

UNDERSTANDING SOAP FORMATION IN PAINT FILMS BY ^{207}Pb , ^{119}Sn AND ^{13}C SOLID-STATE NMR

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Abstract

The formation of lead carboxylates (lead soaps) has been identified as the cause of deterioration of hundreds of oil paintings. Soaps form when heavy metal-containing pigments, for example lead white and lead-tin yellow, react with saturated fatty acids in the oil medium. Understanding the mechanism of the reactions requires chemical information, which can be obtained with solid-state ^{207}Pb , ^{119}Sn and ^{13}C NMR spectroscopy. Using the chemical-shift tensors determined by solid-state NMR we can gain structural insights on the coordination environment of the lead carboxylates and identify and quantify components in a paint film mixture. We have examined the spectroscopy of lead-containing pigments, lead carboxylates, and model paint films that were subjected to accelerated aging. We have also begun to investigate the dynamics of soap formation by ^{13}C NMR spectroscopy. The NMR methods applied to the model paint systems could also be applied to other lead-containing materials.

Introduction

The formation of lead and other heavy-metal carboxylates, also called heavy-metal soaps, has been reported to be the cause of deterioration of hundreds of oil paintings dating from the fifteenth to the twentieth centuries [1-6]. Soaps form when heavy-metal-containing pigments, such as the commonly used lead white, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, and lead-tin yellow type I (LTY-I), Pb_2SnO_4 , react with fatty acids that result from the hydrolysis of glycerides in the oil binder. Soaps can form aggregates or inclusions that can be as large as 100-200 μm in diameter and may break through the paint surface [1-6]. Lead soaps have also been implicated in the increased transparency of paint films [5, 7-9]. Soap formation is not restricted to oil paintings; long-chain fatty acid carboxylates of lead, copper, and zinc have been found as degradation products on the surfaces of metallic cultural artifacts, as a result of treatments or contact with organic substances such as animal fats, oils, or leather [10] and in ancient cosmetics [11]. Despite its widespread occurrence, the chemistry of soap formation is not yet fully understood. The formation of soaps does not take place in all artworks containing potentially reactive materials. What factors trigger the process, what the mechanisms are, and how the processes can be arrested or prevented is not known. Various theories have suggested that the phenomenon may result from peculiarities inherent in the artist's materials and techniques, from conservation procedures, or from the object's exposure to environmental conditions such as high relative humidity and temperature, but these suggestions have not yet been thoroughly studied [2, 8, 9, 12, 13].

Solid-state NMR (ssNMR) can provide structural information on lead soaps. The relationship between ^{207}Pb ssNMR parameters and solid-state structure has been reviewed by Fayon *et al.* [14], Dybowski and Neue [15], and more recently by Dmitrenko *et al.* [16]. There is a

strong dependence of the chemical-shift parameters on local structure, particularly on the coordination geometry around the lead atom. In addition, the ^{13}C chemical shifts are sensitive to crystal symmetry. The conformation and dynamics of the acyl chains of lead carboxylates have been studied in detail using ^{13}C ssNMR [17, 18].

Recently, we have demonstrated ssNMR as a useful technique for obtaining local structural information on lead soaps that cannot be accessed by other methods [19] and for the characterization of lead pigments, LTY-I and lead white, and their impurities [20, 21]. In this proceeding, we further discuss the characterization of lead pigments and lead carboxylates involved in soap formation and state how NMR can be used to answer questions regarding soap formation.

Materials and Methods

Sample Preparation

Lead carboxylates were synthesized as described previously [19]. Lead white (basic lead carbonate) was purchased from Sigma-Aldrich and LTY-I light was purchased from Kremer Pigments (Germany). Paint films of 50% lead white with 50% linseed oil by weight were prepared and dried for 2 weeks under laboratory conditions (approximately 20°C and 40% relative humidity (RH)). The paint films were placed inside a humidity cabinet at 85% RH and 40°C for six months. For one of the lead white paint samples, 0.066 grams of palmitic acid dissolved in 200 μl of ethanol was added to the surface before placing into the humidity cabinet. For the palmitic acid LTY-I paint samples, LTY-I (0.3332 grams) was mixed with 0.1568 grams of linseed oil, and spread on glass slides. After the samples dried for 2 weeks under laboratory conditions, palmitic acid (0.1 grams) dissolved in 500 μl of ethanol was added to the surface of the paint films. The samples were then stored at 40°C and 90% RH for 9 months.

NMR Methods

NMR parameters for lead carboxylates [19] and lead pigments [20, 21] have been described previously. ^{207}Pb ssNMR spectra were recorded at 11.75 tesla (104.63 MHz ^{207}Pb frequency) with a standard Bruker 4-mm probe. Approximately 100 mg of each sample were packed in a 4-mm rotor. Solid lead nitrate was used as a secondary external reference for the ^{207}Pb spectra, the isotropic chemical shift being -3491 ppm relative to tetramethyllead (TML) at 298 K [22]. The spectrum of lead nitrate was recorded at different spinning speeds to compensate for the temperature increase due to spinning. SnCl_2 in HCl was used as a secondary external reference for the ^{119}Sn Spectra, the isotropic chemical shift being -335 ppm [23].

^{207}Pb Wideband Uniform Rate Smooth Truncation – Carr-Purcell Meiboom-Gill (WURST-CPMG) spectra of the paint films were recorded using the parameters of MacGregor *et al.* [24]. WURST pulse widths were 50 μs , with pulse shapes created via the shape tool in Topspin 3.1. Seventy-five Meiboom-Gill loops were acquired for the WURST-CPMG experiments, with a 200- μs echo, and a sweep range of 0.5 MHz in all cases. The recycle delay was 7 s. Multiple WURST-CPMG spectra were collected at different carrier frequencies by shifting the carrier frequency a multiple of the spikelet separation (981.934 ppm) from spectrum to spectrum. The collected spectra were superimposed to form the final spectrum.

The analysis of the ^{207}Pb chemical-shift tensors was performed by fitting the WURST-CPMG envelope. Fits to the WURST-CPMG envelopes were aided by simulation of the powder pattern with the program WSOLIDS [25]. For LTY-I the fitting of the WURST-CPMG envelope was aided by DFT molecular cluster calculations [21].

Results and Discussion

Lead Carboxylates

Soap inclusions in old oil paintings studied by GC-MS and FT-IR have been reported to contain lead carboxylates of the stable saturated C₁₆ (palmitic) and C₁₈ (stearic) straight-chain monocarboxylic fatty acids, and occasionally relatively small amounts of dicarboxylic azelaic acid (C₉) [2, 4, 26]. We collected ²⁰⁷Pb ssNMR spectra and determined ²⁰⁷Pb chemical-shift tensors of these lead carboxylates [19]. The ²⁰⁷Pb NMR spectra, from which chemical-shift tensors were determined, were obtained with spin-temperature alternation with magic angle spinning (STA/MAS) and with the WURST-CPMG [24] pulse sequence (Figure 1a-c and Table 1). The results of these experiments show that the local coordination environment of lead azelate is different from those of lead palmitate and lead stearate; however lead palmitate and lead stearate are very similar to each other. The difference in coordination environment around the lead further supports that incorporation of lead azelate into the ordered structure containing lead palmitate and lead stearate would be unfavorable [4, 27]. In addition, comparing the ²⁰⁷Pb NMR chemical-shift tensors of the lead carboxylates of carbon chain length 6-11, we have shown that crystal packing of the acyl chains is a factor in determining the coordination environment around the lead [28].

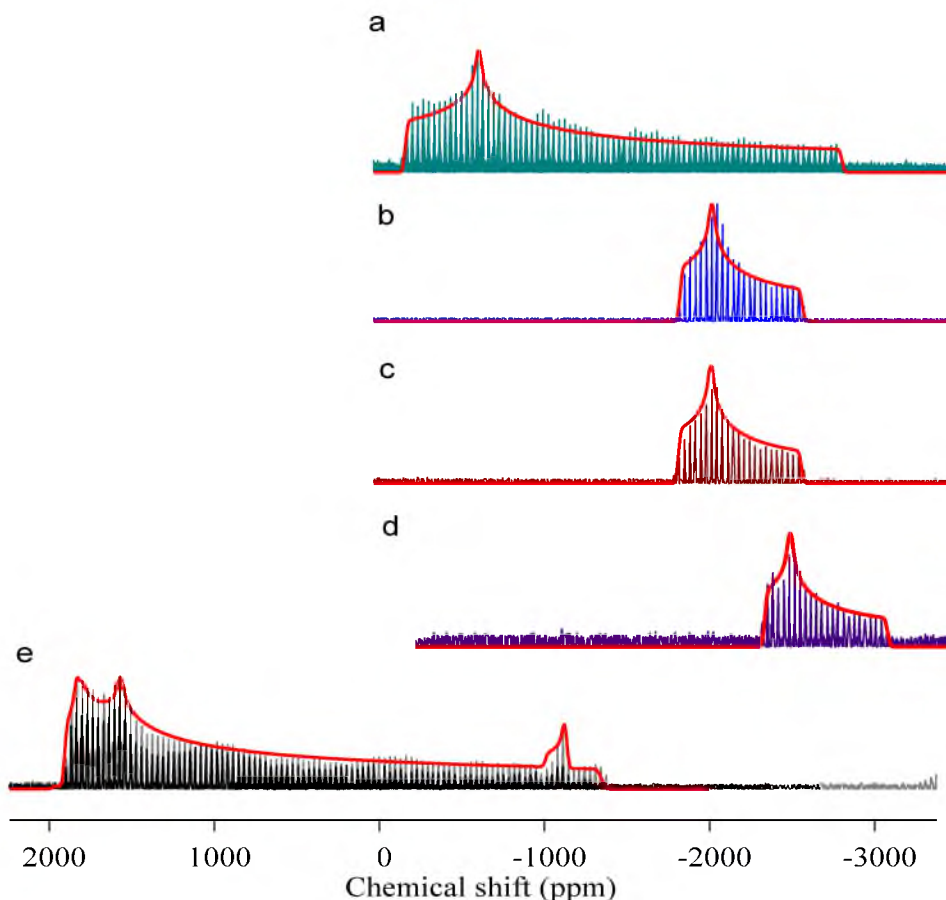


Figure 1. ²⁰⁷Pb WURST-CPMG spectra of lead azelate (a), lead stearate (b), lead palmitate (c), lead white (d) and LTY-I (e). The spectrum of lead white only shows the lead carbonate impurity and the spectrum of LTY-I includes a minium impurity.

Table 1. The Principal Components of the ^{207}Pb and ^{119}Sn Chemical-Shift Tensors of Lead Azelate, Lead Stearate, Lead Palmitate, Lead Carbonate, and Lead-tin Yellow.^a

Compound	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	δ_{iso} (ppm)	Ω (ppm)	κ
Lead Azelate[19]	-160 $\pm$ 7	-604 $\pm$ 11	-2800 $\pm$ 8	-1188 $\pm$ 3	2640 $\pm$ 11	0.66 $\pm$ 0.01
Lead Stearate[19]	-1810 $\pm$ 3	-2007 $\pm$ 6	-2555 $\pm$ 3	-2124 $\pm$ 4	745 $\pm$ 4	0.47 $\pm$ 0.03
Lead Palmitate[19]	-1820 $\pm$ 3	-2013 $\pm$ 5	-2560 $\pm$ 3	-2131 $\pm$ 3	740 $\pm$ 4	0.48 $\pm$ 0.02
Lead Carbonate[22]	-2311 $\pm$ 2	-2481 $\pm$ 2	-3075 $\pm$ 8	-2622 $\pm$ 3	764 $\pm$ 8	0.55 $\pm$ 0.03
Lead-tin Yellow[21] Pb(I)	1810 $\pm$ 7	1565 $\pm$ 10	-1335 $\pm$ 20	690 $\pm$ 23	3145 $\pm$ 21	0.84 $\pm$ 0.02
Pb(II)	1903 $\pm$ 7	1828 $\pm$ 7	-1365 $\pm$ 25	788 $\pm$ 27	3268 $\pm$ 26	0.95 $\pm$ 0.03
Sn	-514 $\pm$ 4	-517 $\pm$ 5	-556 $\pm$ 7	-529 $\pm$ 3	41 $\pm$ 8	0.93 $\pm$ 0.46

^aThe fitting procedure used the isotropic shift, as determined from STA/MAS spectra of the material, with simulation of the values of δ_{11} , δ_{22} , and δ_{33} determined by the edges of the WURST-CPMG spectrum. Span (Ω) and skew (κ) were calculated. $\Omega = |\delta_{33} - \delta_{11}|$ and $\kappa = 3 * (\delta_{\text{iso}} - \delta_{22}) / \Omega$.

Soap formation can be observed by ^{13}C NMR since the carboxyl peak shifts upon lead coordination (Figure 2). This can be used to monitor and quantify soap formation. The ^{13}C NMR spectra of lead palmitate, lead stearate, and lead azelate also show resonance doubling of carbons close to the lead center indicating two possible geometries for the coordination of the fatty acid chain to the lead ion. The presence of two conformers is in agreement with published crystal structures of lead azelate [27] and lead heptanoate [29] that show two fatty acid chains in the asymmetric unit, as well as with previously published ^{13}C spectra of lead decanoate and lead stearate [17].

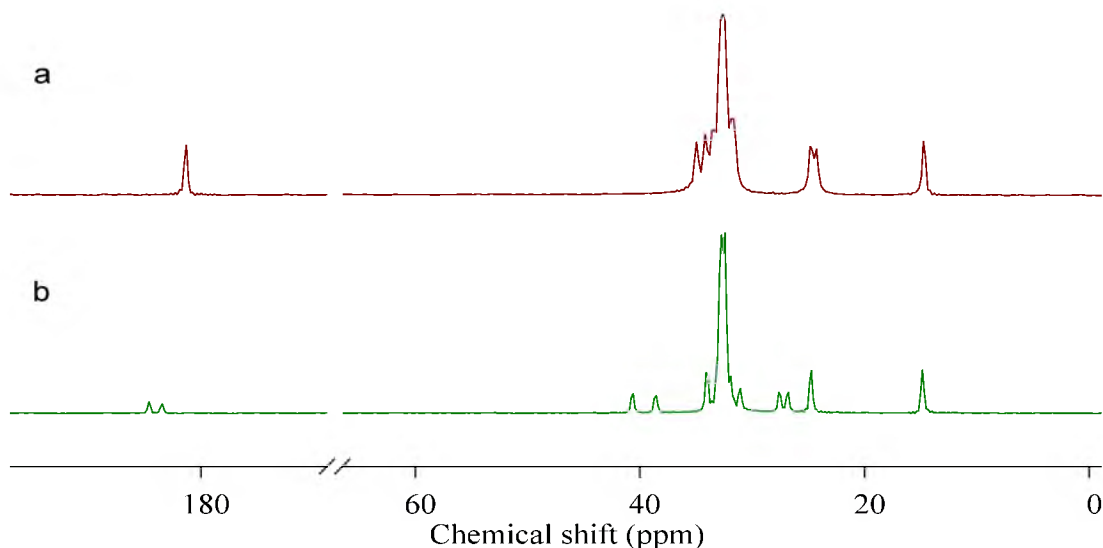


Figure 2. ^{13}C spectra obtained with cross polarization with MAS at 12 kHz of palmitic acid (a) and lead palmitate (b). A comparison of the two spectra shows a shift in the carboxyl (180-185 ppm) region upon binding to lead and a resonance doubling of the carbons closest to the lead in lead palmitate.

Lead Pigments

Two of the lead pigments most commonly involved in soap formation, lead white and LTY-I, have been studied by ^{207}Pb and ^{119}Sn NMR [20, 21]. The ^{207}Pb spectrum of lead white was obtained with the WURST-CPMG experiment (Figure 1d). Only one lead species is observed under the current experimental conditions. Through a series of control experiments with lead nitrate, the lead species detected was determined to be a lead carbonate impurity in lead white [20]. Depending on how lead white is prepared, there usually is a residual amount of lead carbonate present [7]. Possible reasons for not detecting the lead species in lead white include that the chemical-shift tensor is very broad, that the T_1 could be very long compared to the recycle delay, or that T_2 could be very short (which would interfere with the refocusing of the WURST-CPMG experiment).

It has been assumed that minor lead components in LTY-I react with the free fatty acids in the binding medium of oil paintings [2]. The crystal structure of Pb_2SnO_4 shows two distinct but similar lead sites [30]. Iterative fitting of the WURST-CPMG envelope (Figure 1e) of the ^{207}Pb spectrum of LTY-I along with DFT molecular cluster calculations of Pb_2SnO_4 allowed determination of the chemical-shift tensors for the two lead sites (Table 1) and detection of an impurity of the starting material, minium [21]. The ^{119}Sn NMR spectrum of LTY-I, shows evidence of the starting material SnO_2 . The ^{119}Sn chemical-shift tensor of Pb_2SnO_4 is in agreement with the crystal structure that the coordination environment around tin is close to spherically symmetric [30]. Knowledge of the chemical-shift tensors and impurities allows ^{207}Pb and ^{119}Sn ssNMR experiments to determine the reactive species in LTY-I, which is the subject of a separate study [21].

NMR of Paint Films

Free fatty acids in the oil matrix are formed from the hydrolysis of the triglycerides. Because this process starts as soon as a paint film is applied but occurs over years, we have induced soap formation by applying a free fatty acid to the top of a paint film. This simulates a process that has been observed in actual oil paintings, when layers composed of pigments with heavy metals develop soaps by the migration of free fatty acids from oil-rich paint layers that the artist applied above or beneath. Palmitic acid dissolved in ethanol was applied over a dried paint film containing a mixture of linseed oil with lead white or LTY-I. FT-IR, ^{13}C NMR, and ^{207}Pb NMR (Figure 3b and c) showed the formation of lead palmitate. These experiments demonstrate that one may observe the chemistry of soap formation in the paint films with NMR spectroscopy. In addition, one may separate and quantify each component using the corresponding NMR chemical-shift tensors.

Paint films that were subjected to accelerated aging without the addition of free fatty acids were also studied. Soap formation was monitored in these samples by following the characteristic bands in FT-IR spectra [10] and carboxyl peak in the ^{13}C NMR spectrum [19]. However, the ^{207}Pb NMR spectrum (Figure 3a), only shows the lead carbonate impurity visible in lead white. Under the current experimental conditions, 1% lead palmitate would be detected, but not 1% lead azelate [20]. Therefore the initial reaction products do not resemble the crystalline lead soaps studied. In addition, a possible reason for not observing lead soaps could be the same reasons why we are not detecting the resonance of certain species present in lead white, or perhaps the sample is heterogeneous with different soaps.

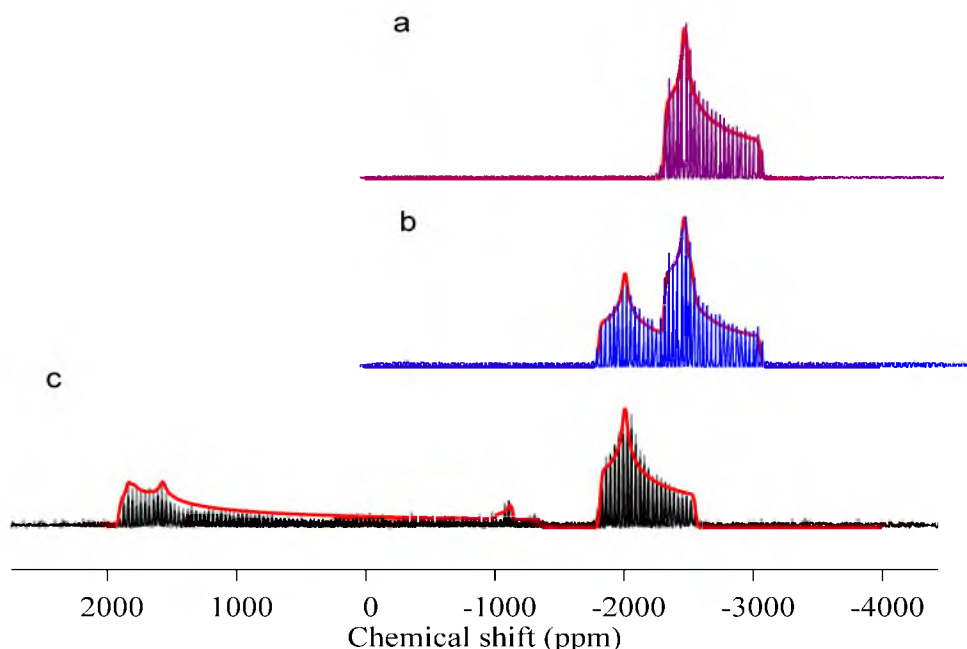


Figure 3. ^{207}Pb lead spectra of paint films subjected to accelerated aging and containing lead white and linseed oil (a), the same as in (a) but with palmitic acid added (b), and LTY-I and linseed oil with palmitic acid added (c). The paint films with palmitic acid (b and c) show the formation of lead palmitate.

Conclusions

Characterization of the lead carboxylates and lead pigments is crucial in understanding the chemistry of soap formation. One may distinguish various lead species with ^{207}Pb NMR spectroscopy. The ^{207}Pb NMR chemical-shift tensors show that the coordination environment around lead azelate is different from lead palmitate and lead stearate. ^{13}C NMR provides structural insight on the coordination of the carboxylate chains that could not be determined by other methods. In particular, the carbon spectra suggest that there are two carboxylate chains in the asymmetric unit of these structures. As the experiments demonstrate, ^{13}C NMR is useful in monitoring and quantifying soap formation. NMR analysis of the pigments has identified and quantified impurities in the formulation as it is received. Although, we cannot detect the lead species for lead white with current methods, we can observe and track the chemistry of soap formation with LTY-I through both ^{207}Pb and ^{119}Sn NMR.

Soap formation has been promoted and detected in model paint samples with the addition of free fatty acids. We caution that these model samples may not be representative of initial reaction products in paint films, where the hydrolysis of the glycerol ester may produce free fatty acids in a different manner and at rates different from the model reactions studied here. The NMR methods, while important for these materials, extend to analysis beyond cultural heritage and are applicable to any lead-based material where species can be distinguished on the basis of NMR spectra.

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