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Mixed Alkyl Dialkylthiocarbamates of Zinc and Cadmium: Potential Precursors for II/VI Materials. X-ray Crystal Structure of [MeZnS$_2$CNEt$_2$]$_2$

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Compounds with the formula RMS$_2$CNR'$_2$ (R or R' = Me or Et, M = Zn; R = Me, R' = Et, M = Cd) have been synthesized and characterized. An X-ray crystal structure for MeZnS$_2$CNEt$_2$ has been determined and shows the complex to be dimeric. The compound crystallizes in space group $P2_1/c$, a = 6.776 (1) Å, b = 10.341 (4) Å, and c = 10.341 (4) Å, α = 90°, β = 97.3 (3)°, and γ = 90°. The zinc complexes may be useful precursors for the deposition of ZnS.

Introduction

There is considerable current interest in the development of novel precursors for the deposition of compound semiconductors by metallo-organic chemical vapor deposition[1] (MOCVD). Conventionally, the growth of metal chalcogens by MOCVD involves the use of metal alkyls, normally dimethylcadmium (DMC)[2] or dimethylzinc (DMZ),[2] and a separate source for the chalcogen, such as hydrogen sulfide or a thiophene.[2] Owing to the reactivity of the metal alkyls, there are often problems with homogeneous prereaction in the apparatus. This can ultimately lead to "snowing" and poor quality films; the problem has, to some extent, been circumvented by careful reactor design[2,3] and the use of adducts of the metal alkyl.[4–7] Both DMC and DMZ are also pyrophoric and toxic: their reactivity also limits the shelf-life.

Single-molecule precursors in which the metallic element and the pnictide (III/V or II/V materials) or chalcogen (II/VI materials) are contained in a single molecule may also overcome the problem of prereaction. The design of such compounds provides a considerable challenge to the chemist; developing chemistry pioneered by Coates,[8] Bradley and Faktor,[9] and Cowley and Jones[10] has produced a range of single-molecule precursors, such as gallium arsenide and indium phosphide, based on mixed alkyl phosphido and aresenido compounds.

We are interested in developing single-molecule precursors for II/VI materials, but the design of coordinatively saturated molecular precursors is more difficult than for III/V materials. A few such precursors have been reported. Takahashi et al.[11] grew cadmium sulfide by using dimethylthiophosphinates M(S$_2$PMe$_2$)$_2$ (M = Cd or Zn); in a subsequent paper Williams demonstrated[12] that highly orientated sulfide films could be grown by using dimethylthiophosphinates as precursors. There is a recent conference report of the growth of sulfide films from zinc and cadmium thiocarbamates,[13] and we have shown[14] that sulfides of excellent crystallinity can be grown by using bis(diethyldithiocarbamates).

Another approach involves the preparation low-coordination-number complexes of cadmium and zinc with sterically hindered thiols and selenols, such as 2,4,6-tri-*tert*-butylbenzenethiol developed by Bochmann.[15] The ternary complex of benzeneselenol and tetramethylethylenediphosphine with cadmium is dimeric and can be used for the low-pressure deposition of CdSe[16] or the deposition of CdSe from solution. Jones has synthesized[17] alkylcadmium/phosphido complexes, which are potentially useful precursors for CdP. A number of thiolates of cadmium and zinc are known to decompose cleanly to the sulfides.[18,19] The volatility of these compounds is extremely limited. There have been no reports of mixed alkyl thiolates of cadmium or zinc, a class of compounds that might make good precursors. In the present paper, we have developed the chemistry of cadmium and zinc complexes containing both an alkyl group and a thiocarbamate ligand to produce a range of molecules that have potential as precursors for CdS and ZnS.

Experimental Section

Metal alkyls were a gift from Epichem; all other chemicals from B.D.H. Solvents were dried before use with molecular sieves or sodium wire as appropriate.

Physical Measurements. Infrared spectra were recorded on a Mattson Polaris FT-IR spectrometer with Nujol mulls; ^{13}C and ^{1}H NMR spectra were recorded by using a Bruker WH 400 or Bruker AM 250 pulsed Fourier transform NMR instrument, and mass spectra were recorded with a Kratos MS50 TC instrument. Microanalyses were performed by the University College, London, Service.

Synthesis of the Compounds. All manipulations were carried by using a vacuum line and standard Schlenck techniques. In a typical experiment, dimethylzinc (33.6 mmol) and diethylamine (33.6 mmol) were stirred and heated in toluene (30 cm^3) under

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Table I. Yields, Melting Points, and Microanalysis Results

compd	% yield	mp, °C	% C	% H	% N	% S
$MeZnS_2CNEt_2$	86	139–140	31.89 (31.59)	5.74 (5.73)	6.04 (6.12)	27.57 (28.04)
$EtZnS_2CNEt_2$	86	115	34.64 (34.64)	6.21 (6.23)	5.67 (5.77)	26.36 (26.42)
$MeCdS_2CNEt_2$[a]	89	>170 dec.	31.46 (26.14)	5.03 (4.74)	5.67 (5.08)	26.95 (23.26)
$MeZnS_2CNMe_2$	62	142	24.02 (23.95)	4.59 (4.52)	7.07 (6.98)	32.11 (31.96)
$EtZnS_2CNMe_2$	59	129	27.75 (27.98)	4.76 (5.17)	6.44 (6.52)	29.92 (29.87)

[a] Reproducible analytical results were hard to obtain as the compound tended to disproportionate to the parent alkyl and the bis(diethyldithiocarbamate).

Table II. Selected Mass Spectrometry Results

compd	M⁺	base peak
$MeZnS_2CNEt_2$	360 (51%)	116
227 (4%)	$Zn(S_2CNEt_2)_2$	$C_5H_{10}NS$
$EtZnS_2CNEt_2$	241 (28%)	143
241 (28%)	$EtZnS_2CNEt_2$	CH_3S_2Zn
$MeCdS_2CNEt_2$	410 (2%)	129
277 (30%)	$Cd(S_2CNEt_2)_2$	CH_3Cd
$MeZnS_2CNMe_2$	304 (24%)	88
199 (0.5%)	$Zn(S_2CNMe_2)_2$	$((CH_3)_2N)_2$
$EtZnS_2CNMe_2$	304 (33%)	88
215 (0.1%)	$Zn(S_2MeEt_2)_2$	$((CH_3)_2N)_2$

Table III. Crystallographic Data for $[MeZnS_2CNEt_2]_2$

Crystal Data	
stoichiometry	$C_{12}H_{26}N_2S_4Zn_2$
MW	457.396
a/Å	6.776 (1)
b/Å	10.341 (4)
c/Å	14.479 (5)
α/deg	90
β/deg	97.3 (3)
γ/deg	90
V/Å^3	1006.33
system	monoclinic
space group	$P2_1/n$
$D_c/(g/cm^3)$	1.509
Z	2
$F(000)$	472
radiation	Mo Kα
λ/Å	0.710 69
μ/cm^{-1}	28.366
Data Collection	
$\theta_{max/min}$	1.5, 2
temp	room temp
total data measured	2102
total data unique	1766
total data obsd	1410
significance test	$F_o > 3\sigma(F_o)$
Refinement	
no. of params	143
abs correction	ψ scan
g[a] (weighting scheme)	0.000 023
final R	0.0375
final R_G	0.0393

[a] $w = 1/[\sigma^2(F_o) + g(F_o)^2]$.

Table IV. Fractional Atomic Coordinates (×10⁴) for $[MeZnS_2CNEt_2]_2$

	x	y	z
Zn(1)	1758 (1)	1163 (1)	4847 (1)
S(1)	970 (2)	−124 (1)	6225 (1)
S(2)	3293 (2)	−516 (1)	4082 (1)
N(1)	−636 (6)	1841 (4)	7060 (3)
C(1)	−960 (7)	867 (4)	6466 (3)
C(11)	−2266 (11)	2706 (6)	7251 (5)
C(12)	−2444 (15)	3857 (8)	6613 (6)
C(21)	1350 (10)	2155 (6)	7527 (4)
C(22)	1812 (16)	1548 (9)	8470 (6)
C(2)	2108 (13)	3025 (6)	5056 (6)

a stream of nitrogen at 70 °C for 12 h. To the cooled solution, a cold solution of CS_2 (33.6 mmol) in toluene (20 cm^3) was added and the mixture warmed to, and kept at, 40 °C for 5 h. Traces of elemental zinc were removed by filtration, and the solvent was removed by evaporation. The product was recrystallized from benzene and gave transparent yellow crystals analyzed as $MeZnS_2CNEt_2$ (1), yield 86% based on dimethylzinc.

All the compounds have been characterized by satisfactory elemental analysis, (Table I), mass spectrometry (Table II), NMR and infrared spectroscopies.

$MeZnS_2CNEt_2$ (1). ^1H NMR ($[^2H_6]C_6H_6$, 45 °C, 250.1 MHz) δ 3.37 (4 H, q, $^3J_{H-H} = 7.1$ Hz, $(CH_3CH_2)_2N$), 0.89 (6 H, t, $^3J_{H-H} = 7.1$ Hz, $(CH_3CH_2)_2N$), −0.02 (3 H, s, $ZnCH_3$). ^{13}C NMR ($[^2H_6]C_6H_6$, 45 °C, 62.9 MHz) δ 202.14 (CS_2), 49.81 ($((CH_{3C}H_2)_2N)$), 12.62 ($((\mathit{C}H_3CH_2)_2N)$), −10.55 ($ZnCH_3$). IR (major bands and tentative assignments) 529, 561 (ν(M—C)), 420 (ν(M—S)), 987 (ν(C—S)), 1503 cm^{-1} (ν(C=N)).

$EtZnS_2CNEt_2$ (2). ^1H NMR ($[^2H_6]C_6H_6$, 45 °C, 400 MHz) δ 3.41 (4 H, q, $^3J_{H-H} = 7.2$ Hz, $(CH_3CH_2)_2N$), 1.69 (3 H, t, $^3J_{H-H} = 8.1$ Hz, CH_3CH_2Zn), 0.92 (6 H, t, $^3J_{H-H} = 7.2$ Hz, $(CH_3CH_2)_2N$), 0.92 (2 H, q, $^3J_{H-H} = 8.1$ Hz, CH_3CH_2Zn). ^{13}C NMR ($[^2H_6]C_6H_6$, 45 °C, 62.9 MHz) δ 200.52 (CS_2), 49.71 ($((CH_3\mathit{C}H_2)_2N)$), 13.95 ($ZnCH_2\mathit{C}H_3$), 12.56 ($((\mathit{C}H_3CH_2)_2N)$), 3.54 ($ZnCH_2CH_3$). IR (major bands and tentative assignments) 510, 563 (ν(M—C)), 423 (ν(M—S)), 986 (ν(C—S)), 1504 cm^{-1} (ν(C=N)).

$MeCdS_2CNEt_2$ (3). ^1H NMR ($[^2H_6]C_6H_6$, 45 °C, 250.1 MHz) δ 3.60 (4 H, q, $^3J_{H-H} = 7.1$ Hz, $(CH_3CH_2)_2N$), 1.03 (6 H, t, $^3J_{H-H} = 7.1$ Hz, $(CH_3CH_2)_2N$), 0.01 (ca, 2 H, broad singlet probably due to methyl exchange at Cd, $CdCH_3$). ^{13}C NMR ($[^2H_6]C_6H_6$, 45 °C, 62.9 MHz) δ 214.45 (CS_2), 51.27 ($((CH_3CH_2)_2N)$), 12.77 ($((\mathit{C}H_3CH_2)_2N)$), no signal observed for CH_3Cd. The composition of the cadmium compound is confirmed by elemental analysis and mass spectrometry. The cadmium complex was much less stable than any of the zinc complexes and on successive recrystallization disproportionated to the bis(diethyldithiocarbamate) complex and dimethylcadmium. IR (major bands and tentative assignments) 561 (ν(M—C)), 427 (ν(M—S)), 987 (ν(C—S)), 1499 cm^{-1} (ν(C=N)).

$MeZnS_2CNMe_2$ (4). ^1H NMR ($[^2H_6]C_6H_6$, 45 °C, 200 MHz) δ 2.81 (6 H, s, $(CH_3)_2N$), −0.23 (3 H, s, $ZnCH_3$). ^{13}C NMR ($[^2H_6]C_6H_6$, 45 °C, 62.9 MHz) δ 204.95 (CS_2), 44.52 ($((CH_3)_2N)$), −9.90 ($ZnCH_3$). IR (major bands and tentative assignments) 529 (ν(M—C)), 444 (ν(M—S)), 973 (ν(C—S)), 1508 cm^{-1} (ν(C=N)).

$EtZnS_2CNMe_2$ (5). ^1H NMR ($[^2H_6]C_6H_6$, 45 °C, 200 MHz) δ 2.80 (6 H, s, $(CH_3)_2N$), 1.62 (3 H, t, $^3J_{H-H} = 8.0$ Hz, $C\mathit{H}_3CH_2Zn$), 0.80 (2 H, q, $^3J_{H-H} = 8.0$ Hz, $(CH_3CH_2)_2N$). ^{13}C NMR ($[^2H_6]C_6H_6$, 45 °C, 62.9 MHz) δ 203.34 (CS_2), 44.48 ($((CH_3)_2N)$), 13.54 ($ZnCH_2\mathit{C}H_3$), 3.67 ($Zn\mathit{C}H_2CH_3$). IR (major bands and tentative assignments) 509 (ν(M—C)), 443 (ν(M—S)), 973 (ν(C—S)), 1508 cm^{-1} (ν(C=N)).

Crystallography. All measurements were made on a sample mounted in a glass capillary by using a CAD4 diffractometer operating in the $\omega/2\theta$ scan mode with graphite monochromated Mo Kα radiation as described previously.[20] The structure was solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods[21] with scattering factors calculated by using the data from ref 22. 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 are given in Table III.

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Table V. Selected Bond Distances (Å) and Angles (deg) for $[MeZnS_2CNEt_2]_2$

S(1)-Zn(1)	2.512 (4)	S(2)-Zn(1)	2.370 (3)
C(2)-Zn(1)	1.958 (8)	C(1)-S(1)	1.732 (6)
C(1)-N(1)	1.325 (6)	C(11)-N(1)	1.475 (8)
C(21)-N(1)	1.463 (7)	C(12)-C(11)	1.503 (12)
C(22)-C(21)	1.498 (10)		
S(2)-Zn(1)-S(1)	97.7 (1)	C(2)-Zn(1)-S(1)	115.6 (4)
C(2)-Zn(1)-S(2)	137.8 (3)	C(1)-S(1)-Zn(1)	95.1 (2)
C(11)-N(1)-C(1)	121.1 (5)	C(21)-N(1)-C(1)	122.4 (5)
C(21)-N(1)-C(11)	116.5 (5)	N(1)-C(1)-S(1)	120.9 (4)
C(12)-C(11)-N(1)	111.6 (7)	C(22)-C(21)-N(1)	113.7 (7)

Positional parameters are given in Table IV. Tables of H atom coordinates, full lists of bond lengths and angles, anisotropic displacement factor coefficients, and F_o/F_c values are included in the supplementary material.

Syntheses of the Compounds

The insertion of CS_2 into the M-N bond of a mixed alkyl thiocarbamate to produce a compound of the stoichiometry RMS_2CNEt_2 was first reported by Noltes[23] (M = Zn, R - Et):

$$MR_2 + HNEt_2 \rightarrow RMNEt_2 + RH \xrightarrow{CS_2} \underset{1-3}{RMS_2CNEt_2}$$

$$M = Zn,\ R = Me\ (1)\ \text{or}\ Et\ (2)$$

$$M = Cd,\ R = Me\ (3)$$

We have confirmed the above chemistry for diethylzinc and extended such a reaction to both dimethylzinc and -cadmium. The same general method was used for each of the compounds and involved the reaction of the parent metal alkyl with the secondary amine, followed by the addition of CS_2 as described in the Experimental Section. The products were recrystallized from benzene and gave transparent yellow crystals: $MeZnS_2CNEt_2$ (1), $EtZnS_2CNEt_2$ (2), $MeCdS_2CNEt_2$ (3), $MeZnS_2CNMe_2$ (4), and $EtZnS_2CNMe_2$ (5). The compounds are all air-sensitive crystalline solids, qualitatively of much reduced reactivity from their parent alkyls.

Structure of $MeZnS_2CNEt_2$. The structure of 1 was determined from a single crystal by X-ray methods and is shown in Figure 1. Selected bond lengths and angles are summarized in Table V.

The structure consists of dimeric molecular units, $[MeZnS_2CNEt_2]_2$; each dithiocarbamate chelates one zinc atom and bridges to the next. The dithiocarbamate groups have no unusual bond lengths or angles. The structure resembles the dimeric structure of bis(diethyldithiocarbamato)zinc(II)[24] with a methyl group replacing the chelating-only thiocarbamate ligand. Each zinc atom is four coordinate, and coordination at the metal is not simply described in terms of any regular polyhedron. Coordination is closest to tetrahedral but is distorted toward a trigonal pyramid with the base defined by C(2), S(2), and S(1). Alternatively, if the chelating thiocarbamate is regarded as a single donor, coordination at the metal is close to trigonal planar.

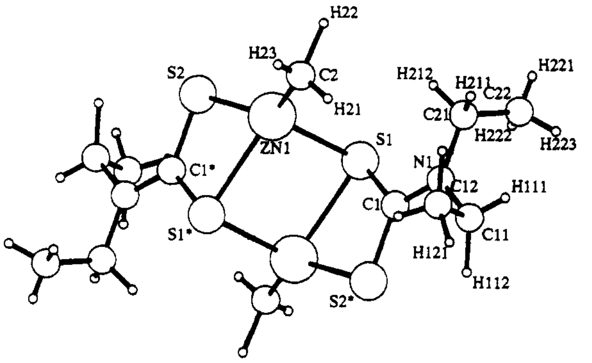

Figure 1. Metal bond lengths (Å) and angles (deg) for $MeZnS_2CNEt_2$: Zn(1)-S(1) 2.512 (4), Zn(1)-S(1′) 2.501 (4), Zn(1)-S(2) 2.370 (3), Zn(1)-C(2) 1.958 (8), S(1)-Zn(1)-S(1′) 92.9 (2), S(1)-Zn(1)-S(2) 97.3 (1), S(1′)-Zn(1)-S(2) 74.3 (2), S(1)-Zn(1)-C(2) 115.6 (4), S(1′)-Zn(1)-C(2) 126.7 (4), S(2)-Zn(1)-C(2) 137.8 (3).

There are relatively few examples of crystallography characterized zinc–alkyl bonds;[25] recent examples include a rotoxane[26] (Zn–C_2H_5, 1.98 Å), a tris(pyrazolyl)borate[27] (Zn–CH_3, 1.89 Å), and the bis adduct of 1,3,5-trimethylhexahydro-1,3,5-triazine with dimethylzinc[28] (Zn–CH_3 1.99 Å); these values are very similar to the 1.98 Å found in the present complex.

Spectroscopic Studies. The compounds have been characterized by ^1H and ^{13}C NMR spectroscopies and by their mass spectra (see the Experimental Section). The zinc complexes have sharp proton NMR spectra, suggesting that the complexes are either in very rapid exchange or inert on the NMR time scale. The cadmium complex is less stable, and the ^1H NMR spectrum is clearly exchange broadened; the spectrum could not be sharpened on cooling to -40 °C. The results for cadmium may suggest that the zinc complexes are fairly inert. The complexes may be either monomeric or dimeric in solution, and we have not sought to clarify this point.

Thiocarbamate stretches are clearly seen in all of the infrared spectra. The mass spectra are particularly interesting and confirm the monomeric molecular species as a component of the fragmentation pattern for all of the compounds; see Table II. For the compounds $MeMS_2CNEt_2$, the molecular ion of the monomer is a major peak, and in the case of $EtZnS_2CNEt_2$, the molecular ion of the monomer was observed as the highest mass peak.

Preliminary Growth Results. All the compounds sublime (10^{-2} Torr, 100–150 °C) and have been successfully used to deposit thin films of the metal sulfide on glass in low-pressure MOCVD experiments (10^{-2}–10^{-3} Torr 450 °C) by using methods described in our earlier paper.[9] Only very thin, submicron thickness, films have been grown to date, and we have not been able to establish their crystallinity by using the X-ray methods available to us. However, the composition of the films has been confirmed by EDAX measurements with the electron microscope; the films all consist of the metal sulfide. Detailed studies of crystal growth from these precursors will be published in a subsequent paper. These compounds represent a new class of precursors for II/VI materials.

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Supplementary Material Available: Tables listing fractional atomic coordinates, anisotropic temperature factors, and bond distances and angles (3 pages); a table listing observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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