Pergamon

Polyhedron Vol. 16, No. 20, pp. 3593–3599, 1997
PII: S0277-5387(97)00116-2
0277–5387/97 $17.00+0.00

© 1997 Elsevier Science Ltd
All rights reserved. Printed in Great Britain

The properties of some volatile alkyl (di-alkylamido)zinc(II) and bis(di-alkylamido) zinc compounds: potential zinc precursors in MOCVD

M. Azad Malik and P. O'Brien*

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AZ. U.K.

(Received 10 January 1997; accepted 19 March 1997)

Abstract—A series of compounds with the general formula $Zn(NR_2)_2$ where R = Et, ^{i}Pr, ^{i}Bu; or $RZnNR'_2$ where R = Me, Et; R′ = Et, ^{i}Pr, ^{i}Bu, $SiMe_3$; and R = Np or ^{t}Bu; R′ = Et, ^{i}Pr, ^{i}Bu; have been synthesized and characterised. Vapour pressure measurements have been carried out to assess the potential suitability of such compounds as zinc precursors. Vapour pressures of alkyl(di-alkylamido)zinc(II) appear to be *ca* 5 Torr at 0°C which makes then suitable zinc precursors for MOCVD (Molecular Organic Chemical Vapour Deposition) whereas bis(di-alkylamido)zinc(II) are viscous liquids with low volatility. © 1997 Elsevier Science Ltd

Keywords: MOCVD; vapour pressure; zincalkylamides.

The development of ZnSe blue lasers has led to an increased interest in II/VI based systems [1–3], until recently lithium was considered the best p-type dopant [4–7] but at present nitrogen is the most promising candidate [8–11]. Simple nitrogen containing sources such as NH_3 have been used with some success in MBE [12–19] (Molecular Beam Epitaxy) but significant incorporation of nitrogen from this precursor is difficult in MOCVD (Molecular Organic Chemical Vapour Deposition) due to: poor thermal decomposition and incorporation at a low growth temperatures, low sticking coefficients, the possibility of adduct formation with organometallic precursors, and a potential for the incorporation of hydrogen into the layers which can cause deep centres with compensation effects. Nitrogen containing metalorganic with low decomposition temperature may enable more effective doping. In 1856 Frankland [20] prepared bis(diethylamido)zinc and since then several such compounds have been reported [21]. Reese *et al.* [22–26] have detailed the synthesis and characterisation of a series of bis(alkylamido)zinc compounds and some of them have been investigated as precursors for the nitrogen-doping of II/VI materials in MOCVD. Among the few structures reported for such compounds are those of: $[MeZnNPh_2]_2$ [27], $Zn[N(Si(CH_3)_3]_2$ [28], $Zn[N(C(CH_3)_3Si(CH_3)_3]_2$ [29]. In this paper we report on the synthesis and characterisation of several new zincalkylamides which may be useful zinc sources for nitrogen doping.

EXPERIMENTAL

Chemicals

Butyllithium, diethylzinc, dimethylamine, diethylamine, di-isopropylamine, di-isobutylamine, zinc chloride and 1,1,1,3,3,3-hexamethyldisilazane were purchased from the Aldrich Chemical Co. Ltd. Dimethylzinc was from Epichem Ltd and solvents from BDH were dried (distilled after boiling with sodium metal and benzophenone for two hours under nitrogen) and degassed (by freezing in liquid nitrogen, used the vacuum to remove any air then defrosting it under

---

* Author to whom correspondence should be addressed.

nitrogen). This process was repeated three times before use.

Physical measurements

NMR spectra were recorded using a Bruker AM250 pulsed Fourier transform instrument. Melting points were measured in sealed tubes with an electrothermal melting point apparatus and are uncorrected. Microanalysis were carried out by the University College London service.

Vapour-pressure measurements

The vapour pressure apparatus used is shown in Fig. 1. It consists of a resistance manometer (Edward model 622 A-1000B-R12) connected to a vacuum system containing a sample holder (A). The sample was frozen under liquid nitrogen and degassed until a background pressure of <0.00 mbar was read. The system was then sealed and the sample allowed to warm up.

The sample tube was placed into the temperature control jacket (E) and the temperature of the sample set by the temperature control unit attached to a thermostat bath containing a mixture of ethylene glycol and water and monitored by using a thermocouple (F). Measurements were recorded as soon as the apparatus had re-equilibrated (20–30 min). The experiments were repeated at least twice to check the reproducibility of the measurements.

Synthesis

All reactions were performed under dry nitrogen using standard Schlenk techniques. Di-neopentylzinc and di-t-butylzinc were prepared as reported previously [30–32].

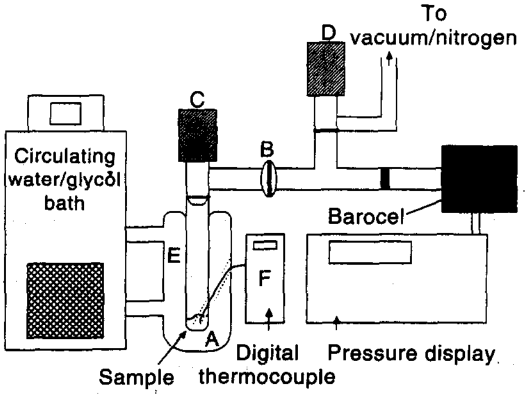

Fig. 1. Schematic diagram of vapour pressure apparatus.

Bis(diethylamido)zinc (**1**)

Attempts to prepare bis(diethylamido)zinc by the reaction of diethylzinc, with excess of diethylamine, as reported in literature [1], gave a mixture of ethyl-(diethylamido)zinc (80%) and bis(diethylamido)zinc (20%). The pure compound was prepared by the following method. A mixture of butyllithium (5.23 g, 80 mmol) and diethylamine (6.2 g, 85 mmol) in pentane (70 cm^3) was reacted at -196°C under nitrogen and allowed to warm slowly to room temperature with stirring. $LiNEt_2$ formed as a white precipitate which was separated by filtration (5.4 g, 68 mmol) and reacted with zinc chloride (4.66 g, 34 mmol) in ether (100 cm^3) at 0°C. A white precipitate of lithium chloride formed which was removed by filtration to give a clear solution of bis(diethylamido)zinc. On complete evaporation of the solvent under vacuum, the product appeared as a viscous liquid which on attempted recrystallization from hexane gave a spongy solid, m.p. 125°C, yield 89% (Found C, 47.3; H, 9.2; N, 13.6. Calculated for $C_8H_{20}N_2Zn$ C, 45.8; H, 9.2; N, 13.4%). NMR data: ^1H NMR([$^2H_6$]C_6H_6), 250 MHz, δ (ppm) 3.18 [8H, broad t, $N(\mathit{CH}_2\text{-}CH_3)_2$], 1.38 [12H, broad q, $N(CH_2\text{-}\mathit{CH}_3)_2$].

Ethyl(diethylamido)zinc (**2**)

Ethyl(diethylamido)zinc was prepared as described in literature [33]. NMR data: ^1H NMR ([$^2H_6$]C_6H_6), 250 MHz, δ (ppm)) 2.80 [4H, broad, $N(\mathit{CH}_2\text{-}CH_3)_2$], 1.11 [6H, broad, $N(CH_2\text{-}\mathit{CH}_3)_2$], 0.51 [2H, broad, $CH_3\text{-}\mathit{CH}_2Zn$], 1.50 [6H, broad, $\mathit{CH}_3\text{-}CH_2Zn$]. ^{13}C-{^1H} NMR ([$^2H_6C_6H_6$), 62.9 MHz, δ (ppm) 48.09 [$N(\mathit{CH}_2\text{-}CH_3)_2$], 18.40 $N(CH_2\text{-}\mathit{CH}_3)_2$], 1.93 [$CH_3\text{-}\mathit{CH}_2Zn$], 13.58 [$\mathit{CH}_3\text{-}CH_2Zn$].

Methyl(di-iso-propylamido)zinc (**3**)

Dimethylzinc (4.30 g, 45.1 mmol) and di-iso-propylamine (4.55 g, 45.1 mmol) in toluene (30 cm^3) were stirred at 40–60°C for 3 h. The solvent was evaporated completely and the product was distilled (50°C, 1 mbar) as a colourless liquid, yield 59%. NMR data: ^1H NMR ([$^2H_6$]C_6H_6), 250 MHz, δ (ppm) -0.36 [3H, s, *Me*Zn], 0.88 [12H, d, $^3J_{H\text{-}H} = 6.4$ -$CH(\mathit{CH}_3)_2$], 2.73 [2H, septet, $^3J_{H\text{-}H} = 6.4$ -$\mathit{CH}(CH_3)_2$. ^{13}C-{^1H} NMR ([$^2H_6$]C_6H_6), 62.9 MHz, δ (ppm) -5.99 [*Me*Zn], 23.32 [$CH(\mathit{CH}_3)_2$], 46.39 [$\mathit{CH}(CH_3)_2$].

Ethyl(di-iso-propylamido)zinc (**4**)

Diethylzinc (14.55 g, 117.9 mmol) and di-iso-propylamine (12.05 g, 118 mmol) in ether (100 cm^3) were stirred at 40–60°C for 5 h. The solvent was evaporated completely and the product was distilled (50°C, 1 mbar) as a colourless liquid, yield 72%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.35 [2H, q, $^{3}J_{H\text{-}H} = 8.1$ CH_2Zn], 1.42 [3H, t, $^{3}J_{H\text{-}H} = 8.1$ CH_3CH$_2$Zn], 0.87 [12H, d, $^{3}J_{H\text{-}H} = 6.4$ -CH(CH_3)$_2$], 2.73 [2H, septet, $^{3}J_{H\text{-}H} = 6.4$ -CH(CH$_3$)$_2$] ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 7.02 [CH_2Zn], 12.51 [CH_3CH$_2$Zn], 23.20 [CH(CH_3)$_2$], 46.47 [CH(CH$_3$)$_2$].

Bis(di-iso-propylamido)zinc (**5**)

A mixture of butyllithium (3.24 g, 50.6 mmol) and di-iso-propylamine (5.12 g, 50.6 mmol) in pentane (70 cm^3) was reacted at −196°C under nitrogen and allowed to warm slowly at room temperature while stirring. A white precipitate of LiN^{i}Pr$_2$ was separated by filtration (4.70 g, 43.9 mmol) and reacted with zinc chloride (2.90 g, 21.3 mmol) in ether (100 cm^3). A white precipitate of lithium chloride formed which was removed by filtration at 0°C to give a clear solution of bis(di-iso-propylamido)zinc. After complete evaporation of the solvent the product appeared as a viscous involatile solid, m.p. 260°C (decomp.), yield 66% (Found C, 53.8; H, 10.5; N, 10.4; calculated for $C_{12}H_{28}N_2Zn$ C, 54.2; H, 10.6; N, 10.5). NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 1.18, 1.60 [12H, d, broad, $^{3}J_{H\text{-}H} = 6.2$ -CH(CH_3)$_2$], 2.33, 3.01 [2H, septet, $^{3}J_{H\text{-}H} = 6.2$ -CH(CH$_3$)$_2$].

Methyl(di-iso-butylamido)zinc (**6**)

Dimethylzinc (12.72 g, 133.4 mmol) and di-iso-propylamine (13.52 g, 133.5 mmol) in ether (100 cm^3) were refluxed at 40–60°C for 3 h. The solvent was evaporated and the product was distilled (50°C, 1 mbar) as a colourless liquid, yield 69%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) −0.35 [3H, s, CH_3Zn], 2.22 [4H, dd, $^{3}J_{H\text{-}H} = 7.0$ N(CH_2-CH], 1.64 [2H, septet, $^{3}J_{H\text{-}H} = 6.7$ NCH$_2$-HC(CH$_3$)$_2$], 0.80 [12H, d, $^{3}J_{H\text{-}H} = 6.7$ HC(CH_3)$_2$],]. ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) −8.83 [CH_3Zn], 58.41 [NCH$_2$-], 28.73 [NCH$_2$-CH(CH$_3$)$_2$], 21.28 [HC(CH_3)$_2$].

Ethyl(di-iso-butylamido)zinc (**7**)

Diethylzinc (3.5 g, 28.4 mmol) and di-iso-butylamine (3.6 g, 28.4 mmol) in toluene (30 cm^3) were stirred at 70°C for 3 h. The solvent was evaporated completely and the product was distilled (50°C, 1 mbar) as a colourless liquid, yield 54%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.42 [2H, q, $^{3}J_{H\text{-}H} = 8.2$ CH$_2$Zn], 2.23 [4H, dd, $^{3}J_{H\text{-}H} = 7.0$ N(CH_2-CH], 1.63 [2H, septet, $^{3}J_{H\text{-}H} = 6.7$ NCH$_2$-CH(CH$_3$)$_2$], 1.51 [3H, t, $^{3}J_{H\text{-}H} = 8.2$ CH_3-CH$_2$Zn], 0.80 [12H, d, $^{3}J_{H\text{-}H} = 6.7$ CH$_3$]. ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 4.83 [CH$_2$Zn], 58.49 [NCH$_2$-CH], 28.79 [NCH$_2$-CH(CH$_3$)$_2$], 13.22 [CH$_3$-CH$_2$Zn], 21.29 [CH$_3$].

Bis(di-iso-butylamido)zinc (**8**)

A mixture of butyllithium (2.93 g, 48.8 mmol) and di-iso-butylamine (6.2 g, 48.8 mmol) in pentane (60 cm^3) was reacted at −196°C under nitrogen and allowed to warm slowly to room temperature while stirring. LiN^{i}Bu$_2$ was formed as a white precipitate which was separated by filtration (4.5 g, 35 mmol) and reacted with zinc chloride (2.32 g, 17 mmol) in ether (100 cm^3) at 0°C to give a clear solution of bis(di-iso-butylamido)zinc. After complete evaporation of the solvent the product appeared as a white viscous involatile solid, m.p. 65°C, yield 76% (Found C, 58.9; H, 11.1; N, 8.6; calculated for $C_{16}H_{36}N_2Zn$ C, 59.7; H, 11.3; N, 8.7). NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 2.98, 2.90 [d, d, $^{3}J_{H\text{-}H} = 6.8$ N(CH_2-CH], 1.73, 1.70 [septet, $^{3}J_{H\text{-}H} = 6.6$ NCH$_2$-CH(CH$_3$)$_2$], 1.13, 0.96 [d, d $^{3}J_{H\text{-}H} = 6.6$ CH_3]. ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 63.78, 65.73 [N(CH_2-CH], 29.13, 31.29 [NCH$_2$-CH(CH$_3$)$_2$], 21.53, 23.01 [CH$_3$].

t-Butyl(dimethylamido)zinc (**9**)

Di-t-butylzinc (2.3 g, 12.8 mmol) and dimethylamine (0.5 g, 12.8 mmol) were reacted in toluene (30 cm^3) at 70–80°C for 4 h. The mixture was allowed to cool and the solvent evaporated to dryness to give a colourless liquid which was identified as t-butyl-(dimethylamido)zinc, yield 73%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (pm) 1.28 [9H, s, C(CH_3)$_3$], 1.88 [6H, s, (CH_3)$_2$]. ^{13}C-{^{1}H} NMR (^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 1.16 [(CH_3)$_3$C], 25.08 [N(CH$_3$)$_2$], 32.54 [C(CH$_3$)$_3$].

t-Butyl(diethylamido)zinc (**10**)

A mixture of di-t-butylzinc (2.8 g, 15.6 mmol) and diethylamine (1.2 g, 16.4 mmol) was stirred in toluene (30 cm^3) at 70°C for 4 h. The mixture was allowed to cool down and the solvent was evaporated to give a colourless liquid identified as t-butyl(diethylamido) zinc, yield 68%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.86 (3H, t, ^{3}JCH$_3$-CH$_2$ = 7.1 Hz NCH$_2$$CH_3$), 1.32 [9H, s, C($CH_3$)$_3$], 2.26 (2H, q, ^{3}JCH$_2$-CH$_3$ = 7.1 Hz NCH_2). ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 1.37 [(CH$_3$)$_3$$C$], 14.91 [CH$_2$$CH_3$], 33.17 [C($CH_3$)$_3$], 44.44 [NCH$_2$].

t-Butyl(di-iso-propylamido)zinc (**11**)

Di-t-butylzinc (1.7 g, 9.5 mmol) and di-iso-propylamine (1.0 g, 9.9 mmol) were stirred in ether (30 cm^3) at 40°C for 8 h. The solvent was removed under reduced pressure and the product was distilled (50°C, 1 mbar) as a clear liquid, yield 65%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.98 [6H, d, ^{3}JCH$_3$-CH = 6.8 Hz CH(CH_3)$_2$], 1.15 [9H, s, C(CH_3)$_3$], 2.84 (1H, m, NCH). ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 2.06 (CH$_3$)$_3$*C*, 23.92 CH(CH_3)$_2$, 32.93 C(CH_3)$_3$, 46.60 N*CH*.

t-Butyl(di-iso-butylamido)zinc (**12**)

A mixture of di-t-butylzinc (2.3 g, 12.8 mmol) and di-iso-butylamine (1.7 g, 13.1 mmol) were stirred in ether (30 cm^3) at 40–60°C for 8 h. The solvent was removed under vacuum at low temperature to give a colourless liquid which was identified as t-butyl(di-iso-butylamido)zinc, yield 79%. Distillation of the product resulted in decomposition. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.84 [6H, d, ^{3}JCH$_2$-CH$_2$ = 6.8 Hz CH(CH_3)$_2$], 1.35 [9H, s, C(CH_3)$_3$], 1.65 (1H, m, CH$_2$*CH*) 2.33 (2H, m, N*CH*$_2$). ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 1.36 [(CH$_3$)$_3$*C*], 28.52 [CH(CH_3)$_2$], 33.59 [C(CH_3)$_3$] 57.99 [NCH$_2$].

Neopentyl(dimethylamido)zinc (**13**)

Di-neopentylzinc (2.8 g, 13.8 mmol) and dimethylamine (0.8 g, 17.7 mmol) were reacted in ether (30 cm^3) at 40–60°C for 15 h. On concentration under vacuum, a white insoluble solid product was obtained, m.p. 260°C (decomp.), yield 79% (Found C, 45.31; H, 9.32; N, 7.59; calculated for C$_7$H$_{17}$NZn C, 46.55; H, 9.49; N, 7.60).

Neopentyl(diethylamido)zinc (**14**)

Di-neopentylzinc (1.4 g, 6.7 mmol) and diethylamine (0.5 g, 6.8 mmol) were stirred in toluene (30 cm^3) at 70°C for 4 h. The mixture was allowed to cool down and the solvent was removed under vacuum to give a colourless liquid which was identified as neopentyl(diethylamido)zinc, yield 69%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.54 (2H, s, ZnCH_2), 0.89 (3H, t, ^{3}JCH$_2$-CH$_2$ = 7.1 Hz NCH$_2$$CH_3$), 1.21 [9H, s, C($CH_3$)$_3$], 2.30 (2H, q, ^{3}JCH$_2$-CH$_2$ = 7.1 Hz NCH_3). ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 2.06 [CH_2Zn], 15.57 [CH$_2$$CH_3$], 32.96 [(CH$_3$)$_3$*C*], 36.58 [C($CH_3$)$_3$], 44.38 [N$CH_2$].

Neopentyl(di-iso-propylamido)zinc (**15**)

Di-neopentylzinc (1.2 g, 5. 8 mmol) and di-iso-propylamine (0.6 g, 5.8 mmol) were reacted in toluene (30 cm^3) at 70°C for 4 h. On concentration under vacuum, a white insoluble solid product was obtained, m.p. 240°C (decomp.) yield 65% (Found C, 54.7; H, 10.5; N, 5.9; calculated for C$_{11}$H$_{25}$N$_2$Zn C, 55.8; H, 10.7; N, 5.9).

Neopentyl(di-iso-butylamido)zinc (**16**)

Di-neopentylzinc (1.5 g, 7.2 mmol) and di-iso-butylamine (1.0 g, 7.7 mmol) were stirred in toluene (30 cm^3) at 70–80°C for 5 h. The mixture was allowed to cool down to room temperature and the solvent was removed under reduced pressure to give a colourless liquid product, yield 75%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.58 (2H, s, ZnCH_2), 0.88 [6H, d, ^{3}JCH$_3$-CH = 6.8 Hz CH(CH_3)$_2$], 1.26 [9H, s, C(CH_3)$_3$], 1.72 (1H, m, CH$_2$*CH*), 2.34 (2H, d, NCH$_2$). ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 2.06 [CH$_2$Zn], 21.33 [C(CH_3)$_3$], 28.81 [(CH_3)$_2$C], 36.64 [CH], 37.12 [*C*(CH$_3$)$_3$], 58.63 [NCH$_2$].

Ethyl(di(trimethylsilylamido))zinc (**17**)

A mixture of diethylzinc (2.57 g, 20.8 mmol) and 1,1,1,3,3,3-hexamethylsilazane (3.36 g, 20.8 mmol) in ether (50 cm^3) was stirred at 50–60°C for 2 h under nitrogen and left overnight at room temperature. Small amounts of elemental zinc settled in a clear solution. Ether was evaporated at low temperature and the product was distilled (20°C, 1 mbar) as a clear liquid, yield 73%. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 250 MHz, δ (ppm) 0.05 [18H, s, (*Me*$_3$Si)$_2$N], 0.12 [1H, q, ^{3}J$_{\text{H-H}}$ = 8.1 CH$_2$Zn], 1.09 [3H, t, ^{3}J$_{\text{H-H}}$ = 8.1 CH_3CH$_2$Zn]. ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) 2.52 [(*Me*$_3$Si($_2$N], 6.51 [CH$_2$Zn], 10.14 [CH_3CH$_2$Zn].

Methyl(di(trimethylsilylamido))zinc (**18**)

Dimethylzinc and 1,1,1,3,3,3-hexamethylsilazane were reacted in ether at 50–60°C for 2 h under nitrogen in 1 : 1 stoichiometric amounts and left overnight at room temperature. Ether was evaporated at low temperature and the product was distilled as clear liquid, yield 61%. Some product was lost while removing the traces of ether under vacuum giving a low yield. NMR data: ^{1}H NMR ([^{2}H$_6$]C$_6$H$_6$), 400 MHz, δ (ppm) −0.69 (3H, s, ZnCH_3), 0.07 [18H, s, N(Si*Me*$_3$)$_2$]. ^{13}C-{^{1}H} NMR ([^{2}H$_6$]C$_6$H$_6$), 62.9 MHz, δ (ppm) −6.51 [CH_3Zn], 2.63 [N(Si*Me*$_3$)$_2$].

RESULTS AND DISCUSSION

The compounds of general formula Zn(NR$_2$)$_2$ where R = Et, ^{i}Pr, ^{i}Bu; and RZnNR$'_2$ where R = Me, Et; R$'$ = Et, ^{i}Pr, ^{i}Bu, SiMe$_3$; R = Np or ^{t}Bu; R$'$ = Et,

^{i}Pr, ^{t}Bu; were prepared as described in the experimental section. All these alkyl(dialkylamido)-zinc(II) are highly volatile air sensitive liquids except for the dimethyl and isoproylamine derivatives of neopentylzinc which were white solids insoluble in common organic solvents and ethyl(diethylamido)zinc(II) which is a viscous liquid. These compounds start to decompose at room temperature, after a few days, to give elemental zinc, but can be stored at 0°C indefinitely. The reactions of these compounds with nitrogenous bases leads to disproportionation and produces the adducts of the alkylzinc. Vapour pressure measurements of the liquid products give the vapour pressure in the region of 5–6 Torr at 0°C which makes them potentially useful as precursors for MOCVD (Table 1).

The bis(di-iso-butylamido)zinc and bis(di-iso-propylamido)zinc are viscous liquids which solidify after a few weeks at low temperature (5°C). These compounds are stable at room temperature over long periods. Reactions of these compounds with pyridine, tetramethylethylenediamine, or triethylamine result in the recovery of the starting material suggesting that no significant adduct formation occurred.

Bis(dimethylamido)zinc has been reported to be a polymeric solid [34] whereas bis(diethylamido)zinc [20] and ethyl(diethylamido)zinc [33] are involatile viscous solids which on repeated crystallisation attempts became yellow, spongy solids. The preparation of bis(diethylamido)zinc by the reaction of diethylzinc and diethylamine has been reported by using two different methods [20,35]. The literature method [20] gave a mixture of bis(diethylamido)zinc and ethyl(diethylamido)zinc even after prolonged reflux. Pure products were prepared using methods described in the experimental section. The products are involatile viscous solids and appeared to be polymers with broad ^{1}H and ^{13}C NMR signals. On repeated crystallisation the NMR signals became broader yielding a yellow solid which may be due to polymerisation.

Spectroscopic studies

^{1}H NMR spectrum of bis(di-ethylamido)zinc (**1**) showed broad signals for both the methyl and methylene protons. After removing the solvent at 60–70°C, under vacuum, the signals became broader. Similarly the ^{1}H NMR spectrum of compound (**2**) gave four broad signals for the N-ethyl and Zn-ethyl groups whereas the ^{13}C NMR spectrum showed reasonably sharp signals.

The ^{1}H NMR spectrum of methyl(di-iso-propylamido)zinc (**3**) and ethyl(di-iso-propylamido)zinc (**4**) gave a doublet and a septet for the iso-propyl group and a singlet for zinc-methyl and a triplet and quartet for zinc-ethyl protons as expected. ^{13}C NMR gave three and four line spectra for (**3**) and (**4**), respectively.

Table 1. Vapour pressure data for alkyl(dialkylamido)zinc compounds

Temp (°C)	Torr
Methyl(di-isopropylamido)zinc	
0.5	10.3
5.2	12.8
9.7	15.7
14.6	19.1
19.5	23.9
25.7	31.6
30.8	39.1
35.3	48.4
38.9	59.2
Ethyl(di-isopropylamido)zinc	
0.1	7.9
5.1	9.8
9.8	11.7
14.7	13.6
19.9	15.4
24.8	19.8
29.7	23.7
34.7	27.9
39.7	33.7
44.9	41.2
Neopentyl(diethylamido)zinc	
5.3	7.9
10.1	10.4
15.0	12.2
19.9	14.5
25.3	16.4
28.7	18.9
41.1	28.5
50.9	37.9
Neopentyl(di-isobutylamido)zinc	
0.3	7.1
5.1	8.1
10.1	9.3
15.1	10.9
20.0	13.1
24.8	14.6
Methyl(di-isobutylamido)zinc	
0.2	7.6
5.5	8.7
10.1	10.2
14.9	12.8
20.0	15.1
24.8	17.6
Ethyl(di-isobutylamido)zinc	
0.6	4.7
5.9	5.6
9.8	6.2
14.9	7.6
20.1	8.3
24.7	9.7
30.0	10.9
35.5	13.1
43.6	15.9
55.0	21.8
Ethyl(di-trimethylsilylamido)zinc	
0.2	16.9
5.3	19.6
10.5	23.1
15.2	26.6
20.3	31.6
24.7	36.8

The ^1H NMR for methyl(di-iso-butylamido)zinc (**6**) and ethyl(di-iso-butylamido)zinc (**7**) showed twice the number of signals expected indicating the presence of two species in solution (dimer and monomer). The presence of two species appears to be a common feature of all iso-butyl derivatives in this series and is well demonstrated by bis(di-iso-butylamido)zinc (**8**). The dimer and monomer equilibrium was investigated by changing the concentration of the amide (Fig. 2a, b, c). Sample (a) was diluted to 50% to give sample (b) which was further diluted to 50% to give sample (c). Figure 2a shows a ^1H NMR spectrum which gives six signals (twice) for an iso-butyl group. Methyl protons give two doublets of different intensities at high field with a close chemical shift. Similarly two sets of doublets of doublets at the lowest field for methylene protons which clearly show that there are two species in solution and that these protons are nonequivalent. Two multiplets at the midfield again with different intensity correspond to methyne proton which couples with methyl and methyl protons. The ^1H NMR spectrum of sample (b) showed a significant change in ratios of two types of signals. On the further 50 : 50 dilution of (b) to give (c) the change was even greater and can be clearly noted from the decrease in intensity of highest field doublet. The signals which decrease in intensity correspond to a dimer and the others which appear with enhanced intensity belong to a monomer (Figure 2a, b, c).

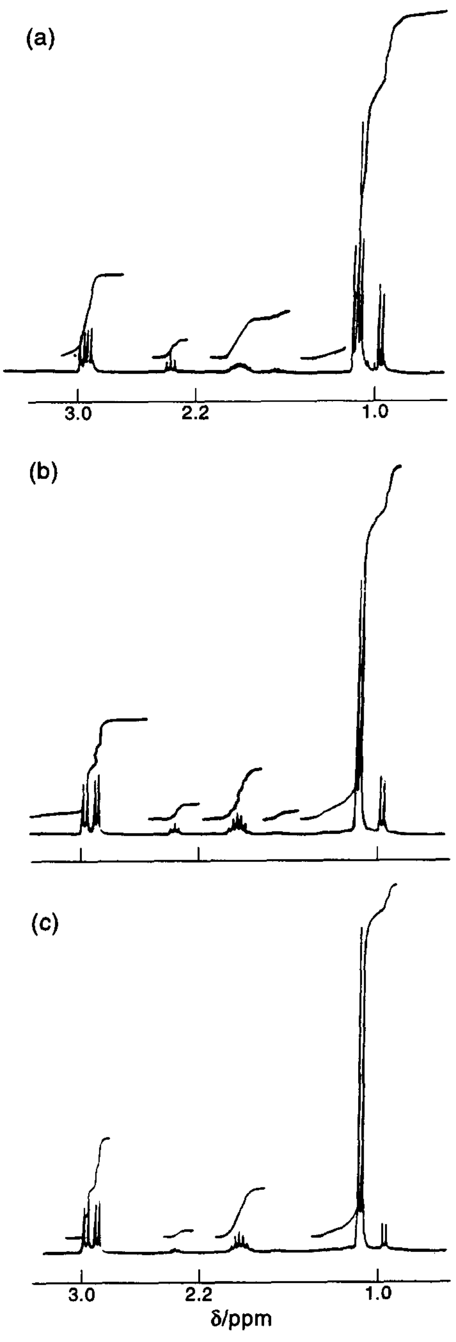

Fig. 2. ^1H NMR spectrum of $Zn(N^iBu_2)_2$ (samples a, b, c).

^1H NMR data for the *t*-butyl and neopentyl derivatives are summarized in the experimental section. ^{13}C and ^1H NMR spectra of methyl(di-trimethylsilylamido)zinc gave two singlets and ethyl(di-trimethylsilylamido)zinc gave a singlet at high field for $SiMe_3$ and a triplet and quartet for EtZn as expected.

Vapour pressure measurements

One of our objectives was to find zincalkylamides with suitable vapour pressures which can be used for the growth of *p*-doped ZnSe layers in MOCVD. Vapour pressure measurements were carried out for all the volatile compounds: methyl(di-isopropylamido)zinc (**3**), ethyl(di-isopropylamido)zinc (**4**), methyl(di-iso-butylamido)zinc (**6**), ethyl(di-iso-butylamido)zinc (**7**), neopentyl(di-ethylamido)zinc (**14**) and neopentyl(di-isobutylamido)zinc (**16**). No vapour pressure measurements were possible for *t*-butyl(di-alkylamido)zinc compounds because of their intrinsic instability.

Vapour pressures were recorded over a range of temperatures. The compounds studied have a wide range of vapour pressure at room temperature. Compounds (**3**) and (**4**) have slightly higher vapour pressures than compounds (**6**), (**7**), (**14**) and (**16**) at 0°C but this difference considerably increases at 25°C. Vapour pressure results are given in Table 1 and some results are plotted (log vapour pressure (Torr) versus temperature (1/K)) in Fig. 3. As the data show all these compounds as reasonably volatile and could be potentially useful zinc sources for MOCVD.

Acknowledgements—We thank the EC for support via a BRITE-EURAM contract BLUEMAT for funding this project and our collaborators in the scheme and their comments.

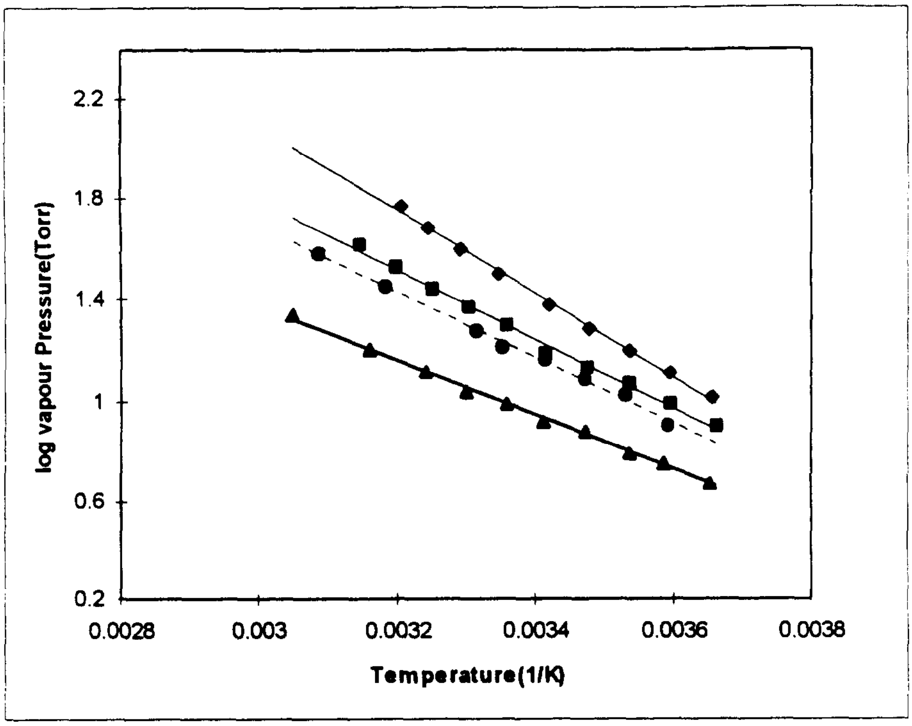

Fig. 3. Vapour pressure (log Torr) *vs* temperature (1/K) of alkyl(di-alkylamido)zinc compounds.

REFERENCES

1. Nakanishi, K., Suemune, I., Kuroda, Y. and Yamanishi, M., *Appl. Phys. Lett.*, 1991, **59**, 1401.
2. Zmudzinski, C. A., Guan, Y. and Zory, P. S., *IEEE Photon Technol. Lett.*, 1990, **2**, 94.
3. Haase, M. A., Qiu, J., DePuydt, J. M., Cheng, H. and Potts, J. E., *Appl. Phys. Lett.*, 1991, **58**, 1173.
4. Haase, M. A., DePuydt, J. M., Cheng, H. and Potts, J. E., *J. Appl. Phys.*, 1990, **67**, 448.
5. Yasuda, T., Mitsuishi, I. and Kukimoto, H., *Appl. Phys. Lett.*, 1988, **52**, 57.
6. Yushikawa, A., Muto, S., Yamaga, S. and Kasi, S., *Jpn. J. Appl. Phys.*, 1988, **27**, L260.
7. Yahata, A., Mitsuhashi, H., Hirahara, K. and Beppu, T., *Jpn. J. Appl. Phys.*, 1990, **29**, L4.
8. Gunshore, R., Nurmikko, A. and Kobayashi, M., *Physics World*, March 1992, p. 46.
9. Yodo, T., Ueda, K., Morio, K., Yamashita, K. and Tanaka, S., *J. Cryst. Growth*, 1991, **107**, 659.
10. Yodo, T. and Tanaka, S., *J. Cryst. Growth*, 1992, **117**, 415.
11. Akimoto, K., Miyajima, K. and Mori, Y., *Jpn. J. Appl. Phys.*, 1989, **28**(4), L528.
12. Stutius, W., *J. Cryst. Growth*, 1982, **59**, 1.
13. Ohki, A., Shibata, N. and Zambutsu, S., *Jpn. J. Appl. Phys.*, 1988, **27**, L909.
14. Ohki, A., Shibata, N., Ando, K. and Katsui, A., *J. Cryst. Growth*, 1988, **93**, 692.
15. Yoshikawa, A., Muto, S., Yamaga, S. and Kasai, H., *J. Cryst. Growth*, 1988, **86**, 279.
16. Yoshikawa, Y., Muto, S., Yamaga, S. and Kasai, H., *Jpn. J. Appl. Phys.*, 1988, **27**, 992.
17. Suemune, I., Yamada, K., Masato, H., Kando, T., Kan, Y. and Yamanishi, M., *Jpn. J. Appl. Phys.*, 1988, **27**, L2195.
18. Taike, A., Migata, M. and Yamamoto, H., *Appl. Phys. Lett.*, 1990, **56**, 1989.
19. Migita, M., Taike, A. and Yamamoto, H., *J. Appl. Phys.*, 1990, **68**, 880.
20. Frankland, E., *Proc. Roy. Soc.*, 1856–57, **8**, 502.
21. Lappert, M. F., Power, P. P., Sanger, A. R. and Srivastava, R. C., *Metal and Metalloid Amides*, Ellis Horwood, Chichester, 1980, 545–566.
22. Reese, W. S. Jr., Green, D. M., Anderson, T. J. and Bretschneider, E. I., *MRS Symp. Proc.*, 1992, **242**, 281.
23. Reese, W. S. Jr., Green, D. M., Anderson, T. J., Bretschneider, E., Pathangey, B., Park, C. and Kim, J., *J. Electronic Material*, 1992, **21**, 361.
24. Reese, W. S. Jr. and Just, O., *MRS Symp. Proc.*, 1994, **334**, 219.
25. Reese, W. S. Jr., Green, D. M., Hesse, W., Anderson, T. J. and Pathangey, B., *MRS Symp. Proc.*, 1993, **282**, 63.
26. Reese, W. S. Jr., Green, D. M., Anderson, T. J. and Bretschneider, E., *MRS Symp. Proc.*, 1992, **242**, 281.
27. Bell, N. A., Shearer, H. M. M. and Spencer, C. B., *Acta Cryst.*, 1983, **C39**, 1182.
28. Haaland, A., Hedberg, K. and Power, P. P., *Inorg. Chem.*, 1984, **23**, 1972.
29. Reese, W. S. Jr., Green, D. M. and Hesse, W., *Polyhedron*, 1992, **11**, 1697.
30. Moorhouse, S. and Wilkinson, G., *J. Chem. Soc., Dalton Trans.*, 1974, 2187.
31. Coates, G. E., Roberts, P. D. and Downs, A. J., *J. Chem. Soc.*, A1967, 1085.
32. Abrahams, M. H., *J. Chem. Soc.*, 1960, 4130.
33. Noltes, J. G., *Rec. Trav. Chem.*, 1965, **84**, 126.
34. Coates, G. E. and Ridley, D., *J. Chem. Soc.*, 1965, 1870.
35. Cuvigny, T. and Normant, M. H., *Comptes rendus*, 1969, **268C**, 835.