is characterized by a Raman line at 215 cm⁻¹, the intensity of which was used to calculate an enthalpy of dimerization as of −17 kJ/mol.

1. Introduction

The vibrational spectra of SCl₂ [2—4], SCl₄ [5], S₂Cl₂ [4, 6, 7, 8, 10, 11] and Se₂Cl₄ [7—9] are well known and, with the exception of SCl₄, the assignment of the fundamental vibrations seems to be well established. In the present investigation the question is addressed whether Raman spectroscopy can be used to detect small concentrations of other species in the above mentioned compounds. These species may arise from certain reversible and temperature dependent reactions such as the following:

(a) Decomposition of SCl₂

\[ 2 \text{SCl}_2 \rightleftharpoons \text{S}_2\text{Cl}_2 + \text{Cl}_2 \] (1)

(b) Possible dimerization of SCl₂

\[ 2 \text{SCl}_2 \rightleftharpoons \text{CIS—SCl}_3 \] (2)

by analogy with the well established reversible dimerization of SF₃ [12], according to equation (3)

\[ 2 \text{SF}_2 \rightleftharpoons \text{FS—SF}_3 \] (3)

(c) Formation and decomposition of SCl₄

\[ \text{SCl}_2 + \text{Cl}_2 \rightleftharpoons \text{SCl}_4 \] (4)

(d) Isomerization of S₂Cl₂

\[ \text{Cl—S—S—Cl} \rightleftharpoons \text{Cl}_2\text{S}=\text{S} \] (5)

by analogy with the spontaneous isomerization of difluorodisulfane (FSSF) to give thiothionylfluoride (F₂SS) [13].

(e) Isomerization or dimerization of Se₂Cl₂

\[ \text{Cl—Se—Se—Cl} \rightleftharpoons \text{Cl}_2\text{Se}=\text{Se} \] (6)

\[ 2 \text{Se}_2\text{Cl}_2 \rightleftharpoons (\text{Se}_2\text{Cl}_3)_2 \] (7)

In the solid state (−87 °C) Se₂Cl₂ has been shown by X-ray structural analysis to consist of cyclic dimers [14].

To determine whether or not such equilibrium reactions occur, we have recorded Raman spectra of the title compounds at temperatures of between 25 °C and −150 °C.

2. Results and Discussion

Dichlorosulfane, SCl₂

SCl₂ is produced by chlorination of S₂Cl₂ with Cl₂ [15], and since this reaction is reversible the commercially available “sulfur dichloride” is a mixture of these three compounds as can be seen from the Raman spectrum shown in Fig. 1a. The strong S₂Cl₂ lines at 436 and 451 cm⁻¹ indicate a molar ratio S₂Cl₂:SCl₂ of ca. 1:6.6±0.5 as was found by comparison of the peak areas at 412—470 cm⁻¹ (S₂Cl₂) and 485—533 cm⁻¹ (SCl₂) with spectra of mixtures prepared from pure SCl₂ and S₂Cl₂. The two Cl₂ lines at 536 and 542 cm⁻¹ (35Cl₂ and 35Cl۵Cl, respectively) are weak due to the weak Raman effect of elemental chlorine. However, the presence of Cl₂ in consider-
Distillation of the commercial sulfur dichloride using a Vigreux column removed the S₂Cl₂, but the Cl₂ concentration was higher in the distilled product than in the original mixture, in agreement with the differing volatilities of the components. Even when only a small middle fraction was collected, the Cl₂ content remained high, indicating SCl₂ decomposition on heating according to equation (1). However, when a little PCl₃ was added to the SCl₂ prior to distillation [16], the product obtained was almost free of Cl₂, and S₂Cl₂ could not be detected any longer as can be seen from the spectra in Fig. 2. The role of PCl₃ obviously is to suppress reaction (1) [16], and to bind Cl₂ as less volatile PCl₅ which will be present in liquid SCl₂ as PCl₅⁻Cl⁻.

The very weak and broad Raman line at 485 cm⁻¹ in Fig. 2a is assigned to the combination vibration 2ν₁−ν₁ of SCl₂ (ν₁ = 517, ν₂ = 208, ν₃ = 515 cm⁻¹); the origin of the weak signal at 341 cm⁻¹ is unknown.

Tetrachlorosulfurane (λ⁴-Tetrachlorosulfurane), SCl₄

The room temperature Raman spectrum of a mixture of pure SCl₂ and Cl₂ in a molar ratio of 1:0.9 in a sealed ampoule did not show any lines attributable to SCl₄ (see Fig. 3a). The very weak feature at 454 cm⁻¹ may be assigned to S₂Cl₂ rather than to SCl₄, since the SCl₄ line at 468 cm⁻¹ is missing (see Fig. 2b). At −140 °C the same sample shows strong SCl₄ lines, and no Raman signals due to elemental chlorine. When the chlorine content was increased to

![Fig. 1. Raman spectra of commercial sulfur dichloride: (a) at 25 °C (bottom); (b) at −100 °C (top); symbols: △ SCl₂, * S₂Cl₂, □ SCl₄, O Cl₂.](image)

![Fig. 2. Raman spectra of SCl₂ distilled after addition of small amounts of PCl₃: (a) bottom: at 25 °C (wavenumbers: 208, 341, 485, 517 cm⁻¹); (b) top: at −140 °C (209, 277, 343, 449, 468, 512 cm⁻¹); symbols as in Fig. 1.](image)

![Fig. 3. Raman spectra of an SCl₂/Cl₂ mixture (molar ratio 1:0.9): (a) bottom: at 25 °C; (b) top: at −140 °C (84, 136, 213, 223, 258, 265, 276, 450, 466, 507 cm⁻¹); symbols as in Fig. 1.](image)
a molar ratio of SCl\textsubscript{2}:Cl\textsubscript{2} = 1:15 the two chlorine lines at 537 and 545 cm\textsuperscript{-1} dominated the room temperature spectrum (see Fig. 4a), but at \(-140 \, ^\circ\text{C}\) strong signals due to SCl\textsubscript{4} appeared (Fig. 4b). At this temperature the sample basically consists of the two solid phases Cl\textsubscript{2} and SCl\textsubscript{4}, which do not form solid solutions [17]. Above 150 cm\textsuperscript{-1} the spectrum is similar to the published spectra [5]; the four lines below 150 cm\textsuperscript{-1} are a superposition of the SCl\textsubscript{4} lines at 84 and 136 (see Fig. 3b) and the lattice vibrations of crystalline chlorine at 77, 94, 113 and 138 cm\textsuperscript{-1} [18, 19].

From powder diffraction data, Kniep et al. concluded that the structure of crystalline SCl\textsubscript{4} [17] may be analogous to that of cubic \(\alpha\)-SeCl\textsubscript{4} [20] which forms tetrameric molecules with chloride anions bridging SeCl\textsubscript{3}\textsuperscript{+} cations in a cubane-like Se\textsubscript{4}Cl\textsubscript{16} cluster with the cations having an exact C\textsubscript{3v} symmetry. However, the Raman spectrum of solid SeCl\textsubscript{4} (Fig. 5) [21, 22] is completely different from that of SCl\textsubscript{4}, while, on the other hand, the spectra of S\textsubscript{2}Cl\textsubscript{2} and Se\textsubscript{2}Cl\textsubscript{2} are completely analogous. Minkwitz et al. assigned the strongest SCl\textsubscript{4} signals to the fundamental vibrations of SCl\textsubscript{4}\textsuperscript{+} cations (A\textsubscript{1}: \(v_1 = 450, v_2 = 279\); E: \(v_3 = 472, v_4 = 228\) cm\textsuperscript{-1} [5a]) which may be bridged by chloride anions. However, the crystal structure seems to be different from that of Se\textsubscript{2}Cl\textsubscript{16} since the Raman lines due to deformation vibrations are much more numerous in SeCl\textsubscript{4} than in the case of SCl\textsubscript{4}. No rigorous vibrational analysis of Se\textsubscript{4}Cl\textsubscript{16} has been published so far.

Our interpretation of the SCl\textsubscript{4} spectrum differs from that of Feuerhahn and Minkwitz [5a] only in the following minor details. The shoulder at 438
should not be assigned to S₂Cl₂ as in [5a], since Fig. 2 shows that S₂Cl₂ is completely removed by distillation. There is also no sign for S₂Cl₂ in the 200–250 cm⁻¹ region of Fig. 3b and 4b. We therefore assume that all features observed in the range 120–520 cm⁻¹ are due to SCl₄ only. Neither the hypothetical SCl₆ molecule nor Cl₅⁻ anions \((v₁ = 268 \text{ cm}^{-1})\) seem to be present. Our results also indicate that the SCl₄ of [5a] may have contained impurities characterized by weak Raman lines at 228 and 132 cm⁻¹, which we did not observe.

**Dichlorodisulfane, S₂Cl₂**

The low temperature Raman spectra of S₂Cl₂ at −100 °C and −140 °C shown in Fig. 6 demonstrate that this compound retains its C₂ symmetry on cooling. In addition, contrary to older reports [24], it neither isomerizes to the known Cl₂SS, which should show Raman lines at 697, 402 and 375 cm⁻¹ [25, 26], nor dimerizes like the analogous Se₂Cl₂ (see below). The first spectrum (−100 °C) is that of glassy S₂Cl₂ while the second one shows it as polycrystalline material (−140 °C). The most remarkable features of the −140 °C spectrum are the six lattice vibrations not observed previously, the high value of 115 cm⁻¹ of the torsion vibration (compared with 104 cm⁻¹ in liquid [7] and 92 cm⁻¹ in gaseous S₂Cl₂ [4]), and the splitting of the signals at 448/435 cm⁻¹ \((v_s\) and \(v_{as}\) of the SCl bonds) and at 216/209 cm⁻¹ \((\delta_s)\). The splitting of \(\delta_s\) into two components must be due to coupling between neighboring molecules in the unit cell which contains 16 molecules [14].

**Dichlorodiselenane, Se₂Cl₂**

So far, only room temperature Raman spectra of Se₂Cl₂ have been recorded [7–9], and these have been assigned on the basis of the molecular symmetry \(C₂\) as follows (wavenumbers in cm⁻¹ [8]):

\[
\begin{align*}
A: v₁ &= 288 \text{ (SeSe)} & B: v₅ &= 367 \text{ (SeCl)} \\
v₂ &= 367 \text{ (SeCl)} & v₆ &= 146 \text{ (SeSeCl)} \\
v₃ &= 130 \text{ (SeSeCl)} & \text{ } & v₄ &= 87 \text{ (torsion)}
\end{align*}
\]

Fig. 7 shows, however, that a new strong and broad signal grows at ca. 215 cm⁻¹ when Se₂Cl₂ (m.p.: −48 °C [14]) is cooled to temperatures of below −50 °C. The relative intensities of all other lines remain constant over the temperature range investigated (+25⋯−110 °C) excepting the weak combination vibration at 407 cm⁻¹ \((v₁ + v₃ [7])\), which disappears on cooling, and the additional weak lines at 306 and 390 cm⁻¹ observed only at −100 °C which may be combinations of the following types: 213 + 97 and 2.213 cm⁻¹, respectively. These effects are completely reversible. According to an X-ray structural
Fig. 7. Raman spectrum of liquid and supercooled Se₂Cl₂ at temperatures of between 25 °C and −100 °C showing the dimerization at low temperatures. Wavenumbers at 25 °C: 88, 131, 147, 289, 356, 407 cm⁻¹; at −100 °C: 97, 134, 148, 213, 289, 306, 353 cm⁻¹.

analysis crystalline Se₂Cl₂ consists of cyclic non-planar dimers of C₂ symmetry at −87 °C [14]:

The six-membered Se₄Cl₂ ring has a chair-like conformation. The shortest intermolecular Se···Cl contacts amount to 332 pm (48 pm less than the van-der-Waals distance but 112 pm more than the intramolecular SeCl bond) [14]. We therefore interpret the 215 cm⁻¹ signal as a characteristic mode of the dimer (caused either by the symmetrical Se···Cl stretching vibration of the Se₄Cl₂ ring or, more likely, by an intermolecular combination of the torsional fundamental ν₄ at ca. 97 cm⁻¹ and the symmetrical bending mode ν₃ at 134 cm⁻¹).

The assignment of the 215 cm⁻¹ line to an Se₂Cl₂ dimer is supported by our observation that the Raman spectrum of a solid solution of Se₂Cl₂ in CS₂ (1:1.4 vv) recorded at −100 °C showed the 215 cm⁻¹ peak with approximately 30% of the intensity (peak area) of that observed with pure Se₂Cl₂ at the same temperature (based on equal intensities at 292 cm⁻¹). The temperature dependence of the 215 cm⁻¹ signal can be used to calculate the enthalpy of formation of the dimer in the presumably supercooled Se₂Cl₂. (Dichlorodiselenane is known for its extreme tendency to form supercooled melts [14].) Since the half width of the lines at 215 and 289 cm⁻¹ (SeSe stretching mode) did not change with temperature, their peak heights were used as a measure for intensity (I) and thus for the relative concentrations of (Se₂Cl₂)₂ and Se₂Cl₂:

\[
K_c = \left( \frac{[Se_2Cl_2]^2}{[Se_2Cl_2]_2} \right) = \frac{I_{215}}{I_{289}}
\]

Since d(lnK_c)/d(T⁻¹) = −ΔH°/R, a semi-logarithmic plot of K_c versus 1/T yields a straight line the slope of which is identical to the negative enthalpy of dimerization, −ΔH (see Fig. 8). For four temperatures between −60 and −100 °C the linear correlation

\[
\ln K_c = 2073 \cdot \frac{1}{T} - 14.44
\]

was obtained (correlation coefficient r = 0.99) resulting in ΔH = −17 kJ/mol (dimer).
3. Experimental

Chemicals: SC\textsubscript{1}\textsubscript{2} (Merck, p.a.) was distilled twice from PC\textsubscript{3} at normal pressure using a 13 cm Vigreux column [27]. S\textsubscript{2}Cl\textsubscript{2} (Alpha-Ventron) was distilled at reduced pressure. Se\textsubscript{2}Cl\textsubscript{2} prepared from SeO\textsubscript{2}, Se and HCl [27] was used without further purification since the \textsuperscript{77}Se NMR spectrum showed only one signal. Chlorine from a steel cylinder was condensed on a cold finger in a vacuum line and collected as a liquid in the Raman sample tube at low temperatures. Weighing before and after filling and sealing the tube provided the masses of SC\textsubscript{1}\textsubscript{2} and Cl\textsubscript{2}. a-SeCl\textsubscript{4} was obtained as a pale-yellow precipitate from the reaction of red amorphous selenium (447 mg) with an excess of SC\textsubscript{1}\textsubscript{2} at 20 °C; the product was washed with dry n-pentane.

Instruments: The two Raman spectrometers Cary 82 (Varian) and U 1000 (Instruments S.A.; equipped with data processing system for peak area integration etc.) were used together with a krypton ion laser (647.1 nm). The samples contained in thin-walled glass tubes were cooled by a stream of cold nitrogen gas produced by evaporation of liquid nitrogen in an electronically controlled home-made system.

References: