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Research Article

Synthesis of ^{13}C-labelled tetramethyltetraselenafulvalene

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Summary

The synthesis of tetramethyltetraselenafulvalene (4,4′,5,5′-tetramethyl $\Delta^{2,2'}$-bis-1,3-diselenole) doubly labelled with carbon-13 in the 2 and 2′-positions is described. Copyright © 2001 John Wiley & Sons, Ltd.

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Introduction

The radical cation salts of tetramethyltetraselenafulvalene (TMTSF) are a fascinating class of materials, where solid state physics phenomena such as metallic conductivity, superconductivity and spin density waves (SDW) can be observed within an isostructural class of salts $(TMTTF)_2^+ X^-$ and $(TMTSF)_2^+ X^-$ depending on the nature of the anion, temperature, applied pressure, and applied magnetic or electrical fields.[1–10]

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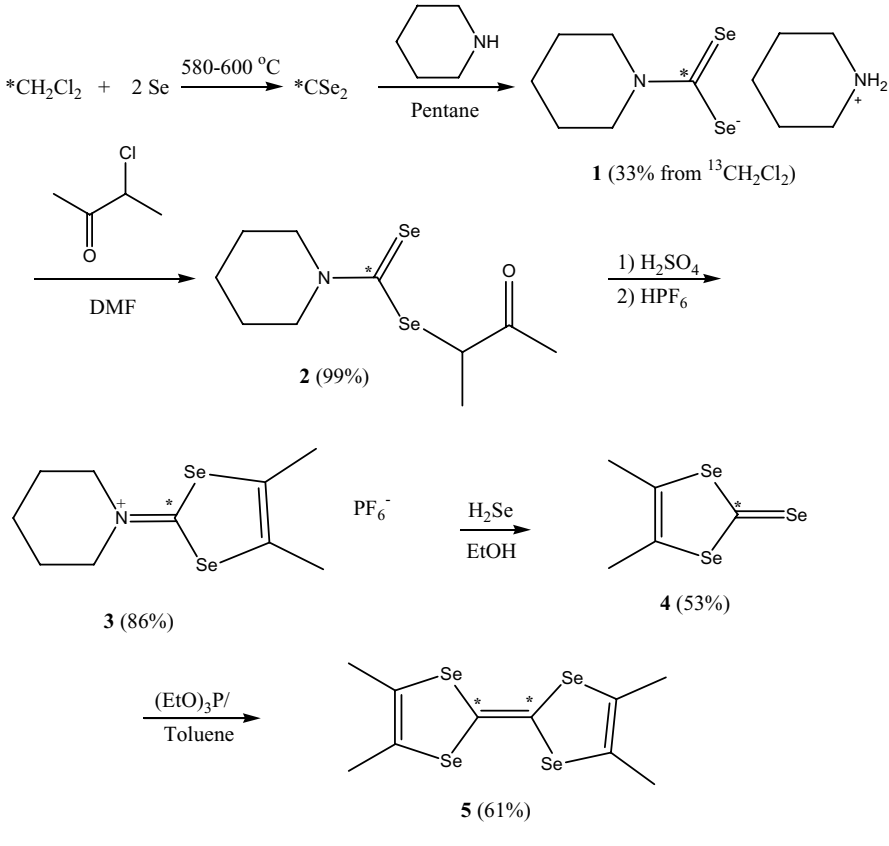
Results and discussion

In order to perform ^{13}C-NMR experiments on $(TMTSF)_2^+ClO_4^-$ in the superconducting solid state access to ^{13}C-labelled TMTSF was needed. Our earlier synthetic work[11] had been directed towards partially labelled material, in order to avoid unwanted intra stack ^{13}C–^{13}C couplings and the synthesis of TMTSF partially ^{13}C-labelled in the 2-position was based on ^{13}C-labelled *N*,*N*-dimethylphosgeneiminium chloride, which was prepared from $^{13}CS_2$. TMTSF obtained by this method might contain traces of sulphur as an impurity, which would affect the superconducting properties of the labelled $(TMTSF)_2^+ClO_4^-$. Therefore, we had to develop the present synthesis shown in Scheme 1.

The synthesis is a ^{13}C-version of one of the published methods.[12,13] Our synthesis starts from $^{13}CH_2Cl_2$, which is converted to $^{13}CSe_2$ by



Scheme 1. Synthetic Procedure (*denotes ^{13}C)

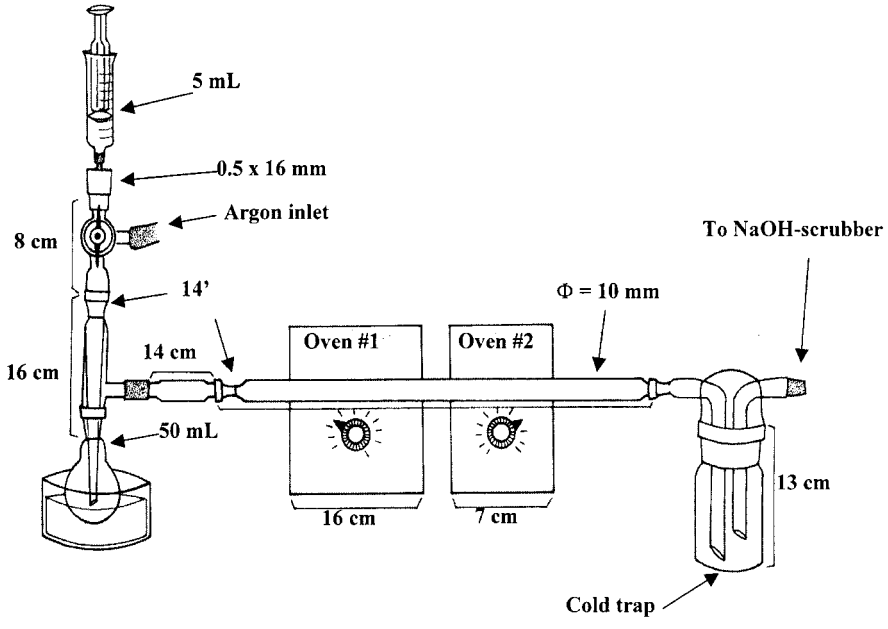


Figure 1. Experimental set-up for the synthesis

reaction with elemental Se in the gaseous phase. The conditions for this reaction had to be carefully studied, because the existing procedures for the synthesis of CSe_2 are all based on the use of a large excess CH_2Cl_2 and operate on up to a 500 g (of CSe_2) scale.[14–16] We decided to optimize the synthesis on a stochiometric scale using 4.00 g (46.6 mmol) of $^{13}CH_2Cl_2$ and 8.0 g (101 mmol) Se. The experimental set-up used is shown in Figure 1.

Experiments showed, that the crucial parameter for obtaining a good yield of CSe_2 is the rate of addition of CH_2Cl_2, and after some experimentation, the present delivery system was developed. It consists of a syringe with a short needle, and allows a slow addition of $^{13}CH_2Cl_2$ driven by its vapour pressure. The $^{13}CH_2Cl_2$ is vaporized in the heated flask and swept into the oven by a slow stream of Ar, where the reaction with Se takes place. The products are collected in a cold trap kept at -60^oC. In order to avoid the problems associated with distillation of the toxic and very bad-smelling CSe_2, the condensate was dissolved in pentane, filtered to remove elemental Se, and converted directly to the piperidinium 1-piperidino diselenocarbamate needed for the synthesis.

Experimental

*Piperidinium 1-piperidine[^{13}C]diselenocarbamate (**1**)*

Selenium powder (8 0 g; 101 mmol) was spread in the pyrolysis tube in the part of the tube placed in oven #1. The system was assembled, and a stream of Ar was passed through for 30 min in order to remove any oxygen. A NaOH-scrubber was included at the outlet from the system in order to remove any traces of H_2Se and CSe_2. The Ar-flow was adjusted to approximately 25 bubles/10 s measured at the NaOH-scrubber. The ovens and the oil bath were turned on, and a syringe containing the $^{13}CH_2Cl_2$ was placed in the septum of the inlet system, when the temperatures were the following: 580°C in the long oven, 600°C in the short oven and approximately 120°C in the oil bath. The addition of $^{13}CH_2Cl_2$ works largely by itself due to the high vapour pressure of CH_2Cl_2, but occasionally some limited warming of the syringe was necessary. The addition took 1.5 h, and after the addition was complete, the flow and heating continued for further a 30 min in order that all $^{13}CSe_2$ was removed from the ovens and into the cold trap. The system was allowed to cool down to room temperature in an Ar-stream, and the yellow–black suspension in the cold trap was diluted with pentane (500 ml in total) and filtered through a paper filter into a flask. Piperidine (8.0 g; 94 mmol) dissolved in pentane (100 ml) was added with stirring to the solution of crude $^{13}CSe_2$ whilst keeping the temperature at 0°C. The yellow precipitate of **1** was filtered and dried in vacuum. Yield: 5.21 g (33%). ^{1}H-NMR (400 MHz; D_2O) δ: 4.33 (m; 4 H); 3.11 (m; 4 H); 1.72 (m; 4 H); 1.63 (m; 8 H). ^{13}C-NMR (100 MHz; D_2O) δ: 194.43 (^{13}C–Se satellite coupling); 193.48 (^{13}C–Se); 192.52 (^{13}C–Se satellite coupling); 56.63; 44.48; 25.44; 23.40; 22.19; 21.44. HRMS (EI): *m*/*z*: calculated for $C_5{}^{13}CH_{10}NSe_2$: 257.9258 (M^+); found: 257.9236.

*1-Piperidine [^{13}C]carbodiselenoic acid, 1-methyl-2-oxopropyl ester (**2**).*

Compound **1** (5.0 g; 16 mmol) was dissolved in degassed DMF (50 ml). Freshly distilled 3-chloro-2-butanone (2.0 g; 19 mmol) was added, and the mixture was stirred at room temperature for 1 h. The mixture was poured into ether (100 ml) and washed with water (150 ml). The organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give crude **2**. Yield: 4.9 g (99%). An analytical sample was purified by crystallization from cyclohexane. ^{1}H-NMR (250 MHz;

$CDCl_3$) δ: 5.21 (m; 1 H); 4.54 (m; 1 H); 4.42 (m; 1 H); 3.86 (m; 2 H); 2.37 (s; 3 H); 1.63 (broad s; 6 H); 1.62 (t, J = 7 Hz; 3 H). ^{13}C-NMR (63 MHz; $CDCl_3$) δ: 194.34 (^{13}C–Se satellite coupling); 193.66 (^{13}C–Se satellite coupling); 192.47 (^{13}C = Se); 191.29 (^{13}C–Se satellite coupling); 190.61 (^{13}C–Se satellite coupling); 160.69; 58.66; 58.49; 55.48; 28.15; 25.99; 25.29; 23.90; 16.19. δ: HRMS (EI): m/z: calculated for $C_9\,^{13}CH_{17}NOSe_2$: 327.9677 (M^+); found: 327.9633.

*2-(1-Piperidinium)-2-[^{13}C]-4,5-dimethyl-1,3-diselenole hexafluorophosphate (**3**)*

The crude diselenocarbamate (**2**) (4.7 g; 15 mmol) was added to cold, concentrated H_2SO_4 (100 ml) with stirring at such a rate that the temperature in the mixture was kept below 0°C. After the addition was complete, the mixture was stirred in an ice bath for 1 h, and poured onto crushed ice (500 ml) containing 60% aqueous HPF_6-solution (25 mL). The precipitated product was filtered, washed with water and dissolved in CH_2Cl_2. The organic phase was separated, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give crude **3** (5.9 g; 86%). An analytical sample was purified by precipitation from CH_2Cl_2 with ether. ^{1}H-NMR (400 MHz; $CDCl_3$) δ: 3.75 (m; 6 H); 2.29 (m; 4 H); 1.92 (m; 4 H); 1.77 (m; 2 H). ^{13}C-NMR (100 MHz; $CDCl_3$) δ: 189.51 (^{13}C–Se satellite coupling); 188.70 (^{13}C–N$^+$); 187.90 (^{13}C–Se satellite coupling); 133.11; 60.12; 25.09; 21.00; 15.60; 15.57. (HRMS (EI): m/z: calculated for $C_9\,^{13}CH_{16}NSe_2$: 310.9649 (M^+); found: 310.9659.

*2-[^{13}C]-4,5-Dimethyl-1,3-diselenole-2-selone (**4**)*

To a stirred suspension of selenium powder (1.1 g;. 14 mmol) in EtOH (50 ml) was added $NaBH_4$ (0.8 g; 21 mmol) in small portions (extensive foaming observed) to give a clear solution. Acetic acid (0.80 ml; 0.84 g; 14 mmol) was added followed at once by addition of compound **3** (5.0 g; 11 mmol). The clear solution turned red immediately, and stirring was continued for 30 min. The mixture was poured into water and filtered. The crude **4** was dissolved in CH_2Cl_2 and dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude selone was crystallized from toluene to give **4** (1.92 g; 53%). ^{1}H-NMR (250 MHz; $CDCl_3$) δ: 2.26 (s; 6 H). ^{13}C-NMR (63 MHz; $CDCl_3$) δ: 220.96 (^{13}C–Se satellite coupling); 208.36 (^{13}C–Se satellite coupling); 207.89 (^{13}C–Se satellite coupling); 206.47 (^{13}C = Se); 205.06 (^{13}C–Se satellite coupling); 204.59

(^{13}C–Se satellite coupling); 188.86 (^{13}C–Se satellite coupling); 144.97; 15.50. HRMS (EI): calculated for $C_4\,^{13}CH_6Se_3$ (M^+): 304.8011; found: 304.8013.

2,2′-[^{13}C]-Tetramethyltetraselenafulvalene (5) (2,2′-[^{13}C]-4,4′,5,5′ tetramethyl $\Delta^{2,2'}$-bis-1,3-diselenole)

Freshly distilled triethyl phosphite (2.0 mL; 1.9 g; 12 mmol) was added to a refluxing solution of **4** (1.92 g; 6.3 mmol) in toluene (25 ml). Reflux was continued for 1 h, and the mixture was cooled in an ice/water bath. The product was filtered, washed with ether and dried. Yield: 0.87 g (61%) of purple crystals. ^{1}H-NMR (250 MHz; $CDCl_3$) δ: 1.98 (s; 6 H). ^{13}C-NMR (63 MHz; $CDCl_3$) δ: 127.13 (^{13}C–Se satellite coupling); 103.53 ($^{13}C = {}^{13}C$); 77.09 (^{13}C–Se satellite coupling); 15.99. HRMS (EI): calculated for $C_8\,^{13}C_2H_{12}Se_4$ (M^+): 451.7683; found: 451.7658.

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References

1. Jerome D. *J Phys IV* 2000; **10**: 69.
2. Jerome D, Mazaud A, Ribault M, Bechgaard K. *J Phys Lett* (*Orsay, France*) 1980; **41**: 95.
3. Bechgaard K, Carneiro K, Rasmussen F, Olsen M, Rindorf G, Jacobsen CS, Pedersen HJ, Scott JC. *J Am Chem Soc* 1981; **103**: 2440.
4. Barthel E, Quiron G, Wzietek P, Jérome D, Christensen JB, Jørgensen M, Bechgaard K. *Europhys Lett* 1993; **21**: 87.
5. Barthel E, Kriza G, Quiron G, Wzietek P, Jérome D, Christensen JB, Jørgensen M, Bechgaard K. *J Phys* (*Paris*) *IV* 1993; **3**: 231.
6. Barthel E, Quiron G, Wzietek P, Jérome D, Christensen JB, Jørgensen M, Bechgaard K. *Synth Met* 1993; **55–57**: 2581.
7. Barthel E, Kriza G, Quiron G, Wzietek P, Jérome D, Christensen JB, Jørgensen M, Bechgaard K. *J Phys* (*Paris*) *I* 1993; **3**: 1501.
8. Barthel E, Kriza G, Quiron G, Wzietek P, Jérome D, Christensen JB, Jørgensen M, Bechgaard K. *Phys Rev Lett* 1993; **71**: 2825.

9. Chow DS, Zamborszky F, Alavi B, Tantillo DJ, Baur A, Merlic CA, Brown SE. *Phys Rev Lett* 2000; **85**: 1698.
10. Merlic CA, Baur A, Tantillo DJ, Brown SE. *Synth Commun* 1999; **29**: 2953.
11. Christensen JB, Jørgensen M, Bechgaard K. *Unpublished work*.
12. Bechgaard K, Cowan DO, Bloch AN. *J Org Chem* 1975; **40**: 746.
13. Engler EM, Patel VV. *J Am Chem Soc* 1974; **96**: 7376.
14. Henriksen L, Kristiansen ES. *Int J Sulfur Chem Part A* 1972; **2**: 13.
15. Brereton MP, Cooper MK, Dennis GR, Ritchie GLD. *Aust J Chem* 1981; **34**: 2253.
16. Pan W-H, Fackler JP Jr, Chen H-W. *Inorg Chem* 1981; **20**: 856.

