Synthesis and Characterization of some Mixed Alkyl–Carbamates of Zinc or Cadmium: Crystal Structures of $[Zn_4Me_2(O_2CNEt_2)_6]$ and $[Zn_4Me_4(O_2CNEt_2)_4]$‡

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Some mixed alkyl–carbamates of formula $[M_4R_2(O_2CNEt_2)_6]$ (M = Zn, R = Me or Et; M = Cd, R = Me) have been synthesized and characterized. The single-crystal structure of $[Zn_4Me_2(O_2CNEt_2)_6]$ consists of an unusual tetranuclear molecule with a plane of zinc atoms. The compound $[Zn_4Me_4(O_2CNEt_2)_4]$ has also been prepared. Its structure is based on an approximately tetrahedral arrangement of zinc atoms.

In a series of recent papers aimed at describing single-molecular precursors for Group II–Group VI materials we have reported the characterization of a number of dimeric diseleno- and dithiocarbamate complexes with alkylmetal fragments. The structures of these compounds are based on dimeric units of stoichiometry $[\{MR(E_2CNR'_2)\}_2]$ (R and R' = alkyl, E = S or Se).[1–6] An initial exception to this stoichiometry was provided by a tetranuclear carbamate $[Zn_4Me_2(O_2CNEt_2)_6]$ prepared by the insertion of CO_2 into the alkylzinc amide $ZnMe(NEt_2)$; a preliminary communication concerning this compound has appeared.[1] In the present paper we report further studies of such systems.

Results and Discussion

Compounds of Stoichiometry $[M_4R_2(O_2CNEt_2)_6]$.—These compounds were prepared by the reaction of diethylamine with either a dialkylzinc or dimethylcadmium to provide the mixed alkyl–alkylamide, followed by insertion of carbon dioxide into the M–N bond of the alkylamide[7,8] [equation (1); M = Zn,

$$NHEt_2 + MR_2 \longrightarrow NMR(NEt_2) \xrightarrow{CO_2(excess)} [M_4R_2(O_2CNEt_2)_6] \quad (1)$$

R = Me **1** or Et **2**; M = Cd, R = Me **3**]. The structure of **1** is shown in Fig. 1 and contains centrosymmetric molecules of formula $[Zn_4Me_2(O_2CNEt_2)_6]$. The core of the molecule contains a plane of zinc atoms forming a parallelogram with four carbamate ligands bridging the zinc atoms along each edge. Two further carbamates bridge across the diagonal of the parallelogram [Zn(1) to Zn(1')] above and below the plane of the zinc atoms; one of the oxygens on each carbamate bonds to a single zinc atom while the other bonds to two. Atom Zn(1) has essentially tetrahedral co-ordination but has a weak contact 2.591 Å to a second oxygen O(4) of one of the edge-bridging carbamate ligands. The tetrahedral co-ordination of Zn(2) is completed by a methyl group. All bond lengths (Table 1) are in typical ranges.

Satisfactory microanalytical results suggest that compounds **2** and **3** have similar structures. The ^1H and ^{13}C NMR spectra of both the zinc complexes, in solution, indicate the presence of two kinds of carbamates, in a 2:1 ratio, as is required by a structure similar to that of **1** in the solid state. The cadmium complex is insoluble in common solvents, but the solid has a remarkably similar infrared spectrum to those of the zinc analogues; the structure may be similar but somehow involves a degree of polymerization between tetrameric units.

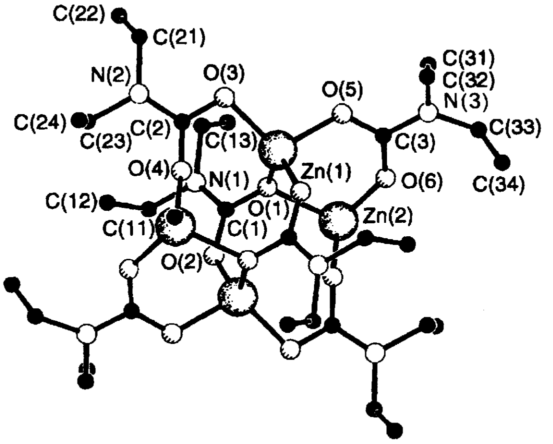

Fig. 1 Crystal structure of $[Zn_4Me_2(O_2CNEt_2)_6]$ **1**

The Compound $[Zn_4Me_4(O_2CNEt_2)_4]$ **4**.—Compound **4** was synthesized by the reaction of **1** with an excess of dimethylzinc [equation (2)]. Its structure is based on tetrameric molecules of

$$[Zn_4Me_2(O_2CNEt_2)_6] + ZnMe_2(excess) \longrightarrow [Zn_4Me_4(O_2CNEt_2)_4] \quad (2)$$

$[Zn_4Me_2(O_2CNEt_2)_4]$ as shown in Fig. 2. In contrast to structure **1** the core of this molecule is based on four zinc atoms in an approximately tetrahedral arrangement. These four metal atoms are joined by bridging carbamates to form two puckered Zn_2O_3C rings which are linked by bridging oxygen atoms. Each carbamate has a co-ordination mode in which one oxygen has a monoatomic contact to one zinc, the other forming a bridge to two different zinc atoms. Unlike structure **1** there are no weak secondary contacts. The bond lengths observed are again in typical ranges.

In contrast to the previous three compounds where two types of carbamates are seen from the ^1H NMR signals for the ethyl groups, three clear signals are observed: a singlet for twelve

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‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Selected contact distances (Å) and angles (°)

Compound **1**			
Zn(1)–O(1)	1.985(6)	Zn(1)–O(2)	1.938(6)
Zn(1)–O(3)	1.937(6)	Zn(1)–O(4)	2.591(7)
Zn(2)–O(4)	1.995(6)	Zn(2)–O(6)	1.934(6)
O(4)–Zn(1)–O(2)	90.6(3)	O(4)–Zn(1)–O(3)	56.3(3)
O(4)–Zn(1)–O(5)	162.5(3)	O(3)–Zn(1)–O(5)	106.8(3)
O(3)–Zn(1)–O(2)	122.3(3)	O(1)–Zn(1)–O(2)	116.1(3)
O(1)–Zn(1)–O(3)	109.1(3)	O(1)–Zn(1)–O(5)	102.3(3)
C(4)–Zn(2)–O(1)	110.4(3)	C(4)–Zn(2)–O(4)	126.3(3)
C(4)–Zn(2)–O(6)	126.5(3)	O(1)–Zn(2)–O(6)	98.3(3)
O(1)–Zn(2)–O(4)	92.0(3)		
Compound **4**			
Zn(1)–O(4)	2.07(1)	Zn(1)–O(6)	2.08(2)
Zn(1)–O(8)	1.96(2)	Zn(1)–C(5)	1.99(3)
Zn(2)–O(1)	2.02(2)	Zn(2)–O(4)	2.04(1)
Zn(2)–O(5)	1.93(2)	Zn(2)–C(6)	1.97(2)
Zn(3)–O(2)	1.99(2)	Zn(3)–O(6)	2.10(2)
Zn(3)–O(7)	2.06(2)	Zn(3)–C(7)	1.95(3)
Zn(4)–O(1)	2.10(2)	Zn(4)–O(3)	1.97(1)
Zn(4)–O(7)	2.08(1)	Zn(4)–C(8)	1.95(3)
C(5)–Zn(1)	1.99(3)	C(6)–Zn(2)	1.97(2)
C(7)–Zn(3)	1.95(3)	C(8)–Zn(4)	1.95(3)
O(4)–Zn(1)–O(6)	92.8(5)	O(4)–Zn(1)–O(8)	98.5(6)
O(4)–Zn(1)–C(5)	116.9(9)	O(6)–Zn(1)–O(8)	100.5(7)
O(6)–Zn(1)–C(5)	117.0(9)	O(8)–Zn(1)–C(5)	125.1(9)
O(1)–Zn(2)–O(4)	93.6(6)	O(1)–Zn(2)–O(5)	96.9(6)
O(1)–Zn(2)–C(6)	118.9(8)	O(4)–Zn(2)–O(5)	102.1(6)
O(4)–Zn(2)–C(6)	108.6(8)	O(5)–Zn(2)–C(6)	130.0(9)
O(2)–Zn(3)–O(6)	94.9(7)	O(2)–Zn(3)–O(7)	99.8(8)
O(2)–Zn(3)–C(7)	128.2(12)	O(6)–Zn(3)–O(7)	95.6(6)
O(6)–Zn(3)–C(7)	119.9(11)	O(7)–Zn(3)–C(7)	112.3(11)
O(1)–Zn(4)–O(3)	96.8(6)	O(1)–Zn(4)–O(7)	95.0(6)
O(1)–Zn(4)–C(8)	115.5(10)	O(3)–Zn(4)–O(7)	97.5(6)
O(3)–Zn(4)–C(8)	128.4(9)	O(7)–Zn(4)–C(8)	117.2(9)

Table 2 Details of the crystallographic refinement for compounds **1** and **4***

	1	**4**
Formula	$C_{32}H_{66}N_6O_{12}Zn_4$	$C_{24}H_{52}N_4O_8Zn_4$
M	988.47	786.18
Crystal system	Triclinic	Tetragonal
Space group	$P\bar{1}$	$P4_1$
a/Å	11.747(1)	10.900(3)
b/Å	11.251(2)	10.900(3)
c/Å	10.422(1)	31.393(15)
α/°	108.43(2)	
β/°	76.48(2)	
γ/°	72.35(2)	
U/Å^3	1159.53	3729.8
Z	1	4
D_c/g cm^{-3}	1.416	1.401
F(000)	516	1632
μ/cm^{-1}	21.51	24.96
(sin θ)/λ for data collection	0.037, 0.630	0.037, 0.595
Minimum, maximum transmission	0.7448, 0.9983	0.6815, 0.9987
Total data recorded	4264	3809
Total data unique	4065	3322
Total data observed $[F_o > 3\sigma(F_o)]$	2310	1885
R_{int}	0.018	0.015
Number of parameters	278	361
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma F_o$	0.0507	0.0631
$R_G = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}$	0.0399	0.0800
Weighting scheme	$2.0173[\sigma^2(F_o) + 0.000\,034F_o{}^2]$	$2.1138[\sigma^2(F_o) + 0.001F_o{}^2]$
Maximum shift/e.s.d.	3.25	1.068
Maximum, minimum, Δρ/e Å^{-3}	0.560, −0.358	0.400, −0.403

* Details in common: absorption correction by EMPABS + DIFABS[13]; full-matrix least-squares refinement.

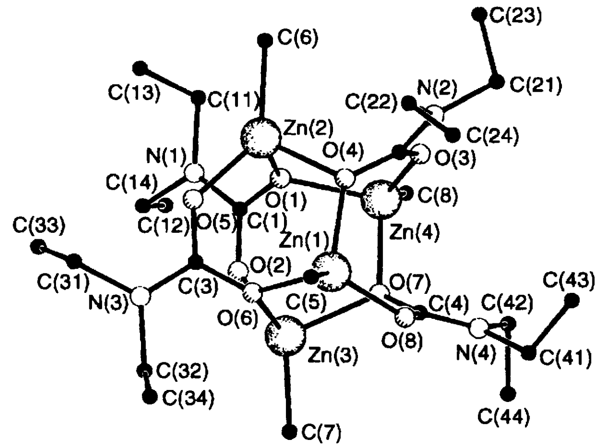

Fig. 2 Crystal structure of $[Zn_4Me_4(O_2CNEt_2)_4]$ **4**

protons at high field for four equivalent methylzinc protons, a triplet for twenty four methyl protons of the ethyl groups, and a quartet for sixteen methylene protons of the ethyl groups. All signals appear at lower field than those for **1**. The ^{13}C NMR spectrum shows four signals, the signal at highest field corresponding to methylzinc carbons being slightly lower (1.54 ppm) than that for compound **1**. The other three signals include two for ethyl carbons and one for carbon bonded to oxygen, all showing similar chemical shifts to those observed for **1**.

Conclusion

A number of structures are known for compounds in which both an alkyl group and oxygen (or other Group VI) atoms co-ordinate to zinc. Co-ordinative saturation at zinc is often attained by some extent of association;[9] common structural units include dimers such as the fused tetrahedra in $K_2[Et_2Zn(OBu^t)_2ZnEt_2]$[10] and $[\{ZnMe(S_2CNEt_2)\}_2]$.[4] Another common geometry is based on a tetrahedral arrangement of zinc atoms as in basic zinc acetate $[Zn_4O(O_2CMe)_6]$[11] and the cubane structure found for neutral alkoxy species such as $[\{ZnMe(OMe)\}_4]$.[12] Compound **1** conforms to none of these established structural types. The tetrahedral system of metal atoms in **4** resembles the disposition of metal atoms in some established cubanes, but the fusing of six- and eight-membered rings is unusual for a compound of this type.

Compounds **1**–**4** are involatile and do not sublime on heating on a vacuum line [10^{-2} Torr (*ca.* 1.33 Pa), < 200 °C]. **CAUTION**: attempts to pyrolyse small quantities of **1** *in vacuo*, on one occasion, led to an explosion, which is quite different to the behaviour of the parent dimeric seleno- or thio-carbamates. These compounds are not likely to be useful precursors for the metal oxides. However, the structures of **1** and **4** are interesting as they do not conform to the structural types observed for the dithio- and diseleno-carbamates.

Experimental

The mixed alkyl–alkylamide was generated *in situ* by the reaction of a stoichiometric amount of diethylamine with the metal alkyl in toluene for 8 h at 70 °C under nitrogen. The resulting solution was cooled to 0 °C and dry CO_2 gas bubbled through it for 0.5 h. The solution was then evaporated to dryness and the solid product recrystallized from toluene to give colourless cubic crystals of compound **1** (R = Me, M = Zn), long slightly sticky needles of **2** (R = Et, M = Zn) and an insoluble microcrystalline solid of **3** (R = Me, M = Cd).

An excess of dimethylzinc (1.42 g, 14.9 mmol) was treated with compound **1** (3.61 g, 3.7 mmol) in toluene solution at room temperature. The mixture was stirred for 0.5 h and the solvent evaporated. Recrystallization from toluene gave white crystals of compound **4**, yield 87%, m.p. 140 °C (Found: C, 36.45; H, 6.70; N, 7.15. Calc. for C, 36.65; H, 6.65; N, 7.15%).

All the other compounds had satisfactory microanalyses and similar infrared spectra. The cadmium complex was apparently insoluble in most common organic solvents and the NMR spectrum was not recorded.

NMR spectra (C_6D_6): $[Zn_4Me_2(O_2CNEt_2)_6]$ **1**, ^1H (250.1 MHz), δ 3.26 [16 H, q, ^3J(H–H) = 7.1, $4(CH_3CH_2)_2N$], 3.08 [8 H, q, ^3J(H–H) = 7.1, $2(CH_3CH_2)_2N$], 1.06 [24 H, t, ^3J(H–H) = 7.1, $4(CH_3CH_2)_2N$], 0.88 [12 H, t, ^3J(H–H) = 7.1 Hz), $2(CH_3CH_2)_2N$] and −0.27 (6 H, s, 2 $ZnCH_3$); ^{13}C (62.9 MHz), δ 164.66, ($4CO_2$), 163.98 ($2CO_2$), 42.90 [$4(CH_3CH_2)_2N$], 42.69 [$2(CH_3CH_2)_2N$], 14.48 [$6(CH_3CH_2)_2N$] and −17.20 ($2ZnCH_3$); $[Zn_4Et_2(O_2CNEt_2)_6]$ **2**, ^1H (250.1 MHz), δ 3.20 [16 H, q, ^3J(H–H) = 7.1, $4(CH_3CH_2)_2N$], 3.11 [8 H, q, ^3J(H–H) = 7.1, $2(CH_3CH_2)_2$], 1.70 [6 H, t, ^3J(H–H) = 8.1, $2(CH_3CH_2)Zn$], 1.03 [24 H, t, ^3J(H–H) = 7.1, $4(CH_3CH_2)_2N$], 0.76 [4 H, q, ^3J(H–H) = 8.1, $2(CH_3CH_2)Zn$] and 0.09 [12 H, t, ^3J(H–H) = 7.1 Hz, $2(CH_3CH_2)_2N$]; ^{13}C (62.9 MHz), δ 164.54 ($4CO_2$), 163.99 ($2CO_2$), 42.96 [$6(CH_3CH_2)_2N$], 14.12 [$4(CH_3CH_2)_2N$], 14.49 [$2(CH_3CH_2)_2N$], 13.77 [$2(CH_3CH_2)Zn$] and −0.63 [$2(CH_3CH_2)Zn$]; $[Zn_4Me_4(O_2CNEt_2)_4]$ **4**, ^1H (250.1 MHz), δ 0.17 (12 H, s), 0.99 [24 H, t, ^3J(H–H) = 7.1 Hz, $(CH_3CH_2)_2N$], and 3.18 [16 H, q, ^3J(H–H) = 7.1 Hz, $2(CH_3CH_2)N$]; ^{13}C (62.9 MHz), δ − 15.66 ($ZnCH_3$), 14.18 [$2N(CH_2CH_3)_2$], 42.79 [$N(CH_2CH_3)_2$] and 164.43 (CO_2).

Crystallography.—Intensity data were collected, at room temperature, on an Enraf-Nonius CAD4 four-circle diffractometer in ω–2θ scan mode. Monochromatic Mo-Kα (λ = 0.710 69 Å) radiation was used throughout. Data for 2310 and 1885 independent reflections, with $I > 3\sigma(I)$, were used in subsequent calculations for compounds **1** and **4** respectively. Data were corrected for Lorentz and polarization factors and an empirical absorption correction was applied prior to refinement. Crystal data and data collection/refinement details are summarised in Table 2.

Structure analysis and refinement. From the crystal data compound **1** was identified as being triclinic and **4** as tetragonal. Systematic absences in the data for **4** led to possible space-group assignments of $P4_1$, $P4_3$, $P4_122$ and $P4_322$. Successful solutions were obtained in $P4_1$ and $P4_3$; that for $P4_1$ is presented here. Both structures were solved by direct methods using SHELXS 86.[14] In both cases the zinc atoms were located first and refined using SHELX 76;[15] the lighter atoms were located in subsequent Fourier-difference maps. The C–C bond distances were constrained in the final refinement for **4** (1.45 + 0.02 Å). Hydrogen-atom positions were refined in geometrically constrained positions for **1** but were not located in **4**. Anisotropic thermal parameters were successfully applied to all heavy atoms with non-unit weights used in the final refinements. The final refined atomic parameters are given in Table 3 with contact distances and angles in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Table 3 Refined fractional atomic coordinates (× 10^4)

Atom	*X/a*	*Y/b*	*Z/c*
Compound **1**			
Zn(1)	38(1)	3 815(1)	1 062(1)
Zn(2)	−569(1)	2 884(1)	−2 024(1)
O(1)	−1 238(4)	4 350(3)	167(4)
O(2)	−1 732(4)	6 313(4)	−134(4)
O(3)	−816(4)	4 644(4)	3 154(4)
O(4)	−710(4)	6 397(4)	2 678(4)
O(5)	497(4)	1 864(3)	422(4)
O(6)	639(4)	1 364(4)	−1 885(5)
N(1)	−3 214(5)	6 032(5)	1 344(6)
N(2)	−1 590(5)	6 713(5)	5 007(5)
N(3)	1 623(5)	−269(5)	−1 254(5)
C(1)	−2 025(6)	5 574(6)	440(7)
C(2)	−1 007(6)	5 914(6)	3 596(6)
C(3)	883(6)	1 054(5)	−893(7)
C(4)	−2 005(6)	2 885(7)	−2 649(7)
C(11)	−4 200(7)	7 386(7)	1 632(8)
C(12)	−4 115(8)	8 410(7)	2 775(9)
C(13)	−3 637(8)	5 326(7)	2 340(10)
C(14)	−4 190(8)	4 696(8)	1 647(10)
C(21)	−1 917(7)	6 165(7)	6 062(7)
C(22)	−3 251(8)	6 423(9)	6 577(9)
C(23)	−2 011(8)	8 264(8)	5 539(8)
C(24)	−1 083(9)	8 550(8)	6 019(9)
C(31)	2 023(7)	−693(6)	−187(7)
C(32)	3 201(7)	−504(7)	−64(8)
C(33)	1 910(7)	−1 393(7)	−2 762(8)
C(34)	3 072(8)	−1 659(9)	−3 648(9)
Compound **4**			
Zn(1)	7 661(3)	7 881(2)	0
Zn(2)	7 185(2)	10 009(2)	800(1)
Zn(3)	4 479(3)	8 054(3)	82(1)
Zn(4)	5 365(2)	11 071(2)	−46(1)
O(1)	5 493(14)	10 417(14)	584(5)
O(2)	3 894(16)	9 148(22)	548(6)
O(3)	7 131(13)	11 317(13)	−137(5)
O(4)	7 866(12)	9 677(11)	205(5)
O(5)	6 813(14)	8 376(14)	999(5)
O(6)	6 132(13)	7 595(13)	384(5)
O(7)	5 235(15)	9 344(13)	−320(5)
O(8)	6 864(19)	8 209(16)	−549(5)
N(1)	4 029(18)	10 504(25)	1 097(7)
N(2)	9 160(16)	11 005(15)	−115(6)
N(3)	5 966(20)	6 506(17)	1 006(5)
N(4)	5 798(21)	9 355(18)	−992(5)
C(1)	4 449(25)	10 022(26)	720(8)
C(2)	8 015(20)	10 636(19)	−22(6)
C(3)	6 310(20)	7 501(21)	798(8)
C(4)	5 990(28)	8 947(24)	−611(7)
C(5)	9 081(27)	6 766(23)	86(9)
C(6)	8 169(23)	11 310(19)	1 067(8)
C(7)	3 563(36)	6 803(30)	−225(10)
C(8)	4 025(26)	12 215(22)	−154(10)
C(11)	4 627(27)	11 606(31)	1 297(10)
C(12)	2 862(20)	10 034(32)	1 291(90)
C(13)	5 165(38)	11 278(60)	1 709(14)
C(14)	1 828(29)	10 861(42)	1 176(17)
C(21)	9 353(27)	12 153(19)	−368(90)
C(22)	10 259(18)	10 341(23)	54(9)
C(23)	9 503(44)	13 193(36)	−63(15)
C(24)	10 994(32)	9 765(37)	−293(11)
C(31)	6 167(29)	6 399(24)	1 479(5)
C(32)	5 485(33)	5 428(25)	760(8)
C(33)	5 108(37)	6 934(40)	1 732(13)
C(34)	6 435(44)	4 437(39)	644(16)
C(41)	6 597(39)	8 925(37)	−1 352(10)
C(42)	4 855(38)	10 266(35)	−1 135(11)
C(43)	7 718(48)	9 685(46)	−1 440(20)
C(44)	3 997(44)	9 437(50)	−1 342(24)

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