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Oxygen and Sulfur Activation

Alkylzinc Carboxylates as Efficient Precursors for Zinc Oxocarboxylates and Sulfidocarboxylates**

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Dedicated to Professor Piotr Sobota on the occasion of his 65th birthday

Zinc compounds supported by carboxylate ligands are of great interest owing to their role in biochemical systems, catalysis, and materials chemistry. For instance, zinc carboxylates, and particularly alkoxyzinc carboxylates, are attracting a great deal of attention owing to their importance as highly active catalysts for the polymerization or copolymerization of a wide range of organic monomers.[1] Zinc oxocarboxylates with the general formula $Zn_4O(O_2CR)_6$ have been known for decades,[2] and interest in them was renewed in the late 1990s primarily by the work of Yaghi and co-workers, who developed the synthesis of metal–organic frameworks (MOFs) with high porosities and tailor-made molecular cavities based on these oxo clusters as secondary building units (SBU).[3] Since then, MOFs based on zinc carboxylates or oxocarboxylates have been studied for a variety of applications, including hydrogen storage, nonlinear optics, and catalysis.[4] In contrast to the rich chemistry of mixed sulfidozinc thiolate complexes,[5] there is a distinct lack of synthetic methods leading to zinc sulfidocarboxylates, which could be used as SBUs in the construction of extended inorganic–organic structures.

The most common synthetic routes for the preparation of extended framework structures with zinc carboxylates as SBUs are based on solvothermal methods and involve inorganic zinc salts as substrates.[4] Our experience in the design, synthesis, and structural characterization of organozinc complexes as models for various transformations[6] prompted us to explore whether alkylzinc carboxylates[7] can be used to synthesize alkoxyzinc carboxylates and other potentially useful clusters. Herein, we present the synthesis and characterization of the novel alkylzinc carboxylate cluster $[EtZn(O_2CPh)]_6$ (**1**) as well as its reactions with dioxygen and elemental sulfur as a new efficient route to zinc oxocarboxylates and sulfidocarboxylates.

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The reaction of Et_2Zn with one equivalent of benzoic acid in toluene affords **1** in essentially quantitative yield. Compound **1** was characterized by spectroscopic and X-ray single-crystal studies. The complex has a hexameric structure with four-coordinate zinc centers (Figure 1). The association of six

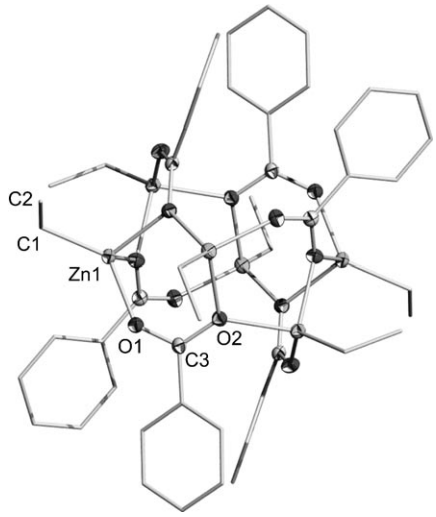

Figure 1. Molecular structure of **1** with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity.

$EtZn(O_2CPh)$ molecules results in a tubular structure containing fused networks of twelve- and six-membered heterocycles. Each carboxylate ligand bridges three zinc centers and adopts an $\eta^1{:}\eta^2{:}\mu_3$ coordination mode. The Zn–O bond lengths of the highly puckered 12-membered $\{ZnOCO\}_3$ rings fall within a narrow range (1.972–2.096 Å). Two $\{ZnOCO\}_3$ rings are further linked through six Zn–O interactions (2.095(1) Å) to give six puckered six-membered rings.[8] The structural motif observed for **1** is analogous to that seen in the methylzinc derivative of *N*-methyl benzamide.[9]

In the course of our studies on the role of supporting ligands in the oxygenation of alkylzinc complexes,[6] we have been interested in finding out whether well-defined zinc alkylperoxides or alkoxides can be synthesized by the selective oxygenation of alkylzinc carboxylates. Therefore, in the next step, we treated **1** with O_2 in [D_8]toluene and monitored the reaction by ^{1}H NMR spectroscopy at 0 °C (Figure 2). The reaction proceeds in two distinct stages. Thus, approximately half the Zn–C bonds in the complex are

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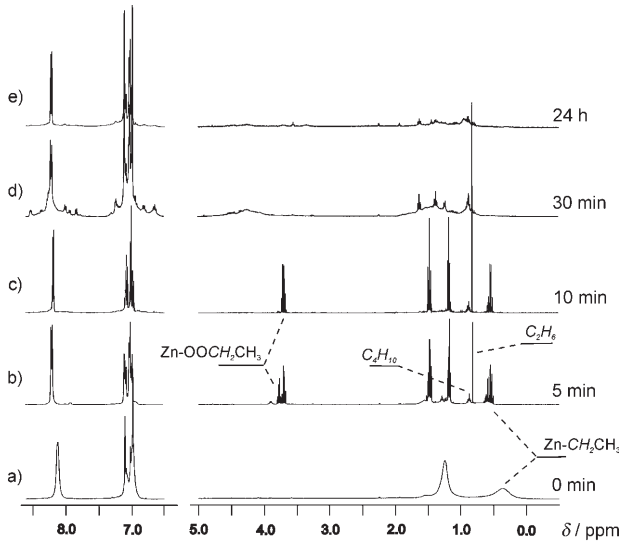
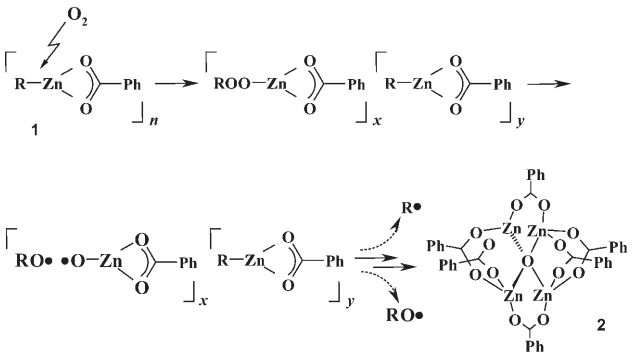


Figure 2. Representative ^{1}H NMR spectra for the oxygenation of **1** in [D$_8$]toluene at 0 °C: a) before introduction of O_2 and during the reaction with O_2 after b) 5, c) 10, and d) 30 min, and e) 24 h.

consumed during the first five minutes to form new clusters with differing stabilities. Although we have no direct evidence for the structures of these clusters, we suggest that they are $[EtZn(O_2CPh)]_x[EtOOZn(O_2CPh)]_y$ aggregates $(x \geq y)$).[10] This proposal is borne out by the ^{1}H NMR spectra, which reveal the presence of well-shaped multiplets of similar intensity characteristic of EtZn and EtOOZn moieties (Figures 2b and 2c). During the next 30 minutes or so the signals assigned to the alkylzinc and alkylperoxozinc species gradually disappear with concomitant evolution of ethane and *n*-butane.[11] At the end of the reaction only signals corresponding to aromatic protons are observed and, strikingly, there are no characteristic signals for ZnOEt species[12] (Figure 2e; the ^{1}H NMR spectra are provided in full as Figure S2 in the Supporting Information).

These observations indicate that the putative $[EtZn(O_2CPh)]_x[EtOOZn(O_2CPh)]_y$ clusters are unstable and undergo further transformations to give the oxocarboxylate species $[Zn_4(\mu_4\text{-}O)(O_2CPh)_6]$ (**2**). Unfortunately, we were not able to isolate any partially oxygenated aggregates in separate experiments carried out in a Schlenk tube. In a control experiment, a solution of $[EtZn(O_2Ph)]_n$ (**1**) in THF at 0 °C was treated with an excess of dry dioxygen and the reaction mixture was stirred for approximately five minutes. The excess of O_2 was then removed and **2** deposited in good yield after several hours. The identity of **2** has been confirmed by X-ray crystallography. The molecular structure of **2**, which has previously been synthesized from zinc benzoate by both thermal decomposition[2d] or serendipitously upon addition of moist acetone,[2c] consists of discrete, monomeric, oxo-centered tetranuclear units with μ-1,2-carboxylate bridges (Figure S1 in the Supporting Information; the redetermined crystal data are also provided).[13]

Thus, in contrast to our expectations, the oxygenation of **1** does not lead to isolable alkylperoxide or alkoxide species. This observation demonstrates that the identity of the supporting ligand can dramatically alter the pathway of oxygenation reactions. These observations are also another instance where the radical-chain mechanism,[14] although widely accepted for decades, fails to explain the product formation in the oxygenation of alkylzinc complexes.[6] Based upon the reaction outcome and our recent extensive studies on the oxygenation of alkylzinc complexes, it is reasonable to propose the reaction mechanism shown in Scheme 1 as a



Scheme 1.

working hypothesis. According to this mechanism,[6c] the initial step in the oxygenation reaction involves the attack of an O_2 molecule at the three-coordinate metal center of an $EtZn(O_2CPh)$ molecule (our recent studies have demonstrated convincingly that higher coordinate species are not active toward O_2[6a,c]). This attack is followed by the insertion of O_2 into the Zn–C bond to give the zinc alkylperoxide species $EtOOZn(O_2CPh)$, which forms the proposed $[EtZn(O_2CPh)]_x[EtOOZn(O_2CPh)]_y$ cage with the parent molecules.

Conventional wisdom states that the reaction of metal alkylperoxides with their metal alkyl precursors should afford isolable MOR alkoxide species. However, the further transformations observed for zinc alkylperoxides supported by carboxylate ligands can be understood by invoking O–O bond homolysis, which produces an alkoxyl radical and a $(PhCO_2)ZnO^{\bullet}$ radical, which likely remains in a cage of the type $[(PhCO_2)ZnO^{\bullet}][EtZn(O_2CPh)]_m$. The nascent $EtO^{\bullet}$ radical diffuses out of the cage and the oxyzinc radical is stabilized by electron transfer from one of the remaining Zn–C bonds. This reaction produces an oxozinc species and gives rise to the release of the ethyl radical, which can abstract hydrogen from the solution bulk to produce ethane or recombine with another $Et^{\bullet}$ or $EtO^{\bullet}$ radical to form butane and diethyl ether, respectively.[11] Consequently, the resulting transient zinc species is a good candidate for involvement in the in-cage rearrangement that leads to the final oxocarboxylate complex **2**.

Encouraged by the results obtained from the oxygenation of **1**, we performed an analogous investigation with elemental sulfur (S_8) to see whether an analogous transformation might lead to the efficient synthesis of a new family of sulfidocarboxylates. The insertion of sulfur into Zn–C bonds has not been studied extensively, and the reported data only concern reactions with dialkylzinc compounds.[15] These latter reac-

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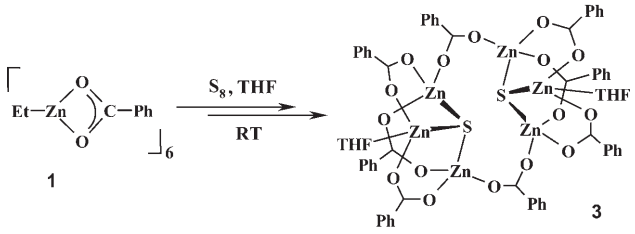
tions generally result in the insertion of sulfur into one Zn–R bond and afford alkylzinc thiolate clusters of the type $[Zn(SR)R]_n$. Interestingly, the reaction of Et_2Zn with two equivalents of sulfur in toluene at room temperature, followed by addition of an excess of 3,5-lutidine (Lut), produced the mixed sulfidozinc thiolates $[Zn_{10}S_4(SEt)_{12}(Lut)_4]$ and $[Zn_2S(SEt)(Et)(Lut)_4]$.[15b] To our knowledge, the interaction of sulfur with monoalkyl RZn(L) complexes (L is a monoanionic ligand) has not been studied before. The reaction of S_8 with **1** in THF solution proceeds with a color change from yellow to colorless after several hours at ambient temperature accompanied by the slow deposition of colorless crystals of the novel zinc sulfidocarboxylate $[Zn_6(\mu_3\text{-}S)_2(O_2Ph)_8(thf)_2]$ (**3**; Scheme 2). Thus, the introduction of sulfur results in the formation of an unusual hexanuclear species instead of giving a tetranuclear analogue of **2** or mixed sulfidozinc thiolate complexes supported by carboxylate ligands.



Scheme 2.

Compound **3** crystallizes as a molecular hexanuclear cluster with C_i symmetry with one uncoordinated THF molecule in the unit cell. The structure consists of a zinc carboxylate cluster in which each central sulfide ion is surrounded by three Zn atoms positioned at the corners of a tetrahedron (Figure 3). The presence of $Zn_3(\mu_3\text{-}S)$ units is striking as the central S atom in most reported structures of mixed sulfidozinc thiolate complexes is found in an $Zn_4(\mu_4\text{-}S)$-type environment and the former coordination mode has hitherto only been observed very rarely.[5] This observation

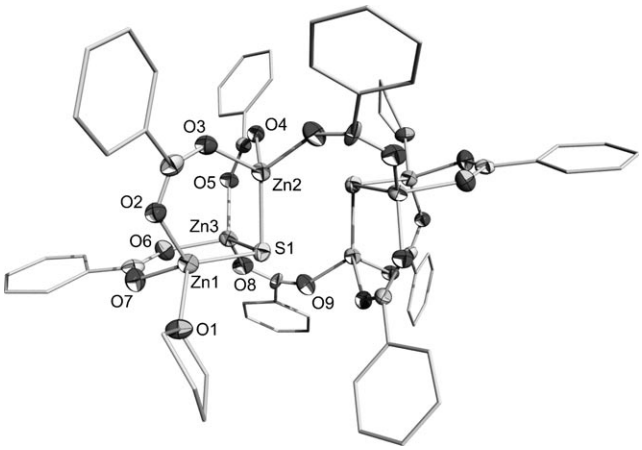


Figure 3. Molecular structure of **3** with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity.

therefore indicates that sulfide ions are not suited to bind to four zinc ions simultaneously in polynuclear zinc carboxylate complexes. The metal centers within each SZn_3 unit are connected by μ-1,2-carboxylate bridges, and two such units are also linked by similar μ-1,2-carboxylate bridges through one of their Zn atoms. Thus, compound **3** may formally be viewed as a dimer of $Zn_3(\mu_3\text{-}S)(O_2CPh)_4(thf)$ moieties where the metal–sulfur framework of these moieties is based on a metal-deficient $\{M\}_4$ tetrahedron lacking one vertex.

All the zinc centers are four-coordinate with an $SZn(O_{carboxylate})_3$ or $SZn(O_{carboxylate})_2(O_{thf})$ environment. The Zn–S bond lengths fall within a narrow range of 2.252–2.275 Å (the shortest Zn···S distance in the vicinity of a μ_3-S center is 3.700 Å). A similar situation is found for the Zn–$O_{carboxylate}$ interactions (av.: 1.967 Å) and the Zn–O_{thf} distances (2.031(5) Å). Both the composition and structure of **3** seem to be without precedent in zinc coordination chemistry. The presence of the peripheral thf ligand coordinated to two zinc centers in **3** holds considerable promise for the development of this unique sulfidocarboxylate zinc cluster as an SBU in the construction of extended inorganic–organic structures.

In conclusion, we have reported a new efficient route to zinc oxo- and sulfidocarboxylate complexes. In addition, the isolation and characterization of **1**–**3** has afforded new insights into the unexplored field of oxygenation and sulfuration of alkylzinc carboxylates.

Experimental Section

1: $ZnEt_2$ (0.494 g, 4.00 mmol) was added to a suspension of benzoic acid (0.488 g, 4.00 mmol) in hexane (7 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and the resulting white slurry was stirred vigorously for a further 6 h. Colorless crystals were obtained from CH_2Cl_2/hexane at −20 °C (0.655 g, 76%); elemental analysis (%) calcd for $C_9H_{10}O_2Zn$: C 50.15, H 4.68; found: C 50.21, H 4.83; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.23$ (q, 2H; $ZnCH_2CH_3$), 1.07 (t, 3H; $ZnCH_2CH_3$), 7.42 (m, 2H; Ar), 7.57 (m, 1H; Ar), 8.09 ppm (m, 2H; Ar); IR (Nujol): $\tilde{\nu} = 1622$(w), 1599(s), 1562(s), 1493(m), 1448(m), 1418(s), 1377(s), 1309(w), 1179(w), 1147(w), 1026(w), 719(s), 681(m), 614(w) cm^{-1}. Our attempts to perform molecular-weight measurements failed owing to the low solubility of this complex in aromatic solvents.

2: A stirred solution of **1** (0.216 g, 1 mmol) in THF (5 mL) was cooled to −20 °C in a Schlenk tube then an excess of dry dioxygen (1 atm) was introduced. After 5 min the excess of O_2 was removed on a vacuum/nitrogen line. Colorless crystals deposited from a THF/hexane mixture after several hours at −20 °C (0.107 g, 64%); elemental analysis (%) calcd for $C_{42}H_{30}O_{13}Zn_4$: C 50.23, H 3.01; found: C 50.31, H 3.08; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.42$ (m, 2H; CH_2), 7.53 (m, 1H; Ar), 8.22 ppm (m 2H; Ar); IR (Nujol): $\tilde{\nu} =$ 1622(w), 1608(s), 1571(s), 1493(m), 1461(m), 1418(s), 1378(m), 1178(w), 1072(w), 1027(w), 716(s), 686(m), 679(m), 605(w) cm^{-1}.

3: A solution of 1/8 S_8 (0.064 g, 2 mmol) in THF was added to a stirred solution of **1** (0.216 g, 1 mmol) in THF (5 mL). The color of the reaction mixture changed immediately to yellow and after two days the solution became colorless. The mixture was concentrated to about 2 mL and stored at 0 °C. Colorless, block-shaped crystals deposited after one day (0.108 g, 55%). Compound **3** is slightly soluble in THF and poorly soluble in CH_2Cl_2 and aromatic solvents; elemental analysis (%) calcd for $C_{32}H_{28}O_9SZn_3$ (sample dried in vacuo for 10 h): C 48.97, H 3.60, S 4.09; found: C 49.06, H 3.69, S 4.06; ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 1.78$ (m, 6H; CH_2), 3.62 (m, 6H; CH_2), 7.36 (m 16H; Ar), 7.47 (m 8H; Ar), 8.11 ppm (m 16H; Ar); IR (nujol): $\tilde{\nu} =$

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1622(w), 1600(s), 1562(s), 1557(s), 1553(s), 1544(s), 1493(m), 1447(m), 1418(s), 1378(m), 1177(w), 1070(w), 1025(w), 718(s), 688(m), 678(m) cm^{-1}.

Crystal data for **1**: $C_{54}H_{60}O_{12}Zn_6$, $M_r = 1293.24$, crystal dimensions $0.42 \times 0.36 \times 0.18$ mm^3, trigonal, space group $R\bar{3}$ (no. 148), $a = 13.5154(6)$, $c = 54.4271(3)$ Å, $V = 8609.5(7)$ $Å^3$, $Z = 6$, $F(000) = 3960$, $\rho_{calcd} = 1.497$ $g\,m^{-3}$, $\theta_{max} = 27.48°$, $R_1 = 0.0283$, $wR_2 = 0.0711$ for 4109 reflections with $I_o > 2\sigma(I_o)$. Crystal data for **2**: $C_{42}H_{30}O_{13}Zn_4$, $M_r = 1004.25$, $0.56 \times 0.38 \times 0.32$ mm^3, cubic, space group $Ia\bar{3}d$ (no. 230), $a = 39.9595(5)$ Å, $V = 63\,808.2(2)$ $Å^3$, $Z = 48$, $F(000) = 22\,320$, $\rho_{calcd} = 1.158$ $g\,m^{-3}$, $\theta_{max} = 18.84°$, $R_1 = 0.0825$, $wR_2 = 0.2251$ for 2019 reflections with $I_o > 2\sigma(I_o)$. Crystal data for **3**: $C_{64}H_{56}S_2O_{18}Zn_6 \cdot C_4H_8O$, $M_r = 1641.80$, $0.48 \times 0.32 \times 0.22$ mm^3, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.5411(8)$, $b = 13.2402(9)$, $c = 13.4481(9)$ Å, $\alpha = 80.522(6)°$, $\beta = 74.576(6)°$, $\gamma = 82.868(4)°$, $V = 1778.0(3)$ $Å^3$, $Z = 1$, $F(000) = 876$, $\rho_{calcd} = 1.60$ $g\,m^{-3}$, $\theta_{max} = 22.46°$, $R_1 = 0.0514$, $wR_2 = 0.1029$ for 2919 reflections with $I_o > 2\sigma(I_o)$. The structures were solved by direct methods using the program SHELXS-97[16] and refined by full-matrix least-squares on F^2 using the program SHELXL-97.[17] H-atoms were included in idealized positions and refined isotropically. CCDC 653815 (**1**), CCDC 654048 (**2**), and CCDC 653816 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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