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Molecular structure models of amorphous bismuth and cerium carboxylate catalyst precursors

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ABSTRACT

As our societal need for materials and energy has grown, so has our need for catalyst processes in hydrogen production. A major function in these applications, for both homogenous and heterogeneous catalysis processes, is the synthesis of an active metal catalyst. It must first be soluble to control the physical properties of the metal being used. Recent work in metal precursors has begun to turn toward these metal carboxylate types of material. Structural models are proposed for bismuth 2-ethylhexanoate and 2,2-dimethyloctanoate and cerium 2-ethylhexanoate. The bismuth compounds have been characterized at different ratios of bismuth to carboxylate as solutions of the free acids. Their structures are most consistent with a Bi4(RCO₂)₁₂ motif where the Bi ions are arranged in a flattened tetrahedron with Bi – Bi distances of about 4.3 Å. There is evidence for Bi – O – Bi linkages at low free acid concentrations. The cerium compound is most consistent with a linear tetracerium molecule where the Ce – Ce distances repeat at about 4.3 Å out to 16.4 Å. The models were generated by analogy with known crystal structures and compared to high-energy x-ray scattering data. To further evaluate the models, DFT calculations were made, and the equilibrium geometries were compared. The vibrational spectra calculated from those geometries are presented and compared to the experimental results. Magnetization vs. temperature data was collected on the cerium compound, and its behavior was consistent with the proposed model. A geometrical approach to determining the dimensionality and relative positions of the metal ions in these structures is presented.

1. Introduction

Metal carboxylates find broad application as catalyst precursors because they are organic-soluble and provide a high weight-density of metal compared to alternatives. Chromium [1], Molybdenum [2], Cobalt [3], Nickel [4], Calcium [5], Potassium [6], Zirconium [7], Tin [8], Manganese [9], and Zinc carboxylates [10], along with several others, all have important applications in this space. Bismuth carboxylates are precursors to acrylate and polyurethane catalysts [11]. Cerium has many important catalytic applications. The cerium compound in this work is also used in the manufacture of P.T.F.E., one of the most widely employed materials in the world [12].

In addition to industrial applications, metal carboxylates are useful precursors for the catalyst designer and researcher. The importance of catalytic activity in an atomic arrangement is displayed by the recent multitude of bottom-up specific methods such as the template, microwave-assisted synthesis, hydrothermal/solvothermal, surfactant-assisted synthesis, sol–gel, and thermal decomposition. These

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methods have been developed, allowing for the creation of superior catalysts [13–15]. Due to their often unusual and sometimes unique structures, metal carboxylates offer a dimension of exploration to the material and catalyst designer. Ceria precursors are of interest due to the persisting need for improved photocatalysts and oxide-shuttle materials for water splitting and fuel cells as green hydrogen energy technology develops [16]. Novel and useful geometries and coordination environments can potentially be achieved using metal carboxylates as starting materials, not only for catalysts but for emerging materials with potential applications as catalysts such as M.O.F.s [17–21].

Organic linkers often contain carboxylate functional groups to drive unique and specialized metal carboxylate frameworks [22,23]. A multitude of these frameworks strongly depend on the localized interaction of the carboxylate to the metal specifically [24]. Thus, this link provides not only a driving force for the overall unique contour of the entire framework but also the overall stability of the material. Yet, unlike typical metal carboxylate organic linkers used to force a selective 3D network, these branched carboxylate ligands typically force lower-dimensionality structures [25–27].

Metal carboxylates are made by a few different routes. Direct neutralization of an oxide, hydroxide, or carbonate starting material is common [28]. Metathesis is often a beneficial route using the aqueous metal salt and the alkali salt of the acid [29]. Less common but sometimes implemented is the dissolution of metal with the acid using air or another oxidant to achieve the reaction. Acidolysis of other metal precursors such as carbonyls or alkoxides is also known but perhaps exclusively implemented in laboratory environments for specific reasons [30]. Two of the most common carboxylic acids used to manufacture metal carboxylates are 2-ethylhexanoic and 2,2-dimethyloctanoic. 2-ethylhexanoic acid is synthetic and is manufactured from propylene [31]. The separation of α -tertiary carboxylic acids from natural hydrocarbon mixtures is industrially achievable with a relatively straightforward process, and the C_{10} fraction has appealing properties of low viscosity and low vapor pressure [32]. The branching at the α -carbon and long sidechains drive both steric and hydrophobic/hydrophilic behavior that is not seen in other materials. These characteristics may provide a unique opportunity for advanced materials in CO₂ utilization, water splitting, and piezoelectric devices [13,18,33-35].

Currently, many carboxylate materials participate as catalysts or are used as a precursor for catalyst processes [36-39]. These specific materials are important in both industrial and academic catalysis fields. Specifically, bismuth and cerium 2-ethylhexanote complexes, as these are base materials, can be used for academic studies and industrial applications. Both cerium and bismuth-based materials are heavily involved in a multitude of key industrial processes used for the production of clean hydrogen, such as methane reforming [40], water-gas-shift [41-43], reforming [44-49], electrodes fuel cells [44, 50], and photocatalysis [33,51]. Given their utility and broad application, surprisingly little is known about the molecular structures of metal 2-ethylhexanoates and 2,2-dimethyloctanoates. In fact, only a couple of papers with convincing structural models exist [29,52]. This situation is due at least in part to the amorphous nature of the products. They are difficult - perhaps impossible - to crystallize, so atomic-resolution structural determination has not been achieved on any of these compounds. Most workers have relied on indirect evidence from spectroscopic or physical measurements, which have been nonetheless useful, if incomplete [28,53–56]. Our approach has been to combine high-energy x-ray diffraction with electronic structure calculation to compare the 1-dimensional pair distribution functions (PDFs) of the models and samples, as well as simulate the vibrational spectra and other data. While a structure solution cannot be claimed in this case, the models are often consistent with the available data, useful for property and process optimization, and predictive of the materials' behaviors.

2. Experimental

2.1. Synthesis of precursors

Bismuth carboxylates for this work were prepared by dissolving bismuth metal in a countercurrent column reactor. The recirculating acid flow was regulated with a resistive heater to 115 + /-5 °C. Excess air was pumped into the bottom of the column. Water is condensed from the overhead and diverted to a receiver. Samples of the resulting yellow to amber solution were collected at bismuth concentrations of 0.33 - 1.8 M (7–28% w/w). The stoichiometries of the organic carboxylate to Bi range from 3.3 to 7.0. If the bismuth concentration is allowed to increase above about 30%, the resulting solutions are cloudy. Bi concentrations were analyzed by EDTA titration to + /- 0.2% Bi w/w.

Cerium 2-ethylhexanoate was prepared by metathesis. Stoichiometric amounts of 2-ethylhexanoic acid and sodium hydroxide were mixed at ambient temperature in the presence of water to give a 1.2 M solution of sodium 2-ethylhexanoate. To this solution was added a stochiometric (acid/Ce = 1/3) quantity of aqueous cerous nitrate solution at 2.6 M with vigorous agitation. The rubbery, pale yellow product was collected on a filter frit and washed several times with excess deionized water until the conductivity of the filtrate reached a constant value. The solid was dried in air at 80 °C until it reached a constant mass. Ce content was analyzed by EDTA titration to 23.01 + /- 0.2% Ce.

2.2. Spectrometric analysis

2.2.1. Field desorption mass spectrometry (FD-MS)

Mass spectra were collected using a Waters Global Quadrupole Timeof-Flight (QToF) instrument. The cerium carboxylate samples were dissolved in HPLC grade acetonitrile and directly infused into the M.S. The source temperature was kept at 100 °C, Cap was at 3.4, and the cone was at 40 V. High-resolution scans were calibrated, and locked mass accuracy was achieved using Na/Cs salts solutions.

2.2.2. FT-IR

FTIR spectra were measured with a Perkin-Elmer G.X. model spectrometer from the neat samples in A.T.R. mode (KBr beam splitter, diamond cell, FR-DTGS detector). Four scans were acquired for each sample in the range of $380-4000 \text{ cm}^{-1}$ at a resolution of 4 cm⁻¹. The resulting S/N was typically better than 320.

2.2.3. Raman

The Raman spectrum of the cerium 2-ethylhexanoate was acquired using a D.X.R. micro-Raman instrument (Thermo Scientific). A diodepumped Nd:YVO₄ laser, maintained at 2.0 mW, was used as the excitation source (532 nm) for Raman characterization. The sample was mounted on a silicon wafer substrate on the sample stage, and the spectrum was constructed by using 20 exposures, 2 s for each.

The Raman spectra of the bismuth 2-ethylhexanoates were acquired using a Mettler-Toledo React Raman 785. The excitation source was a 785 nm Class I.I.I.B. laser with a nominal power of 250 mW. A 9.5 mm diameter probe with a sapphire window was submerged into the samples, and the spectra were built from 20 exposures of 1 s each.

2.2.4. H.E.X.R.D

X-rays with an incident energy of 115 keV were used at beamline 11-ID-C of the Advanced Photon Source (A.P.S.) with a Mar345 image plate or a Varex 4343CT detector. High-energy x-rays (\sim 100 keV) have an appropriate wavelength (\sim 0.1 Å) to diffract from pairs of atoms in condensed phases (liquids and solids) without undergoing significant attenuation or multiple scattering. The diffracted x-rays are collected as a 2-dimensional pattern on the detector. The data were reduced and transformed using FIT2D and Xpdf, generally following the approach of Tomberli et al. [57–59].

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2.2.5. SQUID

The magnetic susceptibility of cerium 2-ethylhexanoate under an applied field of 1 T was measured by SQUID over the temperature range 5–325 K using an MPMS-3 Magnetometer by Quantum Design Inc.

2.2.6. Computational methods

In this work, density functional theory (DFT) calculations were employed to probe the equilibrium geometry of various cerium carboxylate structures. The initial coordinates for the cerium complexes were sourced from Malaestean et al. [60] These crystal structures were truncated to preserve molecular charge, resulting in each system containing four central Ce^{3+} atoms. Each system was balanced with 12 1-charged carboxylate ligands, and neutral groups identified from the crystallography source data were represented with water molecules. The bismuth system's initial coordinates were sourced from S. Troyanov et al. [61]. These initial structures were also truncated to preserve system charge, resulting in systems with 4 or 5 central Bi^{3+} atoms. The bismuth systems were balanced with either 12 (4-bismuth clusters) or 15 (5-bismuth clusters), 1- charged carboxylate ligands, and neutral groups were represented with water molecules.

Once constructed, all systems were centered and converted into simple X.Y.Z. coordinate files. These files were then used to create the geometry optimization inputs that were calculated using the Gaussian quantum chemistry program (version g16e01) [62]. The three-parameter hybrid exchange B3LYP density functional [63,64], with D3 dispersion correction [65] and CEP-31 G basis set [66] as the method in these calculations. The popular B3LYP density functional has been extensively used in modern computational chemistry. Specifically, in the field of conformational research, its accuracy has been extensively verified [67,68]. When combined with the Becke-Grimme dispersion correction, it has also been shown to lead to accurate calculations of non-covalent systems and systems that contain lanthanide species [69, 70]. The B3LYP functional has also been shown to accurately reproduce experimental infrared spectroscopy results [71].

B3LYP functions by combining the three parameters Hartree-Fock exchange-correlation (Pauli repulsion) developed by Becke (B3) with the dynamic electron correlation (interaction between electrons) developed by Lee, Yang, and Parr (L.Y.P.). This combination grants B3LYP its title of "hybrid" functional. The combination of B3LYP being well documented, relatively fast computationally, relatively simple in construction when compared to other "hybrid" functionals (only three parameters), and having a proven accuracy in conformation/spectra studies make it a solid choice for any computational study. A proven track record in lanthanide studies is a bonus.

The CEP-31 G basis set was created to accurately model lanthanidecontaining systems. Its inclusion of a 46-electron effective core potential (ECP) provides a compromise between chemical accuracy and computational speed. The CEP-31 G basis set was parameterized using the most common two and 3 + oxidation states of atoms in the lanthanide group. This basis set model the 5 s and 5p electrons as the outer core (outside of the ECP).

Spectral simulation plots were extracted using Molden 5.2, utilizing broadening parameters to qualitatively match the data [72]. All vibrational spectra were normalized on the frequency axis to the C-H stretch at about 3000 cm^{-1} .

Simulated PDFs of the DFT and crystal structure models were created by snipping appropriate fragments or molecules from the structure of interest and placing them in the center of a large enough box to avoid intermolecular peaks in the resulting PDF, usually $30 \times 30 \times 30$ Å using the routine in Xpdf for this purpose.

3. Results and discussions

3.1. General introduction to structural models

Scheme 1 shows Lewis structures for the models proposed in this paper. The bismuth models have either 4 or 5 bismuth ions. The 4-Bi model derives from the crystal structure in Troyanov et al. The 5-Bi model adds a Bi - O - Bi unit to this structure. The cerium model is a fragment of a polymer after a structure in Malaestean et al.

3.2. Structural and spectroscopic characterization of bismuth 2-ethylhexanoate and 2,2-dimethyloctanoate

Even homoleptic bismuth carboxylates show great structural diversity. For instance, bismuth benzoate and methoxybenzoate both



Scheme 1. Lewis structures for the models used in this work. *Upper left:* 4-Bi model. *Upper right:* 5-Bi model. *Lower:* 1-D polymeric cerium model. The carboxylates are shown as angles, and the terminal Os represent water molecules. "a," "b," and "c" denote the attachments in the repeat unit.

crystallize as 1-D linear polymers [73,74]. Bismuth acetate forms 2-D sheets, yet bismuth formate forms a 3-D extended network. To propose a structural model, we have to evaluate whether any of the extended systems could possibly fit the data. The collected data does not show any strong peaks past about 9 Å. Any extended or polymeric structure will have periodicity past this distance, so the absence of peaks allows us to focus on molecular structures without extended ordering.

Fig. 1 shows the PDFs from the transformed H.E.X.R.D. experimental data (A-F), potential model crystal structures (G-I) [73,75,76], and calculated from the geometry-converged DFT models (J-K). We can identify several features in the experimental data by comparing them to the crystal structures and then point them out in the DFT results. Generally speaking, the DFT results overestimate the interatomic distances. Fig. 2 shows images of DFT-converged geometries of the crystal structure of bismuth models, as well as the core from the crystal structure of bismuth pivalate.

In interpreting the PDFs, we keep in mind that the intensity of the features is roughly proportional to the quantity $f_1f_2c_1c_2$, where f is the scattering factor of the i-th atom, and c is the atomic fraction of the i-th atom. For x-rays, f is approximately proportional to the atomic number. So in the cases of bismuth and cerium, atomic numbers 83 and 58, respectively, any atomic pairs that do not contain at least one metal atom will make a relatively small contribution to the PDF. Additionally, the experiment lasts about a second and is carried out at room temperature. This being the case, the alkyl sidechains distal from the α -carbon, though contributing to the scattering, get averaged out and do not contribute sharp peaks because they are moving rapidly with respect to the rest of the molecule. Thus, the dominant contribution to the PDFs is the metal carboxylate framework, which, while tumbling and translating during the experiment, remains more or less rigid with respect to



Fig. 1. PDFs of (A) bismuth 2-ethylhexanoate 7%, (B) bismuth 2-ethylhexanoate 15%, (C) bismuth 2-ethylhexanoate 29%, (D) bismuth 2,2-dimethyloctanoate 9%, (E) bismuth 2,2-dimethyloctanoate 18%, (F) bismuth 2,2-dimethyloctanoate 30%, (G) bismuth pivalate from Troyanov, et al., (H) bismuth oxide from Ivanov, et al., (I) bismuth benzoate from Rae, et al., (J) DFT 4-bismuth model, and (K) DFT 5-bismuth model.

the atomic pairs closest to the metal ions. Thus, the molecular models used to compare to the experimental data are truncated as the acetates in order to not introduce sharp peaks from the sidechains that will not appear in the experimental results (Table 1 and 2).

These considerations do make normalizing the intensities of the data essentially impossible, so the PDFs are normalized to the maximum peak-to-peak height in each dataset. This precludes the possibility of determining coordination numbers analytically, but since these are so strongly correlated with bond length, this seems inconsequential [77].

The bismuth ions may be imagined to form a flattened tetrahedron or a folded diamond. In Bi_2O_3 the bismuth ions are exclusively connected by Bi - O - Bi linkages, and there is a Bi - Bi distance of 3.7 Å.

Associating the experimental data to strengthen the assertion about extended structures being unsatisfactory, notice how the PDF of the benzoate structure does not have a peak at 5.0 Å. This is because the zigzag arrangement of the bismuths makes the closest Bi – Bi approach 3.7 Å, but the 2nd Bi – Bi distance is out at 7.5 Å, missing the long Bi – Bi distance in the data and in the pivalate model. Further, it can be seen that at low bismuth concentrations, the pivalate model is largely satisfactory. At the highest concentrations of bismuth, the peak at about 3.7 Å can be seen distinctly, which we attribute to the Bi – Bi distance of Bi – O – Bi connections. This suggests that the first step in the dissolution of the bismuth metal is the oxidation of the metal. Further interpretation is that higher acid activity, i.e., concentration, in the reaction mixture is required to depolymerize the resulting bismuth oxide. This is consistent with the product remaining hazy unless some free acid is allowed to remain in the composition.

Since the pivalate model represents the low metal concentration samples well, and we see a plausible explanation for the peak at 3.7 Å in the Bi - O - Bi distances in Bi₂O₃, we sought to corroborate with vibrational spectroscopy. While a simple complexity argument can be made (vide infra), DFT can provide a calculated comparison. The four-bismuth model comes directly from the relevant bismuth pivilate crystal structure, and the five-bismuth model adds the Bi - O - Bi linkage we infer from the PDF. The geometry optimization distorts the structure from what we think is actually in the samples.

The PDFs resulting from the DFT calculations were scaled by 0.81 along the r axis. This was done by comparing the Bi – Bi distances in the geometry converged structures to the same distances in the pivalate model. The factor of 0.81 minimized the average difference between those lengths. As a result, we see the same correlations as above at different distances, but the overall molecular topologies are the same. But the difference between the long and short distances between the Bi ions in the converged geometry is larger than in the input model or the data. So, if the actual geometry is that of a flattened tetrahedron, it is more flattened in the DFT converged geometry. Supplementary Information

For the 5-bismuth cluster, the Bi - Bi distance in the Bi - O - Bi unit is 4.0 Å in the converged calculation, which scales to 3.2 Å. So, while the general impact of the DFT is to overestimate the interatomic distances, especially when there is no covalent bond between the atoms in question, in the case of the Bi - O - Bi subunit, this effect is much less severe.

The purpose of the DFT is not to verify the structure but instead to generate the needed Hessian to calculate the vibrational spectrum. Additional detail about the DFT models is in the Supplementary Information.

Figs. 3 and 4 show the experimental Raman and I.R. spectra with the simulations of the spectra from the models. The vibrational spectra were calculated from the converged 4-Bi, and 5-Bi DFT geometry optimization runs. It can be seen that the increase of Bi concentration leads to a broadening of the features at about 1350 cm^{-1} . This is consistent with an increase in the number and types of local environments in the 5-Bi structure compared to the 4-Bi structure.

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Fig. 2. Images of (left) 5-bismuth DFT converged structure, (center) 4-bismuth DFT converged structure, and (right) bismuth pivalate from Troyanov, et al. Bismuth: violet, oxygen: red, carbon: gray, hydrogen (white).

Table 1

Distance ranges with observed maxima in pair distribution functions.

r (Å)	Atomic pair (s)
2.1–2.3	1st Bi – O
2.6–3.0	Bi – C, 2nd Bi – O
3.9–4.1	Short Bi–Bi
4.9–5.1	Long Bi–Bi

Table 2

Distance ranges in geometry optimized DFT results for selected atomic pairs before and after scaling.

r from the calculation (Å)	r scaled by 0.81 (Å)	Atomic pair (s)	
2.2–2.3	1.8–1.9	1st Bi – O	
2.6-3.7	2.1-3.0	Bi – C, 2nd Bi – O	
4.8-4.9	3.9-4.0	short Bi – Bi	
6.7–6.8	5.4–5.5	long Bi – Bi	



Fig. 3. Raman spectra of: (A) 5-bismuth DFT model, (B) 4-bismuth DFT model, (C) bismuth 2-ethylhexanoate 28%, and (D) bismuth 2-ethylhexanoate 8%.

3.3. Structural, physical, and spectroscopic characterization of cerium 2ethylhexanoate

While the bismuth carboxylates did not show any evidence for longrange ordering, the cerium 2-ethylhexanoate does. There are peaks at 4.3, 8.4, 12.5, and 16.4 Å in the PDF, which is shown in Fig. 5, along with the simulated PDF from the Malestean, et al. crystal structure and the geometry-converged DFT model result. Our initial task was to determine which sort of extended structure might best fit this data. We considered linear (L), square planar (S.P.), primitive cubic (P), body-



Fig. 4. IR spectra of: (A) 5-bismuth DFT model, (B) 4-bismuth DFT model, (C) bismuth 2-ethylhexanoate 28%, and (D) bismuth 2-ethylhexanoate 8%.



Fig. 5. PDFs of (A) experimental data, (B) calculated from Malaestean et al., and (C) calculated from DFT model. The values in the high r region (>9.6 Å) of the experimental data are 20x to show the peaks at 12.5 Å and 16.4 Å.

centered cubic (B.C.C.), and face-centered cubic (F.C.C.) geometries as

Table 3

Distances in units of Ce – Ce correlation from the measured PDF and under assumptions for Ce – Ce packing motif.

-	1	e				
Ce – Ce	Data	L	S.P.	Р	BCC	FCC
1st	1.0	1.0	1.0	1.0	1.0	1.0
2nd	2.0	2.0	1.4	1.4	1.2	1.4
3rd	2.9	3.0	2.0	1.7	1.6	1.7
4th	3.9	4.0	2.2	2.0	1.9	2.0

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potential arrangements of the cerium ions. Normalizing all the Ce – Ce distances to 1, we get the relationships shown in Table 3.

Since the linear arrangement most closely matches the distances in the data, we started our search for structural models with linear compounds. Since the distances in the data are not quite an integer multiples of the first Ce – Ce distance, the structure must not be exactly linear. The simplest approach is to assume the cerium ions lie on an arc. In this case, the arc would have a radius of curvature of about 9.7 Å. We have no evidence that the structure is a loop, but if it were, having this radius, it would contain 13 or 14 cerium ions. To our minds, this degree of curvature does not seem impossible.

Malaestean et al. found several 1-D polymers of cerium carboxylates and reported their structures. We found that one of the isobutanoate forms matched the PDF data reasonably well, especially with respect to the Ce – Ce distances. Therefore, we used a fragment of this polymer as the starting point for the DFT geometry optimization. Unlike the bismuth models, during the geometry optimization, the Ce – Ce distances stayed relatively close to what was observed, so no correction factor to the x-axis was applied in Fig. 5.

Fig. 6 shows images of the Malaestean-derived fragment along with the DFT converged structure as formates for ease of viewing.

Figs. 7 and 8 show the Raman and I.R. spectra of cerium 2-ethylhexanoate with the calculated spectra Reasonably good agreement between the data and calculation can be seen. We cannot say that the simulated Raman peak at about 2000 cm⁻¹ corresponds to the unmatched peak in the data at 2500 cm⁻¹. In the calculation, this arises from a stretching mode of a monodentate carboxylate ligand. It is unreasonable to make this assignment because of the high frequency. The peak in the data is more likely from a mode bearing a proton. The extraneous peak in the I. R. data at about 1500 cm⁻¹ is due to residual free acid in the material, which may or may not be integral to the structure.

In all cases, the stoichiometry of the cerium models is 1:3 for the cerium:carboxylate ratio. This is in good agreement with the mass spectrum result. A peak was observed at 593 Da, consistent with $CeC_{24}H_{45}O_6NaH^+$ ion. No fragments were found with masses consistent with two or more cerium ions. This is seemingly at odds with the diffraction data but may mean that the compounds dissociate under the conditions of the mass spectrometry. To further probe this question, we evaluated the magnetic behavior. The SQUID results, shown in Fig. 9, can be fit into two approximately linear regions. The Curie constants for the low and high temperature regions are 2.3×10^{-3} and 1.3×10^{-3} , respectively. These values are consistent with other cerium bearing solids [7].

For single ion molecular magnets, one usually observes a very steep paramagnetic response, breaking over to saturation at relatively low temperatures [78]. In the Malaestean et al. paper, they observed smooth increases in magnetization with temperature, which are fit to continuum models. Our material seems to be intermediate between these two cases, which could be consistent with an average number of 3–5 cerium ions per molecule, as seen in the PDF data.







Fig. 7. Raman spectra of (A) cerium 2-ethylhexanoate and (B) calculated from the DFT model.



Fig. 8. I.R. spectra of (A) cerium 2-ethylhexanoate and (B) calculated from the DFT model with 2-ethylhexyl sidechains.



Fig. 9. Magnetic susceptibility for cerium 2-ethylhexanoate.

4. Conclusion

As the importance and necessity of hydrogen energy increases, more focus has been placed on superior catalytic routes both to hydrogen itself and for utilization thereof. Novel catalytic precursors, including the carboxylates in this work, will provide an avenue for the synthesis of novel catalysts. Yet, to understand how the catalysts are structured, models for the local atomic arrangements of the precursors must be provided.

Bismuth carboxylates adopt discrete molecular structures without evidence of extended ordering. At low concentrations of metal, the $Bi_4(O_2CR)_{12}$ core, à *la* bismuth pivalate, represents the PDF data reasonably well. At high concentrations of metal, a peak indicating Bi –

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O – Bi units arises. Incorporating this unit back into the electronic structure calculation qualitatively agrees with the vibrational spectroscopy. It may be that these are an intermediate structural motif arising from bismuth oxide, which is then neutralized by the acid present to form the tetrabismuth molecules that compose the liquid.

Cerium 2-ethylhexanote presents periodicity up to at least 16 Å. Geometric analysis shows that a curved, 1-dimensional structure fits this data. Further, local coordination and inter-polyhedral connectivity is consistent with structures reported for other cerium carboxylates. While we cannot calculate the average number of cerium ions per molecule, the magnetic behavior is consistent with a macromolecule that is neither a single-ion magnet nor a continuum like those observed in the 1-D polymers.

Catalyst synthesis and design are advancing as our knowledge and understanding of catalytic processes improve. Improved knowledge of the molecular structures and behaviors of catalyst precursors will aid these efforts. The PDF method has proven to give a helpful view into the important metal-based precursors that are difficult or impossible to crystallize. This method also allows the materials to be studied as they would be used, as sometimes crystallization processes alter the molecular structures. When PDF is combined with geometrical analysis, electronic structure calculation, physical property measurement, and spectroscopy, plausibly convincing models of the atomic-level structures can be proposed.

CRediT authorship contribution statement

Jincan Jin: Writing, analysis, and Interpretation of data. Rebekah Habeger: Writing, analysis, and Interpretation of data. Todd Yoder: Mathematical model construction for carboxyl frameworks. David Coulliette: Mathematical model construction for carboxyl frameworks. Andrew Eisenhart: Computational time and data, Writing. Thomas Beck: Computational time and data, Writing. Udari S. Kodithuwakku: Raman data acquisition. Doo Young Kim: Raman data acquisition. Chris Benmore: Beamline H.E.X.R.D. Acquisition of data. Rob Hart: Conceptualization, Writing – review & editing, R&D Leader. Wilson D. Shafer: Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2022.07.003.

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