Ions clearly transfer between the surfaces during contact. The dependence of the charge of ion content, the correspondence between the sign of the transferred charge and the mobile ion (– for OTs^- and + for Na^+), and the parallel relationship between the $\Delta Q/\Delta M$ values for both the coated and the bare metal surfaces (independent of conductivity) are strong evidence for the ion-transfer mechanism for charging. Ion transfer is consistent with the insensitivity of the $\Delta Q/\Delta M$ to the nature of the second surface, while electron transfer would be strongly influenced by the change in conductivity. Furthermore, these ions (or polymers) do not oxidize or reduce under ambient conditions.[13] Although these results do not disprove the electron-transfer process, there is also no need to invoke it. The occurrence of parallel electron and OTs^- or electron and Na^+ exchange processes for charging would be highly coincidental. The relationship between the sign of the charge and of the mobile ion is observed with an acrylate resin with pendent sulfonic acid groups (mobile H^+)[14] but not with $[P]\text{-}PhSO_3^-Ph_4P^+$ (large, less mobile cation).[7] When the mobility of the principal ions is low, the exchange of extraneous ions and/or ions from moisture will occur to produce the charge which may be the case with these materials which are reported to have minor amounts of ionic impurities.[6] When both ions are mobile[3] or united as with betaines,[15] the situation is even more complicated.

Finally, OTs^- may not be the only ion transferring during contact, and it may be accompanied by the transfer of protons and hydroxide ions from the dissociation of moisture.[16,17] Unlike metal–metal charging where electron transfer has been demonstrated,[18-20] we feel that when mobile ions are present, charging results from the transfer of ions, for polymer–polymer and for polymer–metal contacts.

Acknowledgment. Some of the materials used in this study were available from previous studies with Prof. A. Eisenberg.[3,4]

---

(13) Weinberg, N. L., Ed. *Technique of Electroorganic Synthesis*; Wiley: New York, 1975; Part II, Vol. 5, p 667. The EA and IP levels for this class of stable ions are outside the available ambient energy to undergo spontaneous electron exchange even in electrolyte.

(14) Watanabe, M.; Nagase, H. U.S. Patent 4,883,735, Nov 28, 1989.

(15) Barbetta, A. J.; Doretta, A.; Hoffend, T. R.; Manca, R. D.; Tokoli, E. G. U.S. Patent 4,752,550, June 21, 1988.

(16) Folan, L. M.; Arnold, S.; O'Keeffe, T. R.; Spock, D. E.; Schein, L. B.; Diaz, A. F. *J. Electrostat.* **1990**, *25*, 155.

(17) Matsui, N.; Oka, K.; Inaba, U. The 6th International Congress on Advances in Non-Impact Printing Technologies, 1990; p 45.

(18) Harper, W. R. Proceedings from Static Electrification Conference, 1967; Vol. 4, p 3.

(19) Duke, C. B.; Fabish, T. J. *J. Appl. Phys.* **1978**, *49*, 315.

(20) Seanor, D. A. *Physicochemical Aspects of Polymer Surfaces*; Mittal, K. L., Ed.; Plenum: New York, 1983; Vol. 1, p 477.

Mixed Methyl- and Ethylzinc Complexes with Diethylselenocarbamate: Novel Precursors for ZnSe

M. Azad Malik and Paul O'Brien*

Department of Chemistry
Queen Mary and Westfield College
Mile End Road, London, E1 4NS, U.K.

Received July 24, 1991
Revised Manuscript Received August 26, 1991

Zinc selenide is potentially a particularly important II/VI material having applications in a wide range of roles from blue LEDs[1] to infrared optics.[2] Thin films of zinc selenide can be grown in a number of ways including chemical vapor deposition (CVD),[3] metalloorganic chemical vapor deposition (MOCVD; using precursors such as dimethylzinc[4] or an adduct[5] and usually H_2Se as the selenium source), and molecular beam epitaxy (MBE) from elemental sources.[6]

Developing single-molecule precursors, in which both the chalcogen and the metal are contained within a discrete molecule presents a considerable challenge to the chemist. Sources of this kind have been prepared for III/V materials such as InP and GaAs by Bradley and Faktor[7] and Cowley and Jones.[8] There have also been a number of reports on the deposition of sulfides from single-molecule sources such as thiophosphinates,[9] thiocarbamates,[10] and mixed-metaldialkylthiocarbamates.[11] The latter class of compounds are dimers of the formulae $RMS_2CNR'_2$ (R or R′ = Me or Et; M = Zn; R = Me, R′ = Et, M = Cd). An X-ray structure of $[MeZnS_2CNEt_2]_2$ reveals each dithiocarbamate chelates one zinc atom and bridges to the next. Complexes of cadmium and zinc with very bulky alkyl sulfides, selenides, and tellurides have also been used as single-molecule precursors for some II/VI materials.[12]

In the present communication we report that the new compounds $RZnSe_2CNEt_2$ (R = Me or Et) have been successfully used to deposit thin films of ZnSe. We believe these are the first successful single-molecule precursors for thin films of ZnSe.

The insertion of CS_2 into the M–N bond of a mixed alkylthiocarbamate to produce a compound of the stoichiometry RMS_2CNEt_2 was first reported by Noltes[13] (M = Zn, R = Et):

$$\begin{gathered} MR_2 + HNEt_2 \rightarrow \\ RMNEt_2 + RH \xrightarrow{CS_2} RMS_2CNEt_2 \\ M = Zn,\ R = Me \text{ or } Et \\ M = Cd,\ R = Me \end{gathered}$$

We have earlier confirmed the above chemistry for diethylzinc and extended such reaction to both dimethylzinc and -cadmium.[11] A different strategy was adopted for the synthesis of the selenocarbamate derivatives in order to minimize the handling of CSe_2, which is a particularly noxious material. CSe_2 was prepared by the literature method[14] and immediately converted to the *N,N′*-diethylselenocarbamate as the diethylammonium salt.[15] This was then used to prepare bis(diethylseleno-

---

(1) Kukimoto, H. *J. Cryst. Growth* **1990**, *101*, 953.

(2) Bendow, B.; Gianini, P. D. *Opt. Commun.* **1973**, *9*, 306.

(3) Lewis, K. L.; Cook, B. J.; Roscoe, P. B. *J. Cryst. Growth* **1982**, *56*, 614.

(4) Wright, P. J.; Griffiths, R. J. M.; Cockayne, B. *J. Cryst. Growth* **1984**, *66*, 26.

(5) Wright, P. J.; Parbrook, P. J.; Cockayne, B.; Jones, A. C.; O'Brien, P.; Walsh, J. R. *J. Cryst. Growth* **1990**, *104*, 601.

(6) Yao, T. *J. Cryst. Growth* **1985**, *72*, 21.

(7) Andrews, D. A.; Davies, G. J.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; White, E. A. D. *Semiconduct. Sci. Technol.* **1988**, *3*, 1053.

(8) Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248.

(9) (a) Takahashi, Y.; Yuki, R.; Sugiura, M.; Motojima, S.; Sugiyama, K. *J. Cryst. Growth* **1980**, *50*, 491. (b) Evans, M. A. H.; Williams, J. O. *Thin Solid Films* **1982**, *87*, L1.

(10) (a) Saunders, A.; Vecht, A.; Tyrell, G. *Ternary Multiary Cmpd., Proc., Int. Conf. 7th.* (*1986*) (published 1987). (*Chem. Abstr.* **1988**, *108*, 66226h). (b) Frigo, D. M.; Khan, O. F. Z.; O'Brien, P. *J. Cryst. Growth* **1989**, *96*, 989.

(11) Hursthouse, M. B.; Malik, M. A.; Motevalli, M.; O'Brien, P. *Organometallics* **1991**, *10*, 730.

(12) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 638.

(13) Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 126.

(14) Henriksen, L.; Kristiansen, E. S. S. *Int. J. Sulfur Chem. A* **1972**, *2*, 133.

(15) Henriksen, L. *Int. J. Sulfur Chem. A* **1973**, *8*, 389.

0897-4756/91/2803-0999$02.50/0 © 1991 American Chemical Society

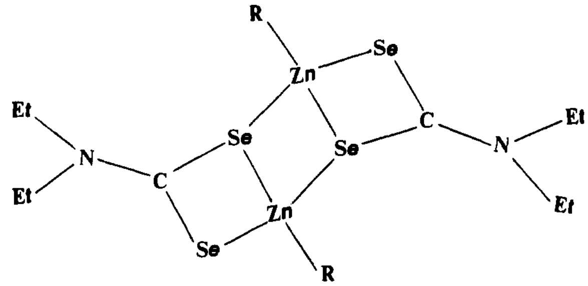

Figure 1. Proposed structure of the mixed alkylzinc ethylselenocarbamates, R = Me or Et.

carbamato)zinc(II) by direct reaction with an aqueous solution of zinc sulfate. Mixed alkyl/selenocarbamates were prepared by the comproportionation of bisalkylzinc and bis(selenocarbamate) in toluene,[16] yields were typically >90%. The compounds could be recrystallized from toluene, but repeated recrystallization can result in the loss of dimethylzinc and reversion to the bis(selenocarbamate). The compounds $[RZnSe_2CNEt_2]_2$ (R = Me (**1**) or Et (**2**)) have both been obtained as crystalline solids; their spectroscopic properties are remarkably similar to those of the corresponding thiocarbamates.[11,16] On the basis of the spectroscopic results[16] and preliminary X-ray crystallographic investigations,[17] dimeric structures, similar to that recently determined[11] for $[CH_3ZnS_2CNEt_2]_2$, are proposed for both **1** and **2** (Figure 1). The monomers do have some stability in the vapor phase, e.g., the mass spectrum of **1** had a large peak for the molecular ion of the monomer (m/z = 323, 53%, $[CH_3ZnSe_2CNEt_2]$).

Zinc selenide was prepared from both **1** and **2** in two different ways: as thin films deposited onto glass microscope slides and by a sealed-tube pyrolysis. Thin films were deposited in a continuously pumped (10^{-2} Torr) tube furnace at 450 °C. A sample of the compound (30–40 mg) was placed at one end of a Schlenck tube (12-mm o.d.) which was inserted into the furnace. The sample end of the tube protruded slightly outside the furnace keeping the precursor at a somewhat lower temperature than the furnace. The glass slide was placed in the hottest part of the furnace. Thin films were grown in about 30 min. The films were specular and electron microscopy showed them to be polycrystalline with small (ca. 1 μm) hexagonal crystallites. Elemental composition was confirmed, as very close to 1:1, by elemental detection by analytical X-rays (EDAX) in the electron microscope. Optical bandgaps were measured as ca. 2.75 eV for films grown from either **1** or **2** (literature 2.7 eV),[18] and reflection high-energy electron diffraction (RHEED) measurements showed the films to be composed of cubic ZnSe with no evidence for preferred orientation (Table I).

Table I. Typical Diffraction Results (d/Å (Intensity)) for ZnSe Prepared from the Precursors

sealed tube pyrolysis at 285 °C[a]		ASTMS		$[MeZnSe_2CNEt_2]_2$ LP-MOCVD 450 °C[b]
$[MeZnSe_2CNEt_2]_2$	$[EtZnSe_2CNEt_2]_2$	hexagonal	cubic	
			3.27 (100)	3.21
3.78 (5)	3.77 (5)			
3.45 (80)	3.44 (85)	3.43 (100)		
3.25 (100)	3.25 (100)	3.25 (90)		
3.01 (65)	3.01 (40)	3.05 (70)	2.84 (<1)	
		2.37 (60)		
2.00 (80)	2.00 (95)	1.99 (100)	2.00 (70)	2.02
1.85 (5)		1.84 (80)		
1.71 (65)	1.70 (65)	1.70 (70)	1.71 (44)	1.72
		1.53 (10)	1.64 (<1)	
	1.42 (5)	1.35 (60)	1.42 (9)	
1.30 (10)	1.30 (10)	1.30 (40)	1.30 (13)	1.30
			1.27 (<1)	
			1.16 (15)	1.16
			1.09 (8)	1.09
			0.96 (8)	0.96

[a] Thermolysis was carried out at various temperatures; the values listed above are for material obtained from a 10-h pyrolysis at 285 °C; similar results were obtained at all temperatures. The absence of some reflections, e.g., 2.37 Å (hkl 102) and 1.84 Å (hkl 103) is believed to be due to the preferred orientation of the material on microscope slide used to record the X-ray powder pattern. During pyrolysis ZnSe deposits along the walls of the tube and when scratched out appears like thin flakes. [b] RHEED measurements on thin films.

Sealed-tube pyrolysis[18] of small quantities of either of the precursors (50 mg, 10 cm^3 in vacuo at temperatures as low as 285–400 °C) gives microcrystalline ZnSe. X-ray powder diffraction analysis of the product showed hexagonal (low temperature) ZnSe. Powder diffraction results and full details are summarized in Table I.

Although adducts of selenides have been used to grow small clusters of CdSe and related materials from solution[19,20] and there is a body of work concerning the solid-state pyrolysis of chalcogen-containing complexes to produce chacogenides,[21-24] we believe that this is the first time that thin films of zinc selenide have been grown from a single-molecule precursor. Further studies of these compounds are in progress.

Acknowledgment. We thank the SERC for a grant to P.O'B. We are extremely grateful to Professor Lars Henricksen of the H. C. Oersted Institute in Copenhagen, CSe_2 was prepared by J. R. Walsh (Q.M.W.) to whom thanks are also due, with his expert guidance and converted to the selenocarbamate for transport. We also thank Dr. A. Brinkman and Paul Brown of the Department of Applied Physics (University of Durham) for RHEED measurements on thin films.

Registry No. **1**, 136629-61-3; **2**, 136629-62-4; ZnSe, 1315-09-9.

---

(16) All reactions were performed in an inert atmosphere using Schlenck techniques and a vacuum line. In a typical preparation a solution of (N,N'-diethyldiselenocarbamato)zinc(II) (5.00 g, 9.1 mmol) in toluene (50 cm^3) was stirred with diethylzinc (1.12 g, 9.1 mmol) at room temperature for 0.5 h. The colorless solution, on concentration under vacuum, gave transparent crystals of ethylzinc N,N-diethyldiselenocarbamate (5.82 g, 17.3 mmol, 95%) mp 131 °C. The methylzinc derivative was prepared in a similar manner mp 155 °C. Both compounds had satisfactory microanalysis $[MeZnSe_2CNEt_2]_2$: Major IR bands (cm^{-1}): 461 (ν Zn–Se), 500, 602 (ν Zn–C), 850 (ν C—Se), 1510 (ν C=N). NMR data: δ ^1H (C_6D_6, 40 °C, 250.1 MHz) 3.33 [4 H, q, $^3J_{H-H}$ 7.2 Hz, $(CH_3CH_2)_2N$], 0.86 [6 H, t, $^3J_{H-H}$ 7.2 Hz $(CH_3CH_2)_2N$], 0.01 [3 H, s, $ZnCH_3$]. ^{13}C NMR δ (C_6D_6, 40 °C, 62.9 MHz) 188.3 [$-CSe_2$], 51.69 [$(CH_3CH_2)_2N$], 12.31 [$(CH_3CH_2)_2N$], −9.42 [$Zn-CH_3$]. $[EtZnSe_2CNEt_2]_2$ Major IR bands (cm^{-1}): 458 (ν Zn–Se), 524, 651 (ν Zn–C), 851 (ν C—Se), 1511 (ν C=N). NMR data: δ ^1H (C_6D_6, 40 °C, 250.1 MHz) 3.44 [4 H, q, $^3J_{H-H}$ 7.2 Hz, $(CH_3CH_2)_2N$], 0.93 [6 H, t, $^3J_{H-H}$ 7.2 Hz $(CH_3CH_2)_2N$] 0.90 [2 H, q, $^3J_{H-H}$ 8.0 Hz, $ZnCH_2CH_3$], 1.65 [3 H, t, $^3J_{H-H}$ 8.0 Hz, $ZnCH_2CH_3$]. ^{13}C NMR δ (C_6D_6, 40 °C, 62.9 (MHz) 188.58 [$-CSe_2$], 52.0 [$(CH_3CH_2)_2N$], 12.39, [$(CH_3CH_2)_2N$], 4.29 [$ZnCH_2CH_3$], 13.88 [$ZnCH_2CH_3$].

(17) Preliminary X-ray crystallographic studies of the compounds (M. Motevalli and M. B. Hursthouse, Q.M.W.) confirm that both structures are based on dimeric units. The results of these studies will be reported in a subsequent paper.

(18) Grovenor, C. R. M. *Microelectronic materials*; Adan Hilger: London, 1989.

(19) Brennan, J. G.; Segrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141.

(20) Brennan, J. G.; Segrist, T.; Carroll, P. J.; Stuczynski, S. M.; Reynders, P.; Brus, L. E.; Steigerwald, M. L. *Chem. Mater.* **1990**, *2*, 403.

(21) Osakada, K.; Yamamoto, T. *J. Chem. Soc., Chem. Commun.* **1987**, 117.

(22) Steigerwald, M. L.; Sprinkle, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 7200.

(23) Hursthouse, M. B.; Khan, O. F. Z.; Mazid, M.; Motevalli, M.; O'Brien, P. *Polyhedron* **1990**, *9*, 541.

(24) Khan, O. F. Z.; O'Brien, P. *Polyhedron* **1991**, *10*, 325.