



^{Communication} ⁷⁷Se and ¹³C NMR Characterization of Selenium Cyanides

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Abstract: Here, we describe a magnetic resonance spectroscopy characterization of selenium cyanide compounds, $Se(CN)_2$, $Se_2(CN)_2$ and $Se_3(CN)_2$. Selenim-77 and carbon-13 nuclides were used to provide data of these species at room temperature. This is the first structural characterization performed using NMR for $Se_3(CN)_2$, while only low-temperature analyses have been conducted so far for $Se(CN)_2$ and $Se_2(CN)_2$. Based on these limitations, a characterization study was deemed mandatory, especially from a synthetic chemistry point of view. In addition to these analyses, we carried out a purity assessment for $Se_3(CN)_2$ according to the melting point parameter along with a solubility evaluation.

Keywords: selenium cyanides; NMR spectroscopy; melting point; solubility



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1. Introduction

Selenium cyanides are a class of inorganic compounds restricted to $Se(CN)_2$, $Se_2(CN)_2$ and $Se_3(CN)_2$ [1–5]. Among them is triselenium dicyanide (TSD), which demonstrates a synthetic utility in organic synthesis by allowing the electrophilic SeCN moiety to be inserted into more complex structures (Scheme 1) [6–8], and can be used for medicinal chemistry (Scheme 1).



Scheme 1. Functionalization of organic compounds by Se₃(CN)₂ prepared in situ.

For example, Kachanov and co-workers developed in 2004 a simple method for the introduction of the SeCN moiety in different aromatic amines containing free *para*position indoles and some active methylene as substrates, furnishing the corresponding selenocyanates compounds in good yields [6]. More recently, Myrboh and co-workers reported a direct and efficient one-step protocol for the selenocyanation of aryl methyl ketones/styryl methyl ketones by selenium dioxide and malononitrile to obtain the desired α -carbonyl selenocyanates, where TSD was employed as a selenocyanating agent formed in situ [8].

Although the in situ generation of TSD represents a fast and efficient pathway by which to insert the SeCN moiety [9], to expand its use in organic synthesis, it is necessary to access the isolated form, mainly due to the presence of unreacted SeO₂ in the reaction medium of the one-pot approach. Consequently, the thermal and moisture sensitiveness of TSD can affect the purification step and the isolated yield and prevent mass and NMR characterizations. In this sense, an X-ray diffraction study of TSD confirmed its triselenide bridge structure, in which it was observed that the CN groups are eclipsed [10]. However, X-ray is not an experimental protocol suitable for purity assessment and/or reaction monitoring.

TSD can be easily prepared via the exothermic reaction between malononitrile and selenium dioxide using DMSO as a solvent [6]. However, no further characterization has been obtained due its poor solubility in organic solvents, [10] and only X-ray crystal and solid-state nuclear magnetic resonance (NMR) analyses have been described [4,5,10,11]. On the other hand, Se(CN)₂ is stable, while Se₂(CN)₂ rapidly disproportionates [6,11]. Additionally, there are ⁷⁷Se and ¹³C NMR analyses of Se(CN)₂ and Se₂(CN)₂ species, but they were collected at low temperatures [10,12], which hamper a selenium chemical shift comparison for a mechanism evaluation and product identification.

In view of these limitations regarding the chemistry of selenium cyanides, and because most of the reactions with TSD have been carried out at room temperature [6–8], we report here the characterization of Se(CN)₂, Se₂(CN)₂ and Se₃(CN)₂ by ⁷⁷Se and ¹³C NMR spectroscopies in DMSO-d₆ solvent at room temperature (25 °C). In order to better understand the practical synthetic methodology used to access TSD from the reaction between malononitrile and selenium dioxide, we also evaluated the solubility and purification step by measuring the TSD melting point (MP) and collecting infrared (IR) absorption data.

2. Results

Se(CN)₂ and Se₂(CN)₂ were prepared according to Woollins and co-workers' methodology (see the Experimental Section) [10]. Se₃(CN)₂ (TSD) was prepared according to Kaminskii and co-workers' procedure (see the Experimental Section) [6]. The NMR analyses were performed at 25 °C, immediately after their preparation, due to the instability and/or disproportionation of selenium cyanide compounds. The samples were prepared by dissolving 5.0 mg of the compound in 0.75 μ L of the solvent. The purity of TSD was evaluated by measuring its melting point after five distinct protocols: washing with water, recrystallization in benzene, washing with ethanol, washing with dichloromethane and without any treatment (see the Experimental Section). Additionally, the solubility of TSD was evaluated in distinct deuterated solvents (CDCl₃, D₂O, Py-d₅, benzene-d₆, D₃COD, D₃CCN and DMSO- d₆). TSD was partially soluble in D₃COD, D₃CCN and DMSO-d₆. Centrifugation was necessary to remove the solid after partial solubilization in the deuterated solvent. Additionally, an infrared spectrum was collected to confirm the presence of the selenium cyanide species and compare it with the literature [10,11].

3. Discussion

The use of NMR spectroscopy to follow a reaction is an effective way to provide evidence for a mechanism [13,14]. NMR can provide structural details about the reactions, visualizing the consumption of starting materials and/or the formation of products, along with kinetic information obtained from the easy quantitative NMR evaluation. Additionally, to obtain more information regarding the reactivity of selenium species, ⁷⁷Se nuclide in NMR analysis is an important tool to for the structural elucidation of products and chemical intermediates [14]. Based on these features, our main idea was to acquire information on the ⁷⁷Se NMR chemical shifts of selenium cyanides, especially TSD, once it could be used to understand the reactivity of this species in the functionalization of heterocycles

(Scheme 1) [6–8]. For this purpose, we prepared TSD, employing SeO₂ (0.34 mmol) in the reaction with malononitrile (0.17 mmol) in 750 μ L of DMSO-d₆ (Scheme 2) [6], and then the ⁷⁷Se{¹H} NMR experiment was performed (Figure 1). It is important to mention that the NMR sample of TSD was centrifuged to eliminate the elemental selenium residue (Figure S1).

$$Se^{0} + SOCl_{2} \xrightarrow{} SeCl_{2} \xrightarrow{} SeCl_{2} \xrightarrow{} SeCN (1.0 \text{ equiv}) \rightarrow Se(CN)_{2}$$

(1.0 equiv) THF, 1 h, r.t.

AgSeCN +
$$I_2$$
 Ar Se₂(CN)₂
(1.0 equiv) (0.5 equiv) THF, 2 h, -20 °C

Scheme 2. Synthesis of Se(CN)₂, Se₂(CN)₂, and Se₃(CN)₂ species.



Figure 1. ⁷⁷Se{¹H} NMR experiments of Se(CN)₂ (red), Se₂(CN)₂. (green) and Se₃(CN)₂ (blue) in DMSO-d₆.

The recorded TSD ⁷⁷Se{¹H} NMR spectrum presented two signals, at δ = 390.7 and 261.3 ppm, which characterize the two types of selenium-77 nuclides in Se₃(CN)₂ (Figure 1). In the ¹³C{¹H} NMR spectrum, we observed a signal of carbon-13 at δ = 102.0 ppm; however, another lower signal at δ = 104.0 ppm was also present (Figure 2). To understand the ⁷⁷Se and ¹³C NMR profiles, Se(CN)₂ and Se₂(CN)₂ were prepared and analyzed using NMR spectroscopy (Scheme 2) [10]. At the beginning, we performed the ⁷⁷Se{¹H} NMR experiments for these selenium cyanide compounds using DMSO-d₆ as a solvent. Se(CN)₂ presented a selenium-77 signal at δ = 440.6 ppm, while Se₂(CN)₂ demonstrated a signal at δ = 261.1 ppm (Figure 1). As can be seen in the ⁷⁷Se NMR spectra, the lower signal frequency of Se₃(CN)₂ was similar to that of the Se₂(CN)₂ compound, while the higher



signal frequency was not close to that observed in the selenium-77 chemical shift of the $Se(CN)_2$ species.

Figure 2. ¹³C{¹H} NMR spectra of Se(CN)₂ (red), Se₂(CN)₂ (green) and Se₃(CN)₂ (blue) in DMSO-d₆.

Next, the ${}^{13}C{}^{1}H$ NMR spectra of Se(CN)₂ and Se₂(CN)₂ were acquired (Figure 2). The ¹³C-NMR spectrum of Se(CN)₂ presented a signal at $\delta = 103.7$ ppm, while Se₂(CN)₂ showed two signals, at $\delta = 101.97$ and 104.08 ppm. According to the literature, Se₂(CN)₂ disproportionates to the $Se(CN)_2$ species, which can be visualized by the presence of the peak at $\delta = 104.08$ ppm, due the higher stability of Se(CN)₂ [10]. Considering that Se₂(CN)₂ has an identical selenium-77 chemical shift with Se₃(CN)₂ (~261 ppm, Figure 1), we assume that the carbon-13 signal at $\delta = 104.48$ ppm in the TSD spectrum was due to the presence of $Se(CN)_2$, once the chemical shifts were similar. Additionally, other possible structures involving isoselenocyanides can be excluded, as observed by infrared (IR) spectroscopy, in which there were no other CN bands (Figures S10–S12) [11]. TSD was isolated, and then the solubility was checked in CDCl₃, D₂O, Py-d₅, benzene-d₆, D₃COD and D₃CCN deuterated solvents. Although TSD was soluble only in D_3COD and D_3CCN solvents, the ⁷⁷Se{¹H} NMR experiment of TSD in D_3 COD did not show signals, and the solution color changed to red (Figure S2). The 77 Se 1 H} NMR spectrum of TSD in D₃CCN demonstrated a variation in the selenium-77 chemical shifts in both ⁷⁷Se NMR signals for a higher frequency region than in DMSO-d₆ (Figure S9: $\delta = 452.8$ and 279.4 ppm).

Although it was possible to characterize all selenium cyanides, the purity of TSD should be evaluated before its proper use as a starting material in organic synthesis. An alternative protocol to check the purity of the TSD compound involves its melting point (MP), which is a practical procedure with a low cost and is properly described in the literature (133–134 °C) [6]. In this sense, TSD was prepared according to Kaminskii and co-workers' procedure [6], and then different purification protocols were evaluated, as can be seen in Table 1. According to the melting point study, the crude product had a distinct MP (Table 1, entry 1), possibly due to the presence of Se(CN)₂ along with the Se₃(CN)₂ starting material, as visualized in the ⁷⁷Se{¹H} NMR spectrum. When the yellow solid was washed with ethanol, the solid became red, exactly as observed in the solubility study, and the measured MP was 132–135 °C (Table 1, entry 4). The solid obtained after washing with water and dichloromethane also presented distinct MPs (Table 1; entries 2 and 5). Only after recrystallization with benzene did the obtained TSD present the correct MP (Table 1, entry 3).

Entry	Purification Protocol	Reference	Melting Point (°C)
1	_	6	134–136
2	Washed with water	7	134–136
3	Recrystallized in benzene	6	133–134
4	Washed with ethanol	_	132–135
5	Washed with dichloromethane	—	130–131

Table 1. Melting points of TSD employing distinct purification protocols ^a.

^a The melting point experiments were performed in triplicate.

Regarding the MP measures, small variations in their values were not sufficiently precise to assess the purity of the prepared TSD. Thus, ⁷⁷Se NMR analyses were performed as well to confirm the purity of the TSD after purification. As can be seen in the Supplementary Materials (Figures S10 and S11), the ⁷⁷Se NMR spectra collected after procedures of entries 2 and 3 (Table 1) demonstrate a great amount of Se(CN)₂, while the methodology of entry 4 (Table 1) did not show signals in the spectrum. Finally, when TSD was washed with dichloromethane, the ⁷⁷Se{¹H} NMR spectrum confirmed the higher purity of this selenium cyanide species. Although the MP experiment can be used to evaluate the synthetic protocol used to obtain TSD (Table 1), ⁷⁷Se NMR spectroscopy is the best choice to confirm its purity.

Once selenium cyanides were synthesized, the NMR experiments were immediately performed due to their instability and/or disproportionation [10,11]. Moreover, the use of TSD in situ minimizes costs and time; nonetheless, depending on the synthetic condition, it could be necessary to isolate TSD. In this case, a careful purification should be carried out once TSD disproportionates easily at room temperature under heating. Additionally, the presence of impurities, such as SeO₂ (Figures S10 and S11; selenium chemical shift δ around 808 ppm), is observed in the purification protocols (Table 1, entries 2 and 3); this accelerates the degradation process, during which the TSD solid rapidly becomes dark. Regarding the sensitivity to light, changes in the prepared TSD were not observed when it was exposed to light. The infrared (IR) analyses were also performed for all the selenium cyanide species, with the following vibrations for Se₃(CN)₂ being observed: strong nitrile stretching at 2130 cm⁻¹ and a weak band at 1646 cm⁻¹ along with a broad unassigned band at 3442 cm⁻¹ [10], which could be due to water and/or impurities, as observed in the $^{13}C{}^{1}H$ NMR spectrum (Figure S8). Se(CN)₂ and Se₂(CN)₂ IR analyses corroborated the literature [10], in which the main bands, such as CN at 2137 and 2139 cm⁻¹, and Se-CN at 668 and 671 cm⁻¹, respectively, could be observed with other band combinations.

4. Materials and Methods

The nuclear magnetic resonance (NMR) data were collected on a Bruker Avance III HD spectrometer operating at 400.0 MHz for ¹H, 100 MHz for ¹³C and 76.0 MHz for ⁷⁷Se. The concentration of all samples was approximately 5.0 mg/0.7 mL of deuterated solvent. NMR data were recorded at 25 °C, with chemical shifts δ reported in parts per million and coupling constants *J* in Hertz. The ⁷⁷Se{¹H} NMR spectra were referenced to diphenyl diselenide (δ = 463.0 ppm) using the substitution method (IUPAC) and the ¹³C{¹H} NMR spectra were referenced to DMSO-d₆ (δ = 39.51 ppm). All data were analyzed using MNova 7.1.1 (2012) software. The infrared analyses were performed with a Fourier Transformed Infrared Bruker Alpha-P spectrometer in the attenuated total reflection mode, and the samples were submitted to KI and placed on the crystal surface obtaining the IR spectra from an average of 24 scans at the range of 4000–1500 cm⁻¹.

All solvents and reagents (SeO₂ and malononitrile) are commercially available (Sigma Aldrich[®], St. Louis, MI, USA) and were used without any previous treatment.

5. Conclusions

In conclusion, we have characterized the selenium cyanide species, $Se(CN)_2$, $Se_2(CN)_2$ and $Se_3(CN)_2$, using NMR (at 25 °C) and IR spectroscopies. This is an important contribu-

tion, as it facilitates the characterization of these starting materials, especially by ⁷⁷Se NMR spectroscopy, spreading their application in organic synthesis and assisting the elucidation of reaction mechanisms through the identification of organoselenium products, byproducts and chemical intermediates. Additionally, we have demonstrated the utility of the melting point parameter to assess the purity of the triselenium dicyanide species in a simple and low-cost procedure. The aggregation of different types of data, as well as the solubility and stability results described here, are imperative to providing new applications for the selenium cyanide species.

Supplementary Materials: The following are available online. Figures S1–S14: ¹³C and ⁷⁷Se NMR spectra, FT-IR spectrum along with the synthetic and purification procedures. Table S1: Melting points results.

Author Contributions: M.S.S. designed and conceived the whole NMR experiment and wrote and reviewed the manuscript; E.J.L. wrote, reviewed and edited the manuscript; J.M.A., S.S.F. and F.P. developed the synthetic methodology and performed the reactions. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Sample Availability: Samples of the compound Se₃(CN)₂ are available from the authors.

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