Low Temperature Raman Spectra of Dichlorosulfane (SCl_2), Tetrachlorosulfurane (SCl_4), Dichlorodisulfane (S_2Cl_2) and Dichlorodiselane (Se_2Cl_2) [1]

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Raman Spectra, Sulfur Chlorides, Selenium Chlorides

The Raman spectrum of commercial "sulfur dichloride" shows strong lines due to SCl_2 and S_2Cl_2 and weak Cl_2 lines at 25 °C, but strong SCl_2 and SCl_4 signals at −100 °C (the latter are superimposed on the S_2Cl_2 lines). Thus, the intense Raman effect of SCl_4 can be used to detect small amounts of chlorine in SCl_2. Mixtures of SCl_2 and Cl_2 (1:15) yield the Raman spectrum of SCl_4 at −140 °C, while at 25 °C not trace of this compound can be detected. The spectra of SCl_4 and α-$SeCl_4$ are quite different, indicating different molecular and/or crystal structures, although ECl_3^+ ions (E = S, Se) are present in both cases. While Se_2Cl_2 dimerizes reversibly below −50 °C, S_2Cl_2 neither dimerizes nor isomerizes on cooling. The S_2Cl_2 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 SCl_2 [2–4], SCl_4 [5], S_2Cl_2 [4, 6, 7, 8, 10, 11] and Se_2Cl_2 [7–9] are well known and, with the exception of SCl_4, 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 SCl_2

$$2\,SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2 \qquad (1)$$

(b) Possible dimerization of SCl_2

$$2\,SCl_2 \rightleftharpoons ClS{-}SCl_3 \qquad (2)$$

by analogy with the well established reversible dimerization of SF_2 [12], according to equation (3)

$$2\,SF_2 \rightleftharpoons FS{-}SF_3 \qquad (3)$$

(c) Formation and decomposition of SCl_4

$$SCl_2 + Cl_2 \rightleftharpoons SCl_4 \qquad (4)$$

(d) Isomerization of S_2Cl_2

$$Cl{-}S{-}S{-}Cl \rightleftharpoons Cl_2S{=}S \qquad (5)$$

by analogy with the spontaneous isomerization of difluorodisulfane (FSSF) to give thiothionylfluoride (F_2SS) [13].

(e) Isomerization or dimerization of Se_2Cl_2

$$Cl{-}Se{-}Se{-}Cl \rightleftharpoons Cl_2Se{=}Se \qquad (6)$$

$$2\,Se_2Cl_2 \rightleftharpoons (Se_2Cl_2)_2 \qquad (7)$$

In the solid state (−87 °C) Se_2Cl_2 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, SCl_2

SCl_2 is produced by chlorination of S_2Cl_2 with Cl_2 [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 S_2Cl_2 lines at 436 and 451 cm^{-1} indicate a molar ratio S_2Cl_2:SCl_2 of *ca.* 1:6.6±0.5 as was found by comparison of the peak areas at 412–470 cm^{-1} (S_2Cl_2) and 485–533 cm^{-1} (SCl_2) with spectra of mixtures prepared from pure SCl_2 and S_2Cl_2. The two Cl_2 lines at 536 and 542 cm^{-1} ($^{35}Cl_2$ and $^{35}Cl^{37}Cl$, respectively) are weak due to the weak Raman effect of elemental chlorine. However, the presence of Cl_2 in consider-

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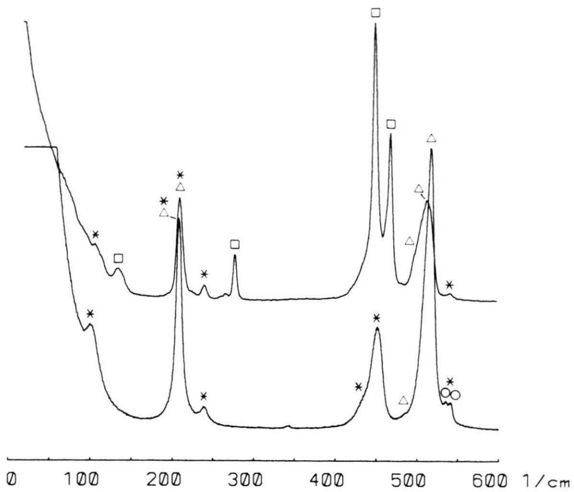


Fig. 1. Raman spectra of commercial sulfur dichloride: (a) at 25 °C (bottom); (b) at −100 °C (top); symbols: △ SCl_2, * S_2Cl_2, □ SCl_4, ○ Cl_2.

Fig. 1b. The strong lines of SCl_4 at 277, 449 and 468 cm^{-1} [5] can thus be used to detect and deter- able concentration can be deduced from the formation of SCl_4 on cooling shown by the low temperature Raman spectrum of the same sample illustrated in

mine even small amounts of chlorine in dichlorosulfane.

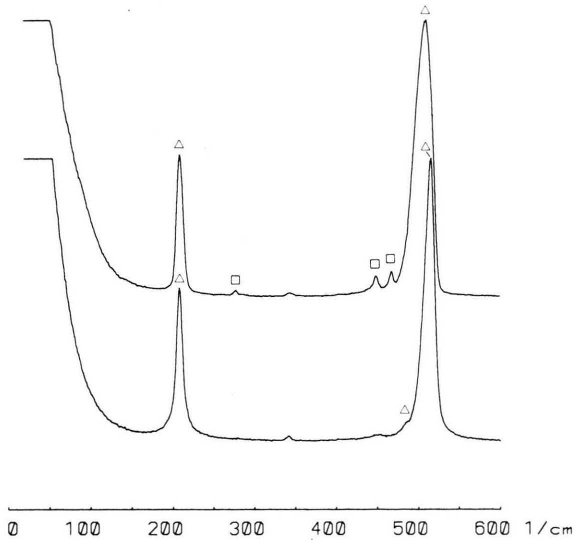


Fig. 2. Raman spectra of SCl_2 distilled after addition of small amounts of PCl_3: (a) bottom: at 25 °C (wavenumbers: 208, 341, 485, 517 cm^{-1}); (b) top: at −140 °C (209, 277, 343, 449, 468, 512 cm^{-1}); symbols as in Fig. 1.

Distillation of the commercial sulfur dichloride using a Vigreux column removed the S_2Cl_2, but the Cl_2 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 Cl_2 content remained high, indicating SCl_2 decomposition on heating according to equation (1). However, when a little PCl_3 was added to the SCl_2 prior to distillation [16], the product obtained was almost free of Cl_2, and S_2Cl_2 could not be detected any longer as can be seen from the spectra in Fig. 2. The role of PCl_3 obviously is to suppress reaction (1) [16], and to bind Cl_2 as less volatile PCl_5 which will be present in liquid SCl_2 as $PCl_4^+Cl^-$.

The very weak and broad Raman line at 485 cm^{-1} in Fig. 2a is assigned to the combination vibration $2\nu_3-\nu_1$ of SCl_2 (ν_1 = 517, ν_2 = 208, ν_3 = 515 cm^{-1}); the origin of the weak signal at 341 cm^{-1} is unknown.

Tetrachlorosulfurane (λ^4-Tetrachlorosulfane), SCl_4

The room temperature Raman spectrum of a mixture of pure SCl_2 and Cl_2 in a molar ratio of 1:0.9 in a sealed ampoule did not show any lines attributable to SCl_4 (see Fig. 3a). The very weak feature at 454 cm^{-1} may be assigned to S_2Cl_2 rather than to SCl_4, since the SCl_4 line at 468 cm^{-1} is missing (see Fig. 2b). At −140 °C the same sample shows strong SCl_4 lines, and no Raman signals due to elemental chlorine. When the chlorine content was increased to

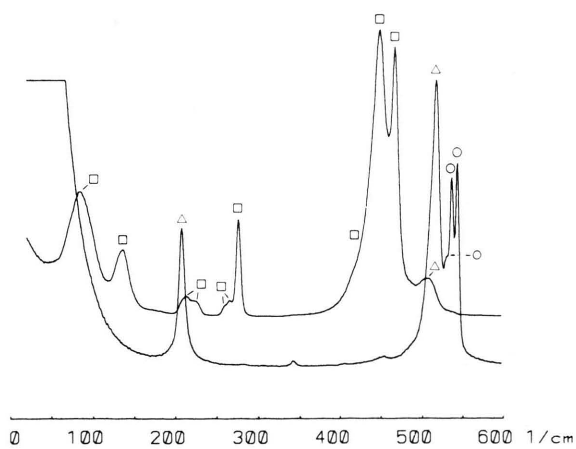


Fig. 3. Raman spectra of an SCl_2/Cl_2 mixture (molar ratio 1:0.9): (a) bottom: at 25 °C; (b) top: at −140 °C (84, 136, 213, 223, 258, 265, 276, 450, 466, 507 cm^{-1}); symbols as in Fig. 1.

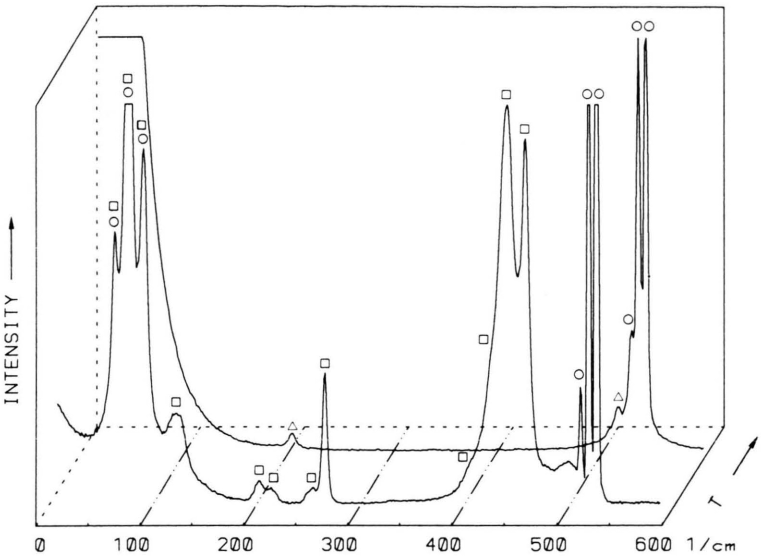


Fig. 4. Raman spectra of an SCl_2/Cl_2 mixture (molar ratio 1:15): (a) background: at 25 °C; (b) front: at −140 °C (75, 88, 103, 136, 214, 226, 259, 266, 278, 421 (sh), 438 (sh), 453, 470, 510, 522, 530, 537 cm^{-1}); symbols as in Fig. 1.

a molar ratio of $SCl_2:Cl_2$ = 1:15 the two chlorine lines at 537 and 545 cm^{-1} dominated the room temperature spectrum (see Fig. 4a), but at −140 °C strong signals due to SCl_4 appeared (Fig. 4b). At this temperature the sample basically consists of the two solid phases Cl_2 and SCl_4, which do not form solid solutions [17]. Above 150 cm^{-1} the spectrum is similar to the published spectra [5]; the four lines below 150 cm^{-1} are a superposition of the SCl_4 lines at 84 and 136 (see Fig. 3b) and the lattice vibrations of crystalline chlorine at 77, 94, 113 and 138 cm^{-1} [18, 19].

From powder diffraction data, Kniep *et al.* concluded that the structure of crystalline SCl_4 [17] may be analogous to that of cubic α-$SeCl_4$ [20] which forms tetrameric molecules with chloride anions bridging $SeCl_3^+$ cations in a cubane-like Se_4Cl_{16} cluster with the cations having an exact C_{3v} symmetry. However, the Raman spectrum of solid $SeCl_4$ (Fig. 5) [21, 22] is completely different from that of SCl_4, while, on the other hand, the spectra of S_2Cl_2 and Se_2Cl_2 are completely analogous. Minkwitz *et al.* assigned the strongest SCl_4 signals to the fundamental vibrations of SCl_3^+ cations (A_1: ν_1 = 450, ν_2 = 279; E: ν_3 = 472, ν_4 = 228 cm^{-1} [5a]) which may be bridged by chloride anions. However, the crystal structure seems to be different from that of Se_4Cl_{16} since the Raman lines due to deformation vibrations are much more numerous in $SeCl_4$ than in the case of

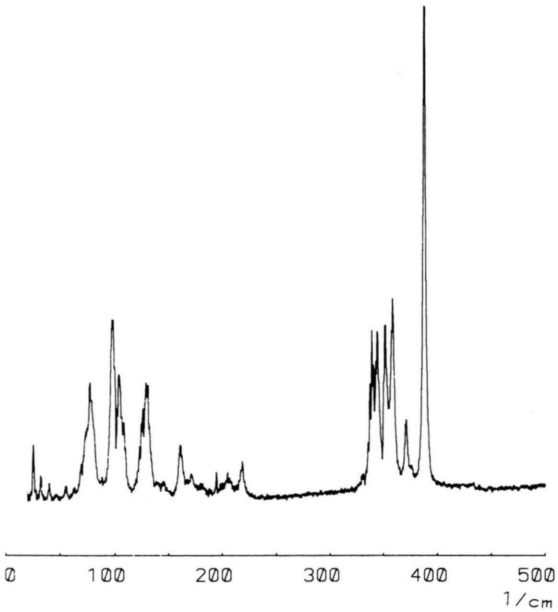


Fig. 5. Raman spectrum of α-$SeCl_4$ at −100 °C (assignment see [21]).

SCl_4. No rigorous vibrational analysis of Se_4Cl_{16} has been published so far.

Our interpretation of the SCl_4 spectrum differs from that of Feuerhahn and Minkwitz [5a] only in the following minor details. The shoulder at 438

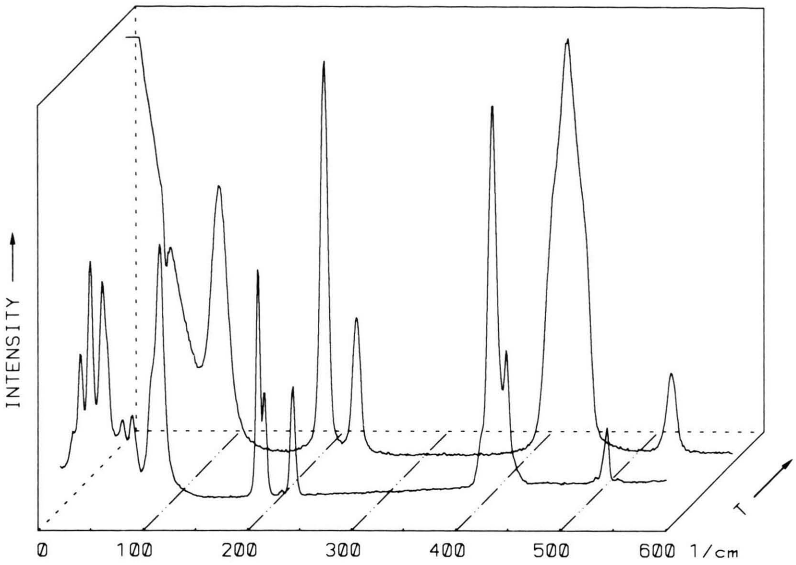


Fig. 6. Raman spectrum of S_2Cl_2: (a) background: at -100 °C (wavenumbers: 109, 210, 241, 430 (sh), 458, 542 (sh) cm^{-1}); (b) front: at -140 °C (wavenumbers: 32, 39, 49, 60, 80, 89, 115, 209, 216, 243, 424 (sh), 435, 448, 544 cm^{-1}).

should not be assigned to S_2Cl_2 as in [5a], since Fig. 2 shows that S_2Cl_2 is completely removed by distillation. There is also no sign for S_2Cl_2 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 SCl_4 only. Neither the hypothetical SCl_6 molecule nor Cl_3^- anions (ν_1 = 268 cm^{-1} [23]) seem to be present. Our results also indicate that the SCl_4 of [5a] may have contained impurities characterized by weak Raman lines at 228 and 132 cm^{-1}, which we did not observe.

Dichlorodisulfane, S_2Cl_2

The low temperature Raman spectra of S_2Cl_2 at -100 °C and -140 °C shown in Fig. 6 demonstrate that this compounds retains its C_2 symmetry on cooling. In addition, contrary to older reports [24], it neither isomerizes to the known Cl_2SS, which should show Raman lines at 697, 402 and 375 cm^{-1} [25, 26], nor dimerizes like the analogous Se_2Cl_2 (see below). The first spectrum (-100 °C) is that of glassy S_2Cl_2 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 S_2Cl_2 [4]), and the splitting of the signals at 448/435 cm^{-1} (ν_s and ν_{as} of the SCl bonds) and at 216/209 cm^{-1} (δ_s). The splitting of δ_s into two components must be due to coupling between neighboring molecules in the unit cell which contains 16 molecules [14].

Dichlorodiselane, Se_2Cl_2

So far, only room temperature Raman spectra of Se_2Cl_2 have been recorded [7–9], and these have been assigned on the basis of the molecular symmetry C_2 as follows (wavenumbers in cm^{-1} [8]):

A: ν_1 = 288 (SeSe)	B: ν_5 = 367 (SeCl)
ν_2 = 367 (SeCl)	ν_6 = 146 (SeSeCl)
ν_3 = 130 (SeSeCl)	
ν_4 = 87 (torsion)	

Fig. 7 shows, however, that a new strong and broad signal grows at *ca.* 215 cm^{-1} when Se_2Cl_2 (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} ($\nu_1 + \nu_3$ [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 $2 \cdot 213$ cm^{-1}, respectively. These effects are completely reversible. According to an X-ray structural

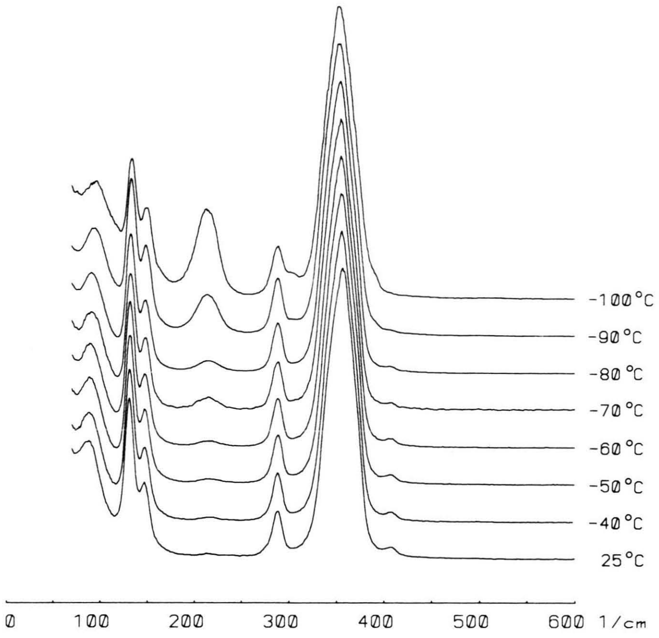
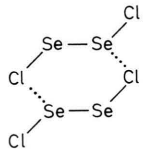


Fig. 7. Raman spectrum of liquid and supercooled Se_2Cl_2 at temperatures of between 25 °C and −100 °C showing the dimerization at low temperatures. Wavenumbers at 25 °C: 88, 131, 147, 289, 356, 407 cm^{-1}; at −100 °C: 97, 134, 148, 213, 289, 306, 353 cm^{-1}.

analysis crystalline Se_2Cl_2 consists of cyclic non-planar dimers of C_i symmetry at −87 °C [14]:



The six-membered Se_4Cl_2 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 interprete the 215 cm^{-1} signal as a characteristic mode of the dimer (caused either by the symmetrical Se···Cl stretching vibration of the Se_4Cl_2 ring or, more likely, by an intermolecular combination of the torsional fundamental ν_4 at *ca.* 97 cm^{-1} and the symmetrical bending mode ν_3 at 134 cm^{-1}).

The assignment of the 215 cm^{-1} line to an Se_2Cl_2 dimer is supported by our observation that the Raman spectrum of a solid solution of Se_2Cl_2 in CS_2 (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 Se_2Cl_2 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 Se_2Cl_2. (Dichlorodiselane 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 $(Se_2Cl_2)_2$ and Se_2Cl_2:

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

Since $d(\ln K_c)/d(T^{-1}) = -\Delta H^\circ/R$, 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, $-\Delta H$ (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).

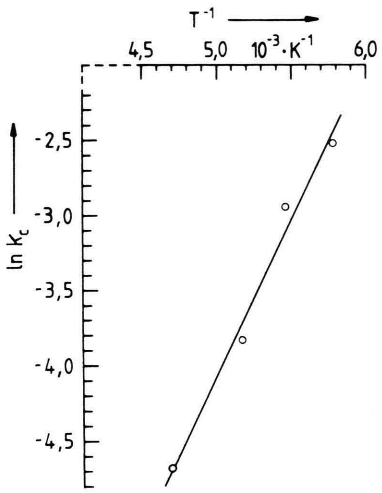


Fig. 8. Semilogarithmic plot of the equilibrium constant K_c of the Se_2Cl_2 dimerization *versus* the reciprocal absolute temperature.

3. Experimental

Chemicals: SCl_2 (Merck, p.a.) was distilled twice from PCl_3 at normal pressure using a 13 cm Vigreux column [27]. S_2Cl_2 (Alpha-Ventron) was distilled at reduced pressure. Se_2Cl_2 prepared from SeO_2, Se and HCl [27] was used without further purification since the ^{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 SCl_2 and Cl_2. α-$SeCl_4$ was obtained as a pale-yellow precipitate from the reaction of red amorphous selenium (447 mg) with an excess of SCl_2 (3.5 ml) 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.

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