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Studies of the thermal decomposition of some diselenocarbamato complexes of cadmium or zinc: molecular design for the deposition of MSe films by CVD

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The compounds $M(Se_2CNEt_2)_2$, M = Zn **1** or Cd **2**, $M(Se_2CNMe^nHex)_2$, M = Zn **3** or Cd **4**, and $ZnEt(Se_2CNEt_2)$ **5** have been investigated by GC-MS and EI-MS in an attempt to determine why **1** and **2** often deposit films containing an excess of selenium by metal organic chemical vapour deposition (MOCVD) whereas **3**, **4** and **5** give MSe (M = Zn or Cd). The EI-MS of all five selenium compounds revealed similar decomposition pathways, which start with loss of an alkyl group. However, studies of compounds **1–5** by pyrolysis GC-MS showed that selenium clusters Se_n, $n = 1–7$, are formed in the vapour phase from **1** and **2**. Compounds **1**, **2** and **5** also form significant quantities of diethyl diselenide ($EtSe_2Et$) in the ratio of 1 : 0.9 : 0.2 respectively, as detected by GC-MS, whereas **3** and **4** do not.

Introduction

A number of approaches have been developed toward the deposition of metal selenide thin films from single source precursors.[1–6] We have been particularly interested in the deposition of thin films of chalcogenide containing materials from diseleno- or dithio-carbamato and related complexes with zinc or cadmium.[7–13]

Although air-stable dithiocarbamate (dtc) complexes such as $M(S_2CNRR')_2$ (M = Zn or Cd, R and R′ are alkyl groups) are useful for the deposition of sulfide films.[9–13] Simpler selenium analogues such as the diethyldiselenocarbamates (dsc) [$M(Se_2CNEt_2)_2$, M = Zn **1** or Cd **2**] are poor precursors as the ZnSe or CdSe films deposited tend to be contaminated with an excess of selenium (*e.g.* at 10^{-3}–10^{-4} Torr, 370–420 °C).[14] More recently we have been able to deposit metal selenides from compounds such as $M(Se_2CNMe^nHex)_2$, M = Zn **3** or Cd **4**, which have two different alkyl substituents at the nitrogen.[15] This paper presents our first efforts to understand the mechanisms which might underlie these observations. Compounds **1–5** have been investigated by EI-MS and high resolution pyrolysis GC-MS in an attempt to understand their behaviour as suitable CVD precursors.

Experimental

Reagents were obtained from Aldrich Chemical Co. and solvents from B.D.H. ^1H NMR spectroscopy was carried out on a Bruker AM500 Fourier-transform instrument. Elemental analysis was performed by the Imperial College Chemistry Departmental service. A Micromass AutoSpec-Q, using Micromass OPUS software was used for EI-MS. FAB spectra were also recorded and the conditions were: matrix, 3-nitrobenzyl alcohol; primary ion beam, 35 keV Cs^+. An electron impact energy of 70 eV at 10^{-7} Torr was used to initiate mass fragmentation. A GC-MS analysis of the samples was carried out using a Hewlett-Packard Series II Gas/Liquid Chromatograph linked to a JEOL JMS AX505W Mass Spectrometer. The chromatography conditions were as follows: column BP1 (Supplied by SGE); bonded phase methyl siloxane, length 25 m, inner diameter 0.22 mm; phase thickness 0.25 μm. The temperature programme employed for analysis was: initial temperature 30 °C, initial time 2 min, 8 °C min^{-1} to 100 °C (first ramp rate), 12 °C min^{-1} (second ramp rate), final temperature 280 °C. The injector temperature was 370 °C and the carrier gas was helium at 12 psi, flow rate 1 $cm^3 min^{-1}$. MS settings were: 3 kV accelerating voltage, 100 μA beam current and 2kV detector voltage. Mass spectra were recorded between 10 and 600 amu with a scan speed of 0.9 s. The precursor (100 mg) was dissolved in chloroform (5 ml) and 1 μl aliquots were injected onto the heated injector with a 30 : 1 split where pyrolysis occurred. Mass spectra of the volatile pyrolysates were recorded as described above.

Preparation of compounds

CSe_2. CSe_2 was prepared by a modification of the method of Henriksen and Kristiansen.[16] **CAUTION**: carbon diselenide is a very toxic, evil-smelling liquid and extreme caution must be observed during preparation and manipulation. All experimental procedures must be carried out in a fume hood and under nitrogen. Approximately 10 g selenium powder yielded approximately 10 g of carbon diselenide. In general, three runs were carried out before purification and isolation of the product. The black residue from the reaction was filtered through neutral alumina and washed through with dichloromethane. The excess CH_2Cl_2 was then removed from the filtrate by distillation (40 °C, atmospheric pressure), leaving a black oily residue which was vacuum distilled (50 °C, 10^{-2} Torr) to give an intensely bright yellow liquid which was collected in a liquid nitrogen trap at −196 °C. Overall yield for the experiment was approximately 30–35 g (69% based on 30 g of selenium). The CSe_2 was placed in an air-tight container and kept indefinitely at −25 °C.

$M(Se_2CNEt_2)_2$, M = Zn 1 or Cd 2. Compounds **1** and **2** were prepared by a slight modification of the methods of Barnard and Woodbridge[17] and Fulrani *et al.*[18] The CSe_2 was used immediately after preparation and allowed to react with an excess of diethylamine in pentane at 0 °C to give diethyldiselenocarbamate as the diethyl ammonium salt.[19] The selenocarbamate was then allowed to react with a stoichiometric quantity of an aqueous solution of zinc sulfate to give an insoluble yellow precipitate of compound **1** $Zn(Se_2CNEt_2)_2$. The crude product was recrystallised from toluene to give yellow cubic crystals. Compound **2** $Cd(Se_2CNEt_2)_2$ was prepared by a similar method using cadmium chloride.

$ZnEt(Se_2CNEt_2)$ 5. All reactions were performed in an inert atmosphere using standard Schlenk techniques and a vacuum line. Compound **5** was prepared as reported previously.[20]

$M(Se_2CNMe^nHex)_2$, M = Zn 3 or Cd 4. Compounds **3** and **4** were prepared using an analogous method to that reported for related compounds.[15]

Results and discussion

EI-MS analysis of compounds 1–4

Initially compounds **1–4** were studied by EI-MS. Fragmentation patterns for $Zn(Se_2CNEt_2)_2$ **1** and $Zn(Se_2CNMe^nHex)_2$ **3** are shown in Scheme 1 and seem to suggest that the major decomposition product should be ZnSe. The EI-MS of $Zn(Se_2CNMe^nHex)_2$ **3** follows a similar fragmentation route to $Zn(Se_2CNEt_2)_2$ **1**. The molecular ion M^+ of $Zn(Se_2CNMe^nHex)_2$ **3** sequentially loses propene, selenium, n-propyl, methane and CN moieties to give a peak at *m*/*z* 430 assignable to $Me^nHexNCSe_2ZnSe^+$ (step 1). The second step of the fragmentation pattern is observed to follow two paths A and B. In path A selenium is first lost followed by the loss of the neutral ZnSe fragment; in path B the reverse is true and ZnSe is lost before selenium. Both paths A and B merge giving the common ion $Me^nHexNCSe^+$ of *m*/*z* 206. The same mechanism is applicable to $Cd(Se_2CNMe^nHex)_2$ **4**.

High resolution pyrolysis GC-MS analysis of compounds 1–5

The observed decomposition mechanisms from EI-MS for $Zn(Se_2CNEt_2)_2$ **1**, $Cd(Se_2CNEt_2)_2$ **2**, $Zn(Se_2CNMe^nHex)_2$ **3** and $Cd(Se_2CNMe^nHex)_2$ **4** are very similar; and thus little can be inferred as to why there is a difference between the two sets of compounds. The key to determining the mechanisms which are governing the success of precursors **3** and **4** over **1** and **2** is carrying out decomposition under conditions similar to those found in an MOCVD reactor. There are a number of techniques that allow such analyses, *e.g. in situ* mass spectrometry within the reactor or TGA-MS; however, the versatile pyrolysis GC-MS technique provides the opportunity to observe the precursor's behaviour over a range of deposition temperatures comparable to those within a CVD reactor.

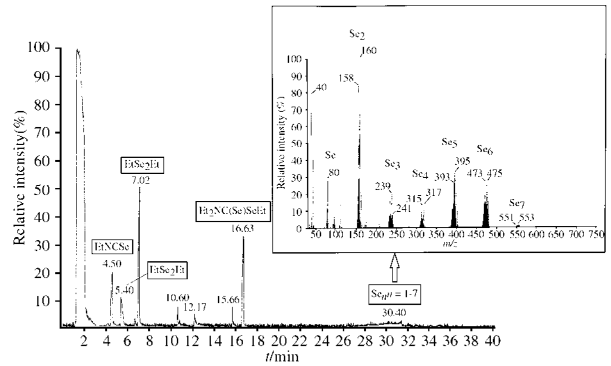
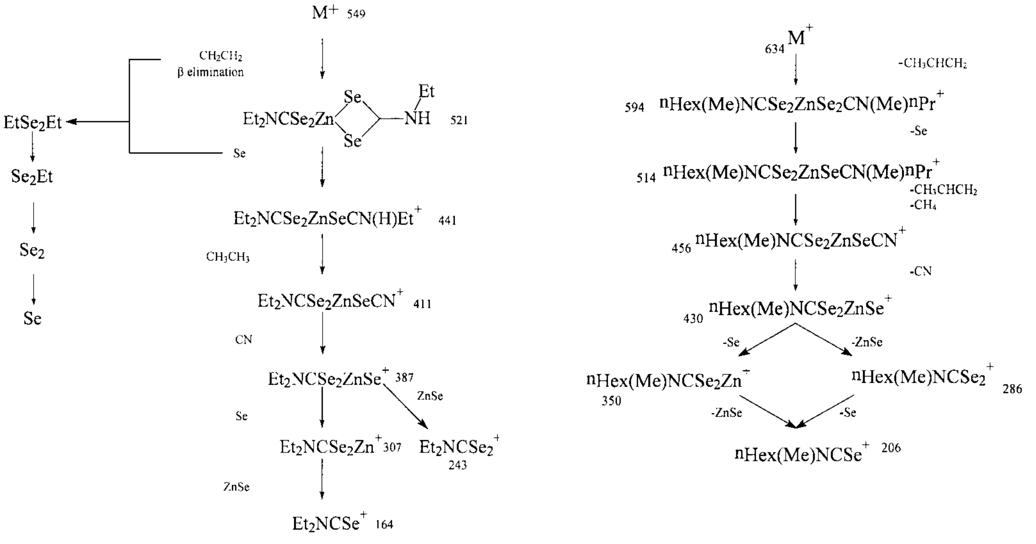


Fig. 1 Gas chromatogram of the volatile pyrolysis products from $Zn(Se_2CNEt_2)_2$ **1**. Inset: mass spectrum of volatile pyrolysate observed at R_t 30.40 min for **1**, showing the presence of selenium clusters. Injector temperature 370 °C, helium at 12 psi, flow rate 1 cm^3 min^{-1}. The precursor (100 mg) was dissolved in chloroform (5 ml) and 1 µl aliquots were injected onto the heated injector with a 30 : 1 split where pyrolysis occurred.

The gas chromatogram of volatile pyrolysis products of $Zn(Se_2CNEt_2)_2$ **1** is shown in Fig. 1. A similar gas chromatogram is observed for $Cd(Se_2CNEt_2)_2$. Fig. 1 shows four main decomposition products with retention times of R_t 4.50, 7.02, 16.63 and 30.40 min. The mass spectrum of the peak at R_t 30.40 (inset to Fig. 1) is interesting. The pattern of this peak (averaged over 110 scans) clearly shows a set of masses with an incremental value of *m*/*z* 78/80 up to 551/553. The GC-MS trace of $Cd(Se_2CNEt_2)_2$ **2** has a peak at the retention time of R_t 23.60 min which shows the same pattern in the mass spectrum (incremental value of *m*/*z* 78/80 to 553/555 averaged over 50 scans). Patterns in these mass spectra strongly suggest that selenium clusters are being formed on pyrolysis of the precursor. These species may be responsible for the deposition of selenium during MOCVD. A GC-MS was undertaken on pure selenium powder to see if a similar GC-trace pattern could be observed; it was found that although selenium has a mp of 217 °C, it does not pass through the gas chromatogram. This result suggests that the selenium clusters are formed *via* an intermediate organo-selenium complex that can pass through the gas chromatogram. One organo-selenium derivative which could decompose to give clusters of selenium is $EtSe_2Et$, which is observed in the pyrolysis experiment. The mass fragmenta-



Scheme 1 Plausible decomposition mechanisms for $Zn(Se_2CNEt_2)_2$ **1** and $Zn(Se_2CNMe^nHex)_2$ **3** combining the steps observed from GC-MS and EI^+ studies of the precursors.

tion pattern for $EtSe_2Et$, taken for the peak at R_t 7.02 min, shows that the $EtSe_2Et$ molecule dissociates Se_2 and Se, eqns. (1) to (4).

$$EtSe_2Et \rightarrow Se_2Et + Et \quad (1)$$

$$Se_2Et \rightarrow Se_2 + Et \quad (2)$$

$$Se_2 \rightarrow 2Se \quad (3)$$

$$Se_2Et \rightarrow SeEt + Se \quad (4)$$

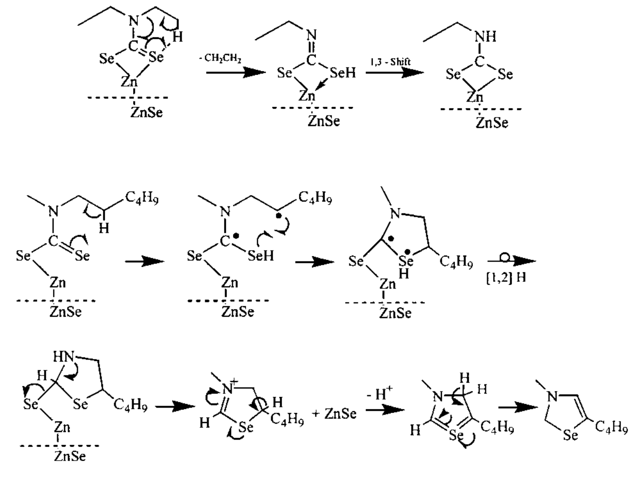
One route for the formation of $EtSe_2Et$ is shown in Scheme 1. Ethene radicals that are lost in the first step can react with the selenium lost in the following step to give the $EtSe^{\cdot}$ radical during the volatilization of the precursor. This $EtSe^{\cdot}$ radical probably dimerises to give $EtSe_2Et$. The GC-MS trace for $Cd(Se_2CNEt_2)_2$ **2** also has a peak (R_t 8.0 min) with a pattern in the mass spectrum consistent with $EtSe_2Et$, eqn. (1).

Combining the steps observed from GC-MS and EI^+ studies of the precursors, a plausible decomposition pathway for $Zn(Se_2CNEt_2)_2$ **1** from the GC-MS data is given in eqns. (5), (6) and (1)–(4) (any ZnSe formed will be involatile which is consistent with the results of thermogravimetric analysis).[21]

$$2Zn(Se_2CNEt_2)_2 \rightarrow EtSe_2Et + Et_2NCSe_2Et + 2ZnSe + 3CNEt + Se_2 \quad (5)$$

$$Et_2NCSe_2Et \rightarrow Et_2NH + CSe_2 + C_2H_4 \quad (6)$$

The formation of diethyl diselenide may be one cause of selenium contamination of films deposited from this precursor; it is also possible that a surface bound diethyl-dsc may lose ethene leaving behind two selenium atoms to one zinc atom coordinated as shown in Scheme 2, again resulting in excess selenium in the film. The ethene could be lost by abstraction of the hydrogen from the primary carbon of the ethyl group by selenium, giving the selenium hydride intermediate. This is followed by a 1,3-shift to return the hydrogen to the nitrogen. Thus there are two complementary pathways that can lead to elemental selenium: (1) the formation of diethyl diselenide, and (2) successive elimination of ethene at the surface to leave behind an excess of selenium on the surface of the film.



Scheme 2 Mechanism for the formation of ethene and the five-membered ring heterocycle from $Zn(Se_2CNEt_2)_2$ **1** and $Zn(Se_2CNMe^nHex)_2$ **3** respectively.

The GC trace of volatile pyrolysates for $Zn(Se_2CNMe^nHex)_2$ **3** is shown in Fig. 2. $Me^nHexNCSe$ was the most abundant species formed (R_t 18.25 min). $Me^nHexNCSe$ was the next most abundant species formed (R_t 8.32, 8.92, 9.67 min). In contrast to $Zn(Se_2CNEt_2)_2$ **1**, there is no evidence for the formation of selenium clusters, or the volatile organo-selenium complex $EtSe_2Et$ from $Zn(Se_2CNMe^nHex)_2$ **3** or $Cd(Se_2CNMe^nHex)_2$ **4**. The first organo-selenium decomposition products from $Zn(Se_2CNMe^nHex)_2$ do not appear until R_t 18.25 min at a temperature of 120 °C. An important peak at 26.39 min is due to a five-membered dihydroselenazole[22] heterocyclic ring system **6**; this species is observed at comparable conditions to those in a LP-MOCVD reactor and may be a key decomposition product.

It is plausible that the dihydroselenazole is formed by the elimination of β-hydrogen which leaves behind a secondary radical which is more reactive and leads to the formation of a five-membered ring intermediate. In this case the five-membered ring formed is stabilised by the n-butyl group resulting in the possibility of clean elimination of the dihydroselenazole ring system leaving behind the metal selenide (refer to Scheme 2). The proton transfer reaction could be achieved in several ways to any neighbouring Lewis base, *e.g.* to surface bound species. One attractive possibility would be if the intact bis-diselenocarbamato complex bound to the surface. In this case transfer of the proton from one side of the complex to the other could lead to clean elimination of the dihydroselenazole, ZnSe and the diselenocarbamic acid; the latter would rapidly decompose to volatile side products (Table 1).

The pyrolysis GC decomposition products of $ZnEt(Se_2CNEt_2)$ **5** have also been compared to those of $Zn(Se_2CNEt_2)_2$ **1**. The major decomposition peaks are similar to those observed for the bis complexes **1** and $Cd(Se_2CNEt_2)_2$ **2**. However for **5**

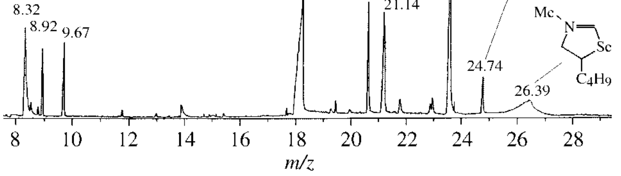


Fig. 2 Gas chromatogram of volatile pyrolysates from $Zn(Se_2CNMe^nHex)_2$ **3**. Injector temperature 370 °C, helium at 12 psi, flow rate $1\ cm^3\ min^{-1}$. The precursor (100 mg) was dissolved in chloroform (5 ml) and 1 μl aliquots were injected onto the heated injector with a 30 : 1 split where pyrolysis occurred.

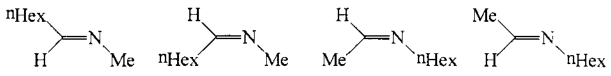
Table 1 GC-MS data of $Zn(Se_2CNEt_2)_2$ **1** and $Cd(Se_2CNEt_2)_2$ **2**

R_t/min				
1	**2**	*m/z* for M^+	Empirical formula	Possible structural assignment
4.50	5.20	135	C_3H_5NSe	EtNCSe
7.02	7.66	218	$C_4H_{10}Se_2$	$EtSe_2Et$
5.40	—	218	$C_4H_{10}Se_2$	$EtSe_2Et$
10.60	—	165	$C_9H_{20}NSe$	$Et_2NC(Se)NEt_2$
12.17	—	265	—	—
15.66	15.71	259	$C_6H_{15}NSe_2$	$Et_2NC(Se)SeMe$
16.63	16.40	273	$C_7H_{15}NSe_2$	$Et_2NC(Se)SeEt$
30.40	23.60	553	Se_7	Se_n, $n = 1–7$

Table 2 GC-MS data of $Zn(Se_2CNMe^nHex)_2$ **3** and $Cd(Se_2CNMe^nHex)_2$ **4**

R_t/min				
3	**4**	*m*/*z* for M^+	Empirical formula	Possible structural assignment
8.32	8.29	126	$C_8H_{16}N$	1
8.92	8.90	126	$C_8H_{16}N$	2
9.67	9.64	126	$C_8H_{16}N$	3
18.25	17.97	207	$C_8H_{16}NSe$	4
20.62		185		$Me^nHexNC+71$
21.14	21.05	301	$C_9H_{19}NSe_2$	$Me^nHexNCSe_2Me$
23.51		320	$C_{15}H_{32}N_2Se$	$Me^nHexNCSeNMe^nHex$
24.74	24.67	371	$C_{14}H_{29}NSe_2$	$Me^nHexNCSe_2{}^nHex$
26.39		207	$C_8H_{16}NSe$	5

1 to 3:



4 and 5:

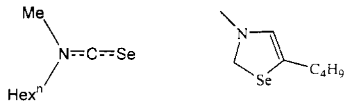


Table 3 Comparative GC-MS data for $Zn(Se_2CNEt_2)_2$ **1** and $ZnEt(Se_2CNEt_2)$ **5**

R_t/min				
1	**5**	*m*/*z* for M^+	Empirical formula	Possible structural assignment
4.50	7.50	135	C_3H_5NSe	EtNCSe
5.40		218	$C_4H_{10}Se_2$	$EtSe_2Et$
	9.46	—	—	—
7.02	10.43	218	$C_4H_{10}Se_2$	$EtSe_2Et$
10.60		165	$C_9H_{20}NSe$	$Et_2NC(Se)NEt_2$
12.17		265	—	—
	14.04	100	—	—
	14.96	209	—	—
15.66	17.68	259	$C_6H_{15}NSe_2$	$Et_2NC(Se)SeMe$
16.63	18.39	273	$C_7H_{15}NSe_2$	$Et_2NC(Se)SeEt$
	26.15	—	—	—
30.40		553	Se_7	Se_n, $n=1$–7

there are no selenium clusters observable even though the organo-selenium species $EtSe_2Et$ is seen (R_t 10.43 min), but only at 18% relative abundance with respect to the parent compound compared to that observed from compound **1**. It is assumed that the response constant for diethyl diselenide passing through the GC column will have a similar value for all three GC runs; and hence the relative concentration of diethyl diselenide determined for **1**, **2** and **5** will be proportional to the area under the peak. The smaller concentration observed for the diethyl diselenide can be attributed to the now smaller ratio of selenium to zinc, previously 4 : 1 in **1**, **2** and 2 : 1 in **5** respectively, and the likely disproportionation to the bis species. It is of interest that in **5**, after loss of the alkyl group, the reactive species on the deposition surface will be similar to that for **1** and **2**. Thus if ethene is lost at the surface as shown in Scheme 2, heavily contaminated films should result as observed from the precursors $Zn(Se_2CNEt_2)_2$ **1** and $Cd(Se_2CNEt_2)_2$ **2**. This however is not the case from the mixed alkyl precursor $ZnEt(Se_2CNEt_2)$ **5**, and may suggest that the formation of diethyl diselenide plays a more prominent role in forming films contaminated with selenium.

The use of pyrolysis GC-MS has allowed us to elucidate some of the reasons why elemental selenium is deposited along with the metal selenide from compounds such as $M(Se_2CNEt_2)_2$ (M = Zn **1** or Cd **2**) whereas $M(Se_2CNMe^nHex)_2$ (M = Zn **3** or Cd **4**) or $ZnEt(Se_2CNEt_2)$ **5** give clean deposits of metal selenides. Selenium clusters [Se_n ($n=1$–7)] are observed on the pyrolysis of **1** or **2**; no such clusters were seen for compounds **3** or **5** (Tables 2, 3).

Conclusion

We have attempted to understand by the use of GC-MS and EI-MS the reason why elemental selenium is deposited along with the metal selenide from the compounds $M(Se_2CNEt_2)_2$ [M = Zn **1** or Cd **2**] whereas $M(Se_2CNMe^nHex)_2$ [M = Zn **3** or Cd **4**]; and $ZnEt(Se_2CNEt_2)$ **5** give clean deposits of metal selenides. The formation of selenium clusters Se_n, $n=1$–7, is observed on pyrolysis of **1** or **2**; no selenium clusters were observed for compounds **3** and **5**. The selenium clusters from the decomposition of **1** and **2** may be connected to the formation of diethyl diselenide $EtSe_2Et$ from the reaction of ethene and selenium. It might be envisaged that **3** and **4** would by analogy give dipropyl diselenide. However, dipropyl diselenide is not seen in the GC-MS of **3** or **4**, but instead a five-membered dihydroselenazole heterocycle was observed to be formed. The formation of the stable compound may explain how the excess of selenium is taken out of the system during the deposition process.

The present report demonstrates that quite subtle changes in substituents at the nitrogen of a diselenocarbamate can markedly affect the thermal decomposition of metal complexes used in the preparation of selenides. The formation of stable ring structures might be expected to be enhanced, by having greater stabilising substituents at the β-carbon to the nitrogen (*e.g.* bulkier alkyl groups), so that when the ring forms it may cleanly eliminate. At present further studies are in hand involving systematic variation of the substituents at the nitrogen.

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