Structural Diversity in the Carbamato Chemistry of Zinc: X-ray Single-Crystal Structures of $[(Me_2NCH_2)_2Zn(O_2CN(C_2H_5)_2)_2]$ and $[C_5H_5NZn_2Me(O_2CN(C_2H_5)_2)_3]$

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Introduction

In several recent papers, we reported the characterization of a number of dimeric diseleno- and dithiocarbamato complexes with metal alkyl fragments of the general type $[RME_2CNR'_2]_2$ (E = S, Se).[1−7] The structural chemistry of these compounds is dominated by the formation of dimeric species. In contrast, the reaction of CO_2 with the alkylzinc alkyamides ($RZnNEt_2$) gave an unusual tetrameric species $[(CH_3)_2Zn_4(O_2CN(C_2H_5)_2)_6]$,[8] which reacts with dimethylzinc to give a distorted cubane $[(CH_3)_4Zn_4(O_2CN(C_2H_5)_2)_4]$.[9] The present note deals with the synthesis and X-ray structures of two more novel carbamates of zinc: $[(Me_2NCH_2)_2Zn(O_2CN(C_2H_5)_2)_2]$ (**1**) and $[C_5H_5NZn_2Me(O_2CN(C_2H_5)_2)_3]$ (**2**).

Results and Discussion

Both compounds are crystalline solids, soluble in common organic solids and stable over a period of months. Compound **1** was isolated by fractional crystallization as the side product is a solid as well. It is interesting to note that the reaction of the tetramer with TMEDA gives monomeric adducts with carbamate and with dimethylzinc, whereas the reaction of pyridine gives a dimeric species.

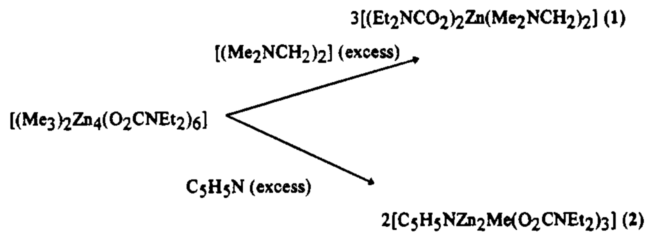

Table 1. Crystal Data and Structure Refinement Parameters

	1	**2**
chem formula	$C_{16}H_{36}N_4O_4Zn$	$C_{21}H_{38}N_4O_4Zn_2$
fw	413.86	573.29
T, °C	20	20
λ, Å	0.71069	0.71069
cryst syst	orthorhombic	triclinic
space group	$Pna2_1$	$P\bar{1}$
a, Å	13.889(1)	10.393(12)
b, Å	10.246(1)	10.680(2)
c, Å	30.802(2)	13.907(13)
α, deg	90	93.30(14)
β, deg	90	109.72((9)
γ, deg	90	103.8(2)
V, Å^3	4382(3)	1395(3)
Z	8	2
D_{calcd}, g cm^{-3}	1.255	1.365
μ, mm^{-1}	1.145	1.758
$F(000)$	1776	600
R^a	0.0405	0.0560
$R_w{}^b$	0.0794	0.1731

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

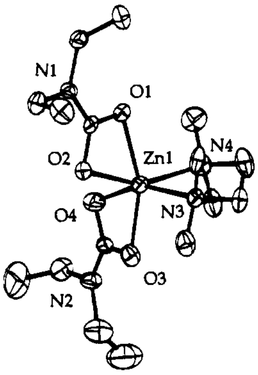

Figure 1. Structure of $[(Me_2NCH_2)_2Zn(O_2CN(C_2H_5)_2]$.

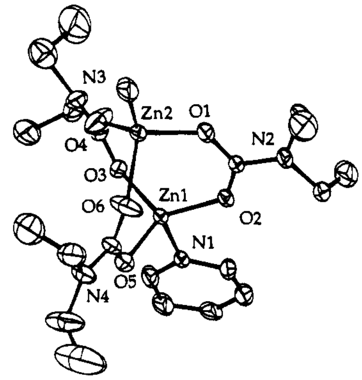

Figure 2. Structure of $[C_5H_5NZn_2CH_3(O_2CN(C_2H_5)_2))_3]$.

Single-crystal X-ray structures of both compounds has been determined by X-ray methods. The structure of **1** contains monomeric molecular units $[(Et_2NCO_2)_2Zn(Me_2NCH_2)_2]$ (Figure 1). The zinc atom is coordinated to four oxygens, two from each chelating carbamate group and two nitrogen atoms from the chelating *N,N,N′,N′*-tetramethylethylenediamine ligand. The coordination around zinc is a distorted octahedron. Selected bond lengths and angles are given in Table 3.

The structure of compound **2** consists of dimeric molecular units $[(Et_2NCO_2)_3MeZn_2NC_5H_5]$ in which each zinc atom is four-coordinate (Figure 2). One of the zinc atoms is coordinated to the nitrogen atom of pyridine and three oxygen atoms, one each from the three bridging carbamato groups, whereas the other zinc atom is linked to one methyl carbon and three oxygen atoms, one each from the carbamato group. Each zinc has

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)^a		*x*	*y*	*z*	*U*(eq)^a
				Compound **1**					
Zn(1)	2333(1)	1496(2)	4(1)	54(1)	C(8)	2982(6)	755(13)	−926(3)	0(4)
Zn(2)	198(1)	6491(2)	2382(1)	55(1)	C(9)	1667(6)	5528(9)	626(4)	76(3)
N(1)	1597(4)	4206(7)	782(3)	56(2)	C(10)	2639(7)	6151(10)	668(3)	3(3)
N(2)	757(6)	−1251(9)	−466(3)	73(3)	C(11)	1361(7)	3982(8)	1235(3)	77(3)
N(3)	3800(4)	1228(8)	243(3)	58(2)	C(12)	2219(7)	3880(10)	1535(3)	2(4)
N(4)	3075(6)	1872(11)	−621(3)	70(3)	C(13)	993(16)	−2577(14)	−383(9)	11(9)
N(5)	1832(6)	3795(8)	2827(3)	71(2)	C(14)	1192(12)	−3345(17)	−742(8)	0(8)
N(6)	950(4)	9193(8)	1596(2)	59(2)	C(15)	−121(9)	−1029(10)	−690(4)	6(4)
N(7)	−572(5)	6790(10)	2998(3)	65(3)	C(16)	−895(9)	−1276(18)	−468(7)	63(13)
N(8)	−1248(4)	6235(8)	2127(2)	57(2)	C(17)	1310(7)	4792(11)	2674(3)	67(3)
O(1)	2067(5)	3447(9)	119(3)	52(2)	C(18)	718(7)	8181(14)	1864(5)	51(4)
O(2)	1779(5)	2038(11)	664(3)	63(3)	C(19)	−203(10)	7962(17)	3223(5)	94(4)
O(3)	2031(4)	−448(6)	−75(2)	75(2)	C(20)	−479(7)	5675(12)	3295(3)	96(3)
O(4)	968(5)	907(7)	−346(2)	90(2)	C(21)	−1568(8)	7024(13)	2855(5)	81(3)
O(5)	1560(4)	5956(6)	2746(2)	76(2)	C(22)	−1869(7)	6098(10)	2498(3)	85(3)
O(6)	526(4)	4567(5)	2457(2)	76(2)	C(23)	−1269(6)	5053(11)	1859(4)	96(4)
O(7)	471(5)	8419(9)	2256(3)	62(2)	C(24)	−1525(11)	7357(11)	1864(7)	90(6)
O(8)	754(5)	7043(11)	1736(4)	67(3)	C(25)	2767(7)	4020(8)	3048(3)	84(3)
C(1)	1801(7)	3235(14)	518(5)	51(4)	C(26)	3621(8)	3752(14)	2783(5)	158(6)
C(2)	1253(7)	−243(10)	−283(3)	67(3)	C(27)	1501(12)	2437(9)	2736(8)	81(7)
C(3)	4114(10)	2326(12)	492(7)	86(6)	C(28)	1299(11)	1697(16)	3143(6)	188(9)
C(4)	3857(6)	77(12)	518(3)	94(4)	C(29)	874(6)	10520(9)	1741(3)	69(3)
C(5)	4385(6)	1076(10)	−147(3)	78(3)	C(30)	−114(7)	11120(8)	1708(3)	89(3)
C(6)	4131(8)	1989(16)	−502(5)	2(4)	C(31)	1209(6)	8965(8)	1147(3)	69(3)
C(7)	2685(11)	3040(18)	−820(5)	7(4)	C(32)	361(6)	8847(11)	842(3)	101(4)
				Compound **2**					
Zn(1)	881(1)	4747(1)	8124(1)	60(1)	C(6)	1132(10)	8793(7)	8641(7)	115(3)
Zn(2)	1464(1)	2013(1)	7164(1)	71(1)	C(7)	958(8)	8988(7)	9547(7)	101(2)
O(1)	2323(7)	3653(5)	6766(5)	116(2)	C(8)	662(10)	7952(7)	10018(7)	113(3)
O(2)	1517(5)	5332(4)	7039(3)	78(1)	C(9)	663(9)	6777(7)	9601(6)	100(2)
O(3)	2168(4)	4307(4)	9336(3)	77(1)	C(10)	2019(10)	6426(9)	5477(6)	104(2)
O(4)	2298(10)	2410(7)	8682(4)	171(3)	C(11)	3249(14)	7565(10)	5995(10	154(4)
O(5)	−1056(4)	3673(4)	7725(4)	88(1)	C(12)	3033(13)	4586(11)	5185(8)	132(3)
O(6)	−462(6)	2261(7)	6972(6)	155(3)	C(13)	2095(20)	3754(16)	4293(10	212(8)
N(1)	835(5)	6539(4)	8715(3)	64(1)	C(14)	4207(13)	1948(14)	434(9)	172(5)
N(2)	2315(7)	5221(6)	5749(4)	93(2)	C(15)	5219(16)	2409(22)	253(17)	340(19)
N(3)	3705(7)	3332(7)	282(4)	108(2)	C(16)	4170(10)	4348(9)	1159(6)	120(3)
N(4)	−2600(6)	1733(6)	7016(6)	106(2)	C(17)	3519(13)	4044(14)	1934(8)	161(4)
C(1)	1992(6)	4691(5)	6530(4)	70(1)	C(18)	−2934(11)	430(11)	6385(12)	153(4)
C(2)	2687(7)	3354(7)	9390(4)	85(2)	C(19)	−2607(19)	−445(14)	7028(16)	226(8)
C(3)	−1311(6)	2573(7)	7267(5)	82(2)	C(20)	−3670(12)	2052(15)	7339(17)	205(9)
C(4)	1626(12)	424(8)	6482(7)	123(3)	C(21)	−4653(24)	2334(22)	6805(23)	374(20)
C(5)	1069(8)	7581(6)	8259(5)	92(2)					

^{a} *U*(eq) is defined as one-third the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

Zn(1)−O(3)	2.044(6)	Zn(1)−N(4)	2.208(9)
Zn(1)−O(1)	2.056(10)	Zn(1)−O(2)	2.227(10)
Zn(1)−N(3)	2.179(6)	Zn(1)−O(4)	2.265(6)
O(3)−Zn(1)−O(1)	157.7(2)	O(3)−Zn(1)−O(4)	60.9(2)
O(3)−Zn(1)−N(3)	96.2(3)	O(1)−Zn(1)−O(4)	100.9(3)
O(1)−Zn(1)−N(3)	103.4(3)	N(3)−Zn(1)−O(4)	155.3(3)
O(3)−Zn(1)−N(4)	99.3(4)	N(4)−Zn(1)−O(4)	91.3(3)
O(1)−Zn(1)−N(4)	93.6(4)	O(2)−Zn(1)−O(4)	102.1(3)
N(3)−Zn(1)−N(4)	83.2(3)	O(3)−Zn(1)−C(2)	30.7(3)
O(3)−Zn(1)−O(2)	106.1(3)	O(4)−Zn(1)−C(2)	30.2(3)
O(1)−Zn(1)−O(2)	62.8(3)	O(1)−Zn(1)−C(1)	31.4(4)
N(3)−Zn(1)−O(2)	92.6(3)	O(2)−Zn(1)−C(1)	31.4(4)
N(4)−Zn(1)−O(2)	154.6(4)		

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **2**

Zn(1)−O(2)	1.921(4)	Zn(2)−O(4)	1.969(6)
Zn(1)−O(3)	1.929(4)	Zn(2)−O(1)	1.969(6)
Zn(1)−O(5)	1.936(6)	Zn(2)−C(4)	1.966(9)
Zn(1)−N(1)	2.057(6)	Zn(2)−O(6)	2.012(6)
O(2)−Zn(1)−O(3)	120.4(2)	O(4)−Zn(2)−O(6)	98.1(3)
O(2)−Zn(1)−O(5)	117.4(2)	O(1)−Zn(2)−O(6)	99.5(3)
O(3)−Zn(1)−O(5)	113.0(2)	C(4)−Zn(2)−O(6)	120.2(4)
O(2)−Zn(1)−N(1)	96.4(2)	C(1)−O(1)−Zn(2)	137.1(5)
O(3)−Zn(1)−N(1)	100.1(2)	C(1)−O(2)−Zn(1)	125.1(4)
O(5)−Zn(1)−N(1)	104.4(2)	C(2)−O(3)−Zn(1)	127.4(4)
O(4)−Zn(2)−O(1)	101.6(4)	C(2)−O(4)−Zn(2)	139.8(5)
O(4)−Zn(2)−C(4)	118.7(4)	C(3)−O(5)−Zn(1)	115.9(4)
O(1)−Zn(2)−C(4)	115.2(3)	C(3)−O(6)−Zn(2)	153.8(7)

distorted tetrahedral coordination. All three carbamato groups act as bridging ligands between the two zinc atoms. Selected bond lengths and angles are given in Table 4.

Zn−O bond distances (2.044(6), 2.057(1), 2.228(1), 2.265(6) Å) in compound **1** are slightly longer than those in compound **2** (1.921(4), 1.929(4), 1.936(6), 1.969(6), 2.012(6) Å). In the dithio-[10,11] or diselenocarbamates,[15] one of the Zn−S or Zn−Se bonds is longer than the other; the same is true for the Zn−O bond distances in compounds **1** and **2**. The Zn−C bond distance in compound **2** is in the typical range (1.89−1.99 Å).[13,14] The

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Zn−N bond distances in adducts such as $Me_2Zn[(CH_2NMe)_3]_2$[14,15] (2.410(4) Å), $Me_2Zn[Me_2N(CH_2)_2NMe_2]_2$[16] (2.260(8) Å), $[Me_2N(CH_2)_3]Zn$[17] (2.307(4) Å), and $(Me_3CCH_2)_2Zn[Me_2N(CH_2)_2NMe_2]$[16] (2.411(4) Å) are much greater than observed in compounds **1** (2.179(6), 2.208(9) Å) and **2** (2.057(6) Å) but are smaller in $C_5H_5N{\cdot}Zn[S_2CNMe_2]_2$[18] (2.079 Å) and $[(CNS)ZnS_2CNMe_2)\ _2]^-$ [19] (1.954(9) Å).

The compounds have been further characterized by NMR (^1H and ^{13}C) spectra. The ^1H NMR spectrum of compound **1** shows a quartet and triplet for the *N*-ethyl protons and singlets for the *N*-methylene and *N*-methyl protons of the TMEDA group. The *N*-methyl protons of the TMEDA are at lower field than the *N*-methylene protons, whereas in the corresponding TMEDA adduct of the dithiocarbamate[20] the methylene protons always appear at lower field than methyl protons. The pattern is reversed in the ^{13}C NMR spectrum; the methyl carbons are at higher field than methylene carbons. The chemical shift for the carbamate carbon ($-CO_2$, δ 164.40) is considerably smaller than that of the corresponding thiocarbamate ($-CS_2$, δ 206.73).

The ^1H NMR spectrum of compound **2** shows two types of carbamates in the ratio of 2:1. For the *N*-ethyl protons, two quartets and two triplets are observed. Only one singlet appears for the *Zn*-methyl protons and three different multiplets are seen at low field for pyridine protons. Similarly the ^{13}C NMR spectrum gives two sets of signals for *N*-ethyl carbons but only one for $-CO_2$ and $Zn-CH_3$ carbons. The chemical shift for the $-CO_2$ carbon (δ 163.98) is very close to that observed for compound **1**.

The carbamato chemistry of the early transition metals is fairly well developed, in contrast, relatively little is known concerning the immediately post transition metals. Our studies of the zinc carbamates have now led to a structurally diverse range of products[8,9] and provide the first example of a simple bis(carbamato)complex of zinc.

Experimental Section

N,N,N',N'-Tetramethylethylenediamine and pyridine were purchased from Aldrich Chemical Co. Ltd. Solvents were obtained from BDH and were dried and degassed before use. All experiments were performed under air-sensitive conditions.

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.

Synthesis. The tetramer $[(CH_3)_2Zn_4(O_2CN(C_2H_5)_2)_6]$[8] was reacted with an excess of tetramethylethylenediamine (TMEDA) or pyridine. The mixtures were heated and stirred to give clear solutions, which were further stirred at room temperature for 0.5 h. The solutions were evaporated to give white solids. The pyridine adduct was dissolved in hexane and gave transparent cubic crystals of **2** (at 0 °C), which were isolated by decanting the solvent: yield 89%; mp 182 °C. Anal. Found: C, 42.76; H, 6.53; N, 9.38. Calcd: C, 43.99; H, 6.68; N, 9.77. The white solid obtained with tetramethylethylenedimaine was dissolved in hexane to give yellowish sticky crystals of $[(Et_2NCO_2)_2Zn(Me_2NCH_2)_2]$ (**1**): yield 47%; mp 208 °C. Anal. Found: C, 45.23; H, 8.67; N, 13.38. Calcd: C, 46.43; H, 8.77; N, 13.53. The material insoluable in hexane was dissolved in benzene and gave a crop of crystals (mp 60 °C) identified as $Me_2Zn(Me_2NCH_2)_2$.

X-ray Studies. X-ray measurements were made on a sample mounted in a glass capillary with an Enraf-Nonius CAD4 diffractometer operating in the $\omega/2\theta$ scan mode with graphite-monochromated Mo Kα radiation as described previously.[21] The structures were solved via standard heavy-atom procedures and refined by using full-matrix least-squares methods[22] with scattering factors calculated by using the data from ref 23. 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 1; atomic coordinates, in Table 2. Tables of H atom coordinates, full lists of bond lengths and angles, and anisotropic displacement factor coefficients are included in the Supporting Information.

NMR Data. $[(Et_2NCO_2)_2Zn(Me_2NCH_2)_2]$ (1). ^1H NMR ($[^2H_6]C_6H_6$, 250.1 MHz): δ 3.42 (8H, q, $^3J_{H-H}$ = 7.1 Hz, $(CH_3\mathit{CH_2})_2N$), 1.15 (12H, t, $^3J_{H-H}$ = 7.1 Hz, $(\mathit{CH_3}CH_2)_2N$), 1.98 (4H, s, NCH_2), 2.25 (12H, s, NCH_3). ^{13}C NMR ($[^2H_6]C_6H_6$, 62.9 MHz: δ 164.40 (CO_2), 46.68 ($((CH_3\mathit{CH_2})_2N$), 14.62 ($((\mathit{CH_3}CH_2)_2N$), 42.67 (CH_3N), 58.98 (NCH_2).

$[C_5H_5NZn_2Me(O_2CN(C_2H_5)_2)_3]$ (2). ^1H NMR ($[^2H_6]C_6H_6$, 250.1 MHz): δ 3.28 (8H, q, $^3J_{H-H}$ = 7.1 Hz, $[(CH_3\mathit{CH_2})_2N]_2$), 3.17 (4H, q, $^3J_{H-H}$ = 7.1 Hz, $(CH_3\mathit{CH_2})_2N$), 1.05 (12H, t, $^3J_{H-H}$ = 7.1 Hz, $[(\mathit{CH_3}CH_2)_2N]_2$), 0.95 (6H, t, $^3J_{H-H}$ = 7.1 Hz, $(\mathit{CH_3}CH_2)_2N$), 0.35 (3H, s, $\mathit{CH_3}Zn$), 6.60, 6.89, 7.08 (NC_5H_5). ^{13}C NMR ($[^2H_6]C_6H_6$, 62.9 MHz): δ 163.98 (CO_2), 42.67 ($[(CH_3\mathit{CH_2})_2N]_2$), 41.06 ($((CH_3\mathit{CH_2})_2N$), 14.48 ($[(\mathit{CH_3}CH_2)_2N]_2$), 16.22 ($((\mathit{CH_3}CH_2)_2N$), 2.03 ($\mathit{CH_3}Zn$), 124.13, 135.81, 150.98 (NC_5H_5).

Acknowledgment. We thank the SERC for a grant to P.O'B.

Supporting Information Available: Complete listings of data collection parameters, bond distances and angles, thermal parameters, and hydrogen coordinates for **1** and **2** (18 pages). Ordering information is given on any current masthead page.

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