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Novel dithio- and diseleno-carbamates of zinc and cadmium as single-molecule precursors for low-pressure metal-organic chemical vapour deposition *

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Four compounds with the empirical formula $M[E_2CN(Me)CH_2CH_2CH_2NMe_2]_2$ (M = Zn **1** or Cd **2**, E = S; M = Zn **3** or Cd **4**, E = Se) have been synthesised and characterised. They are potential single-molecule precursors for growth of Group II–Group VI materials by low-pressure metal–organic chemical vapour deposition (LP-MOCVD). X-Ray crystallographic characterisation of **1**–**3** revealed three fundamentally different structural types in the most readily crystallised forms: **2** consists of discrete dimers, whereas **1** and **3** are polymeric. The LP-MOCVD experiments involving growth of ZnS films from **1** and attempts to grow ZnSe films using **3** are also discussed.

Bis(dialkyldithio- and bis(dialkyldiseleno-carbamates) of zinc and cadmium have been known for many years, and have found applications in the rubber industry[1] and in analysis.[2] More recently, these compounds have found a use as single-molecule precursors in the growth of Group II–Group VI materials by low-pressure metal–organic chemical vapour deposition (LP-MOCVD), leading to a renewed interest in their chemistry and further crystallographic investigations.[3] However, in order to fulfil their potential as precursors in MOCVD it would be useful to have compounds with improved volatility.

The simple dialkyldithio- and dialkyldiseleno-carbamates of zinc and cadmium have dimeric structures in the solid state, but are monomeric in the vapour phase. The dimers can be broken by adduct formation, as illustrated by recent studies of the 2,2′-bipyridyl and 1,10-phenanthroline adducts of $Cd(S_2CNEt_2)_2$ by Airoldi *et al.*[4] and the 1,2-bis(diethylphosphino)ethane adducts of zinc and cadmium bis(diethyldithiocarbamates) by Zeng *et al.*[5] Structure determinations for simple zinc dialkyldithiocarbamates established typical structures as based on five-co-ordinate zinc atoms[6,7] with bridging sulfur atoms in each dimer forming a centrosymmetric core unit consisting of three edge-linked, four-membered rings. However, this is not the case for $[\{Zn(S_2CNMe_2)_2\}_2]$ which was reported as having an eight-membered central ring.[8] An important extension to the chemistry of these compounds involves the replacement of one dithio-/diseleno-carbamate ligand with a simple alkyl group,[9] leading to compounds such as $[\{ZnMe(S_2CNMe_2)\}_2]$ and $[\{ZnMe(Se_2CNEt_2)\}_2]$, which have also shown potential as precursors for MOCVD.[10] Recent work on such mixed-ligand compounds has been extensive, and has included structure determinations on $[\{ZnEt(S_2NCEt_2)\}_2]$[11] and $[\{Zn(CH_2Bu^t)(Se_2CNEt_2)\}_2]$.[12] The mixed-ligand compounds have higher volatility than their parent dithio-/diseleno-carbamates, although dimeric solid-state structures, now characterised by co-ordination numbers of four, are retained. The introduction of alkyl–metal bonds also renders these mixed-ligand compounds air-sensitive, in contrast to the parent dithio-/diseleno-carbamates.

More recently, we have initiated work on zinc and cadmium compounds containing new dialkyldithiocarbamate ligands with dissimilar alkyl groups. By introducing an asymmetric amine function, compounds of the type $[\{M(S_2CNMeR)_2\}_2]$ and $[MR'(S_2CNMeR)\}_2]$ (R = Et, Pr^n, Pr^i or Bu^n; R′ = Me, Et or Bu^s; M = Zn or Cd) have been obtained.[13,14] Several of the air-stable $[\{M(S_2CNMeR)_2\}_2]$ compounds have been shown to be more volatile than the corresponding diethyldithiocarbamates, increasing their utility as MOCVD precursors. Crystallographic characterisation of representative $[\{M(S_2CNMeR)_2\}_2]$ species has confirmed that they have dimeric structures analogous to those of previously studied zinc and cadmium dialkyldithiocarbamates, and $[\{Zn(S_2CNMeBu^n)_2\}_2]$ has been employed in the growth of ZnS films by MOCVD.[13]

In another attempt at increasing the volatility of zinc and cadmium dithio-/diseleno-carbamates, compounds with pendant amine functions of the type $N(Me)CH_2CH_2NMe_2$ and $N(Me)CH_2CH_2CH_2NMe_2$ have been prepared.[15–17] The pendant donor atom in the resulting ligands can interact with the metal centre, and thus potentially alter the extent and nature of any molecular association. In initial work no structural data were reported on homoleptic compounds containing such ligands because of a lack of suitable crystals.[15] However, substitution of one of the dithiocarbamate groups with an alkyl group, in this case methyl, allowed the crystal structure of toluene-solvated $[\{CdMe[S_2CN(Me)CH_2CH_2CH_2NMe_2]\}_2]$ to be determined.[16] This compound is again dimeric, with four-co-ordinate cadmium, and only terminally bound sulfur atoms. Preliminary ZnS and CdS film deposition work involving $N(Me)CH_2CH_2CH_2NMe_2$ derivatives and a hot-wall MOCVD system was also reported.[15–17]

The present paper concerns work on *N,N,N′*-trimethylpropane-1,3-diamine derivatives, and is concerned exclusively with homoleptic compounds. Single-crystal structures are now reported for $[\{Cd[S_2CN(Me)CH_2CH_2CH_2NMe_2]_2\}_2]$ **2** and $[\{Zn[Se_2CN(Me)CH_2CH_2CH_2NMe_2]_2\}_n]$ **3**. Gross features evident from crystallographic characterisation of a low-quality crystal of $[\{Zn[S_2CN(Me)CH_2CH_2CH_2NMe_2]_2\}_n]$ **1** are also discussed. As an extension to our recent film-deposition work with $[\{Zn(S_2CNMeBu^n)_2\}_2]$, ZnS films were grown in a simple LP-MOCVD system using **1** as a single-molecule

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* *Non-SI units employed:* eV ≈ 1.60×10^{-19} J, Torr ≈ 133 Pa.

precursor. Attempts were also made to prepare ZnSe films from **3**.

Experimental

Synthesis and characterisation

All reactions were carried out in fume hoods because of the foul-smelling nature of some of the compounds involved. Chemicals were provided by Aldrich and solvents by BDH. Carbon diselenide was prepared by the reaction of selenium and dichloromethane at 550–600 °C.[18] Zinc and cadmium hydroxide were freshly prepared from the stoichiometric reaction of the metal sulfate with sodium hydroxide, and dried prior to use.

Proton NMR spectra were recorded using a Bruker AM250 pulsed Fourier-transform instrument and ^{77}Se NMR spectra at 30 °C using a JEOL FX 90Q instrument. Samples were dissolved in $CDCl_3$ (external reference tetramethylsilane for ^{1}H and dimethyl selenide for ^{77}Se). Combustion microanalyses were performed at University College or Imperial College, University of London. Infrared spectra were recorded on Mattson Polaris Fourier-transform spectrometers, using KBr media. The TLC analyses were made using silica gel plates, which were developed with iodine vapour.

Compounds 1 and 2. The preparations described give significantly better yields than those previously reported.[15] The infrared bands characteristic of dithio- or diseleno-carbamates were observed for each compound [ν(C=N) 1450–1500; ν(C–S/Se) 950–1000 cm^{-1}].

N,*N*,*N*′-Trimethylpropane-1,3-diamine (5 g, 43 mmol) and carbon disulfide (2.58 g, 43 mmol) were added to a suspension of freshly precipitated zinc hydroxide (2.14 g, 21.5 mmol) in ethanol. The reaction mixture was then stirred and heated at 75 °C for 0.5 h, whereupon the white suspension became a yellow solution, which was cooled, filtered and the ethanol removed *in vacuo* leaving a crude white product which was recrystallised from 1,1,1-trichloroethane. Yield 9.0 g, 94%. M.p. 122–124 °C. δ_H(250 MHz) 1.94 (2 H, qnt, $NCH_2CH_2CH_2N$), 2.28 (6 H, s, NMe_2), 2.38 (2 H, t, $CH_2CH_2NMe_2$), 3.44 (3 H, s, S_2CNCH_3) and 3.90 (2 H, t, $S_2CNCH_2CH_2$) (Found: C, 37.1; H, 7.0; N, 13.0. Calc. for $C_{14}H_{30}N_4S_4Zn$ **1**: C, 37.6; H, 6.7; N, 12.5%). TLC: dichloromethane, single spot, R_f 0.13; acetone, single spot, R_f 0.52; ethyl acetate, single spot, R_f 0.26.

N,*N*,*N*′-Trimethylpropane-1,3-diamine (5 g, 43 mmol) and carbon disulfide (2.58 g, 43 mmol) were added to a suspension of freshly precipitated cadmium hydroxide (3.15 g, 21.5 mmol) in boiling methanol. On stirring for 1 h, the reaction mixture became orange. After filtration to remove unreacted cadmium hydroxide, the methanol was removed *in vacuo* leaving a crude pale yellow product which was recrystallised from 1,1,1-trichloroethane, to give white crystals. Yield 9.46 g, 89%. Decomposes above 130 °C. δ_H(250 MHz) 1.79 (2 H, qnt, $NCH_2CH_2CH_2N$), 2.16 (6 H, s, NMe_2), 2.25 (2 H, t, $CH_2CH_2NMe_2$), 3.16 (3 H, s, S_2CNCH_3) and 3.69 (2 H, t, $S_2CNCH_2CH_2$) (Found: C, 33.5; H, 6.4; N, 10.9. Calc. for $C_{14}H_{30}CdN_4S_4$ **2**: C, 34.0; H, 6.1; N, 11.3%).

Compounds 3 and 4. Triethylamine (1.11 g, 11 mmol) and *N*,*N*,*N*′-trimethylpropane-1,3-diamine (1.28 g, 11 mmol) were added to a solution of carbon diselenide (1.70 g, 10 mmol) stirring in pentane (150 cm^3). The mixture was stirred for 10 min, the precipitate isolated and washed with pentane, then dried *in vacuo* at room temperature. Yield of $[NEt_3H][Se_2CN(Me)CH_2CH_2CH_2NMe_2]$ 2.64 g.

Zinc sulfate (3.55 g, 2.2 mmol) was added to the above salt (1.56 g, 4 mmol) dissolved in water (20 cm^3) at 40 °C. The reaction mixture was centrifuged to remove a small amount of precipitate, then to the resulting yellow solution was added sodium hydrogencarbonate (6 cm^3 of a 1 mol dm^{-3} solution) giving an orange precipitate which was dissolved in dichloromethane. The solution was dried over $MgSO_4$ and the solvent removed to give a yellow oil, which was redissolved in toluene, then saturated in hexane at 50 °C. Yellow-orange crystals were obtained on cooling. Yield 1.24 g, 90%. M.p. 123–125 °C. δ_H(250 MHz) 1.79 (2 H, qnt, $NCH_2CH_2CH_2N$), 2.28 (6 H, s, NMe_2), 2.38 (2 H, t, $CH_2CH_2NMe_2$), 3.51 (3 H, s, Se_2CNCH_3) and 3.99 (2 H, t, $Se_2CNCH_2CH_2$). δ_{Se}(90 MHz) 666 (1 Se, s, CSe) and 642 (1 Se, s, CSe) (Found: C, 27.2; H, 4.8; N, 8.6. Calc. for $C_{14}H_{30}N_4Se_4Zn$ **3**: C, 26.4; H, 4.7; N, 8.8%).

The preparation of $[Cd\{Se_2CN(Me)CH_2CH_2CH_2NMe_2\}_2]$ **4** was almost identical to that above, except that cadmium chloride was employed. The yield was low due to loss during purification. M.p. 146–148 °C. δ_H(250 MHz) 1.96 (2 H, qnt, $NCH_2CH_2CH_2N$), 2.24 (6 H, s, NMe_2), 2.35 (2 H, t, $CH_2CH_2NMe_2$), 3.46 (3 H, s, Se_2CNCH_3) and 3.92 (2 H, t, $Se_2CNCH_2CH_2$). δ_{Se}(90 MHz) 736 (1 Se, s, CSe) and 708 (1 Se, s, CSe) (Found: C, 25.6; H, 4.4; N, 8.0. Calc. for $C_{14}H_{30}CdN_4Se_4$ **4**: C; 24.6; H, 4.4; N, 8.2%).

X-Ray crystallography

Crystals of compounds **2** and **3** were obtained as described above. A crystal of **1** too disordered to allow a fully satisfactory structure determination was grown from benzene solution as detailed elsewhere.[17] The final value of $R1$ $[I > 2\sigma(I)]$ for **1** was 0.1080. Measurements were made at 293(2) K on crystals mounted in glass capillaries using an Enraf-Nonius CAD4 diffractometer operating in ω–2θ scan mode with graphite-monochromated Mo-Kα radiation (λ 0.710 69 Å) as described previously.[19] The structures were solved *via* standard heavy-atom procedures and refined by using full-matrix least-squares methods on F^2.[20] Scattering factors were calculated using data from ref. 21. All non-hydrogen atoms were refined with anisotropic displacement factors; hydrogen atoms were identified in difference maps and included with isotropic displacement factors. Crystal data and details of the intensity measurements and refinement on **2** and **3** are given in Table 1. Important bond lengths and angles for **1**–**3** are given in Table 2.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/53.

LP-MOCVD experiments

Film deposition was conducted in a low-pressure, cold-wall reactor, in which substrates are supported on a graphite susceptor heated by a tungsten–halogen lamp. Basic details of the system have been reported,[10,22] although for these studies and other recent ZnS growth work[13] significant improvements were introduced. A susceptor with a machined, flat-bottomed well accommodating substrates up to 14 × 18 mm is currently used. Also the susceptor temperature is now feedback-controlled, resulting in ± 1 °C stability during growth. Fresh precursor charges, *ca.* 100 mg in the case of compound **1** and *ca.* 50 mg in the case of **3**, were used in each growth run, and standard experiments were 4 h in duration. However, in one experiment involving **1** two successive ZnS layers were deposited on the same substrate over a total deposition period of 8 h, with a change of precursor charge midway through. Substrates were either borosilicate glass cover slips or various monocrystalline materials: Si (100), InP (100), InP (111)P, GaAs (100) and R-plane sapphire. These were solvent-cleaned before use, and no attempts were made to remove native oxide layers from the semiconductors.

Film characterisation

The instruments and procedures used for optical spectrophotometry and scanning electron microscopy (SEM) were reported previously.[13] Plan-view micrographs presented here show the thickest regions of films, where the local thickness is at least twice as great as the average for the whole sample. The θ–2θ X-ray diffraction (XRD) measurements were made using a Siemens D500 diffractometer, operating with monochromated Cu-Kα radiation. For characterisation of films on semiconductor substrates, small θ offsets from the symmetrical Bragg diffraction position were employed, in order to reduce substrate reflections to acceptable intensities. Average film thicknesses were estimated by dissolution of samples in hydrochloric acid, follwed by zinc determination *via* inductively coupled plasma atomic emission spectrophotometry (ICP-AES), using an Applied Research Laboratories 3580B instrument. The ICP-AES analysis procedure and estimates of sample area probably contributed a total error of less than ±5% to the mean thicknesses determined.

Volatilisation experiment with compound 1

To investigate the long-term stability of compound **1** at the vaporisation temperature of 150 °C employed in most MOCVD experiments, the compound was volatilised in a sublimator equipped with a water-cooled cold-finger. A sample (100 mg) was heated at 154–156 °C under a pressure of *ca.* 0.05 Torr. After 2 h *ca.* 20 mg of a viscous yellow oil were recovered from the cold-finger by rinsing with dichloromethane. After removal of the solvent under reduced pressure, the oil solidified over several days at room temperature. Characterisation of this substance indicated the presence of **1** plus at least one other major component (Found: C, 40.3; H, 6.6; N, 13.5. Calc. for **1**: C, 37.6; H, 6.7; N, 12.5%). IR: prominent absorption peaks absent from spectrum of pure **1**[15] at 1563, 1523, 1350 and 987 cm^{-1}. TLC: dichloromethane, two major spots, R_f 0.14 and 0.27; acetone, single diffuse major spot, R_f *ca.* 0.5; ethyl acetate, two major spots, R_f 0.26 and 0.32.

Results and Discussion

Spectroscopic studies

Proton and ^{77}Se NMR spectroscopy was carried out where possible, and in both cases the spectra observed were as expected. The ^{1}H NMR spectrum of compound **1** shows unusually high downfield signals for the methylene and methyl groups adjacent to the C–N bond of the carbamate species. This is due to this bond exhibiting some double-bond character. The other methyl and methylene groups which are bonded to nitrogen show a more usual chemical shift in the region δ 2–2.5. The only other signal (quintet) is that of the methylene protons in the propane-1,3-diamine group. Similar spectra are observed for compounds **2**–**4**. Small upfield chemical shifts are observed from dithio- to diseleno-carbamates and smaller still from zinc to cadmium.

The partial double-bond character of the carbamate group is more lucidly illustrated by the ^{77}Se NMR spectra of compounds **3** and **4**. The two signals observed arise from the combination of the above-said partial double-bond character of the C–N bond, along with the two different groups bonded to nitrogen. The subsequent restricted rotation results in the two selenium atoms in the Se_2CNRR' unit having different environments. The signals are of equal intensity and fall in the range expected.[23]

X-Ray crystallographic results

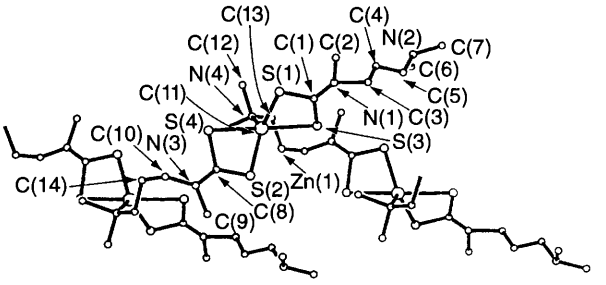

Fig. 1 Solid-state structure of polymeric $[\{Zn[S_2CN(Me)CH_2CH_2CH_2NMe_2]_2\}_n]$ **1**

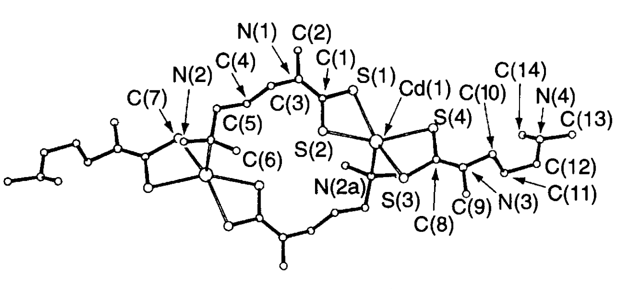

Fig. 2 Solid-state structure of dimeric $[\{Cd[S_2CN(Me)CH_2CH_2CH_2NMe_2]_2\}_2]$ **2**

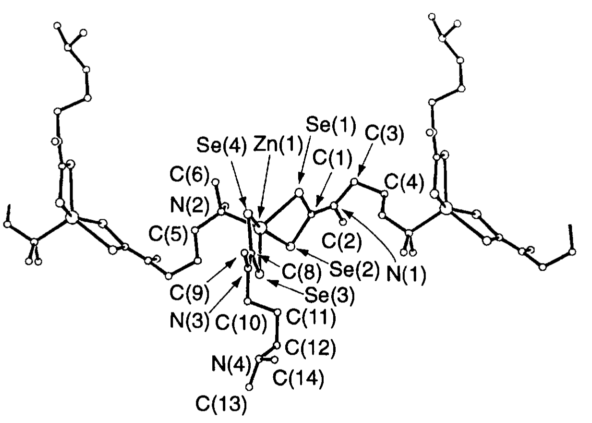

Fig. 3 Solid-state structure of polymeric $[\{Zn[Se_2CN(Me)CH_2CH_2CH_2NMe_2]_2\}_n]$ **3**

The crystal structures of compounds **1**–**3** have been determined and are illustrated in Figs. 1–3. Neither of the fully refined structures of **2** and **3** contains the type of dimeric unit generally observed for bis(dialkyldithio- and bis(dialkyldiselenocarbamates) of zinc and cadmium, characterised by five close metal–sulfur contacts.[6–8,13] In both cases, the structures have been fundamentally altered by the presence of pendant dimethylaminopropyl groups free to co-ordinate to metal centres. The same comments apply to **1**, which was used as a precursor in ZnS film growth experiments. Although only a poorly refined structure was obtained, there is unambiguous evidence that **1** is polymeric, each $Zn[S_2CN(Me)CH_2CH_2CH_2NMe_2]_2$ unit being linear, with one dimethylamino group involved in intermolecular bonding. Bond lengths and angles for **1** are included in Table 2, but the high estimated standard deviations do not justify detailed comparisons with other structures.

The structure of compound **2** is dimeric and centrosymmetric, like those of simple zinc and cadmium bis(dialkyldithiocarbamates). There are no particularly unusual bond lengths or angles. However, each cadmium atom is bonded to only four sulfur atoms, the nitrogen atom occupying the fifth co-ordination position such that the centre of the dimer now contains a more open 16-atom ring. The cadmium atoms are in a square-based pyramidal environment, with apical Cd–N bond lengths of 2.375 Å. This Cd–N distance is shorter than that (2.436 Å) observed in $[CdMe\{S_2CN(Me)CH_2CH_2CH_2N$-

Table 1 Crystal data and structure refinement for compounds **2** and **3***

	2	**3**
Empirical formula	$C_{14}H_{30}CdN_4S_4$	$C_{14}H_{30}N_4Se_4Zn$
M	495.06	635.63
Space group	$P2_1/a$	$P2_1/n$
a/Å	15.871(6)	10.853(9)
b/Å	11.394(5)	12.149(3)
c/Å	11.764(5)	17.187(5)
β/°	94.65(4)	107.64(4)
U/Å^3	2120(2)	2160(2)
D_c/Mg m^{-3}	1.551	1.955
μ/mm^{-1}	1.427	7.883
F(000)	1016	1232
Crystal size/mm	0.21 × 0.12 × 0.26	0.25 × 0.18 × 0.22
θ Range/° for data collection	1.75–25.22	1.98–24.97
hkl Ranges	0–18, −1 to 13, −13 to 13	−4 to 12, −6 to 14, −20 to 19
Reflections collected	4726	4113
Independent reflections (R_{int})	3728 (0.0288)	3790 (0.0336)
Data, restraints, parameters	3715, 0, 226	3790, 0, 227
Goodness of fit on F^2	1.040	0.991
Final *R*, *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0781, 0.2241	0.0572, 0.1350
(all data)	0.1097, 0.2684	0.0992, 0.1456
Largest difference peak and hole/e Å^{-3}	2.570, −1.042	1.428, −1.210

* Details in common: monoclinic; $Z = 4$.

Table 2 Selected bond lengths (Å) and angles (°)

Compound **1**			
Zn(1)–S(1)	2.36(2)	Zn(1)–S(2)	2.30(2)
Zn(1)–S(3)	2.58(2)	Zn(1)–S(4)	2.61(2)
Zn(1)–N(4)	2.56(6)		
S(1)–Zn(1)–S(2)	127.4(6)	S(1)–Zn(1)–S(3)	71.3(5)
S(1)–Zn(1)–S(4)	96.1(6)	S(1)–Zn(1)–N(4)	119(2)
S(2)–Zn(1)–S(3)	106.1(6)	S(2)–Zn(1)–S(4)	70.7(6)
S(2)–Zn(1)–N(4)	114(2)	S(3)–Zn(1)–S(4)	161.8(6)
S(3)–Zn(1)–N(4)	97(2)	S(4)–Zn(1)–N(4)	101(2)
Compound **2**			
Cd(1)–S(1)	2.636(4)	Cd(1)–S(2)	2.581(3)
Cd(1)–S(3)	2.637(4)	Cd(1)–S(4)	2.605(3)
Cd(1)–N(2a)	2.375(11)		
S(1)–Cd(1)–S(2)	69.25(9)	S(1)–Cd(1)–S(3)	157.86(12)
S(1)–Cd(1)–S(4)	101.88(10)	S(1)–Cd(1)–N(2a)	102.0(3)
S(2)–Cd(1)–S(3)	106.20(10)	S(2)–Cd(1)–S(4)	144.88(13)
S(2)–Cd(1)–N(2a)	109.6(3)	S(3)–Cd(1)–S(4)	68.84(10)
S(3)–Cd(1)–N(2a)	99.9(3)	S(4)–Cd(1)–N(2a)	105.5(3)
Compound **3**			
Zn(1)–Se(1)	2.4520(14)	Zn(1)–Se(2)	2.774(3)
Zn(1)–Se(3)	2.4354(14)	Zn(1)–Se(4)	2.779(3)
Zn(1)–N(2)	2.140(7)		
Se(1)–Zn(1)–Se(2)	74.99(5)	Se(1)–Zn(1)–Se(3)	129.70(5)
Se(1)–Zn(1)–Se(4)	95.62(6)	Se(1)–Zn(1)–N(2)	109.9(2)
Se(2)–Zn(1)–Se(3)	97.52(5)	Se(2)–Zn(1)–Se(4)	160.33(5)
Se(2)–Zn(1)–N(2)	101.3(2)	Se(3)–Zn(1)–Se(4)	74.95(4)
Se(3)–Zn(1)–N(2)	120.3(2)	Se(4)–Zn(1)–N(2)	98.2(2)

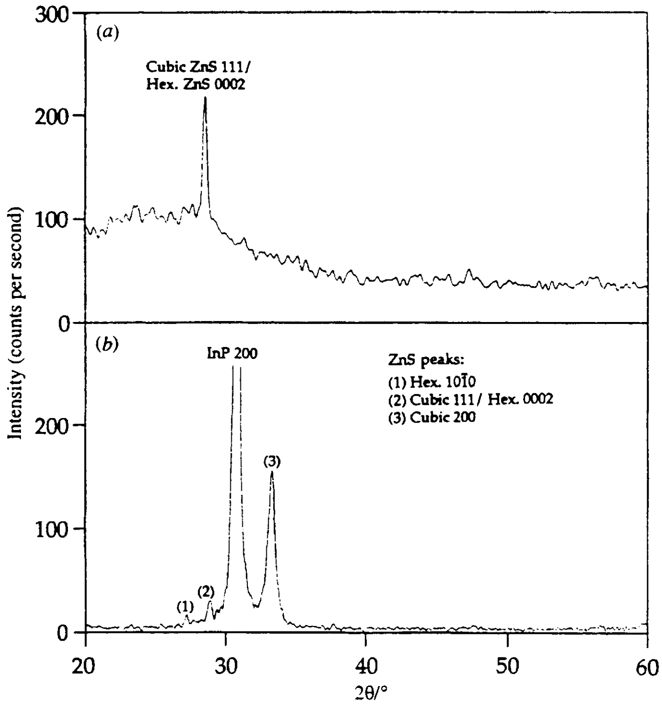

Fig. 4 Indexed θ–2θ XRD traces obtained from ZnS films grown at 500 °C (*a*) over 8 h on a glass substrate, and (*b*) over 4 h on an InP (100) substrate. Trace (*a*) shows a very broad peak centred at 2θ *ca.* 25° attributable to the glass substrate. Trace (*b*) was recorded with a θ offset of 0.05°, and the substrate peak extends off-scale

$Me_2\}]$.[16] The difference is probably partly attributable to the solvation of the latter compound, and also the shortness of the Cd · · · Me interaction restricting the approach of the chelating nitrogen atom through steric effects. The Cd–N bond length in **2** is also slightly less than those found in the 1,10-phenanthroline and 2,2′-bipyridyl adducts of $[\{Cd(S_2CNEt_2)_2\}_2]$, which are 2.402 and 2.430 Å, respectively.[4] However, these differences are unsurprising in view of the very different steric and electronic character of the bidentate N-donor ligands and the dimethylamino group.

The structure of compound **3** is polymeric, but substantially different from that of **1**. Each $Zn[Se_2CN(Me)CH_2CH_2CH_2NMe_2]_2$ unit assumes an L-shaped conformation in a one-dimensional linear chain, with one dimethylamino group again involved in intermolecular bonding. The Zn–N bond length is exceptionally low, and over 0.4 Å less than the analogous distance in **1**. This observation can be rationalised by steric arguments taking account of the disposition of the chalcogen atoms bonded to the zinc centres in **1** and **3**. The four selenium atoms bonded to each zinc in **3** lie roughly in a plane normal to the Zn–N vector.

LP-MOCVD experiments and ZnS film characterisation

The behaviour of compound **1** was investigated partly for comparison with our recent results on $[\{Zn(S_2CNMe$

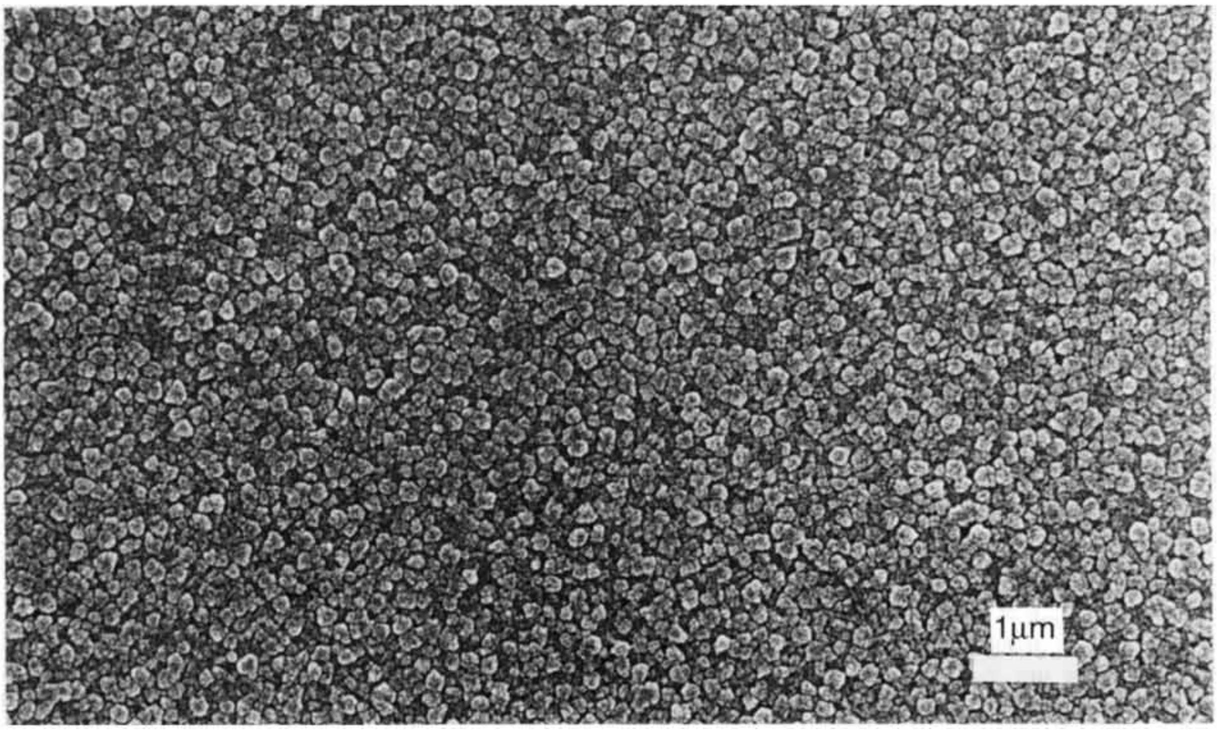

Fig. 5 A SEM micrograph of the ZnS film on glass which produced the diffraction pattern shown in Fig. 4(*a*). Scale marker 1 µm in length

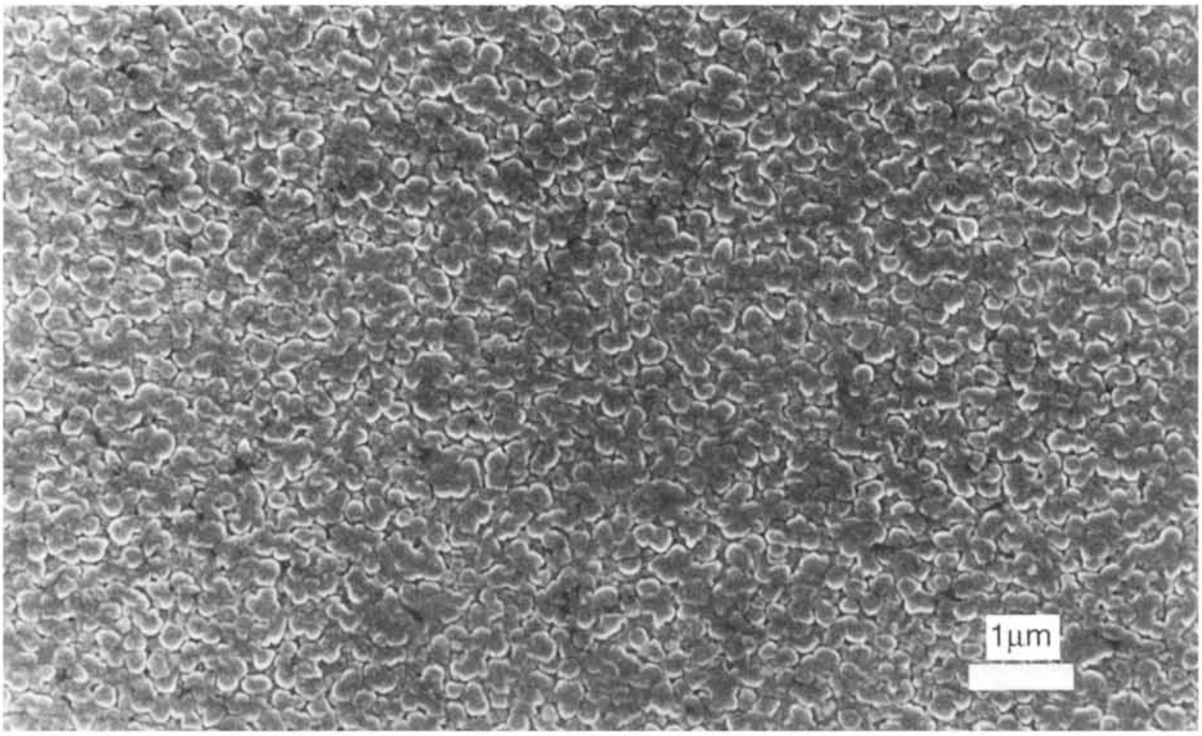

Fig. 6 A SEM micrograph of the ZnS film on InP (100) which produced the diffraction pattern shown in Fig. 4(*b*). Scale marker 1 µm in length

$Bu^n)_2\}_2]$.[13] Standard MOCVD runs involving **1** employed a susceptor temperature of 500 °C and a precursor vaporisation temperature of 150 °C. Under these conditions, specular, transparent films were deposited on all the substrate materials listed in the Experimental section. These films are much more consistent in appearance than those prepared in previous MOCVD work involving zinc bis(dialkyldithiocarbamates), many of which were hazy.[13,24] Initial measurements on films deposited using **1** were made on samples on glass substrates. One such film, from the 8 h growth run, proved sufficiently thick to show a definite optical absorption edge at *ca.* 340 nm (3.65 eV) consistent with the band gap of bulk ZnS (3.68 eV at 300 K).[25] The XRD scans on this film and a similar sample grown over 4 h showed only single ZnS peaks between 2θ 20 and 60°, as illustrated in Fig.4(*a*). The peaks observed can be assigned either to the 111 reflection of cubic ZnS, or the hexagonal ZnS 0002 reflection.[26] These films thus exhibit more extreme preferred orientation than films on glass grown at slightly lower temperatures using $[\{Zn(S_2CNMeBu^n)_2\}_2]$.[13] Fig. 5 shows an SEM micrograph of the film used to obtain the diffraction pattern presented in Fig. 4(*a*). The film shows obvious granularity on a scale of 100–200 nm, and is more strongly textured than similar films deposited from $[\{Zn(S_2CNMeBu^n)_2\}_2]$.[13]

XRD Scans from 2θ 20 to 50 or 60° were also made on films deposited on all the semiconductor substrates listed in the Experimental section. In each case three or four ZnS peaks were observed, demonstrating that the films are not characterised by a single epitaxial orientation of the sort implied in previous reports of MOCVD work involving $[\{Zn(S_2CNEt_2)_2\}_2]$ and GaAs substrates.[27,28] In addition, our studies of films grown using **1** provided further confirmation of the subtlety of factors controlling the particular ZnS phase deposited.[28] The XRD scans on two films, on Si (100) and InP (100) substrates, gave results consistent with the simultaneous presence of cubic and hexagonal ZnS phases. The indexed diffraction pattern recorded from the film on InP (100) is shown in Fig. 4(*b*). Here the most intense film peak is uniquely attributable to the 200 reflection of cubic ZnS.[26] Although the room-temperature lattice mismatch between cubic ZnS and InP is below 8%,[25] the ZnS 200 peak is too weak and broad to suggest epitaxial growth. As illustrated in Fig. 6, the film under discussion has a microstructure significantly different from those of films deposited under similar conditions on glass. Subsequent work on oriented CdS films prepared in the same MOCVD system suggests that this type of morphology is associated with columnar crystal growth.[29]

Estimates of the thicknesses of films obtained from compound **1** under our standard growth conditions were obtained *via* destructive ICP-AES analysis of two films grown on Si (100) substrates, each *ca.* 10 mm square, over 4 h. By assuming a film density of 4.0 g cm^{-3}, similar to that of both bulk ZnS phases,[25] mean thickness estimates of 130 and 200 nm were obtained for the two films. The thicknesses derived are consistent with the interference colour banding shown by these samples, and also illustrate the run-to-run variations in growth rates to be expected when using comparatively crude MOCVD equipment.

The MOCVD experiments involving vaporisation of compound **1** at 150 °C and attempted growth on glass and InP (100) substrates at 400 °C also resulted in the deposition of specular, transparent films. The appearance of the resulting samples suggests that they are much thinner than the corresponding films grown at 500 °C. In contrast, $[\{Zn(S_2CNMeBu^n)_2\}_2]$ deposited no films in duplicate experiments involving attempted growth on glass at 400 °C.[13]

From the volatilisation trial described in the Experimental section, it is obvious that compound **1** decomposes at practical vaporisation temperatures, although monomeric $[Zn\{S_2CN(Me)CH_2CH_2CH_2NMe_2\}_2]$ was presumably the main zinc-containing species transported in our film-growth work. This behaviour contrasts with the thermal stability shown by various simple zinc bis(dialkyldithiocarbamates), which were recovered in analytically pure form after similar volatilisation experiments.[13]

Five MOCVD experiments involving attempted preparation of ZnSe films were performed with compound **3**, using similar conditions to the successful ZnS deposition runs with **1**. In all these experiments insignificant quantities of material were deposited on the substrates, although red-brown deposits, assumed to be elemental selenium, formed on the reactor walls. It is likely that **3** decomposes on heating to give involatile zinc-containing products.

Conclusion

Bis(dithio- and bis(diseleno-carbamates) of zinc and cadmium with *N*,*N*,*N*′-trimethylpropane-1,3-diamine have been prepared by extensions of methods previously used to synthesise simple bis(dialkyldithio- and bis(dialkyldiseleno-carbamates). The present derivatives are of interest as single-molecule precursors for the growth of Group II–Group VI semiconductor films by MOCVD. Spectroscopic and analytical data obtained for the novel selenium compounds are consistent with their formulations. X-Ray crystallographic investigations of compounds **1**–**3** revealed three fundamentally different structure types: polymeric in the case of **1** and **3**, but dimeric in the case of **2**. Dimethylamino groups are involved in bonding to metal centres in all three structures. Unsurprisingly in view of its polymeric nature in the solid state, **1** undergoes partial decomposition on volatilisation. However, MOCVD experiments in which **1** was vaporised at 150 °C resulted in the deposition of ZnS films of consistent specular quality at growth temperatures of 400 and 500 °C. Our experiments to date suggest that the choice of substrate material affects the phase composition, crystallographic orientation and microstructure of ZnS films obtained from **1**, although not in a manner consistent with classical epitaxial growth.

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