FULL PAPER

Synthesis and Isomerisation Reactions of Tetranuclear and Octanuclear (Carbamato)zinc Complexes


Keywords: Carbamato ligands / Chemical vapor deposition / Dialkylcarbamates / Isomerisation / Oxido ligands / Zinc

A new series of (diisopropylcarbamato)(oxido)zinc complexes were obtained by innovative synthetic approaches. The (carbamato)zinc clusters [Zn₄(µ₄-O)(O₂CNPr₂)₆] (1) and [Zn₄(µ₄-O)₂(O₂CNPr₂)₁₂] (2) were synthesised by an identical reaction procedure involving protolysis of ZnEt₂ with iPr₂NH/CO₂ and followed by stoichiometric hydrolysis. Recrystallisation of the reaction product from nitrite solvents yielded the tetrazinc complex 1. Conversely, recrystallisation from alkanone solvents yielded crystals of the octazinc complex 2. The two structural isomers were readily interconverted simply by recrystallisation from the appropriate solvent. Both complexes were structurally characterised by X-ray crystallography. The tetrazinc complex 1 has the quintessential basic zinc acetate type structure. Its dimer, the octazinc complex 2 is a new derivative of the [M₈(µ₄-O)₂(O₂CNPr₂)₁₂] class, examples of which are known for all other first-row transition metals. The solution chemistry was investigated using variable-temperature NMR spectroscopy and ESI-MS. The new synthetic approach offers a route to other similar complexes. Thus, using Et₂NH in place of iPr₂NH yielded the known complex [Zn₄(µ₄-O)(O₂CNEt₂)₆] (3).

Introduction

The tetrahedral [Zn₄O]⁶⁺ core is a common motif in zinc coordination chemistry with examples among the zinc carboxylates,[1,2] carbamates[3–6] and phosphates.[7,8] In the carbamato and carbamato series, this core is extended by bridging oxygen atoms into a framework reminiscent of wurtzite-type ZnO.[9] It is for this reason that the carbamato complex [Zn₄(µ₄-O)(O₂CNEt₂)₆][3] has been described as “a further molecular model of crystalline ZnO”.[10]

Recent studies[6,11] on [Zn₄(µ₄-O)(O₂CNEt₂)₆] and similar complexes showed that the [Zn₄O]⁶⁺ core has a remarkable effect on the reactivity of carbamato ligands, both the carboxylic and amino components possessing intrinsic lability not ordinarily observed in organic carbamates. The [Zn₄(µ₄-O)(O₂CNEt₂)₆] complex and its chemical properties are of interest to us from an electronics perspective: in 2002, we showed[12] that [Zn₄(µ₄-O)(O₂CNEt₂)₆] is volatile under high vacuum and can be used to deposit c-axis-oriented polycrystalline ZnO films by the single-source chemical vapour deposition (SSCVD) process. SSCVD is an unusual deposition technique in that it requires no gas-phase mixing of separate reagents. Instead, it relies on all the desired film constituents being packaged within a specifically designed volatile “precursor” molecule. This technique has been described previously.[11] In our SSCVD depositions of ZnO, we have used zinc carboxylates,[13,14] zinc β-diketonates and zinc oximates[15] as precursors. However, ideal single-source behaviour was only observed with the (carbamato)zinc complex [Zn₄(µ₄-O)(O₂CNEt₂)₆][12] as the other precursors required additional oxygen sources to suppress the formation of high-carbon amorphous ZnO.[16] This singular behaviour of [Zn₄(µ₄-O)(O₂CNEt₂)₆] may be due to the lability of the C–N bond of the diethylcarbamato ligand,[11] which may permit a facile decomposition pathway not available in the other complexes.

The advantage that lability of the C–N bond gives to the ZnO deposition process brings with it stability problems. The sensitivity of carbamates to hydrolysis is well known,[17] with loss of CO₂ being the thermodynamic driving force. The modest stability of [Zn₄(µ₄-O)(O₂CNEt₂)₆] makes it less than ideal as an SSCVD precursor. We found that, for a given sample, its utility for film deposition deteriorated over a period of 2 weeks, even when stored under inert conditions. Moreover, its temperature sensitivity leads to sig-

[a] School of Chemistry, University of New South Wales, Sydney NSW 2052, Australia
[b] Commonwealth Scientific and Industrial Research Organisation, Division of Materials Science and Engineering, Private Bag 33, Clayton South MDC Victoria, 3169 Australia
[c] School of Materials Science, University of New South Wales, Sydney NSW 2052, Australia
[d] School of Chemistry, University of Melbourne, Victoria, 3010 Australia
Fax: +61-3-9347-5180
E-mail: rnlamb@unimelb.edu.au

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

DOI: 10.1002/ejic.200700736
nificant premature decomposition in the Knudsen cell during SSCVD depositions, so that the accompanying outgassing and intra-cell deposition of oxides affects the vapour pressure profile of the precursor, thereby affecting the reproducibility of the deposition.

With this problem in mind, we sought to develop analogous (dialkylcarbamato)zinc complexes with bulkier iPr groups. Our rationalisation was that, as the alkyl groups essentially coat the surface of the typical (oxido)tetrazinc cluster, an increase in alkyl group bulk should have several desirable influences. First, bulkier alkyl groups should provide better steric protection to inhibit hydrolysis of the interior carbamate linkages by ambient water. Second, they should help to weaken polar interactions between clusters by extending the core-to-core distance. Third, there is evidence that the intrinsic thermal stability of the carbamate group increases with the size of the alkyl group.[18]

Our attempts to prepare an (oxido)zinc complex of the sterically bulky iPr2NCO2 ligand were not immediately successful.[19] Adaptations of previously reported syntheses of (carbamato)tetrazinc complexes such as [Zn4(µ4-O)(O2CNPr2)6] proved problematic on several fronts, when applied using the iPr2NCO2 ligand. Difficulties included irreproducibility, low yield, and indications that mixtures of several carbamato products were formed. The well-established Cl/iPr2NCO2 metathesis process, which was used to prepare similar complexes of other divalent transition metal cations,[20,21] proved especially problematic when applied to anhydrous ZnCl2. The low reactivity of this material led to incomplete reactions and partially substituted chloride-containing species, confirming previous outcomes with the Et4NCO2 ligand.[22]

In this paper, the dialkylzinc compound ZnEt2 is found to be a useful starting material for the self-assembly of tetra- and octanuclear (carbamato)(µ-oxido)zinc clusters from HNR2, CO2 and H2O. Specifically, we report the high-yield and reproducible synthesis (Scheme 1) of the first homonuclear (diisopropylcarbamato)(µ-oxido-oxo)zinc complex, [Zn4(µ3-O)(O2CNR2)6] (1), and its closely related dimer [Zn8(µ4-O)2(O2CNiPr2)2]12 (2). The new ZnEt2 method also serves as a more reliable route (Scheme 1) to the known [Zn4(µ3-O)(O2CNPr2)6] (3), and it may prove even more widely applicable.

X-ray diffraction experiments established the mono-(oxido) [Zn4(OH)6]4+ core structure of 1 and 3, and the bis-(oxido) [Zn8(OH)12]24+ core of 2. The tendency of the iPr2NCO2 ligand to form large cluster complexes containing the bis(oxido) core [M8O2]24+ is prevalent; however, the mono(oxido) core of 1 is a novel occurrence for this ligand. Moreover, transition between mono- and bis(oxido) cores has been documented for the first time through the experimental interconversion of 1 and 2. The facility of this interconversion is remarkable as it requires significant reorganisation of Zn-O bonds. The interconversion behaviour outlined in this paper may have a broader significance in considering the solid- and solution-state structures of other polynuclear metallocarbamates.

**Results and Discussion**

**Synthesis and Crystal Structures of (Oxido)zinc Complexes 1–3**

The initial reaction between ZnEt2 and HNR2 (Scheme 1) did not appear to give total conversion to the diamide Zn(NR2)2, instead reaching equilibrium at the partially substituted intermediate [Et2ZN(NR2)(HNR2)] (vide infra), in agreement with previous reports.[23] After addition of CO2, however, complete substitution of the ethyl groups did occur, presumably by ligand transfer with R2NCO2. The white solids precipitated at this stage were deemed to be polymeric [([Zn(O2CNR2)2]12)1n] species due to their insolubility; similar polymeric anhydrous zinc carboxylates have been found in other studies.[22]

The subsequent hydrolysis proceeds in a controlled manner, by the insoluble intermediates reacting slowly with a stoichiometric amount of water diluted in THF, to form the benzene-soluble (oxido)zinc complexes (Scheme 1). The solubility of the products makes this step self-indicating to some extent, but it is crucial to allow the hydrolysis reaction to proceed over a further extended period after dissolution to ensure completion of the reaction, otherwise a mixture of carbamato species is recovered upon concentration of the reaction solution. This insight may explain the low yields incurred in previously reported syntheses of complex 3 with the diethylcarbamato ligand.[8]

[Zn4(µ3-O)(O2CNPr2)6] (3) was isolated from the HNEt2 reaction as a fine, free-flowing white powder. Crystals of 3 were grown by slow cooling of a hot heptane solution of the complex (Table 1, Procedure H). Initially, the complex emerged from solution as solventless cubic crystals (space group I43d), but when left in the mother liquor it converted to give an unstable solvent-containing polymorph, possibly partially characterised tetragonal (43d) form.[3] When out of solution, the solventless crystals were stable, and a full set of reflections were collected. The structural data agree with those previously reported for 3.[6,8]

X-ray diffraction studies of the recrystallised HN/Pr2 reaction product provided interesting yet unexpected results. The structure of the (diisopropylcarbamato)(oxido)zinc...
product was found to vary according to the type of recrystallisation solvent used (Table 1). [Zn₄(µ₂-O)(O₂CN/PtPr₂)₆] (I) was the sole product obtained from CH₃CN and (CH₃)₂CCN recrystallisations (Procedures A and B). The resulting crystals contained varying degrees of lattice solvation and in some cases water, whose origin was most likely adventitious. In its crystal lattices, [Zn₄(µ₂-O)(O₂CN/PtPr₂)₆] is densely packed, trapping smaller nitrile molecules in the basket-shaped cavities created by surface Pr₂ groups. Vacuum removal of all volatiles left 1 as a white, free-flowing powder; 1 is very sensitive to adventitious moisture, although the stability of the material increased when in crystal form. A high level of solubility was noted in most other organic solvents, including higher nitriles such as propanenitrile, butanenitrile and adiponitrile.

In structural terms, the tetrazinc complex 1 (Figure 1) is a new member of an existing family of basic (carbamato)zinc complexes, which already includes the dimethyl,[5] diethyl,[6] dibutyl,[7] tetramethylene,[8] and pentamethylene derivatives. The classic tetrahedral [Zn₄O]⁶⁺ core of 1 (not explicitly shown) is delimitated by Zn–O oxido bonds of 1.939 Å average length. The tetrahedron is stabilised by Zn–O carbamato bonds ranging from 1.923–1.971 Å in length.

Table 1. Recrystallisation parameters for isolated (carbamato)(µ-o xo)zinc complexes.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Starting materials[a]</th>
<th>Recrystallisation conditions</th>
<th>Product</th>
<th>X-ray</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Solvent T [°C]</td>
<td>Composition</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>crude</td>
<td>CH₃CN 90</td>
<td>1·2MeCN</td>
<td>full</td>
</tr>
<tr>
<td>B</td>
<td>crude</td>
<td>(CH₃)₂CCN 100</td>
<td>1·1.3(CH₃)₂CCN·0.2H₂O</td>
<td>full</td>
</tr>
<tr>
<td>C</td>
<td>crude</td>
<td>C₂H₆ 110</td>
<td>2·3C₆H₄(NO₂)·3H₂O</td>
<td>full</td>
</tr>
<tr>
<td>D</td>
<td>crude</td>
<td>C₄H₈ 120</td>
<td>2·3C₆H₄(NO₂)·3H₂O</td>
<td>full</td>
</tr>
<tr>
<td>E</td>
<td>crude</td>
<td>C₆H₁₀ 120</td>
<td>2 (solventless)</td>
<td>full</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>C₇H₁₈ 110</td>
<td>2·C₆H₄Me₂O</td>
<td>unit cell</td>
</tr>
<tr>
<td>G</td>
<td>2</td>
<td>CH₃CN 90</td>
<td>1·2MeCN</td>
<td>unit cell</td>
</tr>
<tr>
<td>H</td>
<td>3</td>
<td>C₂H₆ 110</td>
<td>3 (solventless)</td>
<td>full</td>
</tr>
</tbody>
</table>

[a] crude: HN/Pr₂ reaction product; 1: [Zn₄(µ₂-O)(O₂CN/PtPr₂)₆]; 2: [Zn₄(µ₂-O)(O₂CN/PtPr₂)₂]; 3: [Zn₄(µ₂-O)(O₂CNEt₂)₂].

Figure 1. Molecular structure of 1 showing [ZnO₄] coordination polyhedra. Key: dark tetrahedra = [ZnO₄], black circles = Zn, large dark sphere = O oxido, small dark spheres = O carbamato. Methyl groups and hydrogen atoms are omitted for clarity.

Alternatively, only [Zn₄(µ₂-O)₂(O₂CN/PtPr₂)₁₂] (2) was obtained when the HN/Pr₂ reaction product was recrystallised from alkanes (Procedures C–E). The octazinc cluster 2 was

Table 2. Crystallographic data for selected compounds.

<table>
<thead>
<tr>
<th></th>
<th>1·2CH₃CN</th>
<th>1·1.3(CH₃)₂CCN·0.2H₂O</th>
<th>2·3C₆H₄(NO₂)·3H₂O</th>
<th>2·3C₆H₄(NO₂)·3H₂O</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₄H₁₀N₂O₃Zn₄</td>
<td>C₆H₁₀N₂O₃Zn₄</td>
<td>C₆H₁₈O₃N₂O₃Zn₄</td>
<td>C₆H₁₈O₃N₂O₃Zn₄</td>
<td>C₆H₁₆O₃N₂O₃Zn₄</td>
<td>C₆H₁₆O₃N₂O₃Zn₄</td>
</tr>
<tr>
<td>Formula mass</td>
<td>1224.79</td>
<td>1254.3</td>
<td>2403.5</td>
<td>2682.0</td>
<td>2285.3</td>
<td>974.3</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>trigonal</td>
<td>trigonal</td>
<td>cubic</td>
<td>cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>P1</td>
<td>R₃</td>
<td>R₃</td>
<td>R₃</td>
<td>R₃</td>
</tr>
<tr>
<td>a [Å]</td>
<td>14.355(10)</td>
<td>11.574(1)</td>
<td>20.063(2)</td>
<td>19.724(2)</td>
<td>22.594(2)</td>
<td>23.58(2)</td>
</tr>
<tr>
<td>b [Å]</td>
<td>35.946(2)</td>
<td>13.728(2)</td>
<td>20.063(2)</td>
<td>19.724(2)</td>
<td>22.594(2)</td>
<td>23.58(2)</td>
</tr>
<tr>
<td>c [Å]</td>
<td>24.160(2)</td>
<td>22.959(3)</td>
<td>33.096(9)</td>
<td>33.037(5)</td>
<td>22.594(2)</td>
<td>23.58(2)</td>
</tr>
<tr>
<td>a [°]</td>
<td>90</td>
<td>90.004(5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β [°]</td>
<td>99.462(1)</td>
<td>101.144(5)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ [°]</td>
<td>90</td>
<td>108.253(3)</td>
<td>120</td>
<td>120</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V [Å³]</td>
<td>12297.1</td>
<td>3318.68</td>
<td>11357(4)</td>
<td>11131(2)</td>
<td>11534(2)</td>
<td>13116(1)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>D [Mgm⁻³]</td>
<td>1.323</td>
<td>1.25</td>
<td>1.04</td>
<td>1.20</td>
<td>1.32</td>
<td>1.48</td>
</tr>
<tr>
<td>T [K]</td>
<td>150(2)</td>
<td>150(2)</td>
<td>294</td>
<td>150</td>
<td>150(2)</td>
<td>294</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>20322</td>
<td>2024</td>
<td>6324</td>
<td>2024</td>
<td>6324</td>
<td>2024</td>
</tr>
<tr>
<td>Reflections unique</td>
<td>20574</td>
<td>2024</td>
<td>6324</td>
<td>2024</td>
<td>6324</td>
<td>2024</td>
</tr>
<tr>
<td>Goodness of fit on F²</td>
<td>1.042</td>
<td>1.68</td>
<td>1.46</td>
<td>1.32</td>
<td>0.91</td>
<td>1.33</td>
</tr>
<tr>
<td>R₁</td>
<td>0.0367</td>
<td>0.063</td>
<td>0.053</td>
<td>0.039</td>
<td>0.028</td>
<td>0.044</td>
</tr>
<tr>
<td>wR₂</td>
<td>0.0922</td>
<td>0.088</td>
<td>0.069</td>
<td>0.055</td>
<td>0.039</td>
<td>0.051</td>
</tr>
</tbody>
</table>
also crystallographically identified in crystals grown from C12H26. Varying degrees of lattice solvation were again noted (Table 2), sometimes including water of crystallisation. The lattice arrangements in 2·3C14H30·3H2O and 2·3C8H18·3H2O were very similar with molecules of [Zn4(µ4-O)2(O2CNPr2)12] regularly spaced between 3-D planes of alternating alkane and H2O molecules. Crystals grown from C12H30 contained no solvent. The general physical characteristics of 2 are similar to those observed for 1.

In a variation on the basic (carbamato)zinc structure, the octazinc complex 2 (Figure 2) essentially consists of two [Zn4O]6+ cores lashed together by a web of bridging iPr2NCO2− ligands. As a result of the extended bridging, only two zinc atoms remain in a tetrahedral {ZnO4} environment. Each of the other zinc atoms is bound in a distorted trigonal-bipyramidal {ZnO5} coordination. The [Zn8(µ4-O)2(O2CNPr2)12] structure belongs to the 3 symmetry group. Its envelope is an ovoid shape, with an approximate volume of 3500 Å3. Its bis(oxido) [Zn8O2]12+ core (Figure 3) consists of two counterfacing [Zn4O]6+ tetrahedra aligned on a threefold axis in a staggered fashion. Symmetry rules dictate that two discrete types of zinc atoms exist: Zn1 on the threefold axis, and Zn2. Zn1 is bridged by one type of carbamato ligand to Zn2. The second type of carbamato ligand holds the [ZnO3]12+ core together by binding a Zn2 from each tetrahedron with one oxygen atom (O12), whilst its other oxygen atom (O22) binds a single Zn2. Bond lengths and angles of 2 closely resemble those of previously reported [Zn2Ni6(µ4-O)2(O2CNPr2)12].[25]

Figure 2. Molecular structure of 2 showing {ZnO4} and {ZnO5} coordination polyhedra. Key: dark tetrahedra = {ZnO4}, light trigonal bipyramids = {ZnO5}, black circles = Zn, large dark spheres = O carbamato, methyl groups and hydrogen atoms are omitted for clarity.

The new octazinc complex 2 matches the [M4(µ4-O)2(O2CNPr2)12] structure found for every divalent metal ion along the 4th period, and complexes isostructural with [Zn8(O2CNEt2)12] and its dinuclear dissociation isomer [Co4(O2CNEt2)12] were studied intensively using UV/Vis techniques, with the result that the lower-nuclearity dinuclear species dominates in solution.[27] Despite this dominance, the existence of a facile isomerisation

metallic compound [Zn2Ni6(µ4-O)2(O2CNPr2)12] has also been reported, but was obtained only in low yield.[25] The structure of [Cu8(µ4-O)2(O2CNPr2)12] is somewhat anomalous, it having eight pentacoordinate Cu2+ ions, two of them in square-pyramidal and six in trigonal-bipyramidal configurations.[25] This aberration is presumably due to the electronic stabilisation of the d9 configuration by the square-pyramidal coordination of two Cu2+ ions.

Interconversion of (Diisopropylcarbamato)(oxido)zinc Complexes

Isolation of crystallographically pure samples of the (carbamato)zinc isomers 1 and 2 allowed the systematic investigation of the isomerisation process. Thus, the tetranuclear complex 1 easily dimerised to give octazinc 2 as the respective solvate, simply by recrystallising it from heptane (Table 1, Procedure F). Likewise, the octazinc complex 2 reverted to its monomeric form when recrystallised from acetonitrile (Procedure G). The combination of these steps is a reversible cycle, the facile interconversion of 1 and 2 [Equation (1)].

2 [Zn4(µ4-O)(O2CNPr2)12] ↔ [Zn6(µ4-O)2(O2CNPr2)12] [Equation (1)]

Although this type of process has not yet been observed for molecules of the [M4(µ4-O)(O2CNR)12] type, the fragmentation and recombination of metallocarbamates is not an entirely new concept. The solution dynamics of the hexanuclear complex [Co6(O2CNEt2)12] and its dinuclear dissociation isomer [Co4(O2CNEt2)12] were studied intensively using UV/Vis techniques, with the result that the lower-nuclearity dinuclear species dominates in solution.[27]
pathway allowed the deposition of the hexanuclear isomer as the sole solid product. This isomerisation pathway was reported to be necessary to the formation of mixed-metal [Co₈Mg₆₋₆(O₂CNEt₂)₁₂] complexes.\[27\]

Heterodimetallic carbamato complexes are attractive from a metal oxide film growth perspective. The homonuclear complex [Mg₆(O₂CNEt₂)₁₂] is already a proven precursor for MgO thin-film growth.\[28\] and when mixed with the (µ-oxido)zinc analogue [Zn₄(µ₄-O)(O₂CNEt₂)₆] has been used to deposit dimetallic ZnₓMg₂₋ₓO films of high quality and reproducibility.\[29\] The next logical step is thus to exchange when bonded to [Zn₄O]₆⁺,\[11\] we could not rule out an analogous exchange environment involving [Zn₃O₂]¹⁺ or other intermediates; such a process could also give rise to similar spectral features. Hence, we took to investigating the iPr₂NCO₂ ligand environment over a temperature range of 193–368 K. During the course of these experiments, a slight degree of decomposition occurred, as indicated by trace amounts of ZnO powder in the NMR tube and “free” HN/iPr₂ appearing in the spectra. This decomposition was slightly accelerated at high temperatures (308–368 K); no other significant spectral changes were observed in this temperature range.

Low-temperature ¹H NMR studies (Figure 4, inset) revealed a classic case of exchange between inequivalent iPr groups. A ¹³C NMR experiment at 193 K (Figure S1) confirmed that the methine carbon resonance had resolved into two broad signals at δ = 47.2 and 43.9 ppm, while the carboxyl resonance remained sharp and stationary at δ = 161.9 ppm. The methyl ¹³C NMR signals were obscured by solvent peaks and could not be assigned. The chemical shifts of these NMR signals tend towards those of the crystalline-state structure of tetrazinc complex 1, in which each iPr₂NCO₂ ligand clearly presents two inequivalent iPr environments (Figure 5). The variable-temperature NMR results could be explained by a conformational exchange, whereby the iPr groups are projected towards (endo) and away (exo) from the inner [Zn₄O]⁶⁺ core of the molecule. While the relatively open structure of 1 accommodates a staggered alkyl conformation (Figure 5), the tightly packed surface of octazinc complex 2 results in only exo-oriented iPr groups.

In order to further characterise the solution chemistry of the (diisopropylcarbamato)zinc system, a sample of 2 in THF was analysed using high-resolution ESI-MS. On the positive-ion spectrum, peaks of several di-, tri- and tetraclear zinc species were detected in the range m/z = 850–1300 (Figure 6). The tetrazinc complex [Zn₄(µ₄-O)(O₂CN/iPr₂)₆] [M₁] was observed as its proton adduct [M₁ + H]⁺ at m/z

### Solution Analysis of (Oxido)zinc Complexes 1–3

The solution dynamics of diisopropyl complexes 1 and 2 were investigated by ¹H and ¹³C NMR spectroscopy in [D₆]-chloroform, [D₆]benzene, and [D₈]toluene solvents. A striking observation was made from room-temperature experiments; each complex gave identical solution spectra. This suggests that a common solution species is being formed, a process made possible through the exceptional fluxionality of the complexes. This common species was thought to be the tetrazinc complex [Zn₄(µ₄-O)(O₂CN/iPr₂)₆], whose symmetry agrees with the characteristically simple ligand spectra we observed (Figure 4, foreground).

However, given the propensity of dialkylcarbamato ligands to exchange when bonded to [Zn₄O]⁶⁺,\[11\] we could not rule out an analogous exchange environment involving [Zn₃O₂]¹⁺ or other intermediates; such a process could also give rise to similar spectral features. Hence, we took to investigating the iPr₂NCO₂ ligand environment over a temperature range of 193–368 K. During the course of these experiments, a slight degree of decomposition occurred, as indicated by trace amounts of ZnO powder in the NMR tube and “free” HN/iPr₂ appearing in the spectra. This decomposition was slightly accelerated at high temperatures (308–368 K); no other significant spectral changes were observed in this temperature range.

Low-temperature ¹H NMR studies (Figure 4, inset) revealed a classic case of exchange between inequivalent iPr groups. A ¹³C NMR experiment at 193 K (Figure S1) confirmed that the methine carbon resonance had resolved into two broad signals at δ = 47.2 and 43.9 ppm, while the carboxyl resonance remained sharp and stationary at δ = 161.9 ppm. The methyl ¹³C NMR signals were obscured by solvent peaks and could not be assigned. The chemical shifts of these NMR signals tend towards those of the crystalline-state structure of tetrazinc complex 1, in which each iPr₂NCO₂ ligand clearly presents two inequivalent iPr environments (Figure 5). The variable-temperature NMR results could be explained by a conformational exchange, whereby the iPr groups are projected towards (endo) and away (exo) from the inner [Zn₄O]⁶⁺ core of the molecule. While the relatively open structure of 1 accommodates a staggered alkyl conformation (Figure 5), the tightly packed surface of octazinc complex 2 results in only exo-oriented iPr groups.

In order to further characterise the solution chemistry of the (diisopropylcarbamato)zinc system, a sample of 2 in THF was analysed using high-resolution ESI-MS. On the positive-ion spectrum, peaks of several di-, tri- and tetraclear zinc species were detected in the range m/z = 850–1300 (Figure 6). The tetrazinc complex [Zn₄(µ₄-O)(O₂CN/iPr₂)₆] [M₁] was observed as its proton adduct [M₁ + H]⁺ at m/z

Figure 4. Foreground: room-temperature ¹H NMR spectrum of 2 in [D₆]toluene. Inset: variable-temperature ¹H NMR stack plot for the same solution.
Tetranuclear and Octanuclear (Carbamato)zinc Complexes

Figure 5. Ellipsoidal diagram of an \( \text{iPr}_2\text{NCO}_2^- \) ligand from 1·1.3(CH\(_3\))\(_3\)CCN·0.2H\(_2\)O. Thermal ellipsoids represent the 30% probability level.

\[ m/z = 1137.3409 \] and its diisopropylammonium adduct \([\text{M}_1 + \text{H}_2\text{NiPr}_2]^+\) at \( m/z = 1238.4641 \). Also detected were the fragment ions \([\text{M}_1 - \text{ZnO} + \text{H}]^+\), \([\text{M}_1 - \text{ZnO} - \text{L}]^+\) and \([\text{M}_1 - 2\ \text{ZnO} - \text{L} + 2\ \text{H}]^+\), where \( \text{L} = \text{iPr}_2\text{NCO}_2^- \). Our interpretations of their structural formulae are provided in Figure 6.

Each peak was computationally simulated utilising the monoisotopic mass, isotopic distribution and background chemistry of the ions in question. As an example, the expanded peak at \( m/z = 1137.3409 \) is shown above the corresponding simulation for \([\text{M}_1 + \text{H}]^+\) in Figure 7. Additional simulation results are given in the Supporting Information (Figures S2–S5). In general, our simulations match the experimental data within 5–11 ppm, which is a reasonable instrumental error for the equipment used. Several zinc species of higher nuclearity (\( \text{Zn} > 4 \)) were observed close to the baseline in the mass range \( m/z = 1300–1800 \) (Figure S6), but the low signal-to-noise ratio hampered conclusive identification of those species. No peaks for molecular ions or adduct species were noted for \([\text{Zn}_8(\mu_4-\text{O})_2(\text{O}_2\text{CNiPr}_2)_2]^-\) \([\text{M}_2]^-\). On the negative-ion spectrum, a cluster of peaks were also detected close to the baseline at \( m/z = 990–1050 \), which according their distributions also appeared to be from tetrarazine species.

The present ESI technique has predominantly detected ionic species of low nuclearity (\( 2 \leq \text{Zn} \leq 4 \)), with most peaks exhibiting a degree of protonation. Although this technique did not directly show the concentration of neutral species such as 1 and 2, we were presented with a rich variety of fragment species, a consequence of the labile chemistry of the system. Other researchers studying the related cobalt complex \([\text{Co}_8(\mu_4-\text{O})_2(\text{O}_2\text{CNiPr}_2)_2]\) using DCI-MS reported only octanuclear anions and a singly charged fragment appearing to be \([\text{Co}_4(\mu_4-\text{O})(\text{O}_2\text{CNiPr}_2)_6]^-\).\[20\] From their data, the observed ratio of octanuclear to tetrarazine ions was 1.8:1. We are continuing to employ other techniques to characterise solution kinetics of the newly discovered diisopropyl derivatives 1 and 2. \(^1\text{H}\) and \(^{13}\text{C}\) NMR solution spectra of complex 3 agree with literature data.\[6\]

Figure 6. High-resolution positive ion ESI mass spectrum of 2 dissolved in tetrahydrofuran (\( m/z = 825–1300 \)).

---

Monoisotopic mass: 850.3815 (exp), 850.3862 (calc), error 5.5 ppm
Formula: \( \text{C}_{32}\text{H}_{72}\text{N}_{18}\text{O}_{27}\text{Zn}_{12} \)
Assignment: \([\text{Zn}_2(\text{O}_2\text{CNiPr}_2)_3]^-(\text{H})^+\)

Monoisotopic mass: 912.2925 (exp), 912.2997 (calc), error 7.9 ppm
Formula: \( \text{C}_{32}\text{H}_{72}\text{N}_{18}\text{O}_{27}\text{Zn}_{12} \)
Assignment: \([\text{Zn}_2(\text{O}_2\text{CNiPr}_2)_3]^-\)

Monoisotopic mass: 1057.4213 (exp), 1057.4100 (calc), error 10.7 ppm
Formula: \( \text{C}_{32}\text{H}_{72}\text{N}_{18}\text{O}_{27}\text{Zn}_{12} \)
Assignment: \([\text{Zn}_2(\text{O}_2\text{CNiPr}_2)_3]^-(\text{H})^+\)

Monoisotopic mass: 1137.3409 (exp), 1137.3340 (calc), error 6.1 ppm
Formula: \( \text{C}_{32}\text{H}_{72}\text{N}_{18}\text{O}_{27}\text{Zn}_{12} \)
Assignment: \([\text{Zn}_2(\text{O}_2\text{CNiPr}_2)_3]^-(\text{H})^+\)

Monoisotopic mass: 1238.4641 (exp), 1238.4545 (calc), error 7.8 ppm
Formula: \( \text{C}_{32}\text{H}_{72}\text{N}_{18}\text{O}_{27}\text{Zn}_{12} \)
Assignment: \([\text{Zn}_2(\text{O}_2\text{CNiPr}_2)_3]^-(\text{H})^+\)
Figure 7. Expanded molecular adduct region for \([M_1 + H]^+\), where \(M_1 = [Zn_4(\mu_4-O)(O_2CNiPr_2)_6] \). (a) Experimental isotopic distribution; (b) calculated isotopic distribution for \(C_{42}H_{85}N_{6}O_{13}Zn_4^+\).

Conclusion

A convenient new route has been developed for the synthesis of (carbamato)zinc complexes. The (diisopropylcarbamato)(\(\mu\)-oxo)zinc complexes participate in an unusually facile isomerisation that allows selective isolation of its tetrazinc or octazinc isomers by choice of recrystallisation solvent. The amount of bond breaking and forming required for the isomerisation between tetrazinc complex \(1\) and octazinc complex \(2\) would appear, superficially, to be a significant barrier to the process. However, when the general lability of carbamato ligands\(^{[31]}\) is appreciated, the tetra/octazinc interconversion finds its place comfortably among other dialkylcarbamato-associated phenomena including metal-centre lability,\(^{[32]}\) transamination,\(^{[6]}\) and \(CO_2\) scrambling.\(^{[6]}\)

The subtle solvent effects discovered in this work may stimulate a re-examination of carbamate chemistry of other metals. In particular, the lability of the (carbamato)zinc complexes offers a route to mixed-metal clusters with possible applications in SSCVD deposition of dimetallic oxide films.

Experimental Section

Materials: Secondary amines were distilled from KOH and stored under argon. Neat ZnEt\(_2\) was purchased from Aldrich and used as received. Caution: Diethylzinc is pyrophoric and must be handled with care under an inert gas! Anaerobic-grade \(CO_2\) was obtained from BOC Gases and used without further purification. Acetonitrile, benzene, \(n\)-heptane and trimethylacetonitrile were dried using standard procedures and stored under argon. Other alkanes were purchased from Aldrich and used as received. [D]\(\)Chloroform was purchased from Aldrich and distilled from CaH\(_2\) under argon. [D\(_3\)]-Benzene and [D\(_3\)]toluene were purchased from Aldrich and used as received. MilliQ-grade water was deoxygenated by distillation under argon prior to use. All preparative reactions and product manipulations were carried out under argon using standard Schlenk techniques, unless otherwise specified.

Instrumentation: \(^1\)H and \(^{13}\)C NMR spectra were recorded with Bruker DMX 500 and DPX 300 instruments. Mass spectra were recorded with a Q-TOF Ultima API instrument. Ionic distributions were simulated using iMass and MassLynx\textsuperscript{SM} software packages.\(^{[33,34]}\)

Synthesis of (Dialkylcarbamato)(\(\mu\)-oxido)zinc Complexes \([Zn_4(\mu_4-O)(O_2CNiPr_2)_6] \) (1) and \([Zn_8(\mu_4-O_2)(O_2CNiPr_2)_12] \) (2): Under an inert gas, diethylzinc (10.0 mL, 98 mmol) was added to a 250-mL 3-necked flask fitted with a reflux condenser. Benzene (100 mL) and diisopropylamine (200 mmol) were added to the flask, and the mixture was refluxed for 2 h, during which the solution became yellow. Diethylamine (16.8 mL, 160 mmol) was added to a solution of diethylzinc (8.2 mL, 80 mmol) in benzene (100 mL) in a 250-mL three-necked flask fitted with a reflux condenser under an inert gas. The resulting clear solution was heated under reflux for 2 h, during which the solution became yellow.
low, with concomitant evolution of a colourless gas. The solution was cooled, then stirred whilst a stream of CO\textsubscript{2} gas was passed over it overnight, to give a white cloudy mixture. After cooling to 0°C, a solution of H\textsubscript{2}O (300 \textmu L, 17 mmol) in THF (30 mL) was added dropwise to the stirred mixture, leading to an increase in turbidity. After stirring at room temperature for 48 h, the mixture had become a clear solution. Volatiles were removed under reduced pressure to give a white solid. The tetranuclear complex 3 was isolated as a white powder (16.8 g, 86%) by recrystallisation of the solid from hot heptane and subsequent removal of solvent under reduced pressure. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ = 1.08 (t, 6 H, CH\textsubscript{3}), 3.27 (q, 4 H, CH\textsubscript{2}) ppm. \textsuperscript{13}C NMR (76.6 MHz, CDCl\textsubscript{3}): δ = 162.4 (CO\textsubscript{2}), 41.54 (CH\textsubscript{2}), 13.58 (CH\textsubscript{3}) ppm.

X-ray Crystallography

Recrystallisation Procedure: The experimental setup consisted of a B-type bushing 38-mL heavy-walled glass pressure tube (Ace Glass) containing stirrer bar and recrystallisation materials under argon. A volume of 10 mL of solvent per gram of (dipropylcarbamato)zinc complex was found to give crystals of adequate quality. For 1\textcdot2CH\textsubscript{3}CN, a sealed vial containing 1 or 2 and CH\textsubscript{3}CN was heated and stirred up to 90 °C, the white powder dissolving to give a colourless solution. Heating was ceased, and the tube was cooled slowly at the cooling rate of the bath; 24 h later a crop of colourless solution was done with SIR92 \cite{37} and the refinement with RAELS \cite{38} ORTEP-II\cite{39} for eMac was used for the structural data collection. The authors are also very grateful to the UNSW Analytical Centre NMR facility for assistance with variable-temperature NMR spectroscopy experiments and the Bioanalytical Mass Spectrometry Facility (BMSF) for conducting ESI-MS experiments.

Acknowledgments

The authors wish to thank Paul Jensen from the Crystal Structure Analysis Facility at Sydney University for low-temperature single-crystal X-ray data collection. The authors are also very grateful to the UNSW Analytical Centre's NMR facility for assistance with variable-temperature NMR spectroscopy experiments and the

---

\[ R_w = \frac{\sum I - \sum I_{o}}{\sum I_o} \]

\[ \delta = 1.08 \text{ (t, 6 H, CH}_3\text{)}, 3.27 \text{ (q, 4 H, CH}_2\text{)} \text{ ppm.} \]

\[ \delta = 162.4 \text{ (CO}_2\text{), 41.54 \text{ (CH}_2\text{), 13.58 \text{ (CH}_3\text{) ppm.}} \]

\[ R_w = \frac{\sum I - \sum I_{o}}{\sum I_o} \]

\[ \delta = 1.08 \text{ (t, 6 H, CH}_3\text{)}, 3.27 \text{ (q, 4 H, CH}_2\text{)} \text{ ppm.} \]

\[ \delta = 162.4 \text{ (CO}_2\text{), 41.54 \text{ (CH}_2\text{), 13.58 \text{ (CH}_3\text{) ppm.}} \]


[38] A. D. Rae, RAELS, University of New South Wales, Sydney, 1996.


Received: July 12, 2007
Published Online: March 13, 2008
(Since its publication in Early View, a few minor changes have been made.)