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Conversion Between Doubly and Triply Carboxylate-Bridged Di(ethylzinc) Complexes and Formation of the (μ-Oxo)tetrazinc Carboxylate [Zn₄O(ArᵀolCO₂)₆]

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Abstract

Ethylzinc 2,6-bis(p-tolyl)benzoate converts between two forms in solution. Through NMR spectroscopic techniques and X-ray crystallography, the species in equilibrium were identified as [Zn₂(2,6-bis(p-tolyl)benzoate)₂] (1), [Zn₂(2,6-bis(p-tolyl)benzoate)_₃] (2), and diethyl zinc (Arᵀol = 2,6-bis(p-tolyl)phenyl). The equilibrium provides a model for understanding the speciation between doubly and triply m-terphenylcarboxylate-bridged diiron(II) and mononuclear iron(II) complexes. Evidence is presented for the occurrence of coordinatively unsaturated trigonal zinc species in solution. Both 1 and 2 decompose in air to form the T-symmetric oxozinc carboxylate, [Zn₄O(ArᵀolCO₂)₆] (3).

The steric bulk of m-terphenylcarboxylates facilitates assembly of biomimetic diiron(II) complexes that act as models for the active site of soluble methane monoxygenase. These complexes share the general formula, [Fe₂(RCO₂)₄(L)₁-2], where R is an m-terphenyl group and L is a neutral donor (Scheme 1). Within this diiron family, doubly, triply, and quadruply carboxylate-bridged compounds have been isolated as solids, but the role, if any, of the neutral ligand L in modulating the number of bridging carboxylates remains unclear. In particular, reaction of [Fe₂(ArᵀolCO₂)₄] (4) (Arᵀol = 2,6-bis(p-tolyl)phenyl) with N,N-dimethylethylenediamine (N,N-Me₂en) produces a mixture of doubly-bridged [Fe₂(ArᵀolCO₂)₄(N,N-Me₂en)] (5), triply-bridged [Fe₂(ArᵀolCO₂)₄(N,N-Me₂en)] (6), and [Fe₂(ArᵀolCO₂)₄(N,N-Me₂en)] (7), all characterized in the solid state (Scheme 1). A ¹⁹F NMR spectroscopic study of a fluorinated analog of 4 revealed interconversion between doubly- and quadruply-bridged forms, for which triply-bridged intermediates were proposed. The speciation of these diiron(II) complexes in solution during the oxidation of tethered substrates remains unclear, however, and is important for understanding their reactivity.

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ASSOCIATED CONTENT
Supporting Information
NMR spectra and X-ray crystallographic data for 1-3 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

Notes
The authors declare no competing financial interests.
One approach to studying the solution dynamics of 2-m-terphenylcarboxylate-bridged diiron(II) complexes is through parallel work on the redox stable dizinc(II) analogs. With the use of diamagnetic zinc complexes, NMR spectroscopic techniques can be employed to probe solution structures. An excellent candidate for such a study is the ethylzinc 2-m-terphenylcarboxylate, [Zn$_2$(Ar$_{3}$CO$_2$)$_2$(Et)$_2$(THF)$_2$] (1), which we discovered during pursuit of a dizinc analog of the biomimetic diiron(II) carboxylate, [Fe$_2$(PIM)(Ar$_{3}$CO$_2$)$_2$] (8) (see Figure S12 for the structure of PIM$^3$). NMR spectroscopic experiments revealed the presence of a dynamic equilibrium between doubly-bridged 1 and the triply carboxylate-bridged complex [Zn$_2$(Ar$_{3}$CO$_2$)$_3$(Et)(THF)] (2), which forms together with diethylzinc (Et$_2$Zn) in solution (Scheme 1). This equilibrium may be relevant to related diiron carboxylate complexes like 4-7. Compound 1 can lose its coordinated THF molecules, and evidence for a THF-free species having trigonal-planar zinc centers is also presented here. We further describe the oxozinc 2-m-terphenylcarboxylate complex, [Zn$_4$O(Ar$_{3}$CO$_2$)$_6$] (3), formed in air by decomposition of 1 or 2, which has a unique structure of $T$ symmetry constructed by alignment of $T_h$ and $T_d$ local symmetries.

Ethylzinc carboxylate 1 was prepared by addition of one equiv of Et$_2$Zn to a solution of Ar$_{3}$CO$_2$H in THF. X-ray diffraction quality crystals of 1 formed directly from the reaction mixture and the solid-state structure was determined (Figure 1). In 1, the two carboxylates bridge in a μ-1,3 mode, creating an 8-membered ring with a Zn⋯Zn distance of 4.06 Å. The ring adopts a chair conformation, with the ethyl groups and the THF molecules trans to each other across the ring as required by a crystallographic inversion center in the middle (Figure 1). Further details about the crystal structure, including selected bond distances and angles, are provided in the Supporting Information (SI, Table S4).

Compound 1 is a member of the well-known class of alkylzinc carboxylates, interest in which has increased in recent years because of their use as starting materials for oxozinc carboxylates and in polymerization catalysis.$^6$-$^9$ Original work on alkylzinc carboxylates dates back to the 1960’s, and in 1974 it was demonstrated that the simple ethylzinc carboxylates of acetate, trifluoroacetate, and benzoate have increased reactivity toward methanol compared to Et$_2$Zn itself.$^{10}$ Although aggregation in solution was described, structures of the simple ethylzinc carboxylates with acetate and benzoate reported in recent years display large variations in nuclearity and overall structure. Ethylzinc acetate exists as [Zn$_5$(CH$_3$CO$_2$)$_6$(Et)$_4$] (9) in C$_6$H$_6$ or toluene and as [Zn$_2$(CH$_3$CO$_2$)$_2$(Et)$_2$] (10) in THF.$^7$-$^8$ Additional solution studies revealed that these two motifs convert upon heating in an appropriate solvent. Ethylzinc benzoate also has two forms. From non-coordinating solvents, a hexazinc barrel-shaped compound, [Zn$_6$(PhCO$_2$)$_6$(Et)$_6$] (11),$^6$ is obtained with a carboxylate-to-ethyl ratio of 1:1. From THF, a dizinc complex, [Zn$_2$(PhCO$_2$)$_3$(Et)(THF)] (12),$^9$ crystallizes, with a ratio of 3:1. One report of an ethylzinc m-terphenyl carboxylate, [Zn$_2$(Ar$_{3}$MesCO$_2$)$_2$(Et)$_2$] (13),$^{11}$ is particularly interesting because it features two trigonal zinc centers (Ar$_{3}$Mes = 2,6-bis(mesityl)phenyl). The structure of 1 differs from that of 13 in that the latter has an 8-membered ring in a boat conformation (Figure 1), trigonal planar zinc, and a Zn⋯Zn distance of 3.58 Å. The $^1$H NMR spectrum of 13 in C$_6$D$_6$ supports the persistence of this structure in solution.$^{11}$ A summary of the carboxylate-to-ethyl ratios of the simple ethylzinc carboxylates is presented in Table S2.
When crystals of 1 are dissolved in C₆D₆ or toluene-d₈, more than one species is observed in the ¹H NMR spectrum (Figure 2, SI). In the aromatic region, two sets of peaks from the 2,6-bis(p-tolyl)phenyl groups are present, but the signals are not fully resolved. Resolution is obtained for the two tolyl methyl groups (2.08 and 1.97 ppm) and two ethyl groups (−0.28/1.28, and 0.17/1.23 ppm for the CH₂/CH₃ resonances, respectively). The upfield CH₂ resonances suggest that both ethyl groups are bound to zinc. Large, broad THF resonances occur at 3.49 and 1.37 ppm. Another set of broad resonances, appearing at 2.80 and 1.14 ppm, is also assigned as THF. Because a chemical shift of 2.80 ppm is unusual for the OCH₂ resonance of THF, 1 was prepared from THF-d₈ and its ¹H NMR spectrum acquired. The disappearance of peaks at 3.49, 2.80, 1.37, and 1.14 ppm confirmed the THF assignments (Figure S2). Heating the mixture in toluene-d₈ to 100 °C results in coalescence to a single species (Figure S3), which suggests that the compounds either exchange ligands, are in equilibrium, or both.

The species with methyl group resonances at 2.08 and 1.97 ppm are hereby referred to as A and B, respectively. Adding THF has an effect on the speciation of A and B (Figure S4). Resonances corresponding to B and the ethyl group at −0.28/1.28 ppm decrease in intensity with addition of increasing amounts of THF and are most likely the same species. The THF resonances at 2.80/1.14 ppm also disappear, presumably due to increased exchange with excess THF. The methyl resonance of species A increases and shifts from 2.08 to 2.14 ppm upon addition of 50 equiv of THF, and the broad Et₂Zn ethyl group CH₂ resonance shifts from 0.17 to 0.27 ppm. The changes upon addition of THF suggest a shift in equilibrium from B toward A.

To gain a deeper insight into the nature of the species present, DOSY spectra were recorded at different concentrations of THF. In C₆D₆ or toluene-d₈ and with no extra THF added, three species are observed: m-terphenyl carboxylate complexes A and B, and another having an ethyl group, C (Figures 3, S9). Species C has a calculated hydrodynamic radius (R_H) of 3.31 Å, which is close to, but larger than, the X-ray-determined radius (R_X-ray) of Et₂Zn (3.14 Å), calculated from the crystal structure of Et₂Zn.¹² Because we expect Et₂Zn to coordinate THF under these conditions, an R_H value larger than R_X-ray is reasonable. Isolated Et₂Zn in C₆D₆ resonates at 0.10 and 1.08 ppm. The slight deviation of the resonances in our system from the values for Et₂Zn, 0.17 and 1.23 ppm, may indicate an interconversion or exchange process. As the amount of THF is increased, the diffusion coefficient of C decreases (Table S1, Figures S9-S10). This observation implies that Et₂Zn is in equilibrium with larger species in solution, such as A and/or B. The possibility that Et₂Zn self-associates into oligomers cannot be ruled out. Because Et₂Zn is on the same side of the equilibrium as B (see following paragraphs), and the proportion of B decreases with increasing amounts of THF, there must be an ethyl group associated with A. Thus, the observed ethyl group resonance of C is a mixture of species A and Et₂Zn. As A becomes the dominant species in solution with increasing THF, the calculated hydrodynamic radius of 6.38 Å is consistent with the formulation of 1 (R_X-ray = 6.47 Å), supporting the assignment of A as 1.

The equilibrium described above will shift upon removal of Et₂Zn from solution under vacuum. When crystals of 1 are dissolved in toluene, stripped to dryness, and redissolved in
deuterated solvent, the $^1$H NMR spectrum in C$_6$D$_6$ reveals the presence of species B, for which the THF and ethyl group resonances can now be confidently assigned. The carboxylate/ethyl/THF ratio in B is 3:1:1. This ratio is the same for 12 (Table S2) and supports the formulation of B as [Zn$_2$(Ar$_{Tol}$CO$_2$)$_3$(Et)(THF)] (2). Preparation of 2 in bulk quantities and its subsequent crystal growth by slow diffusion of pentane into a benzene solution of the compound produces colorless plates suitable for X-ray diffraction. The structure confirms the assigned formula (Figure 4). The molecule is a triply $m$-terphenylcarboxylate-bridged dizinc compound with a Zn···Zn distance of 3.32 Å. This value is smaller than that in 1, as expected following the addition of a third bridging carboxylate. A pseudo-C$_3$ symmetry axis exists along the Zn-Zn vector, which, in conjunction with the lack of a collinear improper axis of rotation, produces $\Lambda$ and $\Delta$ isomers, both of which occur in the crystal structure (Figure S13). The DOSY NMR spectrum of 2 was also obtained and the calculated hydrodynamic radius of 7.81 Å is larger than $R_{X\text{-ray}}$ (7.20 Å), but still consistent with retention of this structure in solution. With the formula of the species in solution now in hand, a balanced equation (eq 1) describing the solution equilibrium can be written:

$$
3 \left[ \text{Zn}_2\left(\text{Ar}^{\text{Tol}}\text{CO}_2\right)_2\left(\text{Et}\right)_2(\text{THF})\right] + 2 \text{Et}_2\text{Zn} + n \text{THF} \\
2 \left[ \text{Zn}_2\left(\text{Ar}^{\text{Tol}}\text{CO}_2\right)_3\left(\text{Et}\right)(\text{THF})\right]
$$

To further test the presence of this equilibrium in solution as well as its reversibility, Et$_2$Zn and THF were added to isolated 2 in an attempt to produce 1. Addition of THF to a sample of 2 in C$_6$D$_6$ does not afford any 1, and the only observable change in the $^1$H NMR spectrum is a broadening of the THF resonance of 2 owing to exchange with free THF (Figure S8). When Et$_2$Zn is added to a solution of 2 in C$_6$D$_6$, however, 1 is clearly detectable along with a THF OCH$_2$ resonance at 3.30 ppm (Figures 5, S8). This experiment proves that extra THF is not required for the conversion of 2 to 1. Integration of the methyl and THF OCH$_2$ resonances in 2 reveals that 2 retains all its bound THF. Based on the stoichiometry of the balanced equation between 1 and 2, only $\frac{2}{3}$ of a THF molecule is available per molecule of 1. It therefore appears that THF-free 1, [Zn$_2$(Ar$_{Tol}$CO$_2$)$_2$(Et)$_2$] (1'), may exist in solution. In combination with DOSY experiments that confirm dinuclearity of these species in solution and the crystal structure of 13, 1' most likely contains two coordinatively unsaturated trigonal planar zinc centers. Generation of such potentially reactive zinc centers suggests that zinc $m$-terphenylcarboxylates might be good catalysts. Addition of both THF and Et$_2$Zn to a sample of 2 in C$_6$D$_6$ restores the $^1$H NMR spectrum to that of a mixture of 1 and 2 similar to the one obtained upon dissolution of crystals of 1 in C$_6$D$_6$ or toluene-$d_8$ (Figure S8). Again, THF is not required for the conversion of 2 to 1 although it promotes the conversion between 1' and 1.

The conversion between solvated species of 1, [Zn$_2$(Ar$_{Tol}$CO$_2$)$_2$(Et)$_2$(THF)$_0$], probably occurs through simple association and dissociation of THF molecules. However, the mechanism of conversion of 1 to 2 is still unclear and more than one pathway may be involved. The demonstrated interconversion between doubly and triply carboxylate-bridged...
species 1 and 2 depends on the amount of THF present. The diiron complexes, 5, 6, and 7, represent analogs of 1, 2, and Et₂Zn respectively, where the ethyl groups are replaced by Ar⁹TolCO₂⁻, and THF by N,N-Me₂en. Thus, the equilibrium between 1, 2, and Et₂Zn provides insight into why iron complexes 5, 6, and 7 could be isolated from the same reaction mixture. These equilibria are crucial when considering oxidation reactions supported by diiron complexes in solution because a species different from that observed in the solid state structure may be responsible for the reactivity.

Unlike the interconversion between ethylzinc carboxylate compounds 9 and 10, which occurs at elevated temperatures,⁸ interconversion between 1 and 2 occurs readily at room temperature. The reason for this difference may be a higher energy barrier associated with formation and disassembly of 9, owing to its tightly packed pentazinc cluster core. Thus, modification of the carboxylate R group in ethyl zinc carboxylates may change the kinetics of structure interconversion as well as the nuclearity of the corresponding complex.

Understanding these simple zinc compounds can provide insight into the manner by which carboxylates can be used effectively for producing well-defined metal complexes.

Upon exposure to air, compounds 1 and 2 decompose into the oxozinc carboxylate [Zn₄O(Ar⁹TolCO₂)₆] (3). Colorless crystals of 3 were obtained by allowing an NMR spectroscopic sample of 1/2 in C₆D₆ to slowly react with air over the course of a week. Compound 3 crystallizes in the rhombohedral space group R₃ with 1/6th of a molecule in the asymmetric unit. The six m-terphenyl wings align with Tₕ symmetry (Figure 6). The Zn₄O core has Tₐ symmetry, however, and the alignment of Tₕ and Tₐ symmetries limits the symmetry of 3 to T. This concept can be visualized with stereographic projections shown in Figure 6. To the best of our knowledge, the superposition of Tₕ and Tₐ symmetries to produce T symmetry in a molecule is unique. None of the 45 T symmetric molecules contained in the CSDSymmetry database¹³ provide similar examples. The two enantiomers in the crystal lattice are related by the crystallographic inversion center. Variations of the orientation of the tolyl groups show that the symmetry in the solid state is only pseudo-T-symmetric. In the ¹H NMR spectrum of 3 in CD₂Cl₂, the tolyl CH₃ resonance is observed at 1.43 ppm, which is 1 ppm upfield from that of the free carboxylate. The large shift is attributed to positioning of the methyl groups above a neighboring m-terphenyl benzene ring and is consistent with the crystal structure. Because a single set of resonances is observed in the NMR spectrum, the molecule must have T symmetry on average in solution at 25 °C.

This report reveals that that two formulations of ethylzinc 2,6-bis(p-toly)benzoate, 1 and 2, readily convert in solution. This behavior differs from that of the ethylzinc acetate complexes, which require heat to convert them between 9 and 10. With the knowledge of the solution equilibrium between 1, 2, and Et₂Zn, we can now propose interconversion of doubly and triply carboxylate-bridged diiron(II) and mononuclear iron(II) complexes, such as those observed in discrete solid state complexes 5, 6, and 7. Furthermore, the use of sterically demanding m-terphenyl substituents provides access to coordinatively unsaturated zinc centers, providing a possible strategy for use in zinc-catalyzed reactions.
Experimental Section

General

Diethylzinc (1 M in heptane or hexanes) was purchased from Aldrich and used as received. A solution of Et$_2$Zn in toluene-$d_8$ for NMR spectroscopic experiments was prepared by adding toluene-$d_8$ to Et$_2$Zn in hexanes and distilling off the hexanes. Solvents were saturated with argon, passed through two columns of activated alumina, and stored over activated 3 or 4 Å molecular sieves. The compound 2,6-bis$(p$-tolyl)benzoic acid (ArTolCO$_2$H) was prepared by a literature procedure.$^{14}$ All manipulations of compounds 1 and 2 were performed under a nitrogen atmosphere in an MBraun drybox. IR spectra were obtained on a ThermoNicolet Avatar 360 spectrometer using the OMNIC software. Details about NMR spectroscopy and X-ray data collection and refinement are provided in the SI.

Synthesis

$[\text{Zn}_2(\text{ArTolCO}_2)_2(\text{Et})_2(\text{THF})_2]$ (1). ArTolCO$_2$H (50.8 mg, 168 μmol) was dissolved in 1 mL of THF. Diethylzinc (170 μL, 1 M in heptane) was injected into the reaction mixture with stirring. After 20 s, stirring was stopped and the solution was allowed to sit overnight, forming colorless crystals of 1. The solution was decanted and the crystals were washed twice with 1 mL of pentane before drying under vacuum to yield 67.1 mg (71.7 μmol, 85.4%) of 1. NMR: Compound 1 does not exist as the only species in solution. See text for discussion. IR (KBr): 3055, 3025, 2980, 2924, 2881, 2850, 2808, 1917, 1597, 1515, 1453, 1410, 1381, 1111, 1037, 986, 883, 842, 819, 802, 784, 768, 734, 703, 605, 583, 544, 517 cm$^{-1}$. Anal. Calcd for C$_{54}$H$_{60}$O$_6$Zn$_2$: C 69.31, H 6.46. Found: C 68.88, H 6.32. Decomposes above 136 °C (turns yellow-brown).

$[\text{Zn}_2(\text{ArTolCO}_2)_2(\text{Et})_2(\text{THF-d}_8)_2]$ (1·THF-$d_8$). The same procedure was used for the synthesis of 1 except that THF-$d_8$ was used as the solvent. Yield: 46.2 mg (48.5 μmol, 57.8%).

$[\text{Zn}_2(\text{ArTolCO}_2)_3(\text{Et})(\text{THF})]$ (2). A sample of 1 (48.0 mg, 51.3 μmol) was dissolved in 2.5 mL toluene and the solvent was removed under vacuum. The crude material was dissolved in 800 μL benzene and pentane was allowed to slowly diffuse into the solution slowly. After 5 d, colorless plates of 2 (31.5 mg, 81.2%) were obtained. $^1$H NMR (C$_6$D$_6$): δ 7.40 (d, $^3$J$_{HH}$ = 8.1 Hz, 12H), 7.27 (d, $^3$J$_{HH}$ = 7.7 Hz, 6H), 7.12 (t, $^3$J$_{HH}$ = 7.7 Hz, 3H), 7.02 (d, $^3$J$_{HH}$ = 7.7 Hz, 12H), 2.80 (t, $^3$J$_{HH}$ = 6.4 Hz, 4H), 1.97 (s, 18H), 1.28 (t, $^3$J$_{HH}$ = 8.1 Hz, 3H), 1.13 (t, $^3$J$_{HH}$ = 6.6 Hz, 4H), −0.28 (q, $^3$J$_{HH}$ = 8.1 Hz, 2H). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ 178.2, 140.8, 139.3, 136.7, 129.4, 128.8, 128.6, 69.55, 25.0, 21.0, 13.1, −2.4. IR (KBr): 3054, 3022, 2920, 2849, 2807, 1727, 1604, 1544, 1515, 1454, 1408, 1385, 1151, 1109, 1033, 1028, 845, 817, 801, 789, 767, 733, 706, 585, 540 cm$^{-1}$. Anal. Calcd for C$_{69}$H$_{64}$O$_7$Zn$_2$: C 72.95, H 5.68. Found: C 73.33, H 5.96, N 0.05. Decomposes above 246 °C (turns yellow-brown).

Reactivity

Exposure of 1 and 2 to air. An NMR solution of 1 dissolved in C$_6$D$_6$ was allowed to slowly react with air through a plastic cap over a week. Colorless prisms of [Zn$_4$O(ArTolCO$_2$)$_6$] (3)
were obtained. NMR was used to confirm that the crystals correspond to a single species in solution. No further attempts were made to isolate the compound in bulk quantities.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.

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**REFERENCES**


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Figure 1.
X-ray crystal structure of 1 (top) with thermal ellipsoids at 50% probability, showing the chair and boat conformations of 1 and 13 (bottom), respectively. Hydrogen atoms are omitted for clarity.
Figure 2.
Upfield region of the $^1$H NMR spectrum (500 MHz) of 1 dissolved in C$_6$D$_6$. Labels A, B, and C are used to distinguish between the three species present in equilibrium. The ethyl resonances at 3.26 and 1.11 ppm correspond to a minor zinc ethoxide impurity.
Figure 3.
DOSY NMR spectrum (400 MHz) of 1 dissolved in toluene-$d_8$. Species A, B, C, and THF are indicated by the colored lines.
Figure 4.
Structure of a single isomer of 2 (top) with 50% thermal ellipsoids. Hydrogen and disordered atoms are omitted for clarity.
Figure 5.
Upfield region of the $^1$H NMR spectrum (500 MHz) of 2 in C$_6$D$_6$ upon addition of Et$_2$Zn. The red arrows indicate the presence of 1. The peaks between 0.8-1.0 ppm and an underlying multiplet at 1.19-1.23 ppm correspond to hexane and methylcyclopentane impurities in the Et$_2$Zn solution.
Figure 6.
On top are stereographic projections of $T_d$ (red) and $T_h$ (blue) symmetry and their superposition which preserves the elements of $T$ symmetry (purple). On bottom are the $T_d$ core structure of 3 with the Ar$^{\text{Tol}}$ groups removed for clarity (left) and space filling diagram of 3 showing the $T_h$ shell created by the Ar$^{\text{Tol}}$ groups (right). Disordered atoms are removed for clarity.
Scheme 1.

(A) Diiron ArTolCO2− complexes and (B) the equilibrium between 1, 2, and Et2Zn.