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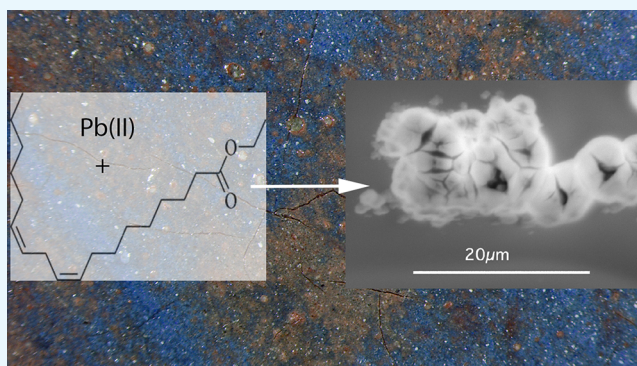
Reaction of Pb(II) and Zn(II) with Ethyl Linoleate To Form Structured Hybrid Inorganic–Organic Complexes: A Model for Degradation in Historic Paint Films

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ABSTRACT: To investigate soap formation in drying oils in historic paints, the reaction between metal acetates (K^+ , Zn^{2+} , Pb^{2+}) and ethyl linoleate (EL) was studied using optical microscopy, X-ray powder diffraction, and electron microscopy. Pb(II) and Zn(II) react rapidly with EL to form highly structured, spherulitic, luminescent crystallites that aggregate. Evidence from Fourier transform infrared (FTIR) and scanning electron microscopy/energy dispersive X-ray analysis and high-resolution synchrotron powder X-ray diffraction indicates that these are organic–inorganic hybrid complexes or coordination polymers. FTIR absorbance peaks at ca. 1540 cm^{-1} for Pb(II) and ca. 1580 cm^{-1} for Zn(II) are consistent with the formation of carboxylate complexes. The complexes formed offer insight into the degradation processes observed in oil paint films, suggesting that soap formation is rapid when metal ions are solubilized and can occur with unsaturated fatty acids that are present in fresh oils. These complexes may account for the atypical luminescence observed in lead-containing cured oil paint films.



INTRODUCTION

Properly formulated, cured oil paint films are remarkably stable natural polymer systems, lasting hundreds of years. Lead-containing paints, made from lead white ($Pb(OH)_2 \cdot 2PbCO_3$) or red lead (Pb_3O_4), have noteworthy stability. Despite their longevity, the propensity of lead-containing oil paints to form “soaps”, generally defined as the metal salts of fatty acids, which arise from reaction with free fatty acids in the oil medium is well known. Soap formation has been most closely associated with zinc- and lead-containing pigments, although it occurs with other metal ions in paints, such as copper or calcium. Formation of zinc soaps has long been blamed for the brittleness of zinc white paint.¹ Salt “soaps” can result in a variety of other problems in paintings: these include formation of aggregates that can protrude through the painted surface as whitish “pustules” and an increase in transparency of the oil paint film.^{2,3} Analysis of the pustules indicates that they are primarily composed of salts of palmitic and stearic acids and a smaller proportion of oleic acid.^{4,5} Delamination of paint layers, often associated with zinc soap formation, may occur.^{6,7} Recent work has shown that a variety of zinc alkanoates with sheet structures can form in oil, which might account for this phenomenon.⁸

Considerable research is being undertaken to characterize and understand the mechanism and rate of “soap” formation in oil paint films.^{9,10} However, debate remains over whether it is a long-term, slow reaction, and is therefore possibly preventable,

or it occurs early in the curing process, and if so, what are the factors that initiate the reactions to form soaps. To investigate these questions, we set out to understand the time frame of lead and zinc carboxylate formation through a competition experiment between the oligomerization of oil and the salt formation pathways.

Ethyl linoleate (EL), 9,12-linoleic (9,12-octadecadienoic-*(Z,Z)*acid-, ethyl ester), has been shown to be an appropriate model to study the curing of linseed and other natural drying oils;¹¹ therefore, we used EL to simplify the study of the curing reaction in the presence of metal ions. Potassium, lead, and zinc acetates were used to add quantifiable amounts of soluble metal ions found in pigments and driers to the model system. This model is different from others that have been used for studying soap formation as the fatty acid is polyunsaturated.

Reaction of methanolic solutions of EL and $M^{n+}(CH_3COO)_n$ [$M = Pb^{2+}, Zn^{2+}$] in air on quartz plates resulted in both oxidation of EL and formation of discrete spherulites within hours. These are colorless, ordered structures that luminesce in the visible region upon near-UV/visible irradiation. Their properties suggest that they may be thought of as hybrid inorganic–organic complexes or coordination polymers, which contain both inorganic and organic moieties bonded into a

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network with long-range connectivity in at least one dimension.¹² In particular, the complexes described here seem to be similar to those described in the reports of lead(II) alkanooates and zinc(II) carboxylates, which are two-dimensional and three-dimensional (3D) framework complexes.¹³ This article presents preliminary characterization of the structural and luminescence properties of Pb(II)–EL and Zn(II)–EL complexes and briefly discusses the possible importance of these findings to understanding the preservation state of oil paintings.

■ EXPERIMENTAL SECTION

EL (Sigma-Aldrich, 1 g ampules), Zn(CH₃COO)₂ (Aldrich, 99.99%), K(CH₃COO) (Sigma), and Pb(CH₃COO)₂·3H₂O (Mallinckrodt) were used as received. Mixtures of EL and metal acetates (M = Pb²⁺, K⁺, and Zn²⁺) in methanol (Fisher, Analytical Grade) were made up under an atmosphere of dry nitrogen or argon. The gases were purified by passage through columns of BASF R3-11 catalyst and 4 Å molecular sieves. Samples of metal acetates in approximately 0.1, 0.25, and 0.5 mole ratios to EL were prepared under N₂(g). Metal acetate samples were weighed and transferred into a dry box. In the dry box, 45.5 μL of EL was measured and added to vials containing the weighed metal acetate, which were then capped, sealed, and kept in the freezer until use. The mixtures were taken up in a minimum amount of dry CH₃OH (<0.5 mL), and in air, the solution was placed dropwise onto quartz plates. After only a few minutes, the clear solution became cloudy and bubbles evolved. The resulting films were allowed to cure in air overnight and then monitored using the methods described below. All analyses of the products except the X-ray powder diffraction measurements were recorded in situ in the film on quartz plates. This means that in most cases the spectra obtained are a combination of those from the EL film and the metal-containing product.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded using a Nexus 670 FTIR bench with a SpectraTech Continuum microscope (Thermo Nicolet) equipped with a 15× ATR objective with a silicon crystal slide-on attachment. Spectra were collected at 8 cm⁻¹ resolution, 256 scans were integrated, and the sample area was 100 μm × 100 μm. Spectral analysis was performed using OMNIC software. Transmission and luminescence spectra of EL–metal acetate mixtures curing on spectral grade quartz plates (Wilmad) were obtained. Absorbance spectra were acquired using a Cary 1G UV–visible spectrophotometer (Varian/Agilent Technologies) between 200 and 800 nm; the analysis of the spectra was carried out using Cary Win UV software. Macroscale luminescence spectra were obtained using a Fluorolog FL3-22 spectrofluorometer (Horiba Jobin Yvon) equipped with external fiber optic cables to collect emission and excitation–emission spectra of the films on the plates. A standard experiment used λ_{ex} = 250–600 nm with 25 nm steps and 5 nm slit width and acquired λ_{em} between 300 and 800 nm with 2 nm steps and 5 nm slit width. Measurements at the microscopic scale were made using a Craic XDi 100 microspectrophotometer (CRAIC Technologies, Altadena) with a 36× Cassegrain objective (field of view 4 μm × 4 μm). QDI GRAMS was used for spectral analysis. Transmission was typically measured from 350 to 750 nm. Plane and polarized transmitted light microscopy (PLM) was carried out on a Leica DMRX microscope with PL Fluotar D 20×/0.48 and 50×/0.85 20× objectives. Leica filter cubes D, I2/3, and M

were employed for fluorescence microscopy. Photomicrographs were acquired using a Canon EOS D1 camera.

For scanning electron microscopy/energy dispersive X-ray analysis (SEM/EDX), each sample was placed onto a pressed carbon stub (Ted Pella Inc.) using a double-sided carbon sticky tab (Ted Pella Inc.). Back-scattered electron (BSE) images were acquired on a Hitachi S 3400-N variable-pressure scanning electron microscope. An Oxford INCA X-act detector (80 mm², resolution 129 eV at 5.9 keV) and an INCA 300 X-ray spectrometer were used for EDX analysis. The accelerating voltage was 20 kV, the pressure was 40–60 Pa, and the working distance was 10 mm. The samples were not coated.

For X-ray powder diffraction studies, samples containing lead(II) or zinc(II) acetates in methanol with EL were prepared in air. After several weeks, the aggregates that had formed were separated as best as possible but not completely from the EL film and loaded into 1.5 mm diameter Kapton capillary tubes. High-resolution synchrotron powder X-ray diffraction (HR SP-XRD) data were collected using the mail-in program on beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, IL.¹⁴ Scans were collected in transmission mode on spinning Kapton capillaries using a fixed wavelength of 0.41384 Å. Patterns were collected at 250, 273, and 285 K.

■ RESULTS AND DISCUSSION

Films prepared from methanol solutions of EL with and without added K(CH₃COO) behaved similarly, curing to give transparent, featureless films. In contrast, Pb(CH₃COO)₂ and Zn(CH₃COO)₂ reacted rapidly with EL, evolving acetic acid as bubbles, and within hours translucent spots that contained crystalline compounds had formed in the films. We did not observe any effect on the relative rate of salt formation compared to that of oxidation on increasing the molar ratio of the metal acetates to EL over the time frame of our measurements, nor did we observe any effect on the nature of the products, although the initiation of the reaction between saturated fatty acids and Pb(II) has been shown to be related to the chain length of the fatty acid.¹⁵ Polarized light micrographs of the Pb(II) product after ca. 2 h are shown in Figure 1 and of the aggregated Zn(II) product, in Figure 2. Concomitant oxidation of EL occurred, which was monitored by a decrease in UV absorbance at 280 and 225 nm and the disappearance of a methylene C–H stretch in the FTIR spectra at 3007 cm⁻¹. In films prepared from solutions of neat EL and those containing K⁺, UV–vis and FTIR measurements showed that oxidation had neared completion within 4 weeks and in films containing zinc or lead ions it took 9 weeks.

SEM/EDX results showed that the metal ions became entirely sequestered into the compounds formed. The crystallites of Pb–EL, which self-limit in size at ca. 5 μm diameter (Figure 3), and Zn–EL, which are acicular needles, did not grow in size over time; rather over a period of 1–3 days, they flocculated into aggregates up to 500 μm in diameter. Representative images of the aggregates are illustrated in Figures 4 and 5. Dispersions of colloidal particles, such as the crystallites formed in the reaction of EL with Pb²⁺ or Zn²⁺, are metastable, and the particles tend to move and separate from a host fluid,¹⁶ which is EL in this case, but for paintings, it would be a plastic oligomeric cured seed or nut oil.

The formation of metal–carboxylate bonds in the reaction mixture was determined by measuring the development of strong absorbance bands in the IR spectrum between 1489 and

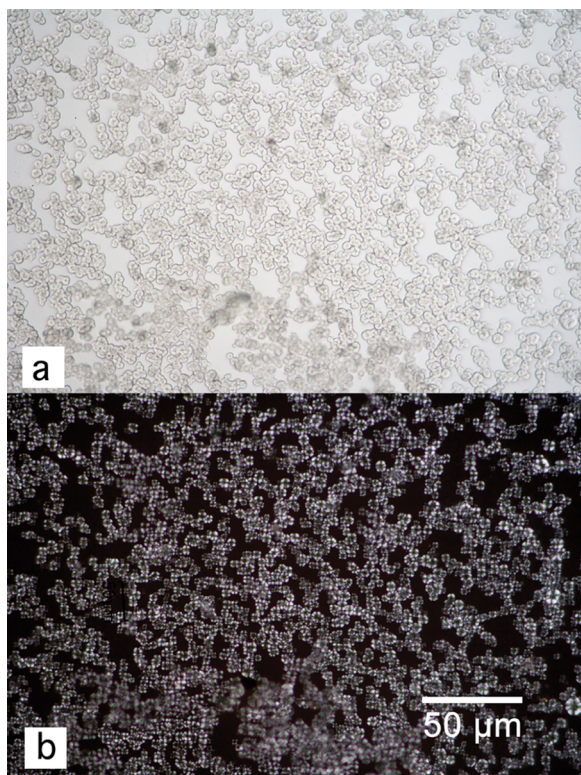


Figure 1. Photomicrograph of the spherulitic product formed on mixing methanolic EL and $\text{Pb}(\text{CH}_3\text{COO})_2$ in air after ca. 2 h: (a) transmitted plane-polarized light and (b) cross-polarized light (same field of view).

1590 cm^{-1} due to $\nu_{\text{as}}\text{ COO}^-$.¹⁷ Until large aggregates of the metal soaps had formed, the spectra were dominated by the absorbance of the EL film as the field of view was large compared to the size of the crystals. The FTIR spectrum of a Pb–EL aggregate 2 weeks after mixing is shown in Figure 6. Absorbance bands initially appeared at 1505 and 1547 cm^{-1} that coalesced over time to a single broad band centered at ca. 1540 cm^{-1} . For the final lead product, $\nu_{\text{s}}\text{ COO}^-$ is $1390/1370\text{ cm}^{-1}$.

The FTIR spectrum of the mixture of Zn(II) with EL is shown in Figure 7. The spectrum obtained from the area of an aggregate, shown in black, contains peaks due to absorbances of carboxylate anion groups as well as unreacted ester carboxylate, which is present in the clear film, whose spectrum is shown in red. Initially, the spectrum of the aggregate contained a peak at 1541 cm^{-1} perhaps due to an intermediate acetate-containing species; after 1100 h, this stretch had broadened and moved to ca. 1580 cm^{-1} ; it has shoulders at ca. 1634 , 1562 , and 1541 cm^{-1} . The $\nu_{\text{s}}\text{ COO}^-$ absorbances occur at 1463 and 1441 cm^{-1} . The values reported for $\nu_{\text{as}}\text{ COO}^-$ of salts of lead(II) and zinc(II) with saturated and monounsaturated fatty acids, specifically the stearates, palmitates, and oleates, range between 1542 and 1504 cm^{-1} for lead complexes and 1547 and 1538 cm^{-1} for zinc soaps;^{18–20} the oleates and zinc linoleate have doublets for this stretch.¹⁷ The change we observed in the IR spectra over time might be an indication of an acetate-containing species, a secondary reorganization on oxidation to give a more stable product, or changes as the EL ligand oxidizes. The values of $\nu_{\text{as}}\text{ COO}^- \text{ cm}^{-1}$ for Zn–EL are significant in light of the observations made that zinc soap aggregates in real paint films and models prepared using linseed

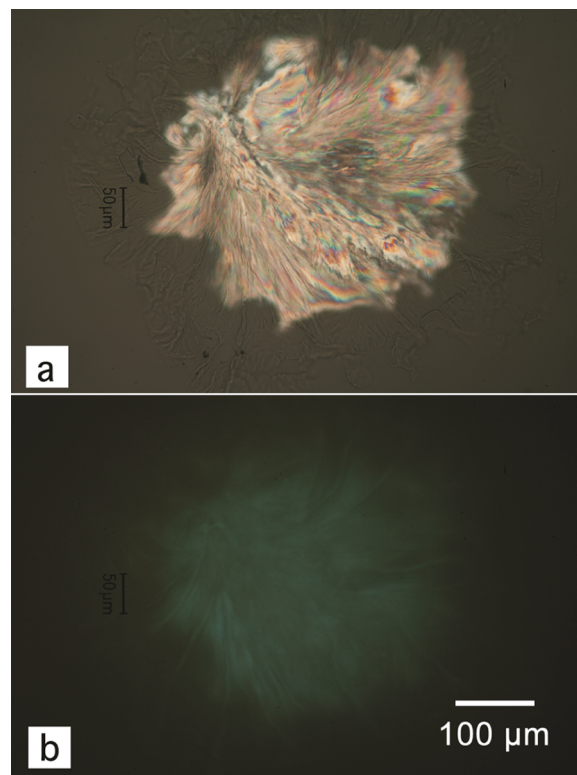


Figure 2. Large aggregate of the reaction product formed from the reaction between methanolic $\text{Zn}(\text{CH}_3\text{COO})_2$ and EL: (a) transmitted cross-polarized light and (b) visible-induced fluorescence (Leica filter cube with bandpass filter of $\lambda_{\text{ex}} 450\text{--}490\text{ nm}$ and transmission longpass filter of $\lambda_{\text{ex}} 515\text{ nm}$).

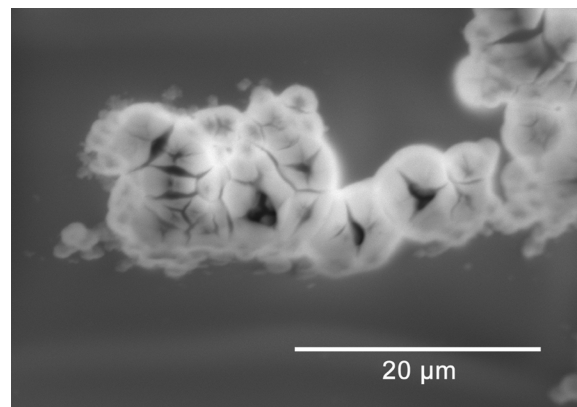


Figure 3. BSE image of the complex formed on mixing $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ in methanol with excess EL prior to aggregation. The spherulitic structure surrounding a central void or cavity (black) can be seen.

oil have a broad peak at $1570\text{--}1590\text{ cm}^{-1}$, a value much more similar to that for Zn–EL than that for saturated fatty acid zinc soaps.^{5,18}

Hermans et al.¹⁸ have discussed the differences in the IR spectra of simple soap salts, mixed metal salts, model Zn-paint films, and real paint films and the possible reasons for them. They dismissed the hypothesis that broadening of the $\nu_{\text{as}}\text{ COO}^-$ stretch in real paint films is owing to the interaction of fatty acids or triglycerides with ZnO particles. An interesting suggestion, based on the observation that on melting a single sharp peak for the asymmetric carboxylate stretch in zinc

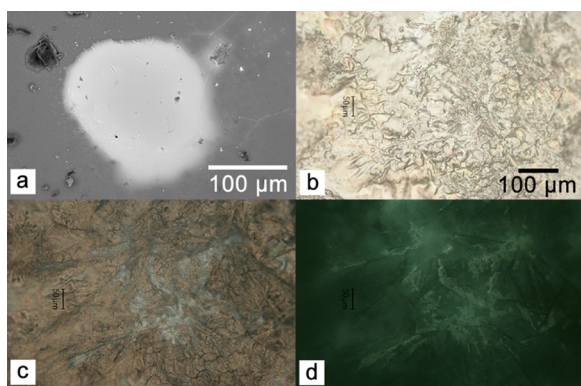


Figure 4. Aggregate of crystallites formed by the reaction of Pb(II) with EL: (a) BSE image, (b) plane-polarized transmitted light image, (c) the same field of view as (b) in transmitted cross-polarized light, and (d) fluorescence using Leica filter cube D (excitation bandpass filter of 355–425 nm, dichroic filter of 455 nm, and longpass filter of 470 nm).

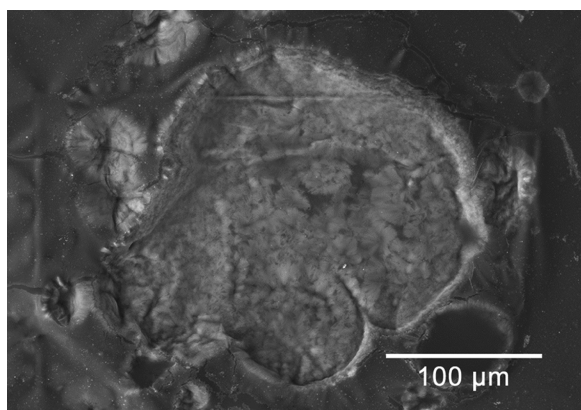


Figure 5. BSE image of an aggregate of Zn-EL, which comprises spherulitic clusters of acicular crystallites.

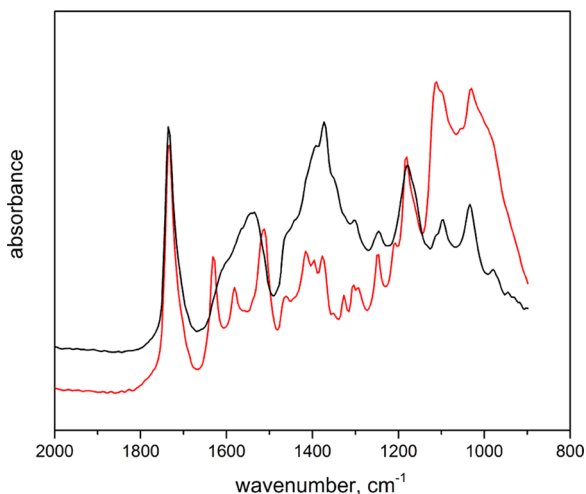


Figure 6. FTIR spectrum of an aggregate of the Pb-EL complex aged 2 weeks (black) and the surrounding film, which does contain some unaggregated crystals (red). The $\nu_{\text{as}} \text{COO}^-$ has a maximum intensity at 1540 cm^{-1} and shoulders at 1610 and 1567 cm^{-1} .

palmitate is replaced by three higher-energy peaks, is that broadening is indicative of distortions in a tetrahedral geometry around Zn(II) ions. This may also occur in some solid-state

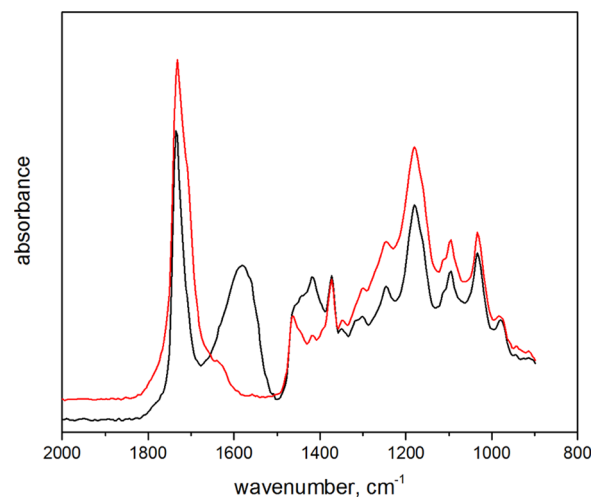


Figure 7. FTIR spectrum of an aggregate of the Zn-EL complex aged 2 weeks (black) and the clear film surrounding it (red). The $\nu_{\text{as}} \text{COO}^-$ has a maximum intensity at 1581 cm^{-1} and shoulders at 1634 , 1562 , and 1541 cm^{-1} .

carboxylates as it is known that certain Zn(II) complexes can have polynuclear (e.g., zinc acetyl acetonate) or polymeric structures. Another possibility raised by Hermans et al. is that the oxidized linoxyn film that forms the paint binder may be thought of as an ionomer, which can be neutralized by free ions, including Zn(II), in the paint matrix. In such a system, zinc ions could occupy several geometrically distinguishable sites; therefore, broadening of the absorbances associated with carboxylate stretches would occur.

The similarity in the $\nu_{\text{as}} \text{COO}^-$ peaks of the complex models, real paint, and the simple model, EL, for drying oil used in this study suggests that the aggregates formed in the more complex systems may involve unsaturated fatty acids such as linolenic acid during part of their development and may have comprised salts of unsaturated fatty acids, which oxidize over time and therefore would not be identified in historic paints using various analytical methods. The absence of metal ions in the noncrystalline phase in the model system and the absence of any carboxylate ion absorbances in that phase mean that we cannot speculate about the proposed presence of noncrystalline alkanooates in real paint systems.

HR SP-XRD measurements were performed on the material recovered from the films to obtain average information on their structures. The aggregates of the crystallites were separated manually from the EL film, but not rinsed, and then loaded into the Kapton capillary. The SP-XRD patterns (Figure 8) contain broad peak features because of the presence of noncrystalline material, which most likely is the EL film that could not be entirely removed, although the presence of noncrystalline soaps ought not be ruled out. Sharp diffraction peaks at low 2θ indicate that the systems possess long-range structures, as expected for coordination polymers. The diffraction patterns did not change significantly between 250 and 285 K, indicating that no phase changes occurred over this range. It is a narrow and low-temperature range but was chosen to decrease the movement of the particles within remaining viscous EL. Corbeil et al. have shown that zinc linoleate has an XRD pattern which at $2\theta = 2\text{--}18^\circ$ is similar to that of soaps formed between zinc(II) and stearate, palmitate, and oleate.²¹ The fact that these are all needlelike crystals also supports the inference that

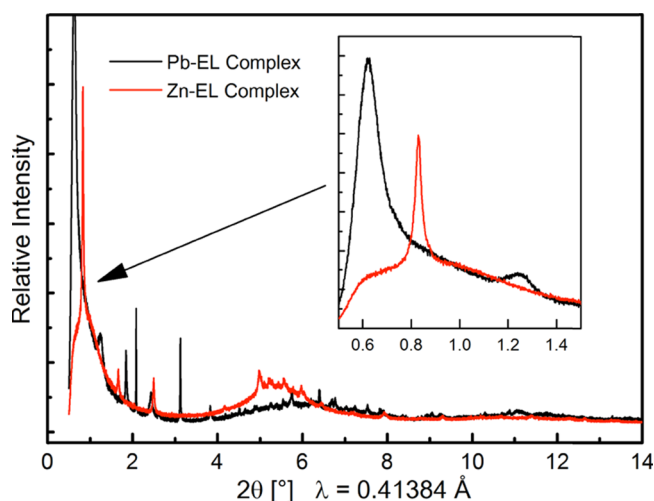


Figure 8. HR SP-XRD patterns of the products of the reaction of Pb(II) and Zn(II) with EL. The broad features may be due to unreacted EL coating the crystallites.

these complexes are structurally similar. However, the lead complex is different.

For some cases, it has been proposed that it is possible to determine the bonding mode of a carboxylate to a metal ion, that is to determine if it is unidentate, bidentate, bridging, or pseudobridging, by measuring the energy difference between the symmetric and antisymmetric C=O stretching modes in the IR spectrum.^{22,23} However, we believe that as the exact energy of specific stretches can be dependent on the surrounding crystallographic symmetry as well as the bonding mode a comparison between these complexes, that have different symmetries as well as different metal ions, is not warranted with the information available in this study. Furthermore, given the complex shape of the Pb-EL species (seen in Figures 1 and 3), it is likely to have multiple bonding modes. For comparison, the recorded crystal structures of neodymium alkanooates show that these complexes have two or more forms of coordination of the carboxylate group, a fact that was not evident from their infrared spectra.²⁴

Metal carboxylate coordination polymers have many different structures,²⁵ but even so we are surprised that for these simple systems the structures of Zn-EL and Pb-EL complexes are very different, which is clear from PLM and SEM. The Zn-EL crystallites are needlelike and the crystallographic point group has not been determined, but the crystal habit is similar to that of the complexes formed with saturated fatty acids. In contrast, the Pb-EL coordination polymer appears to have a complex starchlike helical structure. The BSE image of the Pb-EL complex shows, as does PLM, that the structure has a void in the center (Figures 1 and 3). This is consistent with the compound having characteristics similar to some 3D metal-organic hybrid framework structures that are porous. Lead azelate has a 3D polymeric network (monoclinic) with 7-fold symmetry around lead(II) ions that are arranged in stacks bridged by carboxylate groups.²⁶ The ability of lead to support expanded coordination might be the factor that allows this structure to be formed.²⁷ The FTIR spectra indicate some changes at the early stage of the reaction, but we have no information from other techniques such as optical microscopy on the structural changes in the M-EL systems, and the changes observed may be associated with curing of EL rather

than major crystallographic changes or formation of ionomers, which Hermans et al. have observed in model systems of metal soaps in linseed oil.²⁸ Short-chain lead(II) carboxylates have been reported to convert from a crystalline to a smectic phase over the temperature range of 343–379 K.²⁹ Changes in the structure over time have been reported for short-chain lead(II) alkanooates.³⁰ In these systems, conformational changes occur between solid and condense phases with concomitant changes in X-ray diffraction patterns and infrared spectra, but, as noted, we do not have evidence for this kind of change in the M-EL systems over the time frame and temperature range employed here.

The Pb-EL and Zn-EL species luminesce. We measured the emission of the lead-EL complex to see if the species formed might be related to those responsible for the atypical luminescence that has been described for lead white paint films. Whereas cured linseed oil itself has a weak emission at ca. 510 nm,³¹ lead white paint films have an atypical strong, broad emission at ca. 500–550 nm.³² An excitation–emission spectrum obtained from the entire plate of Pb-EL (crystals and curing EL) has three bands: $\lambda_{\text{ex/em}} = 296/462$, 366/442, and 483/572 nm. The emission spectrum of Pb(II)-EL upon irradiation at 360 nm has broad maxima at ca. 485 and 555 nm (black trace in Figure 9). The emission spectrum is broader and

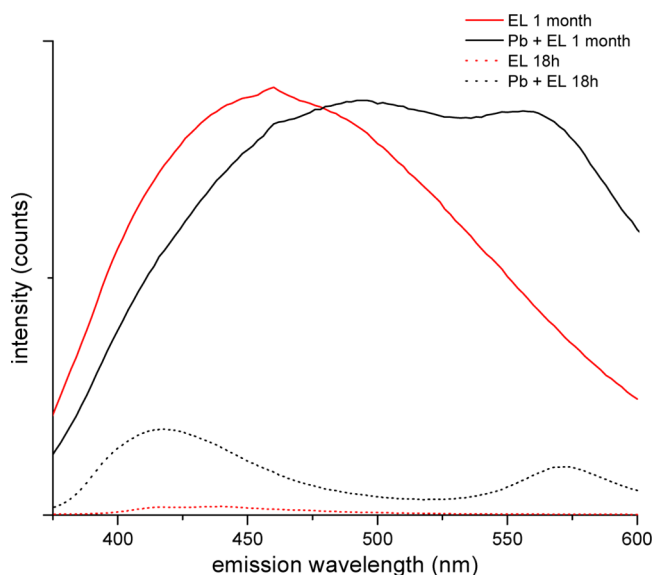


Figure 9. Macroscopic emission spectra, $\lambda_{\text{ex}} = 360$ nm, of EL (red) and EL mixed with Pb(CH₃COO)₂ (black) after 18 h (dotted) and 1 month (solid). (Collected using a fiber optic attachment on a Fluorolog spectrophotometer.)

has a longer wavelength than that of oxidized EL, which develops an emission maximum at ca. 450 nm. A photomicrograph of the emission from an aggregate of the Zn-EL complex upon near-UV/visible excitation is shown in Figure 2b. The strong emission from zinc oxide itself has precluded noticing a soap-related emission in paint films, and this remains to be studied.

Coordination polymers and metal-organic hybrid complexes are often luminescent,³³ including some that contain lead. Lead soaps exhibit weak fluorescence at low temperature³⁴ and Martínez Casado et al. have shown that the glass states of lead alkanooates phosphoresce.³⁵ Compounds prepared from lead(II) with a variety of aromatic carboxylic acids emit in the blue to

green (420–520 nm) region, depending on the structure and nature of bonding of the carboxylate group.³⁶ Pb(II) complexes of butyric acid and N-donor ligands have several emission bands deep into the visible region.³⁷ These observations suggest that the presence of carboxylate complexes of lead may account at least in part for the observed luminescence of lead white paint films.

We propose that two apparently unrelated observations regarding lead white paints, “soap” formation and atypical luminescence, are connected. Traditionally, the pigment lead white was prepared from metal coils or buckles using the so-called stack process through the reaction in air with acetic acid vapors, which ultimately gives the white basic carbonate. To obtain a pure product, the scrapings were washed to remove metal and lead acetates.^{38,39} Insufficient washing would leave soluble salts and metal particles in the pigment. Although it has not been specifically noted that soluble lead salts remaining in lead white contribute to soap formation in paints, Pb(CH₃COO)₂ added to cobalt stannate and vine black paints as a drier did appear to be correlated with the development of defects in the paint films.^{4,40} Keune and Boon⁴¹ reported that paintings by the Hudson River School painter Frederic Edwin Church quickly developed issues because of lead soaps, the formation of which was related to the presence of lead acetate as a drier in the paint. Using EL as the model for a drying oil, we have shown that Zn(II) and Pb(II) form complex coordination compounds with unsaturated fatty acids. These products, unlike soaps formed with saturated fatty acids, luminesce at room temperature.

Reactions between metal ions and drying oils to form the so-called soaps occur across a broad range of paintings and are sometimes more and sometimes less obvious in paint films containing lead white, lead tin yellow, red lead, and zinc white. A large study of 108 17th and 18th century English paintings showed that the phenomenon of lead soap formation cannot yet be related to the factors such as treatment or environment, although it appears that leaner paint films have less soap formation.⁴² The results from the simple system used in this study clearly demonstrate that the reaction between an unsaturated fatty acid ester, a model for oil, and soluble metal ions is rapid and in the case of Zn(II) and Pb(II) leads to the precipitation of crystals that aggregate. The fact that not all paintings equally present the evidence for lead soap formation might be related to the comparative purity of the lead white available in specific places at particular times and the presence of mobile ions. Lead white that has been washed well, thereby removing Pb(CH₃COO)₂, which is easily solubilized, along with the unreacted metal, might provide a paint film that is less prone to rapid formation of particles of insoluble lead carboxylates and their subsequent aggregation.

CONCLUSIONS

On mixing EL, used as a simple model for linseed oil paint, with lead(II) or zinc(II) acetates, crystallites of luminescent complexes rapidly formed and aggregated into flocs within 48 h. These consist of metal carboxylates, but they are not simple salts. The luminescence and structural properties indicate that the Pb(II)–EL and Zn(II)–EL complexes are coordination polymers that have long-range structures. There are significant differences in the physical behavior of the EL complexes compared to that of the soaps formed with saturated or monounsaturated fatty acids, evident from their FTIR spectra as well as luminescence behavior and structural information.

The EL complexes have properties, such as luminescence behavior, that are between those of the simple soaps and the “soaps” found in paints. We believe that this work may be a valuable model for future studies of the problem of paint reactivity. The lead complex formed on reaction with the unsaturated fatty acid has an interesting complex structure that is different from the structures formed on reaction with straight-chain unsaturated carboxylic acids and adds information regarding the possibility of reaction with unoxidized fatty acids. The observation that simple systems of a divalent metal ion with an unsaturated fatty acid ester give rise to stable, highly structured products provides insight into the studies of metal ion sequestration, stabilization, and toxicity in biological and ecological research.¹⁵

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Author Contributions

M.G.M. designed the experiments and carried out FTIR and PL experiments. M.G.M., M.R.P., and B.H.B. performed SEM/EDX and OM. M.R.S. performed XRD. B.H.B. and M.G.M. wrote the paper with input from M.R.S. and M.R.P. All authors read and approved the paper.

Notes

The authors declare no competing financial interest.

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