Oxygenation of alkylzinc complexes with pyrrolylketiminate ligand: access to alkylperoxide *versus* oxo-encapsulated complexes†‡

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By variation of the zinc bonded alkyl group significantly different post-oxygenation products, the novel zinc alkylperoxide and the tetranuclear zinc oxo-encapsulated cluster, were derived from the controlled oxygenation of the corresponding alkylzinc complexes with a pyrrolylketiminate ligand.

Zinc complexes supported by monoanionic *N,N*-bifunctional ligands are currently receiving considerable attention due to their increasing role in various stoichiometric and catalytic transformations.[1] Very recently, we have identified a particularly intriguing family of main-group metal complexes based on pyrroloimines, which exhibit a diversity of bonding modes to metal centers[2] as well as appearing to be an interesting building block for supramolecular architecture through self-assembly.[3] In our ongoing efforts to gain a more intimate view of the role of supporting ligands in the reactions of zinc alkyls with O_2, we turned our attention to this group of complexes, and herein we report the synthesis and structural characterization of a novel trinuclear zinc alkylperoxide and a zinc oxo cluster, the formation of which was mediated by the identity of the zinc bonded alkyl substituents in parent alkylzinc complexes supported by an *N,N*-bidentate ligand.

The reaction of R_2Zn with 1 equiv. of 2,2′-(1′-pyrroliny1)-pyrrole[4] (*Pyr-pyrl*H) in toluene at 20 °C affords the alkylzinc complexes, [RZn(*Pyr-pyrl*)] [where R = Et (**1**) and ^tBu (**2**)].

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Cryoscopic molecular weight determinations showed that both compounds are monomeric in benzene solution. Although we were not able to obtain single crystals of **1**, the NMR data are fully consistent with the anticipated formula (see ESI: Fig. S1†). In the solid state, the structure of **2** was determined by X-ray diffraction, which revealed that it occurs as a centrosymmetric dimer with the unsymmetrical $Zn_2(\mu\text{-}N)_2$ bridges formed by the pyrrole nitrogen and with each zinc having a distorted tetrahedral geometry (Fig. 1). In the crystal structure adjacent dimeric moieties of **2** self-assemble in chains by the double C–H···π hydrogen bonds (Fig. S3†). It is interesting to note that the related *tert*-butylzinc complex with *N*-phenylpyrrolylaldiminate forms a noncovalently-bonded dimer in which the association of the molecular units is attained through a pair of intermolecular Zn–pyrrole π interactions.[2a] Thus, a slight modification in the backbone of bifunctional pyrrolylaldiminate ligands may lead to both significant changes in their coordination mode to a metal center and in the assembly of the RZn(*N,N*) species.

In the next step, a solution of **2** in toluene at −20 °C was treated by dry dioxygen for approximately 20 min. Then, the excess of O_2 was removed and colorless crystals of the alkyl-peroxide [^{t}BuOOZn(*Pyr-pyrl*)]$_2$[Zn(*Pyr-pyrl*)$_2$] (**3**) precipitated after several hours in good yield. The reaction affords the trinuclear zinc alkylperoxide, which formally may be viewed as an adduct formed from the two oxygenated moieties of **2** and the dichelate zinc complex. Surprisingly, the analogous reaction of the ethyl complex **1** with O_2 under similar conditions leads to the tetranuclear zinc oxo cluster $Zn_4(\mu_4\text{-}O)(Pyr\text{-}pyrl)_6$ (**4**), which precipitates from the post reaction mixture after several days.
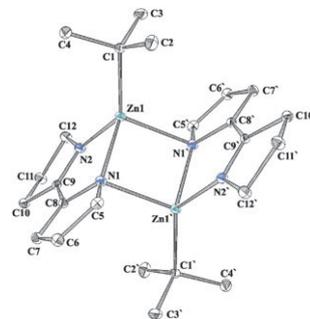

Fig. 1 Molecular structure of **2** with thermal ellipsoids at the 30% level; hydrogen atoms omitted for clarity. Selected dimensions (Å): Zn1–N1, 2.119(2); Zn1–N2, 2.058(1); Zn1–C1, 1.989(1); Zn1–N1′, 2.264(6).
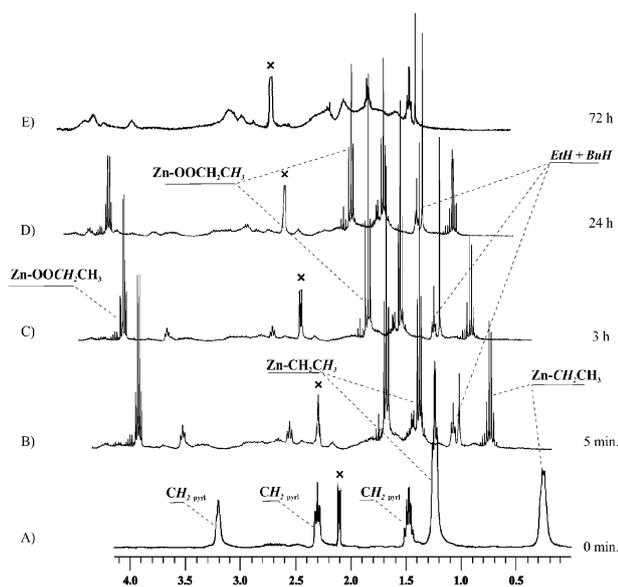
Fig. 2 Representative ^{1}H NMR spectra for the oxygenation of **1** in toluene-d[8] at −20 °C: before introduction of O$_2$ (A); during the reaction with O$_2$: 5 min. (B), 3 h (C), 24 h (D) and 72 h (E); peaks marked with × represent the deuterated protons solvent signal.

To gain further insight into the oxygenation of **1**, the reaction was monitored by ^{1}H NMR spectroscopy at −20 °C (Fig. 2, the spectra are provided in full as Fig. S7†). It is clear from NMR-tube experiments that the reaction proceeds in two distinct stages. The insertion of O$_2$ into the Zn–C bond is fast, proceeding within the first five minutes, leading to an EtOOZn(Pyr-pyrl) intermediate. However, only approximately half the amount of the Zn–C bonds supplied in the form of **1** are consumed, as indicated by the presence of well-resolved multiplets of similar intensity for the Et–Zn and EtOOZn groups (Fig. 2B). In the next 2–3 days the signals assigned to the alkylzinc and alkylperoxozinc species gradually disappear completely with concomitant evolution of ethane and *n*-butane.

On the basis of the reaction outcome and the spectroscopic data, the reaction can be rationalized by assuming the following pathways. In the first stage, O$_2$ reacts with the three-coordinate **1** to generate the ethylperoxide species that efficiently forms, with the parent metal alkyl complex, a relatively stable adduct
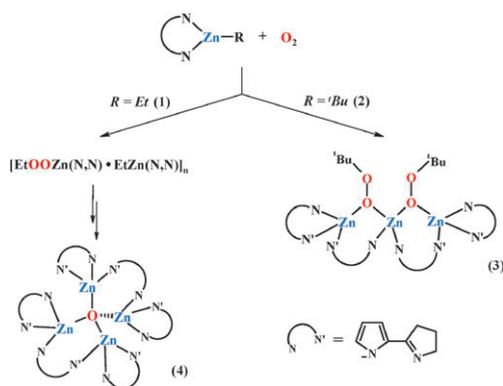
[EtOOZn(Pyr-pyrl)·**1**]$_n$ (Scheme 1). This view is supported by the aforementioned spectroscopic data as well as by the previously isolated and structurally characterized analogue [ROOZn(O,N)·RZn(O,N)]$_2$ cluster, derived from the oxygenation of the ethylzinc complex with aminoalkoxide ligand.[5] The putative [EtOOZn(Pyr-pyrl)·**1**]$_n$ cage likely comprises the four-coordinate ZnEt centers as it is resistant toward further reaction with O$_2$ under studied conditions.[5,6] In this case, however, the resulting ethylperoxide moiety supported by the *N,N*-ligand is presumably relatively unstable and slowly decomposes to the Zn$_4$O cluster *via* initial in-cage homolysis of the O–O bond, generating the (Pyr-pyrl)ZnO• and EtO• radical species. The oxyzinc radical cannot be stabilized by oxidation of the metal center and is likely further stabilized by electron transfer from one of the remaining Zn–C bonds, and this cage reaction leads to the release of Et• radical[7] and produces a zinc oxo species. We observed similar in-cage transformations for the EtZn/ZnOOEt system supported by a carboxylate ligand, though the homolytic cleavage of the ZnO–OEt bond responsible for formation of the oxo-encapsulated moieties was considerably faster under analogous conditions.[8] In our opinion, the contrasting reactivity of **1** and **2** with O$_2$ is an additional instance that highlights the role of an intermediate cage involving the resulting alkylperoxide species and the parent alkyl complex; in the oxygenation process of **2**, this type of intermediate aggregate is likely not sufficiently rigid due to steric encumbrances, and reacts further toward the complete oxygenation of the Zn–C bonds. It is also worth noting that Wheatley *et al.* recently reported on the isolation and structure characterization of a number of alkoxide and oxo-encapsulated products from the reaction of O$_2$ with various mixed lithium-zinc systems containing 2-pyridylamide ligands, however the origin of a diversity of oxo-capture modes and the nature of the reactive intermediates has essentially remained unclear.[9]

The identity of **3** and **4** has been confirmed by X-ray crystallography. The molecular structure of **3** consists of discrete asymmetric dinuclear units with Zn atoms coupled by the μ-OO^{t}Bu and μ-1,2-*N,N* bridges, and the terminal zinc atoms are further coordinated by an asymmetrically chelating *Pyr-pyrl* ligand (Fig. 3). Both the Zn–O and O–O distances are similar to the corresponding bond lengths found in zinc μ$_2$-alkylperoxide complexes.[1f,6a] Adjacent monomeric moieties

Scheme 1 Two competing reaction pathways that the alkylzinc complexes with the *N,N*-bifunctional ligand can undergo in the presence of O$_2$.

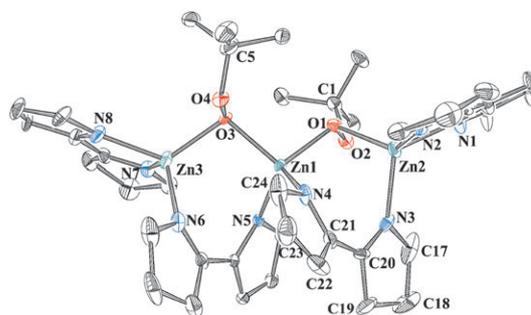
Fig. 3 Molecular structure of **3** with thermal ellipsoids set at the 30% level; hydrogen atoms omitted for clarity. Selected dimensions (Å): Zn1–O1, Zn2–O1, 2.068(6); 1.983(6); Zn1–O3, 1.974(2); Zn3–O3, 1.966(2); O1–O2, 1.477(8); O3–O4, 1.491(4); Zn2–N1, 2.015(3); Zn2–N2, 1.991(3); Zn2–N3, 1.996(4); Zn1–N4, 1.993(3); Zn1–N5, 2.000(3); Zn3–N6, 1.993(3); Zn3–N7, 2.036(3); Zn3–N8, 1.994(3).
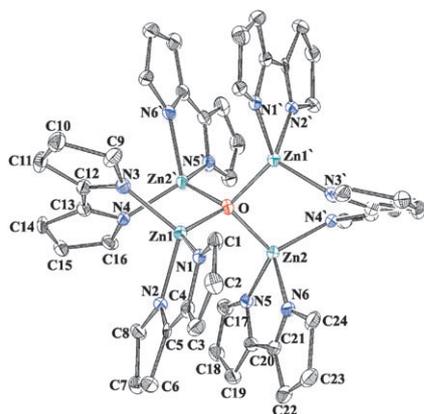
Fig. 4 Molecular structure of **4** with thermal ellipsoids at the 30% level; hydrogen atoms omitted for clarity. Selected dimensions (Å): Zn1–N1, 2.008(1); Zn1–N2, 2.048(7); Zn1–N3, 2.007(8); Zn2–N4′, 1.998(1); Zn2–N5, 2.001(8); Zn2–N6, 2.041(8); Zn1–O, 1.956(3); Zn2–O, 1.957(3).
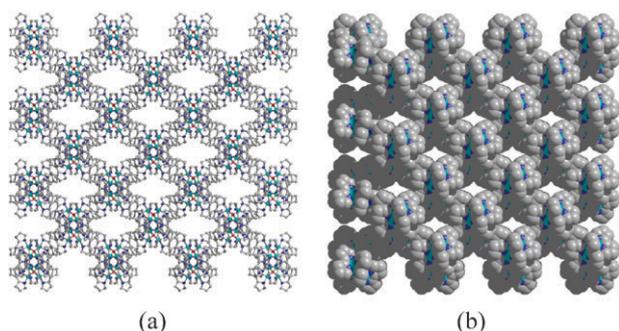

Fig. 5 Crystal structure of **4** viewed along *c* axis: (a) wire-frame model, (b) space-filling diagram of the framework.

of **3** are held together in chains by the cooperative C–H⋯π hydrogen bonds (Fig. S5†); the oxygen centers are not involved in intra- and intermolecular non-covalent interactions.

The molecular structure of **4** consists of discrete monomeric oxo centered tetranuclear units with the zinc centers paired up by the μ-1,2-*N,N*-bridges and additionally chelated by *Pyr-pyrl* ligand (Fig. 4). The observed diversity of coordination modes of the *N,N*-bifunctional ligand is striking as, to our knowledge, for all previous examples of the tetranuclear zinc oxo-encapsulated clusters the metal centers within OZn$_4$ units were connected by bifunctional ligands of μ-1,2-binding mode.[8,9] Furthermore, a detailed analysis of the crystal structure of **4** revealed that the Zn$_4$O clusters self-assemble *via* complementary supramolecular interactions to produce an extended 3D network with ellipsoidal channels of 12 Å and 14 Å equatorial radii (Fig. 5). This microporous material is particularly intriguing as, in recent years, the extensive studies have concentrated on the storage of H$_2$ in microporous metal–organic frameworks incorporating [Zn$_4$O]$^{6+}$ tetrahedra linked by organic connectors.[10] Moreover, the Zn$_4$O nodal regions of the framework have been identified as the principal sites for the hydrogen gas adsorption.[11] Thus, this work suggests a new way to engineer nanostructured materials composed of connected [Zn$_4$O]$^{6+}$ tetrahedra under mild conditions. Exploration of these possibilities, including gas sorption properties, is currently underway.

In conclusion, 2,2′-(1′-pyrroliny1)pyrrole appears to be a very promising, versatile *N,N*-bifunctional supporting ligand which, to our surprise, has not essentially been explored in the coordination chemistry and self-assembly processes.[12] The controlled oxygenation of alkylzinc complexes with *Pyr-pyrl* provided the novel zinc alkylperoxide and the tetranuclear zinc oxo-encapsulated cluster. This unprecedented reaction outcome switching was simply achieved by changing the character of the alkyl substituent of the zinc complex. The composition and structure of these significantly different post-oxygenation products, as well as the spectroscopically detected intermediates, may be of importance in comprehending the mechanisms operating in oxygen capture processes by metal alkyl complexes.

Notes and references

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7 The presence of ethane and butane in the reaction mixture indicates that Et• radicals undergo an in-cage recombination with each other to give butane or the alkyl radical can diffuse away from the cage with concomitant hydrogen abstraction from the bulk.

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