

Correlation between Rheological Properties of Zinc Carboxylate Liquids and Molecular Structure

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Using Fourier transform infrared spectroscopy (FTIR), the viscosity of zinc 2-ethylhexanoate liquid has been found to correlate with the intensity of an asymmetric COO stretching resonance at 1632 cm^{-1} . This is consistent with the presence of the zinc carboxylate polymer, *catena*-2-ethylhexanoato-(*O,O'*)-tri- μ -2-ethylhexanoato-(*O,O'*)-dizinc(II) as the origin of the viscosity, a conclusion that is further supported by theoretical predictions. Density functional theory has been used to assign the IR spectra of the zinc carboxylate dimer, *catena*-2-ethylhexanoato-(*O,O'*)-di-(tri- μ -2-ethylhexanoato-(*O,O'*)-dizinc(II)-formic) acid, and the model of the molecular liquid, μ -4-oxo-hexakis-(μ -2-ethylhexanoato)-tetrazinc(II). The predicted spectra indicate that the decreased symmetry of the polymer relative to the zinc 2-ethylhexanoate liquid increases the intensity of the asymmetric carboxylate stretch at 1632 cm^{-1} and leads to the observed correlation.

Introduction

Zinc carboxylates are the building blocks for an array of materials that exhibit vast structural diversity, arising from a small number of chelation modes.¹ The structures that form from the simple reaction of Zn and a carboxylic acid are sensitive to the reaction conditions and can be manipulated according to the zinc carboxylate stoichiometric ratio,² temperature,³ method of recrystallization,⁴ and solvent choice.⁵ The basic (acid deficient) zinc carboxylate structure is a μ -4-oxo-centered tetrahedron of zinc cations surrounded by an octahedron of syn-syn bridging carboxylate anions.⁶ This common structural motif has been implemented in the formation of high surface area metal organic framework materials⁷ and been studied as a molecular analog of ZnO in order to understand its photoluminescent properties.⁸ Reaction of zinc with carboxylic acids that have long, branched, alkyl groups leads to products that are used industrially as high density sources of zinc that are soluble in organic solvents. This material has properties that resemble both a molecular liquid (low viscosity at room temperature) and a molten polymer (a relatively high flow activation energy). In this study, we use Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT) calculations to gain a better understanding of the specific molecular structures that control the viscosity of the product of a reaction between ZnO and 2-ethylhexanoic acid.

Our results indicate that the viscosity of zinc 2-ethylhexanoate liquids can be correlated with the intensity of a band at 1632 cm^{-1} in the FTIR spectra. As no satisfactory assignment of this band exists in the literature, we have turned to DFT to characterize the vibrational motion and help understand the chemical and structural reasons for the fluid behavior. Two candidate structures have been examined, each with salient features that can be reasonably correlated with viscosity of zinc

2-ethylhexanoate. The first model complex is μ -4-oxo-hexakis-(μ -2-ethylhexanoato)-tetrazinc(II), μ -Zn₄O- μ -(O₂C₈H₁₅)₆ molecule, (**1**), which is representative of the basic zinc acetate structure wherein the carboxylate ligands bridge two zinc atoms in a syn-syn configuration.^{9–11} The second model is representative of the 1-dimensional 3,1 polymer formed from an anionic dizinc cluster with three bridging syn-syn carboxylate ions joined by a syn-anti bridging carboxylate ligand, *catena*-2-ethylhexanoato-(*O,O'*)-tri- μ -2-ethylhexanoato-(*O,O'*)-dizinc(II), [Zn₂(μ -O₂C₈H₁₅)₃(μ -O₂C₈H₁₅)_n], (**2**). This polymer is modeled with a dimeric molecule, *catena*-2-ethylhexanoato-(*O,O'*)-di-(tri- μ -2-ethylhexanoato-(*O,O'*)-dizinc(II)-formic) acid, [Zn₂(μ -O₂C₈H₁₅)₃(HO₂CH)]₂-*catena*- μ -O₂C₈H₁₅, (**3**) (Figure 1).

Experimental

Sample Preparation, Analysis, and Spectroscopy. To prepare samples A–M for this study, zinc oxide (99.99%, Aldrich, Milwaukee, WI) and 2-ethylhexanoic acid (99% Aldrich, Milwaukee, WI) were combined in a molar ratio of 2:3 (13 samples) or 1:2 (one sample, α) in a round-bottom flask and heated to 90 °C under reduced pressure (\sim 5 mmHg) while the flask was mechanically rotated. Exact ratios of ZnO to 2-ethylhexanoic acid are given in Table 1. Water of reaction and excess acid were distilled away from the reaction mixture after allowing sufficient residence time to promote the completion of reaction.¹² 25 g of each of the 14 zinc 2-ethylhexanoates were obtained as colorless oils after 2 h. The products were analyzed for metal content by extraction of the zinc into aqueous solution with HCl and titration of the aqueous phase by EDTA (Table 1). Typically 0.6 g of zinc 2-ethylhexanoate was weighed to within $\pm 0.0001\text{ g}$ and titrated with standardized EDTA solution of 0.0503 mol/dm.³ The solution was buffered with hexamethylenetetramine and the pH was adjusted with NaOH solution and acetic acid as needed to maintain pH 5.5. This method allows an accuracy of $\pm 0.002\text{ mol/dm}^3$ Zn with a

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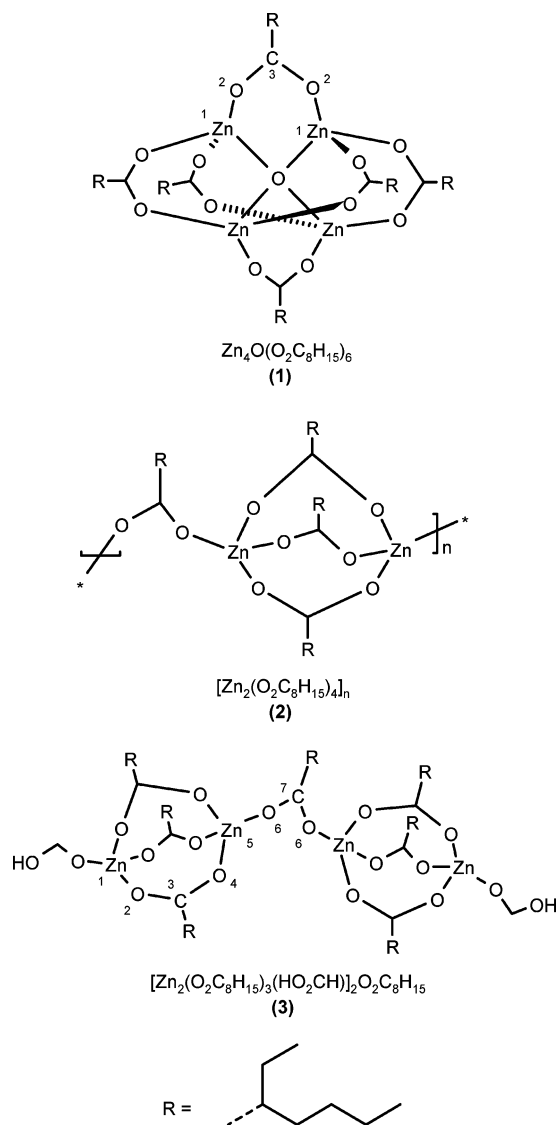


Figure 1. Structure and atomic labels of μ -Zn₄O-(O₂C₈H₁₅)₆ (**1**), [Zn₂(μ -O₂C₈H₁₅)₃(μ -O₂C₈H₁₅)]_n (**2**), and [Zn₂(μ -O₂C₈H₁₅)₃(HO₂CH)]₂-catena- μ -O₂C₈H₁₅ (**3**).

TABLE 1: Viscosities and [Zn] for Zinc 2-Ethylhexanoate Solutions A–M Formed from the Shown Ratios of Zinc Oxide and 2-ethylhexanoic Acid at 25 °C as Described in the Experimental Methods

sample	Zn:O ₂ CR reactants	[Zn] (mol/dm ³)	viscosity (Pa·s)
A	0.667	3.96	7.860
B	0.667	4.01	3.648
C	0.667	3.99	5.620
D	0.633	3.97	3.640
E	0.649	3.99	2.240
F	0.664	3.97	6.180
G	0.661	3.99	8.200
H	0.659	4.03	2.300
I	0.662	3.99	6.458
J	0.663	3.94	4.959
K	0.662	3.94	5.946
L	0.664	3.96	2.974
M	0.659	4.04	2.218
α	0.501	3.34	high

standard deviation of 0.004 mol/dm³ Zn.¹³ The residual water contents were determined by TGA mass loss (TA Instruments, SDT2960). Mass loss to 160 °C at 10 °C/min in air was less than 3% by mass for all samples. The viscosities were measured under conditions of constant temperature in calibrated Cannon-

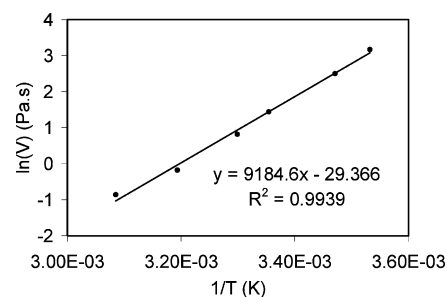


Figure 2. Viscosity as a function of temperature for zinc 2-ethylhexanoate solution sample A.

Fenske capillary tubes at temperatures of 10, 15, 25, 30, 40, and 50 °C. FTIR spectra were measured with a Perkin-Elmer GX model spectrometer from the neat samples in ATR mode (KBr beamsplitter, diamond cell, FR-DTGS detector). Four scans were acquired for each sample in the range of 380–4000 cm⁻¹ at a resolution of 4 cm⁻¹. The resulting S/N was typically better than 320.

Computational Methods. The geometries of 2-ethylhexanoic acid, HO₂C₈H₁₅, 2-ethylhexanoate anion, ⁻O₂C₈H₁₅, the zinc 2-ethylhexanoate, μ -Zn₄O-(O₂C₈H₁₅)₆ (**1**), and the model Zn dimer [Zn₂(μ -O₂C₈H₁₅)₃(HO₂CH)]₂-catena- μ -O₂C₈H₁₅ (**3**), were optimized using DFT with the B3LYP combination of exchange and correlation functionals^{14,15} as implemented in the Gaussian03 quantum chemistry code.¹⁶ The 6-31G* basis set^{17–19} was used for all main group elements, while the LANL2 pseudopotential and LANL2DZ basis set²⁰ was used to describe Zn. The initial geometry for **1** was based upon the Koyama and Saito crystal structure of basic zinc acetate⁶ for the μ -Zn₄O-(O₂CR)₆ core, while the initial geometry of **3** was based upon the 3,1 zinc crotonate polymer reported by Clegg, et al.²¹ Normal mode coordinate analysis confirmed each structure to be a local minimum, with no imaginary vibrations or a single imaginary vibration less than 10 cm⁻¹. The atomic displacements of vibrational motion were used to assign the normal modes, and a scaling factor of 0.9613 was applied to the frequencies.²²

Results and Discussion

IR Spectroscopy and Viscosity. Thirteen samples A–M of zinc 2-ethylhexanoate were prepared at a molar ratio of 2:3 for zinc oxide and 2-ethylhexanoic acid. The ratios were varied from 0.633 to 0.667 in order to study the effect of composition on material property. It is interesting to note that the batch composition is essentially uncorrelated with either the viscosity or the zinc concentration in the product. The measured viscosities at 25 °C are collected in Table 1. It can be seen that the viscosity varies by about 6.0 Pa·s among these samples, even though their compositions are measured to be within $\pm 2\%$, and they were prepared under nearly identical conditions. The values for the 3:2 samples (A–M) agree reasonably well to the value published by Andor et al.²³ For these samples, there is essentially no correlation between composition and viscosity. However, for a sample prepared at a zinc oxide to 2-ethylhexanoic acid ratio of 1:2 sample (α), the resulting product was too viscous to measure with our apparatus.

As shown in Figure 2, for sample A, the viscosity as a function of temperature can be fit to a line with the mathematical form $L = K + (\Delta G/RT)$, yielding a ΔG value of 76.36 kJ mol⁻¹. Such temperature dependence is similar to that expected for a solution of dilute polymer.²⁴ This suggests that the high viscosity sample prepared at 1:2 zinc oxide to 2-ethylhexanoic acid ratio has a polymer as its major component, while the samples

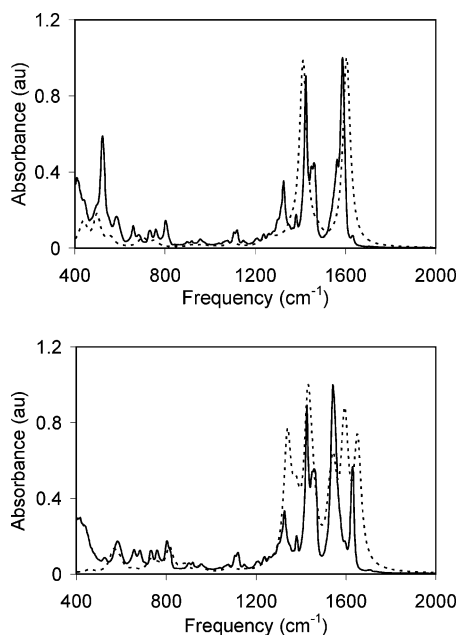


Figure 3. IR spectra for (top) the least viscous sample (M in Table 1, solid) with the B3LYP calculated spectra of **(1)** (dash) and (bottom) the most viscous sample (α in Table 1, solid) with the B3LYP calculated spectra of **(3)** overlaid (dash). Absorbance intensities have been normalized to 1.

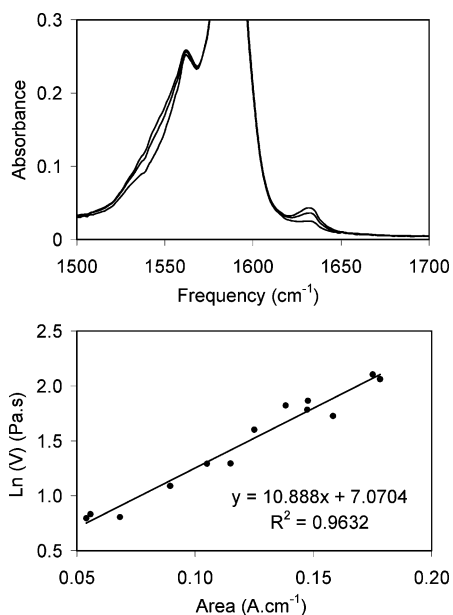


Figure 4. Top: IR spectra from 1500–1700 cm^{-1} for samples G, C and M. Bottom: correlation between peak area and $\ln(\text{viscosity})$ at 1632 cm^{-1} corresponding to the observable $(\text{COO})_{\text{as}}$ vibration in the polymer.

prepared at 2:3 zinc to acid ratio have a molecular species as their major component and that a small, uncontrolled amount of polymer is responsible for the increased viscosity.

The IR spectrum of a low viscosity 2:3 Zn: O_2CR sample is shown in the upper portion of Figure 3, superimposed with the DFT calculated spectrum for the molecular model **1**. The lower portion of this figure also illustrates the same data for the 1:2 sample and the computational results for the polymer model **3**. Absorption as a function of viscosity in the 2:3 samples is shown for the 1500 – 1700 cm^{-1} region the upper portion of Figure 4. Samples with higher viscosity absorb more strongly at 1632 cm^{-1} , with the lowest viscosity samples showing little absorption at this wavelength. The background of the strong peak at 1587

TABLE 2: B3LYP/6-31G*/LANL2DZ Optimized Structural Parameters $\text{Zn}_4\text{O}(\text{O}_2\text{C}_8\text{H}_{15})_6$ (1**) and the Model Dimer (**3**), Using the Numbering System Shown in Figure 1^a**

	1		3
$r_{1,2}$	2.0028	$r_{1,2}$	1.9734
$r_{2,3}$	1.2702	$r_{2,3}$	1.2755
$r_{1,1'}$	3.2684	$r_{3,4}$	1.2666
$r_{1,\mu-40}$	2.0014	$r_{4,5}$	2.0056
$\alpha_{1,2,3}$	132.00	$r_{1,5}$	3.2963
$\alpha_{2,3,2'}$	125.21	$r_{5,6}$	1.9846
$\alpha_{1,\mu-40,1'}$	109.47	$r_{6,7}$	1.2724
		$\alpha_{1,2,3}$	127.38
		$\alpha_{2,3,4}$	124.53
		$\alpha_{6,7,6'}$	120.03

^a Average quantities are reported for the Zn–O bond lengths and angles in **1** and **3**.

cm^{-1} was subtracted, and the areas of the 1632 cm^{-1} peaks were found by summation. Figure 4 (lower) shows a logarithmic fit to these areas as a function of viscosity. The R^2 value of this fit is 0.9632 indicating an exceptionally strong relationship between the two observables.

Optimized Geometry and Normal-Mode Analysis. Geometry optimizations of 2-ethylhexanoic acid, $\text{HO}_2\text{C}_8\text{H}_{15}$, 2-ethylhexanoate anion $^-\text{O}_2\text{C}_8\text{H}_{15}$, the tetranuclear complex, **1**, and the model Zn-dimer, **3**, were performed without symmetry constraints (coordinates given in the Supporting Information). The average calculated bond lengths and angles are presented in Table 2. In general, good agreement is observed between the DFT predicted structural parameters of the Zn complexes and those obtained from X-ray crystallography for the basic zinc carboxylate motif⁶ and zinc carboxylate 3,1 chain polymer.¹⁹ The optimized structural parameters for both **1** and **3** have Zn–O bond lengths that deviate on average by 0.05 Å from experimental structures, with overestimation of the calculated distances, while remaining bond lengths deviate by 0.01 Å and all bond angles are within the range reported experimentally.

The DFT simulated IR spectra of zinc 2-ethylhexanoate, $\mu\text{-Zn}_4\text{O-}\mu\text{-(O}_2\text{C}_8\text{H}_{15})_6$, **1**, is shown overlaid with the experimental spectrum of the least viscous sample (M) in Figure 3 (top). Model complex **1** has 459 normal modes, 396 of which are associated solely with the carboxylate alkyl chains. For the purposes of this paper, the vibrations associated with the carboxylates, and not their alkyl chains, are emphasized, as their characteristic absorptions form the basis of the correlation of rheological properties and molecular structure. Each carboxylate group contributes three stretching modes, two symmetric and one asymmetric, which leads to 18 total COO stretches in **1** that may contribute to the FTIR spectrum. Although the symmetry of **1** is only C_1 , the $\mu\text{-Zn}_4\text{O-}\mu\text{-(O}_2\text{CR})_6$ core formed from the four Zn ions and six carboxylate groups has near T_d symmetry. In this context, the symmetric carboxylate stretches form five sets of vibrations (12 modes of motion) at distinct but nearly degenerate energies: t_1 , $t_2^{(1)}$, e, a_1 , and $t_2^{(2)}$. Three of the sets (t_1 , e and a_1) are essentially unobservable by IR. The other two groups of vibrations have substantial transition dipole moments and lead to calculated bands between 1406 and 1409 cm^{-1} ($\nu_{310} - \nu_{314}$) and 1422 cm^{-1} (ν_{315}) from $t_2^{(1)}$, and $t_2^{(2)}$ (Figure 3, Table 3).²⁵ These bands are observed experimentally at 1423 and 1455 cm^{-1} , respectively. The asymmetric vibrations contribute two sets of three modes that are essentially degenerate as well, a t_1 and a t_2 . The t_2 leads to the calculated band between 1601 and 1603 cm^{-1} and the t_1 is IR silent. The t_2 band is observed experimentally at 1585 cm^{-1} . Finally, the central oxygen of the Zn_4O cage is predicted to have a significant IR

TABLE 3: Frequencies (Scaled by 0.9613) and Assignments of the Vibrational Modes Associated with the COO Groups of μ -Zn₄O- μ -(O₂C₈H₁₅)₆, (1), and [Zn₂(μ -O₂C₈H₁₅)₃(HO₂CH)]₂-catena- μ -O₂C₈H₁₅, (3), Based upon B3LYP/6-31G*/LANL2DZ Optimized Structures^a

1				3			
mode	assignment	symmetry ^b	frequency (cm ⁻¹)	mode	assignment	symmetry ^c	frequency (cm ⁻¹)
$\nu_{172}-\nu_{179}$	(Zn ₄ O) _{str}	<i>t</i> ₂	496–498 (521)	$\nu_{381}-\nu_{384}$	syn–syn (COO) _{sym}	^a	1409–1413 (1426)
$\nu_{310}-\nu_{314}$	(COO) _{sym}	<i>t</i> ₂	1406–1409 (1423)	ν_{387}	syn–anti (COO) _{sym}	^a	1429 (1456)
ν_{315}	(COO) _{sym}	<i>t</i> ₂	1422 (1455)	ν_{448}	syn–anti (COO) _{as}	^b	1560 (1542)
$\nu_{367}-\nu_{369}$	(COO) _{as}	<i>t</i> ₂	1601–1603 (1585)	$\nu_{449}-\nu_{450}$	syn–syn (COO) _{as}	^b	1618–1626 (1632)

^a Experimental values are given in parenthesis and are based upon the IR spectra of zinc 2-ethylhexanoate liquid; the sample with the highest concentration of μ -Zn₄O- μ -(O₂C₈H₁₅)₆, (1); and [Zn₂(μ -O₂C₈H₁₅)₃(μ -O₂C₈H₁₅)_n], polymer 2. ^b Assuming *T_d* local symmetry of the Zn₄O cage. ^c Assuming *C_{2v}* local symmetry of the COO unit.

absorption of *t*₂ modes between 496 and 498 cm⁻¹ (521 cm⁻¹ experimental), in reasonable agreement with Braga and Longo.²⁶ The net result of the DFT description is that the local *T_d* symmetry of the μ -Zn₄O- μ -(O₂CR)₆ core gives rise to the two observed COO region IR bands between 1406 and 1422 and 1601–1603 cm⁻¹, attributable to symmetric and asymmetric stretches, respectively.^{27,28}

The DFT simulated IR spectra of model dimer, (3), is shown in Figure 3 (bottom) overlaid with the experimental spectrum of the most viscous sample (α). In the model dimer there are 561 normal modes, 462 of which are associated solely with the carboxylic C₇H₁₅ alkyl chains. Two of the nine carboxylic acid groups are associated with the formate groups that terminate the polymer chain. These are the intense bands at 1757 and 1143 cm⁻¹ in Figure 3. The remaining seven carboxylate bridging groups give rise to 14 symmetric and 7 asymmetric stretching modes. Of the symmetric modes, only 5 have a large predicted IR intensity, with the syn–syn carboxylic modes (bridging Zn metals) occurring between 1409 and 1413 ($\nu_{381} - \nu_{384}$) cm⁻¹ and at syn–anti carboxylic vibration (bridging the two Zn clusters) at 1429 cm⁻¹ (ν_{387}) (Figure 3B, Table 3). This compares to experimental values of 1423 and 1456 cm⁻¹, respectively. The asymmetric COO stretches are predicted to be higher in energy than the symmetric stretches by \sim 200 cm⁻¹, similar to that observed in (1). Of the 7 asymmetric vibrations, 3 are calculated to have significant IR intensity with the syn–anti mode appearing at 1560 cm⁻¹ (ν_{448}) and the syn–syn symmetric vibrations absorbing between 1618 and 1626 cm⁻¹ ($\nu_{449} - \nu_{450}$). The observed experimental values are 1542 cm⁻¹ and 1632 cm⁻¹.

Figure 4A shows the experimental FTIR region of interest from 1500 to 1700 cm⁻¹ for three of the samples synthesized at a Zn:O₂CR ratio of 2:3. The logarithmic correlation between the areas of the peaks at 1632 cm⁻¹ and the sample viscosity is shown in Figure 4. Since the calculation results for 1 and 2 show this peak to be assignable to 3,1 linear zinc 2-ethylhexanoate polymer, and the samples behave thermally as dilute polymer solutions, we propose that the samples are dilute solutions of the linear 3,1 polymer 2-ethylhexanoate analog of zinc crotonate in basic zinc 2-ethylhexanoate molecular liquid. This assignment offers a chemically reasonable interpretation of this material and its behavior.

Two-dimensional polymers are an unlikely viscous component, as they are insoluble,^{29–33} and no precipitate was observed. It is also possible that a known 8,5 zinc carboxylate polymer forms,¹² and this could be the form responsible for the viscosity increase and observed IR spectra since it has low symmetry.

These assignments and interpretation of zinc carboxylate vibrational spectra allow reinterpretation of previous results. Specifically, small bands that cannot be attributed to Zn₄O(O₂CR)₆ in the *T_d* group may be due to polymer contamination rather than partitioning of the Zn₄O(O₂CR)₆ molecules into *T_d* and *T* (or lower) symmetry molecules in the samples.⁹

Conclusions

In the product of the neutralization reaction between ZnO and 2-ethylhexanoic acid, a large variation of viscosity was observed despite very similar synthetic conditions and product compositions. The correlation between the intensity of the IR feature at 1632 cm⁻¹ and the sample viscosity implies that a high molecular weight component is responsible for this resonance. Symmetry arguments and DFT calculations indicate that a linear 3,1 polymer dissolved in basic zinc 2-ethylhexanoate is consistent with the material behavior and observed IR spectra. Finally, the calculations presented offer the least ambiguous assignments of the vibrational bands in zinc carboxylates.

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Supporting Information Available: Tables showing B3LYP/6-31G* optimized structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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