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^{13}C NMR and FT-IR spectra of thiocyanogen, $S_2(CN)_2$, selenocyanogen, $Se_2(CN)_2$, and related compounds

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Abstract

The pseudohalogens thiocyanogen [$(SCN)_2$], sulfur dicyanide [$S(CN)_2$], selenocyanogen [$(SeCN)_2$], selenium dicyanide [$Se(CN)_2$] and selenium diselenocyanate [$Se(SeCN)_2$] have been prepared and studied by ^{13}C NMR spectroscopy for the first time. The ^{13}C NMR results confirm the structure previously assigned to these compounds on the basis of vibrational spectroscopy. Thiocyanogen, sulfur dicyanide, selenocyanogen and selenium dicyanide have been also studied as liquid film on KBr plate in the solid state (KBr pellet) by FT-IR spectroscopy and the data collected have been compared and discussed with previous results recorded on solutions in organic solvents. Good agreement with early results has been obtained. It has been confirmed by solid state ^{13}C NMR–MAS that under mild conditions selenocyanogen disproportionates into selenium dicyanide and selenium diselenocyanate. By heating selenocyanogen above 180°C it polymerizes irreversibly into a brown polymer known as paraselenocyanogen whose FT-IR spectrum is surprisingly very similar to that of parathiocyanogen or polythiocyanogen, the product of self-polymerization of thiocyanogen.

Keywords: Pseudohalogens; Selenocyanogen; Thiocyanogen

1. Introduction

The chemistry of pseudohalogens has always been a fascinating and rather briefly treated subject in textbooks of inorganic chemistry [1–4]. Thiocyanogen [$S_2(CN)_2$] was discovered by Soderback 81 years ago [1,5], whereas selenocyanogen [$Se_2(CN)_2$] was prepared in pure form only in 1925 [1,6,7].

Infrared (IR) and Raman spectra of thiocyanogen [8–10] strongly suggest structure **1**, which has a disulfide bridge, NC–S–S–CN, rather than structure **2**, which has the isothiocyanate form S=C=N–N=C=S, even though, according to certain authors [9], on the basis of the position of the IR band due to a –SCN or –NCS group, structure **2** is favoured in polar solvents such as ether while structure **1** is largely predominant in non-polar aprotic solvents. This consideration is not negligible because the addition of thiocyanogen to ethylenic double bonds of organic substrates involves the addition of both –SCN and –NCS groups [11]:

$$R\text{–}CH{=}CH\text{–}R + S_2(CN)_2 \rightarrow$$

$$NC\text{–}S\text{–}C(R)\text{–}C(R)\text{–}S\text{–}CN\ (\mathbf{3})$$

$$+NC\text{–}S\text{–}C(R)\text{–}C(R)\text{–}N{=}C{=}S\ (\mathbf{4})$$

However, in contrast to the above suggestion, the product with structure **4** can be formed in both polar and non-polar solvents [11,12]. Recently, the matter has been rationalized [12], and it has been shown that the IR band shift of thiocyanogen observed previously in ether could reasonably be due to a charge-transfer interaction of thiocyanogen with solvent rather than to the presence of isomer **2**.

Moreover, it has been pointed out [12] that the heat of formation of thiocyanogen found experimentally coincides with the value theoretically calculated for isomer **1** rather than compound **2** [13], and similar conclusions were obtained from the gas-phase UV spectrum of thiocyanogen, in agreement with theoretical calculations [14].

Thus, to explain the different addition behaviour which leads simultaneously to structures **3** and **4**, it is possible that the thiocyanogen radical derived from S–S homolysis has a bifunctional behaviour, as has been previously postulated [11,15–17]:

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•S–CN (**5**)↔•N=C=S (**6**)

Bhatnagar et al. [18] have shown by magnetic susceptibility measurements that freshly prepared solutions of thiocyanogen in carbon disulfide and other solvents are diamagnetic but that on standing they become paramagnetic. In certain solvents such as cyclohexane, thiocyanogen is less stable and paramagnetism is observed also in freshly prepared solutions. The paramagnetism can be attributed to the formation of thiocyanogen radicals due to homolysis of S–S bonds during solution ageing. Probably these radicals induce the irreversible self-polymerization of thiocyanogen to a brick-red solid known as parathiocyanogen or polythiocyanogen whose structure seems to be very peculiar [15–17,19].

Selenocyanogen [$Se_2(CN)_2$] was isolated for the first time in 1925 thanks to the work of Birkenback and Kellermann ([6,7]). Fundamental studies of the structure of selenocyanogen and related compounds have already been published [20,21] and are based on IR spectroscopy; some short reviews on selenocyanogen and related compounds are also available [22–24]. Selenocyanogen and related compounds belong to the class of pseudohalides and are the selenium analogues of the thiocyanogen family of compounds. In comparison to thiocyanogen, selenocyanogen and its homologues have received much less attention by investigators, but the available data show that the selenocyanogen family has the same chemical structure as the thiocyanogen family of compounds.

Some unexpected differences between thiocyanogen and selenocyanogen can be immediately outlined here. While thiocyanogen is unstable and cannot be isolated in the pure state unless special conditions at low temperatures are adopted, selenocyanogen is rather more stable and can be isolated at room temperature as a yellow powder; it can also be re-crystallized from CH_2Cl_2 solutions and remains unchanged for months if stored in a closed flask at +5°C in the absence of humidity or solvent impurities. Thiocyanogen heated above 0°C or isolated by solvent evaporation at room temperature quickly turns into a brick-red solid [17]; however, selenocyanogen when heated in solution with carbon disulfide undergoes a unique disproportionation reaction as follows [21–24]:

$$2Se_2(CN)_2 \rightarrow Se(CN)_2 + Se_3(CN)_2 \qquad (1)$$

When heated at higher temperatures, selenocyanogen liberates a sublimate (see below) and is polymerized into a brownish material. Practically nothing is known about the selenocyanogen polymerization products or about the strong sensitivity of selenocyanogen to certain molecules and solvents which cause its polymerization to a deep-red solid [25].

The difference in stability between thiocyanogen and selenocyanogen is quite striking notwithstanding that the two molecules should have the same geometrical structure, and in general it is expected that the S–S bond strength is comparable to that of the Se–Se bond strength. However, the dissociation energy of a Se–Se bond in diselenides is about 73 kcal mol^{-1} [24], which is larger than that for a S–S bond, which requires 63 kcal mol^{-1} [26]; in any case, these data should be considered only as approximations. Taking into account the rich organic chemistry of selenium [23,24], the C–Se bond should be as stable as the C–S bond; moreover, the Pauling electronegativity of selenium is slightly lower than that of sulfur [24], thus the C–Se bond should have at least the same degree of covalency as the C–S bond.

2. Experimental

^{13}C NMR spectra in $CDCl_3$ solution were performed with a Bruker AMX-600 spectrometer operating at 150.9 MHz; 7 s relaxation delay with 0.7 s of acquisition time and 90° pulse angle were applied. Spectra were obtained with 64 000 words. All reagents and solvents used were from Aldrich or Fluka.

Solid state ^{13}C MAS–NMR spectra were recorded at room temperature on a Bruker AC-200 spectrometer, equipped with an HP amplifier, ^{1}H 200 MHz, 120 W continuous wave and a pulse amplifier M3205. Samples were packed into 4-mm zirconia rotors and sealed with Kel-F caps. The spin rate was 8 kHz. Spectra were obtained with 512 words in the time domain, zero-filled and Fourier-transformed with a size of 1024 words; 20 000 scans were performed.

FT-IR spectra were recorded on a Perkin-Elmer 1710 spectrometer. Samples were studied embedded in KBr pellets. All reagents and solvents were from Aldrich or Fluka and were used as received.

2.1. Lead thiocyanate preparation

Lead thiocyanate was prepared by adding ammonium thiocyanate solution to an aqueous solution of lead(II) nitrate in stoichiometric amounts. The white precipitate was collected by filtration, washed with water and dried in an oven at 105°C.

2.2. Silver cyanide preparation

Similarly, silver cyanide was prepared by precipitation from silver nitrate and sodium cyanide in stoichiometric amounts. The white precipitate was collected by filtration, protected totally from light and dried in a desiccator under dynamic vacuum.

2.3. Thiocyanogen preparation

Thiocyanogen [$S_2(CN)_2$] was prepared as previously reported [17], by suspending 6.8 g of dry lead(II) thiocyanate in 50 ml of $CDCl_3$ (deuterated chloroform) by magnetic stirring and adding dropwise 3.36 g of bromine. The freshly prepared thiocyanogen solution was decanted and immediately used to record the ^{13}C NMR spectrum. On standing the solution polymerized to the insoluble and brick-red solid polythiocyanogen [15–17].

2.4. Sulfur dicyanide preparation

Sulfur dicyanide [$S(CN)_2$] was prepared by suspending 4.5 g of silver cyanide in 50 ml of $CDCl_3$ by vigorous stirring and by adding dropwise 1.0 ml of sulfur dichloride (SCl_2). The mixture was stirred for 30 min at room temperature and then the silver chloride formed was separated by decantation. The $CDCl_3$ solution of $S(CN)_2$ was used to record the ^{13}C NMR spectrum.

2.5. Preparation of silver selenocyanate

Silver selenocyanate was prepared by adding a solution of potassium selenocyanate to a solution of silver nitrate in stoichiometric amounts. The precipitate formed was collected by filtration, washed with water and dried into a desiccator under dynamic vacuum. Care should be taken to avoid exposure to light.

2.6. Preparation of selenocyanogen

Selenocyanogen was prepared by suspending 13.5 g of silver selenocyanate [Ag(SeCN)] in 100 ml of dichloromethane with vigorous stirring. Then an iodine solution in dichloromethane was added (6.0 g of iodine per 160 ml of dichloromethane). Very rapid discolouration of the iodine was observed. The mixture was stirred for 2 h at +13°C and then it was decanted. The silver iodide collected was yellow while the $Se_2(CN)_2$ solution was orange. Dichloromethane was then distilled off under reduced pressure in a water-bath to leave a canary-yellow powder. Yield: 2.77 g (55.9% over iodine used).

Selenocyanogen was dissolved in $CDCl_3$ to record the ^{13}C NMR spectrum in solution immediately after preparation. The solid-state ^{13}C NMR spectrum was recorded 3 weeks after preparation.

2.7. Stability of selenocyanogen

Selenocyanogen is rather stable when stored in closed flasks in the dark at +5°C. When stored in this way no decomposition can be observed (visually and by IR spectroscopy) even after months. However, humidity, heat and certain solvents greatly accelerate the decomposition and polymerization of selenocyanogen [10].

2.8. Preparation of selenium dicyanide and paraselenocyanogen

Selenocyanogen (0.217 g) was mixed with 15 ml of decalin and heated in a oil-bath for 2 h at 210°C and 1 h at 180°C. The initially yellow decalin solution quickly became orange and then during heating turbid and brown. In the refrigerator, a discrete crystalline sublimate was deposited; this was collected and identified as selenium dicyanide by its IR spectrum. The dark-brown precipitate formed in the flask was easily separated from decalin by settling and decantation. The collected precipitate was washed several times with dichloromethane and then dried in air. The precipitate was paraselenocyanogen or polyselenocyanogen.

2.9. Stability of selenium dicyanide

The white and tabular crystals of selenium dicyanide are stable for months when stored in a tightly closed flask at room temperature. Exposure to light causes the formation of an orange colour. Also moisture and certain solvents cause a change in colour.

3. Results and discussion

In previous work we have concentrated our efforts on the study of the structure of parathiocyanogen or polythiocyanogen [$(SCN)_x$], the inorganic polymer resulting from spontaneous polymerization of thiocyanogen [15–17]. In these studies we reported evidence about the peculiar and probably linear structure of parathiocyanogen. With FT-IR and electronic spectroscopy we have also studied thiocyanogen [$(SCN)_2$] with the aim of understanding some aspects of its spontaneous polymerization [17].

3.1. ^{13}C NMR spectrum of thiocyanogen

The ^{13}C NMR spectrum of freshly prepared thiocyanogen (see Table 1) is characterized by a sharp singlet at 107.36 ppm. The thiocyanate ion of potassium thiocyanate is reported to show a ^{13}C NMR signal at about 133.3 ppm [27,28], but alkyl thiocyanates such as methyl-, ethyl- and butylthiocyanate give an NMR signal at higher fields, namely at 113.5, 112.1 and 112.1 ppm, respectively [27]. On the other hand, organic isothiocyanates are detected at 128–136 ppm [27,28], in the same range where the inorganic thiocyanate ion of KSCN gives an NMR signal, hence at considerably lower fields than organic thiocyanates (see Table 1).

Based on these data, it can be concluded that thiocyanogen has structure **1**, with a disulfide bridge connecting the two cyanide groups because its NMR signal is comparable to that of alkylthiocyanates. In fact, for isomer **2** of ‘isothiocyanogen’ we should expect a singlet NMR signal at 128–132 ppm, while for isomer **7** of ‘thiocyanogen–isothiocyanogen’ (NC–S–N=C=S) we would expect two different signals, one due to the thiocyanate group at about 107 ppm and the other due to the isothiocyanate group at 128–132 ppm. Since we observe a unique signal at 107.36 ppm we can conclude that structure **1** is the correct structure of thiocyanogen.

Additionally, our NMR spectrum does not show any evidence for the presence of thiocyanate (**5**) and isothiocyanate

Table 1
^{13}C NMR synopsis

Compound name	Structure (see text)	NMR signal (ppm)	Reference
Thiocyanogen	**1**	107, 36 (singlet, in $CDCl_3$)	this work
Sulfur dicyanide	**8**	126 (singlet, in $CDCl_3$)	this work
Selenocyanogen	**10**	89, 92 (singlet, in $CDCl_3$)	this work
Selenium dicyanide	see Eq. (2)	130 (broad, solid-state MAS–NMR)	this work
Selenium diselenocyanate	see Eq. (2)	98,3 (broad, solid-state MAS–NMR)	this work
Potassium thiocyanate	KSCN	133.3	[27,28]
Methyl thiocyanate	Me–SCN	113.5	[27]
Ethyl thiocyanate	Et–SCN	112.1	[27]
Potassium cyanide	KCN	168.5	[28]
Alkyl nitrile	R–CN	112–126	[28]
Alkyl isonitrile	R–N=C	157–167	[27,28]
Alkyl isothiocyanate	R–N=C=S	128–136	[27,28]

(**6**) radicals, which means that these radicals are only present at very low concentrations in our system.

Ageing of thiocyanogen solution in $CDCl_3$ causes the formation of an orange-coloured solution, and also a brick-red precipitate starts to appear in suspension and at the bottom of the solution. As mentioned in Section 1, Bhatnagar et al. [18] have shown that freshly prepared thiocyanogen solutions are diamagnetic but become paramagnetic upon ageing due to free radical formation. The ^{13}C NMR spectrum of aged thiocyanogen solution still shows the signal at 107 ppm due to thiocyanogen but a new feature at 169.6 ppm starts to appear. We have already shown [17] that thiocyanogen polymer (polythiocyanogen) has a unique feature at 186 ppm in dimethylformamide (DMF) solution, where it has some degree of solubility; however, polythiocyanogen is not soluble in chloroform. Thus the signal at 169.6 ppm (in $CDCl_3$) could be due to a low molecular weight and soluble oligomer of thiocyanogen.

Other possible interpretations involve the presence of isothiocyanate ion, which we suppose should absorb in this field from the observation that isocyanides give NMR signals at 157–165 ppm (see Table 1). If the assignment of the feature at 169.6 ppm to the isothiocyanate group is correct, we have the first direct indication that thiocyanogen undergoes the scission of its S–S bond followed by a rearrangement to an isothiocyanate group. This could explain the simultaneous N and S addition to the double bonds of organic substrates (see structures **3** and **4**). However, a simpler and more convincing explanation exists for the feature at 169.6 ppm. In fact, cyanide ion absorbs at 168.5 ppm (see Table 1); hence, instead of scission of the S–S bond, we have evidence of scission of the C–S bond which leads to the cyanide group. Scission of the C–S bond of thiocyanogen would imply the formation of thiocyanate ion and free sulfur. Unfortunately, there is no evidence of the presence of free thiocyanate in our NMR spectrum because no signal at 113.5 ppm was observed. Thus, the NMR spectroscopy data suggest that the degradation of thiocyanogen in chloroform involves the formation of cyanide ions and free sulfur.

3.2. *^{13}C NMR spectrum of sulfur dicyanide*

We have also studied by ^{13}C NMR spectroscopy the lower thiocyanogen homologue sulfur dicyanide, which has the structure NC–S–CN (**8**) (V-shaped, not linear), which was assigned on the basis of vibrational spectroscopy and X-ray studies [22,23], rather than NC–N=C=S (**9**) or other possible structures.

Freshly prepared sulfur dicyanide shows a unique and sharp singlet at about 126 ppm (see Table 1) in $CDCl_3$ solution. Even if the ^{13}C NMR signal of this molecule appears at lower fields than that observed for thiocyanogen, we can immediately exclude structure **9**, which requires two different signals at lower fields, namely one at least at 157 ppm [27,28] for the isocyanide group, which was not observed, and the other above 130 ppm for the isothiocyanide group [27,28]. Since only one signal was detected we can conclude that structure **8** is the correct structure of sulfur dicyanide. To explain why the signal of sulfur dicyanide appears at 126 ppm and that of thiocyanogen at 107 ppm we must assume that some conjugation between the triple bonds of the two cyano groups occurs through the sulfur bridge in the case of sulfur cyanide, while this is absent in the case of thiocyanogen, which has two sulfur atoms per bridge. Therefore, conjugation causes an NMR signal closer to the thiocyanate ion in the case of sulfur dicyanide (133.3 ppm for thiocyanate versus 126 ppm for sulfur dicyanide), while for thiocyanogen the NMR signal at 107 ppm is comparable to that of organic alkyl thiocyanates which in fact absorb in that region [20,21]. The general observation that sulfur dicyanide is more stable than thiocyanogen could be ascribed to the fact that the former is stabilized also by conjugation while the latter is not. In fact, sulfur dicyanide can be isolated in the form of crystals by sublimation [22], whereas thiocyanogen can be isolated in crystal form only under more complex conditions at −50°C [10] and at temperatures above 0°C shows a certain stability only in solution. When thiocyanogen in solution is concentrated by evaporating the solvent at room temperature under reduced pressure, it polymerizes very quickly [17], sometimes with detonation [17]. Upon prolonged ageing in solution at room temperature, sulfur dicyanide begins self-polymerization. The ^{13}C NMR spectrum shows a resonance at 129 ppm, but also a new line appears at 124 ppm and complicated resonances are observed in the 147–165 ppm region with the main peak at 155.5 ppm. Additional features are observed in the 171–182 ppm region. These aged spectra will be interpreted and discussed elsewhere [25].

3.3. ^{13}C NMR spectra of selenocyanogen and selenium dicyanide

As reported in Table 1, the ^{13}C NMR spectrum of freshly prepared selenocyanogen [$Se_2(CN)_2$] in $CDCl_3$ solution shows a sharp singlet at 89.92 ppm. The presence of a unique singlet is in complete agreement with the fact that the correct structure of selenocyanogen is analogous to that assigned to thiocyanogen, NC–Se–Se–CN (**10**).

All other possible structures involving isoselenocyanide, Se=C=N–N=C=Se (**11**), and selenocyanide isoselenocyanide, Se=C=N–Se–CN (**12**), can be excluded completely. What is somewhat surprising is that the resonance of selenocyanogen appears at higher fields than that of thiocyanogen (89.92 ppm for the former versus 107.36 ppm for the latter), notwithstanding that these two compounds have the same general structure and that selenium and sulfur are very close in their chemical properties. At present we have no clear explanation for this difference, but it may be that if the Se–Se–C angle is different from the S–S–C angle this difference could affect the electronic shielding of the carbon nucleus leading to a difference in chemical shift.

As mentioned in Section 1, selenocyanogen is relatively stable at room temperature and we have tried to record also its solid-state ^{13}C NMR spectrum. This spectrum (see Table 1), was recorded only 3 weeks after selenocyanogen preparation. It is characterized by two main resonance peaks, one lying at 98.3 ppm and a doublet at about 130 ppm. Since only one resonance was detected in freshly prepared selenocyanogen solution, it is likely that some disproportionation or decomposition occurred in the solid during the 3 weeks after the preparation so that the solid-state spectrum now shows at least two resonance peaks. Since the well-known disproportionation reaction of selenocyanogen described in the literature [22–24] involves the reaction (Eq. (1)) showing that selenocyanogen is transformed into selenium dicyanide and selenium diselenocyanate in mild conditions, we tentatively assign the resonance due to selenium diselenocyanate the peak at 98.3 ppm, while the peak at about 130 ppm is assigned to selenium dicyanide by observing that sulfur dicyanide has a ^{13}C NMR signal (in solution) at 126 ppm.

3.4. FT-IR spectra of thiocyanogen and sulfur dicyanide

As shown in Table 2, the strong thiocyanogen band due to antisymmetric stretching of the –CN group has been observed

Table 2
Infrared band summary; values in cm^{-1}

Thiocyanogen film on KBr plate [a]	Thiocyanogen solution in carbon tetrachloride [b]	Thiocyanogen solution in carbon disulfide [b]	Thiocyanogen solution in ether [b]	Sulfur dicyanide [c]	Sulfur dicyanide (KBr pellet) [d]
2162 vs	2175 s	2171 s	2177 ms	2179 s (with 2188 sh)	2180 s
2073 m	1990 m		2030 m		
	1735 vw, br				
1660 s					
1415 mw					
	1350 vw, br				
1300 sh					
1220 m					
					1140 br
1060 mw					
780 sh					790 mw
					740 mw
670 m	668 s	673 s		684 s	685 m
600 w		667 s		665 vs	
				635 m	620 m
					600 w
					550 w
					525 w
440 vw		490 mw		499 vvw	465 w
					420 vw
	368 w	359 vw		374 w	
				329 w	

[a] From [17].
[b] From [9,10].
[c] From [8].
[d] This work.

in the range 2171–2177 cm^{-1} by various authors when the pseudohalogen was dissolved in organic solvents. By leaving some drops of thiocyanogen solution in CH_2Cl_2 to evaporate onto a KBr disk, it is possible to record the spectrum of almost ‘dry’ and still not polymerized thiocyanogen [17]. Under these special conditions, the strong band due to antisymmetric stretching appears at 2162 cm^{-1} while the band presumably due to symmetric stretching is detected at 2073 cm^{-1}. This is at a significantly higher frequency than the value detected in CCl_4 solution (1990 cm^{-1}) and in ether solution (2030 cm^{-1}) reported by other authors [9,10]. This suggests that this band is very sensitive to the nature of the solvent in which the molecule is dissolved [12]. The intense band at about 670 cm^{-1} is due to a C–S stretching band, confirming structure **1**.

An alternative and reasonable interpretation suggests that the band at 2073 cm^{-1} could be assigned to cyanide ion. In fact, sodium cyanide shows an IR band at 2060 cm^{-1} [15]. This assignment seems to confirm the NMR interpretation we have given in the preceding section about the decomposition of thiocyanogen in chloroform.

Table 2 shows also that the FT-IR spectrum of sulfur dicyanide is in reasonable agreement with previously published spectra. In particular, only one nitrile stretching band is observed at 2180 cm^{-1} in the solid state (KBr pellet). Thermodynamic calculations using the group increment method [29] give for thiocyanogen $\Delta G_f^o = 63.7$ kcal mol^{-1} and $\Delta H_f^o = 69.8$ kcal mol^{-1} (literature experimental data: $\Delta H_f^o = 74.3$ kcal mol^{-1}). Sulfur dicyanide is a slightly less endothermic compound, with $\Delta G_f^o = 61.4$ kcal mol^{-1} and $\Delta H_f^o = 64.0$ kcal mol^{-1}.

3.5. FT-IR spectra of selenocyanogen and selenium dicyanide

The IR spectrum of selenocyanogen in solution has been studied by several authors [20,21,23]. In this work we have recorded for the first time the FT-IR spectrum of selenocyanogen in KBr pellet. As shown in Table 3, there is generally good agreement between the main bands of $Se_2(CN)_2$ measured in solution and in the solid state. The nitrile stretching band of selenocyanogen was reported at 2152 cm^{-1} when measured in organic solvents [20], while it is shifted to 2143 cm^{-1} in KBr pellet followed by a weaker band at 1992 cm^{-1}. If the former stronger band is assigned to nitrile antisymmetric stretching then the weaker band at lower frequency is assignable to nitrile symmetric stretching. There are no indications about the presence of an isoselenocyanate group, since it is characterized by out-of-phase stretching at 2182 cm^{-1} and in-phase stretching mode at 983 cm^{-1} [30], which are completely absent from our spectra. The symmetric Se–C(N) stretching is reported as a strong band at 521 cm^{-1} in organic solvents whereas in KBr pellet it appears at 505 cm^{-1}; in the solid state we observe also another band at 580 cm^{-1} which could be due to antisymmetric Se–C(N) stretching. In the solid state we were able to observe also Se–CN bending at 436 cm^{-1}. Additionally, we have recorded other intense bands in the FT-IR spectrum of selenocyanogen in KBr. These bands were never reported previously because the spectra were recorded in organic solvents so that some spectral regions were buried by the intense absorption of the solvent, or at the time of the early measurements certain spectral regions were not accessible to the spectrophotometers or were not considered by the researchers. In fact, we observe additional bands at 3650, 3540 and 3434 cm^{-1}; these bands are strong and may be are only overtones or combination bands, but additionally we observe other two bands at 1640 and 1610 cm^{-1} which, however, remain unassigned. There are several other weak and very weak infrared bands (see Table 1) which were detected for the first time but which could also be due to impurities.

Also for selenium dicyanide (see Table 1), for the IR spectrum (in KBr) recorded on the sublimate formed by thermal decomposition of selenocyanogen there is a good general agreement between early reported spectra and the FT-IR reported here. The nitrile stretching appears in KBr pellet as a sharp peak at 2181 cm^{-1}, hence at higher frequency than selenocyanogen, in agreement with previous values reported at 2171 and 2183 cm^{-1} [20,21]. In agreement with previous measurements [20,21] we observe the antisymmetric C–Se stretching at 605 cm^{-1} and the symmetric C–Se stretching at 507 cm^{-1}. At 462 and 436 cm^{-1} we observe the C–Se bending mode. Again also in the case of selenium dicyanide we observe new IR bands never reported before, namely at 3649, 3589, 3581, 3453, 2922, 2851 cm^{-1} and at 1638, 1612 cm^{-1}. These bands remain unassigned; some of them could be due to impurities.

3.6. FT-IR spectrum of paraselenocyanogen

Concerning paraselenocyanogen or polyselenocyanogen there are no precise data available in the literature. In Section 2 we have shown that selenocyanogen undergoes a thermal decomposition reaction when heated at high temperature with liberation of a sublimate which was identified as selenium dicyanide by IR spectroscopy as just discussed, and the formation of a dark-brown insoluble product which is paraselenocyanogen and can be described by the general formula of $[Se_y(CN)_2]_x$ with $0 < y < 3$ and x very large. We will examine in more detail the paraselenocyanogen formation mechanism and its structural aspects elsewhere [25]. However, here we would like to report that the IR spectrum of paraselenocyanogen is very peculiar and is very similar to the spectrum of parathiocyanogen [17].

In fact, the spectrum of paraselenocyanogen is characterized by a very intense and broad band at 1200 cm^{-1} with a shoulder at 1263 cm^{-1}, two medium bands at 1444 and 1412 cm^{-1} and medium-weak bands at 1619 and 881 cm^{-1}. Weak bands are detectable at 801, 638, 609, 525 cm^{-1} as well as at 2262, 2184 and 2148 cm^{-1}. Since selenium diselenocyanate [$Se_3(CN)_2$] has only three main IR lines (see Table 3) which do not coincide at all with the spectrum of para-

Table 3
Infrared band summary; values in cm^{-1}

Selenium diselenocyanate (KBr) [a]	Selenocyanogen (KBr pellet) [b]	Selenocyanogen (chloroform) [a]	Selenium dicyanide (KBr pellet) [b]	Selenium dicyanide [a]	Selenium dicyanide [c]
	3650 ms		3649 vs		
	3625 sh		3627 sh		
	3583 sh		3589 vs		
	3540 vs		3544 sh		
			3518 vs		
	3434 vs		3435 m		
	2935 mw		2922 vs		
	2867 w		2851 ms		
	2656 w				
	2523 vw				
	2500 vw				
			2181 s	2171 s (KBr) [d]	2183
2131 ms	2143 vs	2152 vs			
	1992 br				
	1721 sh				
	1640 m		1638 m		
	1610 s		1612 vs		
	1503 vw				
	1460 vw		1449 ms		
			1345 w		
			1308 w		
	1280 m, br		1260 w		
			1228 w		
	1120 vw		1140 w		
	1080 vw		1055 w		
	1020 w		1020 w		
	990 sh		973 mw		
			925 mw		
	870 sh				
			839 mw		
	745 vw				
	580 br		605 br	608 m	608
513 s	505 vvs	521 vs	507 vvs	516 vs	516
			462 w		
	436 mw		436 w	436 w	
364 and 360 w	412 w	357 w		345 w	345
		333 w		336 w	
				312 w	310
				302 w	

[a] From [20].
[b] This work.
[c] From [21].
[d] In acetonitrile the bands are resolved at 2183 (sh) and 2175 (m).

selenocyanogen, we can conclude that the disproportionation reaction (Eq. (1)) happens under very mild conditions, while under strong heating the decomposition reaction of selenocyanogen is as follows:

$$2x\mathrm{Se}_2(\mathrm{CN})_2 \rightarrow x\mathrm{Se}(\mathrm{CN})_2 + [\mathrm{Se}_y(\mathrm{CN})_2]_x + x\mathrm{Se} \qquad (2)$$

$$(\text{with } 0<y<3)$$

The coincidence between the FT-IR spectra of paraselenocyanogen and parathiocyanogen shows only that selenocyanogen polymerizes like thiocyanogen by forming a polymer which should have the same structure of parathiocyanogen. Since we have proposed [15–17] that parathiocyanogen could have a linear structure rather than a triazine-based structure, we can conclude that paraselenocyanogen also has a linear structure because its spectrum is impressively similar to that of parathiocyanogen.

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