solid-state detector, the latter eliminating the need for beam monochromatization. Measurement of a standard reflection showed no variation greater than 2 standard deviations throughout, and hence there was no evidence of crystal decay. In a number of cases, 2-4 equiv were measured for particular reflections. In the few cases where significant differences occurred, the reflections concerned were assessed individually. Intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The crystal used for data collection could be inscribed in a rectangular block of dimensions 0.19 × 0.23 × 0.30 mm, but part of the surface was curved and it was not possible to use any of the standard routines for calculating absorption factors. It is thought that the low μ and the reasonable regularity of the dimensions means that the absence of absorption corrections has not seriously affected the structural details obtained. A total of 4040 reflections were measured, which after averaging gave 3498 unique reflections of which 2126 had $I > 3\sigma(I)$ and these were used for the structural analysis.

The structure was solved by the heavy-atom method and refined in three block matrices by using least-squares procedures which minimized the function $\sum w\Delta^2$. The weight for each reflection, w, in the final cycles of refinement is given by $w = (5.0 + 0.5|F_o| + 0.006|F_o|^2)^{-1}$. For this scheme average values of $\sum w\Delta^2$ for ranges of increasing $|F_o|$ were nearly constant. A difference map revealed one of the perchlorate ions and two of the lattice water molecules to be disordered. Occupancies for partial atoms were assigned on the basis of peak heights in the difference map. After isotropic refinement a further difference map yielded the approximate positions for the hydrogen atoms of the cation with the exception of those attached to N(33), the pendant nitrogen atom of the coordinated triamine. Attempts to locate these hydrogen atoms or those of the water molecules during subsequent refinement were unsuccessful nor could they be positioned unambiguously by calculation. The positions of the other hydrogen atoms were optimized, assuming C-H and N-H to be 1.0 Å and assuming the appropriate geometry of the atom to which they are bonded. The anisotropic refinement process was terminated when the minimization factor changed by <0.1% and a final difference map showed no residual electron density greater than |0.5| e Å^{-3}. The final R was 0.078 and R' [$=(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$] was 0.107.

The structural solution and analysis calculations were carried out on a FACOM M340S computer using programs written by F.S.S. Neutral-atom scattering factors, corrected for anomalous dispersion, were taken from ref 15. The final atomic coordinates for non-hydrogen atoms are given in Table I, and selected interatomic parameters are presented in Table II.

Physical Measurements. Electronic and CD spectra were recorded by using a Perkin-Elmer Lambda 5 spectrophotometer and a Jobin-Yvon CNRS Dichrographe III instrument, respectively. AAS measurements were carried out on a Varian AA 274 instrument. NMR spectra of samples dissolved in D_2O were recorded at 360 MHz for ^1H and at 90 MHz for ^{13}C by using a Bruker WM 360 spectrometer at 21 °C, with standard Bruker software. Chemical shifts (δ) are given in ppm relative to TPS as internal standard.

Nuclear Overhauser effects (NOE's) were measured by the difference method. Low-intensity presaturation pulses (3 s) were applied before each acquisition (16K data points over 3300 Hz, 90° observation pulse, 10-s relaxation delay), accumulating 40 sets of data, each containing two "dummy" scans and eight acquired scans for each irradiation position and a "blank" position. A line-broadening of 1 Hz was applied to the subtracted FID's before Fourier transformation. Quantitative values for the enhancements were determined from integrals, wherever possible. Pseudo-INDOR effects were determined in a similar way, but with an observation pulse of 30° and the irradiation power reduced by 20 db. ^1H COSY-45 spectra were measured by using 2K data points over 3300 Hz in f_2 and 512 points zero-filled to 1K in f_1. $^{13}C-^1H$ correlation was carried out by using the Bruker XHCORRD routine optimized for a coupling constant of 135 Hz, collecting 1K data points over 14 500 Hz in f_2 and 256 points in f_1 with zero-filling in both dimensions.

Acknowledgment. We thank the Royal Society, the Science and Engineering Research Council and the Macquarie University Research Grant Scheme for financial support.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, and complete molecular dimensions and contact distances (6 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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Deoxygenation of Carbon Dioxide to Diethylformamide in the $Zn/HNEt_2/CO_2$ System. Crystal and Molecular Structure of $[Zn_4O(O_2CNEt_2)_6]$

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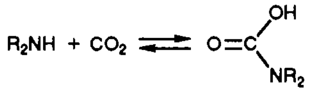
Carbon dioxide chemistry is an active field of research, and much interest is devoted to the use of metal systems to modify its reactivity.[1] Energy demanding transformations such as the carbon dioxide deoxygenation (1), can be realized, for example,

$$CO_2 + 2e^- \rightarrow CO + O^{2-} \qquad (1)$$

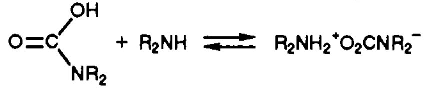
when the reducing equivalents are provided by a metal, either in a heterogeneous system[2] or as part of a soluble coordination compound.[3] Metals themselves[2,3] can also act as oxygen acceptors, the formation of a metal-oxygen bond thus controlling the overall thermodynamic balance.[2-4]

Metal carbamato complexes, $[M(O_2CNR_2)_n]$, can be readily prepared from carbon dioxide and a metal precursor in the presence of a secondary amine. In recent years, we became interested in the chemistry of these compounds, and in addition to synthetic and structural aspects,[5] we pointed out their utility for accomplishing incorporation[6] and deoxygenation[7] reactions of carbon dioxide. In continuation of these studies, we decided to prepare the still unknown homoleptic zinc(II) dialkylcarbamato complexes. Since usual synthetic techniques, such as the reaction of metal chlorides with the CO_2/HNR_2 system[5] or the formal CO_2 insertion into the $M-NR_2$ bond,[8] proved to be unsuitable,[9] a different method of preparation became necessary.

The alternative method of preparing *N,N*-dialkylcarbamato complexes from metal hydrides[10] or from metal-alkyl precursors[11] can be regarded as a proton abstraction from $HOC(O)NR_2$ or from $NH_2R_2^+O_2CNR_2^-$, both arising from equilibria 2 and 3,


(2)

$$R_2NH + CO_2 \rightleftharpoons O{=}C(OH)NR_2 \qquad (2)$$


(3)

$$O{=}C(OH)NR_2 + R_2NH \rightleftharpoons R_2NH_2^+O_2CNR_2^- \qquad (3)$$

respectively. We therefore reasoned that zinc metal itself might be able to carry out an electron transfer to the protic reagents present in the R_2NH/CO_2 system, leading finally to the required homoleptic zinc(II) *N,N*-dialkylcarbamato derivatives. However, we soon realized that, while this was the fundamental reaction pathway, a deoxygenation reaction of CO_2 was also occurring.

We here report the results of these studies and the X-ray crystal structure of a tetranuclear μ_4-oxo diethylcarbamato complex of zinc(II) formed in the $Et_2NH/CO_2/Zn$ system.

Experimental Section

All of the operations were carried out under an inert atmosphere, or under CO or CO_2, as specified. Carbon oxides (CO and CO_2) were purchased as high-purity gases and used as such; labeled $^{13}CO_2$ was prepared by decomposing $Ba^{13}CO_3$ (CEA, 90% enriched) with concentrated sulfuric acid. $HNEt_2$ was distilled from sodium-potassium alloy and kept over sodium sand. Metallic zinc powder was etched with con-

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Table I. Summary of Crystallographic Data for $[Zn_4O(O_2CNEt_2)_6]$

formula	$C_{30}H_{60}N_6O_{13}Zn_4$	Z	16
MW	974.4	T, K	293
cryst system	tetragonal	λ, Å	0.71069
space group	$I4_1/a$	D_c, g cm^{-3}	1.422
a, Å	21.928 (6)	scan type	
c, Å	37.86 (2)	scan range, deg	$3 < \theta < 6$
V, Å^3	18202.5	μ, cm^{-1}	21.927
$F(000)$	8096.0		

no. of reflns measd	4805
no. of reflns with $I > 2\sigma(I)$ in structure solution	1495
no. of reflns with $I > 4\sigma(I)$ in structure refinement	1140
secondary extinction coeff	2.3×10^{-8}
no. of parameters refined	238
R, R_w	0.061, 0.065

centrated HCl, washed with water and THF, and dried under reduced pressure. Infrared spectra were measured with a Perkin-Elmer 283 spectrophotometer, gas analyses were carried out with a Dani 3200 gas chromatograph, and GC-MS spectra were obtained with a Dani 3800 gas chromatograph coupled to a Hewlett-Packard 5970 mass analyzer.

Reactions of Zn with $HNEt_2$ and CO_2. Synthesis of $[Zn_4O(O_2CNEt_2)_6]$. A 100-mL stainless-steel autoclave, charged with 2.410 g of zinc (36.9 mmol), 8 mL of $HNEt_2$ (77.7 mmol), 25 mL of toluene, and 50 atm of CO_2, was heated at 150 °C for 48 h: a maximum value of 180 atm was noted for the pressure at 150 °C. After the system was cooled to room temperature, gas-chromatographic analysis of the gas phase showed the presence of dihydrogen, but no significant amounts of CO were detected. The liquid phase was siphoned out and evaporated under reduced pressure. The volatiles were collected in a cold trap and both Et_2NH and $Et_2NC(O)H$ were detected by IR spectroscopy and GC-MS. A small amount of Et_3N was also found in the GC-MS spectra. The solid residue (5.62 g) contained only a small amount of unreacted metallic zinc: it was treated with 200 mL of heptane and 40 mL of toluene, the mixture was heated to 80 °C, and the resulting solution was filtered while still hot. Colorless crystals were obtained by cooling to about −30 °C: they were collected by filtration and dried under reduced pressure (3.18 g, 35% yield). Infrared spectrum (Nujol): 2980–2840 vs, 1570 vs, 1510 vs, 1460 s, 1430 s, 1380 s, 1320 s, 1220 s, 1090 m, 1070 sh, 980 m, 940 m, 810 sh, 790 ms, 780 m, 770 m, 660 m, 630 ms, 520 s, 470 sh, 450 ms cm^{-1}. Anal. Calcd for $Zn_4O(O_2CNEt_2)_6$, $C_{30}H_{60}N_6O_{13}Zn_4$: C, 37.0; H, 6.2; N, 8.6; CO_2, 27.1; Zn, 26.8; CO_2/Zn, 1.5. Found: C, 36.6; H, 6.1; N, 8.5; CO_2, 26.7; Zn, 26.7; CO_2/Zn, 1.49.

A similar experiment was repeated by using $^{13}CO_2$ (5 mmol for 2.5 mmol of zinc) and pressurizing the autoclave with dinitrogen at 10 atm. The presence of $Et_2N^{13}C(O)H$ in the distilled solution was confirmed by IR spectroscopy ($\tilde{\nu}_{CO}$ 1640 cm^{-1}, calcd 1643 cm^{-1}) and GC-MS analysis ($M^+ = 102$). The same result was obtained by using CO (100 atm) instead of dinitrogen.

Table II. Positional Parameters for the Non-Hydrogen Atoms of $[Zn_4O(O_2CNEt_2)_6]^a$

atom	x/a	y/b	z/c	B, Å^2
Zn(1)	0.2343 (1)	0.0783 (2)	0.54284 (8)	5.36 (7)
Zn(2)	0.1941 (1)	−0.0497 (2)	0.51099 (7)	5.26 (7)
Zn(3)	0.2023 (1)	0.0659 (1)	0.46143 (7)	5.11 (7)
Zn(4)	0.3225 (1)	0.0064 (2)	0.49196 (8)	6.02 (8)
O	0.2393 (8)	0.0220 (7)	0.5019 (4)	5.2 (4)*
O(11)	0.3144 (8)	0.0970 (8)	0.5599 (5)	6.9 (5)*
O(12)	0.1931 (9)	0.0380 (9)	0.5815 (5)	7.5 (5)*
O(13)	0.1943 (8)	0.1543 (8)	0.5313 (4)	6.3 (4)*
O(21)	0.1665 (9)	−0.0532 (9)	0.5586 (5)	8.5 (5)*
O(22)	0.1232 (8)	−0.0588 (8)	0.4815 (4)	6.2 (4)*
O(23)	0.2466 (7)	−0.1168 (8)	0.5040 (4)	6.0 (4)*
O(31)	0.2628 (8)	0.0793 (8)	0.4241 (4)	6.4 (4)*
O(32)	0.1361 (8)	0.0208 (8)	0.4432 (4)	6.5 (4)*
O(33)	0.1666 (8)	0.1425 (8)	0.4738 (5)	6.8 (5)*
O(41)	0.376 (1)	0.039 (1)	0.5266 (6)	10.8 (7)*
O(42)	0.3472 (9)	0.0423 (9)	0.4476 (5)	7.5 (5)*
O(43)	0.3384 (8)	−0.0781 (8)	0.4908 (4)	6.0 (4)*
N(1)	0.326 (1)	−0.177 (1)	0.5011 (8)	11.0 (8)*
N(2)	0.052 (1)	−0.039 (1)	0.4400 (6)	7.4 (6)*
N(3)	0.157 (1)	−0.032 (1)	0.6176 (6)	7.8 (6)*
N(4)	0.136 (1)	0.224 (1)	0.5047 (7)	8.7 (7)*
N(5)	0.353 (1)	0.096 (1)	0.3994 (6)	9.2 (7)*
N(6)	0.416 (2)	0.093 (2)	0.573 (1)	15 (1)*
C(1)	0.303 (1)	−0.117 (1)	0.4971 (8)	8.4 (8)*
C(2)	0.105 (1)	−0.024 (1)	0.4558 (7)	6.1 (7)*
C(3)	0.175 (1)	−0.015 (1)	0.5830 (7)	7.4 (7)*
C(4)	0.168 (1)	0.170 (1)	0.5018 (8)	6.5 (7)*
C(5)	0.317 (1)	0.074 (1)	0.4243 (8)	8.0 (8)*
C(6)	0.371 (2)	0.082 (2)	0.5480 (8)	9.3 (9)*
C(11)	0.293 (2)	−0.238 (2)	0.506 (1)	13 (1)*
C(12)	0.392 (2)	−0.195 (2)	0.489 (1)	16 (2)*
C(13)	0.295 (2)	−0.249 (2)	0.547 (1)	15 (1)*
C(14)	0.422 (3)	−0.179 (3)	0.512 (2)	23 (2)*
C(21)	0.016 (1)	−0.096 (1)	0.4497 (7)	7.7 (8)*
C(22)	0.029 (1)	−0.001 (1)	0.4115 (7)	7.8 (8)*
C(23)	−0.080 (2)	−0.072 (2)	0.4812 (8)	9.5 (9)*
C(24)	0.054 (2)	−0.016 (2)	0.375 (1)	13 (1)*
C(31)	0.170 (2)	0.008 (2)	0.6491 (9)	10 (1)*
C(32)	0.161 (2)	−0.112 (2)	0.6260 (9)	10 (1)*
C(33)	0.118 (2)	0.051 (2)	0.6511 (9)	11 (1)*
C(34)	0.097 (2)	−0.112 (2)	0.625 (1)	16 (2)*
C(41)	0.139 (1)	0.261 (1)	0.5379 (7)	7.0 (7)*
C(42)	0.087 (2)	0.241 (2)	0.476 (1)	13 (1)*
C(43)	0.089 (2)	0.240 (2)	0.5635 (9)	10 (1)*
C(44)	0.119 (2)	0.281 (2)	0.457 (1)	13 (1)*
C(51)	0.421 (2)	0.092 (2)	0.3990 (9)	10 (1)*
C(52)	0.322 (1)	0.132 (1)	0.3700 (8)	8.5 (9)*
C(53)	0.446 (2)	0.148 (2)	0.414 (1)	17 (2)*
C(54)	0.317 (2)	0.089 (2)	0.339 (1)	13 (1)*
C(61)	0.402 (5)	0.131 (5)	0.627 (3)	17 (3)*
C(61)′	0.401 (3)	0.105 (3)	0.619 (2)	10 (2)*
C(62)	0.480 (2)	0.042 (2)	0.567 (1)	17 (2)*
C(63)	0.409 (3)	0.169 (3)	0.605 (2)	22 (2)*
C(64)	0.492 (3)	0.088 (3)	0.547 (1)	19 (2)*

[a] Starred values indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

X-ray Data Collection and Refinement of $Zn_4O(O_2CNEt_2)_6$. Crystals suitable for the X-ray study were grown by slowly cooling a hot heptane solution. A crystal of approximate dimensions (mm) 0.2 × 0.2 × 1.2 was sealed under argon in a glass capillary for intensity data collection. An Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation was used. Lattice constants were determined on the basis of 25 accurately centered reflections; crystal data and some details of data collection and refinement are given in Table I. The space group is $I4_1/a$ (No. 88[12]), origin in $\bar{1}$, with the following systematic conditions: integral

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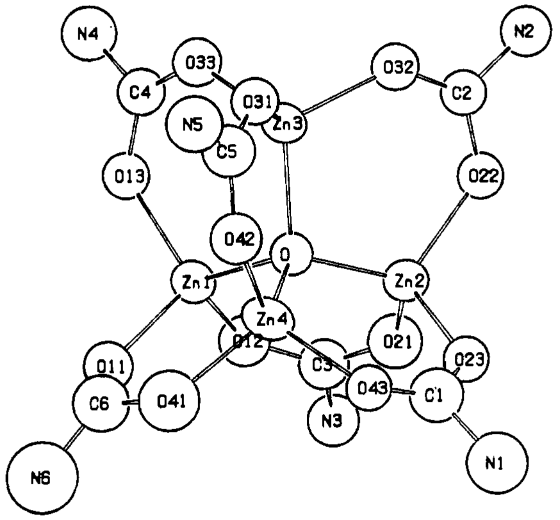

Figure 1. ORTEP view of the molecular structure of the tetranuclear complex $[Zn_4O(O_2CNEt_2)_6]$. The ethyl groups have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

$h + k + l = 2n$; for $00l$, $l = 4n$; for $h0l$, $h = 2n$. In the scan range θ = 3–26°, a total of 4805 reflections were measured. Since diffraction intensity was poor, data collection was slow and only the minimum of the reflection sphere was scanned ($+h$, $+k$, $+l$; $h \leq k$). Only 1495 reflections met the condition $I > 2\sigma(I)$ and were used in the subsequent structure solution. Direct methods[13] gave the positions of the Zn atoms. Their positional and isotropic parameters were refined to a conventional agreement factor of 0.29. The structure was completed by two difference Fourier and refinement cycles.[14] No absorption correction was applied. In the final refinement with anisotropic thermal parameters for the Zn atoms and isotropic thermal parameters for all other atoms, 1140 reflections with $I > 4\sigma(I)$ were used for 238 parameters. Due to this quite low reflection/parameter ratio, no refinement with anisotropic temperature factors for the other atoms was attempted, and we did not try to locate the hydrogen atoms. A correction for secondary extinction[15] was applied to F_c. Some disorder was still present in the ethyl groups; however, no attempt was made to improve the situation, this being a common feature for this class of compounds.[5] Atomic coordinates are reported in Table II.

Results and Discussion

Although, in principle, dialkylcarbamato complexes could be prepared, with dihydrogen evolution, from those metals which have a standard reduction potential $E°$ lower than zero, this route has seldom been used, except for dialkylcarbamato complexes of alkali metals.[6b] We here describe our experiments with zinc.

Carefully cleaned zinc powder was suspended in toluene with diethylamine and CO_2 (50 atm), and the mixture was heated to 150 °C for 2 days. Dihydrogen was evolved, and workup of the toluene solution gave colorless crystals whose IR spectrum indicated the presence of the carbamato group and the absence of coordinated or lattice amine. Analytical data were not consistent with the $Zn(O_2CNEt_2)_2$ minimal formulation; especially the CO_2/Zn molar ratio of about 1.5 suggested the presence of a μ-oxo ligand. An X-ray analysis was therefore undertaken.

The structure was found to consist of discrete tetranuclear units of $Zn_4O(O_2CNEt_2)_6$, whose outstanding feature is the presence of a central oxygen atom, μ_4-bonded to four zinc atoms, which are placed at the vertices of a nearly regular tetrahedron. The four zinc atoms are joined by six bridging carbamato groups along the six edges of the tetrahedron.

The molecular structure of the tetranuclear carbamato complex is shown in Figure 1, together with the numbering scheme used.

Table III. Selected Bond Distances (Å) and Angles (deg) in $[Zn_4O(O_2CNEt_2)_6]$

Zn(1)–O	1.985 (5)	O(11)–C(6)	1.35 (1)
Zn(1)–O(11)	1.916 (6)	O(12)–C(3)	1.231 (9)
Zn(1)–O(12)	1.936 (6)	O(13)–C(4)	1.309 (9)
Zn(1)–O(13)	1.935 (5)	O(21)–C(3)	1.260 (9)
Zn(2)–O	1.890 (5)	O(22)–C(2)	1.297 (8)
Zn(2)–O(21)	1.905 (6)	O(23)–C(1)	1.26 (1)
Zn(2)–O(22)	1.924 (5)	O(31)–C(5)	1.19 (1)
Zn(2)–O(23)	1.889 (5)	O(32)–C(2)	1.286 (8)
Zn(3)–O	1.982 (5)	O(33)–C(4)	1.221 (9)
Zn(3)–O(31)	1.962 (5)	O(41)–C(6)	1.25 (1)
Zn(3)–O(32)	1.888 (5)	O(42)–C(5)	1.30 (1)
Zn(3)–O(33)	1.912 (5)	O(43)–C(1)	1.18 (1)
Zn(4)–O	1.895 (5)	N(1)–C(1)	1.41 (1)
Zn(4)–O(41)	1.895 (7)	N(2)–C(2)	1.358 (9)
Zn(4)–O(42)	1.934 (6)	N(3)–C(3)	1.414 (9)
Zn(4)–O(43)	1.886 (5)	N(4)–C(4)	1.377 (9)
Zn···Zn (mean)	3.163 (1)	N(5)–C(5)	1.33 (1)
		N(6)–C(6)	1.40 (1)

Zn(2)–Zn(1)–Zn(3)	59.65 (3)	O–Zn(3)–O(33)	113.8 (2)
Zn(2)–Zn(1)–Zn(4)	59.81 (3)	O(31)–Zn(3)–O(32)	109.6 (2)
Zn(3)–Zn(1)–Zn(4)	59.96 (3)	O(31)–Zn(3)–O(33)	108.9 (2)
Zn(1)–Zn(2)–Zn(3)	60.09 (3)	O(32)–Zn(3)–O(33)	103.6 (2)
Zn(1)–Zn(2)–Zn(4)	59.67 (3)	Zn(1)–O–Zn(4)	108.6 (3)
Zn(3)–Zn(2)–Zn(4)	60.06 (3)	Zn(2)–O–Zn(3)	109.3 (3)
Zn(1)–Zn(3)–Zn(2)	60.27 (3)	Zn(2)–O–Zn(4)	113.0 (3)
Zn(1)–Zn(3)–Zn(4)	59.68 (3)	Zn(3)–O–Zn(4)	109.2 (3)
Zn(2)–Zn(3)–Zn(4)	59.92 (3)	Zn(1)–O(11)–C(6)	132.2 (7)
Zn(1)–Zn(4)–Zn(2)	60.52 (3)	Zn(1)–O(12)–C(3)	128.3 (7)
Zn(1)–Zn(4)–Zn(3)	60.36 (3)	Zn(1)–O(13)–C(4)	128.7 (6)
Zn(2)–Zn(4)–Zn(3)	60.02 (3)	Zn(2)–O(21)–C(3)	128.4 (6)
O–Zn(1)–O(11)	110.3 (2)	Zn(2)–O(22)–C(2)	128.2 (5)
O–Zn(1)–O(12)	109.5 (2)	Zn(2)–O(23)–C(1)	128.8 (8)
O–Zn(1)–O(13)	112.6 (2)	Zn(3)–O(31)–C(5)	130.8 (7)
O(11)–Zn(1)–O(12)	105.7 (3)	Zn(3)–O(32)–C(2)	132.1 (6)
O(11)–Zn(1)–O(13)	107.9 (2)	Zn(3)–O(33)–C(4)	130.0 (6)
O(12)–Zn(1)–O(13)	110.6 (2)	Zn(4)–O(41)–C(6)	132.8 (8)
O–Zn(2)–O(21)	112.0 (2)	Zn(4)–O(42)–C(5)	131.4 (6)
O–Zn(2)–O(22)	113.8 (2)	Zn(4)–O(43)–C(1)	125.4 (9)
O–Zn(2)–O(23)	107.6 (2)	O(23)–C(1)–O(43)	134 (1)
O(21)–Zn(2)–O(22)	106.7 (2)	O(22)–C(2)–O(32)	124.7 (8)
O(21)–Zn(2)–O(23)	107.2 (3)	O(12)–C(3)–O(21)	129.8 (9)
O(22)–Zn(2)–O(23)	109.3 (2)	O(13)–C(4)–O(33)	128.0 (9)
O–Zn(3)–O(31)	110.6 (2)	O(31)–C(5)–O(42)	124 (1)
O–Zn(3)–O(32)	110.0 (2)	O(11)–C(6)–O(41)	118 (1)

A selection of bond distances and angles is provided in Table III. The central oxygen atom has a nearly perfect tetrahedral geometry. The distances between the central oxygen and the four crystallographically independent zinc atoms vary from 1.890 (5) to 1.985 (5) Å, which may be compared to the average Zn–O bond distance of 1.978 Å in ZnO.[16a]

Although pentacoordinated bridging oxides are now known,[16] μ_4-oxo ligands are rather uncommon.[17] In the case of zinc, reported examples include $[VZnO(O_2CPh)_3L]_4$,[18] $Zn_4O(B_6O_{12})$,[19] and $Zn_4O(S_2P(OR)_2)_6$,[20] but the obvious comparison is with the basic carboxylate $M_4O(O_2CR)_6$. They have a well-known archetype in $Be_4O(O_2CMe)_6$,[21] but analogous structures have been suggested for $Co_4O(O_2CCMe_3)_6$[22] and $Zn_4O(O_2CR)_6$.[22,23] An X-ray crystal structure is available for $Zn_4O(O_2CMe)_6$,[24a] whose

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absorption and emission spectra were recently described;[24b] a comparison of the geometrical parameters with those of our oxo carbamato complex shows a close resemblance between the two compounds. The only apparent difference is a slight shortening of the $Zn-O_2CNEt_2$ average distance (1.915 (6) Å) with respect to the $Zn-O_2CMe$ value (1.98 Å). This can be rationalized on the basis of an increased electron density on the diethylcarbamato ligand, with a consequent stronger interaction with the cation.

It is interesting to note that the compound reported in this paper is highly symmetrical, and the diethylcarbamato groups are of one type only, namely bridging bidentate. This is a unique feature within tetranuclear compounds of this category; usually only mononuclear species, such as $Si(O_2CN^iPr_2)_4$[25] or $Hf(O_2CN^iPr_2)_4$,[26] or dinuclear species, such as $Cu_2(O_2CNEt_2)_4 \cdot 2NHEt_2$,[27] have a homogeneous set of ligands, i.e. terminal monodentate (Si), terminal bidentate (Hf), or bridging bidentate (Cu).

In view of this unique structural feature and considering the difficulties encountered[5] in structural assignments by IR spectroscopy for this type of compound, the tetranuclear μ_4-oxo species can be regarded as an IR standard for the absorptions associated with the dialkylcarbamato group between 1600 and 1300 cm^{-1}.

μ-Oxo carbamato complexes are not new, and some examples have already been prepared in these laboratories: $U_4O_2(O_2CNEt_2)_{12}$[28] and $Cu_8O_2(O_2CNPr^i_2)_{12}$.[27] These complexes were obtained in low yields during the preparation of the homoleptic carbamates, and their formation was attributed to the presence of an adventitious hydrolytic process. This was confirmed by the experimental observation that good yields of the μ-oxo products could be obtained when the starting dialkylcarbamato complexes were reacted with the required amount of water.[27]

In our case, the synthesis of the zinc diethylcarbamato complex was repeated several times, and special care was taken to avoid the presence of moisture; however, the yields of the μ-oxo derivative roughly corresponded to those obtained (35% of recrystallized product) under the standard operative conditions. Water was therefore unlikely to be responsible for the presence of the μ-oxo ligand in our zinc compound, and a different explanation had to be found. Some literature data were considered first. Zinc metal and carbon dioxide are known[29] to be in equilibrium with ZnO and CO. Moreover, the most convenient route to the $Zn_4O(O_2CR)_6$ carboxylates is the high-temperature reaction between zinc oxide and the carboxylic acid.[23] These facts suggested that the oxygen in our structure could be derived by an analogous route, but the analysis of the reaction products showed that no CO was formed, and diethylformamide was found instead. The identified products thus justify the stoichiometry of eq 4. Labeling experiments with $^{13}CO_2$ confirmed that the carbonyl carbon atom in the formamide originated from CO_2. It therefore seems safe to conclude that the missing oxygen after formamide formation is released as the μ-oxo ligand in the zinc tetramer (cf. eq 1).

$$4Zn + 7Et_2NH + 7CO_2 \rightarrow Zn_4O(O_2CNEt_2)_6 + Et_2NC(O)H + 3H_2 \quad (4)$$

The formation of diethylformamide and the μ-oxo tetramer is probably a concerted process. The possibility that the formation of the μ_4-oxo is accompanied by evolution of CO, which in a subsequent step forms diethylformamide, is unlikely on the basis of the following experimental evidence: (a) the μ-oxo complex and the formamide were obtained, albeit in low yields, even under atmospheric pressure of CO_2 and at lower temperature (70 °C), i.e. where deoxygenation of CO_2 to CO seems unlikely; (b) the reaction between Zn, CO, and $NHEt_2$ under 100 atm of CO at 200 °C did not yield diethylformamide; (c) if Zn and $NHEt_2$ were allowed to react with a stoichiometric amount of labeled $^{13}CO_2$, but in the presence of a large excess of ^{12}CO, labeled diethylformamide was still formed.

The presence of diethylformamide also indicated that the μ-oxo complex could not simply be formed by thermal decomposition of the homoleptic carbamato complex, by analogy with a possible route from $M(O_2CR)_n$ to $MO(O_2CR)_{n-2}$ and carboxylic anhydride.[23] This would have produced the carbamic anhydride, which would decompose to CO_2 and tetraethylurea, rather than to diethylformamide.

To conclude, we believe that free carbon monoxide is not involved in our reaction and suggest that the μ-oxo atom and the formamide are the result of a yet unclear unique transformation of the carbamato group over the zinc surface. This transformation constitutes, beyond any mechanistic speculation, the first example of a CO_2 deoxygenation with simultaneous formation of a metal-oxygen bond and incorporation of CO into an organic molecule.[30]

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Supplementary Material Available: Complete tables of bond distances, bond angles, and thermal parameters (10 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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Behavior of Phosphoryl Trifluoride toward Dry Trimethylamine Oxide: Complex Formation and Disproportionation, and Action of Lewis Acids

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A recent study of the behavior of $SiCl_4$ and SiF_4 toward dry trimethylamine oxide (hereinafter TMAO)[1] implied the possibility that similar work with $POCl_3$ and POF_3 also would be interesting. For the present study, POF_3 was chosen because steric inhibitions would be minimal and its high volatility would make possible the use of high-vacuum methods to determine combining ratios at low temperatures; also, NMR spectra would aid interpretation. One exploratory experiment did show interesting results for $POCl_3$, but it was not feasible to prove the detailed chemistry by NMR spectra.

It was found to be easy enough to demonstrate clean formation of the 1:1 complex $TMAO \cdot POF_3$ at temperatures in the -80 °C region. This complex, warmed rapidly to 25 °C and then finally to 50 °C for removal of all volatiles, decomposed to give PF_6^- and

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