Unusual Products from Carbon Dioxide Insertion Reactions into Group 12 Alkyls–Alkylamides: the X-Ray Structure of a Tetrameric Alkylzinc Carbamate $[Me_2Zn_4(O_2CNEt_2)_6]$

Michael B. Hursthouse,*† M. Azad Malik, Majid Motevalli and Paul O'Brien*

Department of Chemistry, Queen Mary and Westfield College, University of London, Mile End Road, London E1 4NS, UK

The reaction of CO_2 with mixed alkyls–alkylamides $RMNEt_2$ (R = Me or Et, M = Zn and R = Me, M = Cd) leads to solid tetrameric products; an X-ray structure is reported for $[Me_2Zn_4(O_2CNEt_2)_6]$ which contains two tetrahedral and two trigonal bipyramidal zinc atoms.

In attempts to develop useful, single-molecule, precursors for materials such as ZnSe we have prepared a number of mixed alkyl, dialkylchalcogen carbamates;[1-3] crystallographic studies have shown these compounds are typically dimers with approximately tetrahedral coordination at the metal (ME_3C)[1-3] (E = S or Se). One route to such species involves, in a formal sense, the insertion of CS_2 or CSe_2 into the appropriate mixed alkyl-alkylamide.[1-5] We have now attempted the analogous insertion reactions into $RMNR'_2$ with CO_2 [R = Me (Zn and Cd), R = Et (Zn), and R' = Et in all cases] and report the formation of tetrameric species with a unique structure.

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

$[R_2M_4(O_2CNEt_2)_6]$
1 R = Me, M = Zn
2 R = Et, M = Zn
3 R = Me, M = Cd

The structure of **1** has been solved by X-ray methods‡ and consists of tetrameric molecular units $[Me_2Zn_4(O_2CNEt_2)_6]$ (Fig. 1). The zinc atoms lie in a plane and the unit is centrosymmetric with two independent zinc atoms. Four carbamates bond along the edge of the Zn_4 parallelogram with normal Zn–O distances. 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 in each bonds *via* a monoatomic bridge to Zn(2) [and Zn(2')], and tetrahedral coordination at Zn(2) is completed by a methyl group. The other zinc atom [Zn(1)] is five-coordinate with a weak monoatomic bridge (2.591 Å) from one of the edge-bridging carbamates Zn(1)–O(4). The coordination at zinc can be viewed either as a flattened tetrahedron consisting of the normal zinc–oxygen contacts with O(4) coordinating to the opened-up face of the tetrahedron, or as a distorted trigonal bipyramid with weak axial ligation from O(4). There are a number of crystallographically characterized Zn–C bonds; bond lengths are typically in the range[7,8] 1.93–2.00 Å, similar to that reported in the present study.

Spectroscopic studies (IR and ^{13}C and ^{1}H NMR), and satisfactory microanalytical results suggest that the compounds **2** and **3** have similar structures.§ In particular the

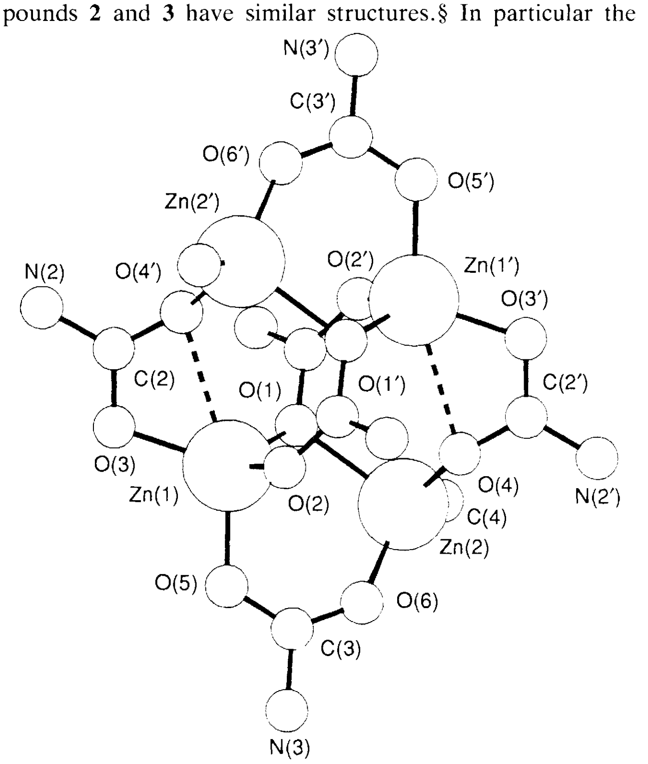

Fig. 1 Structure of $[Me_2Zn_4(O_2CNEt_2)_6]$ (for clarity the ethyl groups of the carbamates and all hydrogen atoms have been omitted), important bond lengths (Å) and angles (°): Zn(1)–O(1) 1.985(6), Zn(1)–O(2) 1.938(6), Zn(1)–O(3) 1.937(6), Zn(1)–O(4) 2.591(7), Zn(1)–O(5) 1.934(5), Zn(2)–C(4) 1.945(8), Zn(2)–O(1) 2.132(6) 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)

---

† *Present address*: Department of Chemistry, University of Wales, College of Cardiff, Cardiff CF1 3TB.

‡ *Crystal data* for **1**, $C_{32}H_{66}O_{12}N_6Zn_4$, $M = 988.469$, $a = 1.747(1)$, $b = 11.251(2)$, $c = 10.422(1)$ Å, $\alpha = 108.43(2)$, $\beta = 76.48(2)$, $\gamma = 72.35(2)°$, $V = 1159.53(43)$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_c = 1.416\ g\ cm^{-3}$, $\lambda(Mo\text{-}K\alpha) = 0.71069$ Å, $\mu = 21.511\ cm^{-1}$. Data were recorded with a CAD4 diffractometer in the $\omega/2\theta$ scan mode; 4065 unique reflections measured, 2310 observed with $F_o > 3\sigma(F_o)$. Structure solved by direct methods, and refined with the inclusion of hydrogen atoms to $R = 0.0507$, $R_w = 0.0400$ for 244 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1991.

§ All the compounds had satisfactory microanalyses and similar IR spectra. The cadmium complex was insoluble in most common organic solvents and NMR spectra were not recorded.

NMR spectra (*J* values in Hz): **1**, ^{1}H (C_6D_6, 250.1 MHz) δ 3.20 {16H, q, $^3J_{H\text{-}H}$ 7.1, $[(CH_3C\mathit{H}_2)_2N]_4$}, 3.11 {8H, q, $^3J_{H\text{-}H}$ 7.1, $[(CH_3C\mathit{H}_2)_2N]_2$}, 1.03 {24H, t, $^3J_{H\text{-}H}$ 7.1, $[(C\mathit{H}_3CH_2)_2N]_4$}, 0.09 {12H, t, $^3J_{H\text{-}H}$ 7.1, $[(C\mathit{H}_3CH_2)_2N]_2$}, 1.70 {6H, t, $^3J_{H\text{-}H}$ 8.1, $[(C\mathit{H}_3CH_2)Zn]_2$} and 0.76 {4H, q, $^3J_{H\text{-}H}$ 8.1, $[(CH_3C\mathit{H}_2)Zn]_2$}, ^{13}C (C_6D_6, 62.9 MHz), δ 164.54 $(CO_2)_4$, 163.99 $(CO_2)_2$, 42.96 $[(CH_3C\mathit{H}_2)_2N]_6$, 14.12 $[(\mathit{C}H_3CH_2)_2N]_4$, 14.49 $[(\mathit{C}H_3CH_2)_2N]_2$, 13.77 $[(\mathit{C}H_3CH_2)Zn]_2$ and −0.63 $[(CH_3\mathit{C}H_2)Zn]_2$.

For **2**, ^{1}H (C_6D_6, 250.1 MHz), δ 3.26 {16H, q, $^3J_{H\text{-}H}$ 7.1, $[(CH_3C\mathit{H}_2)_2N]_4$}, 3.08 {8H, q, $^3J_{H\text{-}H}$ 7.1, $[(CH_3C\mathit{H}_2)_2N]_2$}, 1.06 {24H, t, $^3J_{H\text{-}H}$ 7.1, $[(C\mathit{H}_3CH_2)_2N]_4$}, 0.88 {12H, t, $^3J_{H\text{-}H}$ 7.1, $[(C\mathit{H}_3CH_2)_2N]_2$} and −0.27 {6H, s, $(C\mathit{H}_3Zn)_2$}; ^{13}C, (C_6D_6, 62.9 MHz) δ 164.66 $(CO_2)_4$, 163.98 $(CO_2)_2$, 42.90 $[(CH_3\mathit{C}H_2)_2N]_4$, 42.69 $[(CH_3\mathit{C}H_2)_2N]_2$, 14.48 $[(\mathit{C}H_3CH_2)_2N]_6$ and −17.20 $(\mathit{C}H_3Zn)_2$.

spectra of the two zinc complexes in solution indicate the presence of two kinds of carbamates, in a 2 : 1 ratio, exactly as required by the solid state structure of **1**.§ The cadmium complex is insoluble in common solvents, but the solid has a remarkably similar IR spectrum to those of the zinc analogues; the structure may be similar but involving some degree of polymerization between tetrameric units.

There are a number of structures known for compounds in which both an alkyl group and oxygen (or other group 6) atoms coordinate to zinc. Coordinative saturation at zinc is often attained by some degree of association,[6] and common structural units include dimers such as the fused tetrahedra in $K_2[Et_2Zn(OBu^t)_2ZnEt_2]$[7] and $[MeZn(S_2CNEt_2)]_2$.[1] Another common geometry is based on a tetrahedral arrangement of zinc atoms as in basic zinc acetate $[Zn_4O(O_2CMe)_6]$[9] and the cubane structure found for neutral alkoxy species such as $[\{MeZn(OMe)\}_4]$.[10] The present structure conforms to none of these established structural types.

The compounds **1**–**3** are involatile and do not sublime on heating on a vacuum line (10^{-2} Torr; <200 °C). Attempts to pyrolyse small quantities of compound **1** *in vacuo* have, on one occasion, led to the explosion of the tube, behaviour which is quite different from that of the parent dimeric seleno- and thio-carbamates. These compounds are not likely to be useful precursors for the metal oxides. However, the structure of **1** is, to our knowledge, unique in containing a planar tetramer of zinc atoms involving the fusion of tetrahedral and trigonal pyramidal zinc sites.

We thank the SERC for a grant to P. O'B. and the support of crystallography at Q. M. W. We thank Dr Peter Thornton (Q. M. W.) for helpful discussions.

Received, 13th August 1991; Com. 1/04243B

References

1 M. B. Hursthouse, M. A. Malik, M. Motevalli and P. O'Brien, *Organometallics*, 1991, **10**, 730.
2 M. A. Malik and P. O'Brien, *Mater. Chem.*, 1991, in the press.
3 M. B. Hursthouse, M. A. Malik, M. Motevalli and P. O'Brien, unpublished crystal structures for $[RME_2CNR'_2]_2$ (R' = Et, M = Zn or $Zn_{0.5}Cd_{0.5}$ and R = Me and R = Et, M = Zn) QMW, 1991.
4 J. G. Noltes, *Rec. Trav. Chim. Pays-Bas*, 1965, **84**, 126.
5 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Strivastava, *Metal and Metalloid Amides*, Ellis Horwood, Chichester, 1980.
6 N. A. Bell and P. T. Moseley, *J. Organomet. Chem.*, 1987, **325**, 47.
7 R. M. Fabicon, M. Parvez and H. G. Richey Jr., *J. Am. Chem. Soc.*, 1991, **113**, 1412.
8 M. B. Hursthouse, M. Motevalli, P. O'Brien, J. R. Walsh and A. C. Jones, *Organometallics*, 1991, in the press.
9 L. Hiltunen, M. Leskela, M. Makela and L. Niinisto, *Acta Chem. Scand., Ser. A*, 1987, **41**, 548.
10 H. M. M. Shearer and C. B. Spencer, *Acta Crystallogr., Sect. B*, 1980, **36**, 2046.