Analysis of Lead Carboxylates and Lead-Containing Pigments in Oil Paintings by Solid-State Nuclear Magnetic Resonance

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ABSTRACT

Soap formation in traditional oil paintings occurs when heavy metal-containing pigments, such as lead white, $2Pb(CO_3)_2 \cdot Pb(OH)_2$, and lead-tin yellow type I, Pb_2SnO_4, react with fatty acids in the binding medium. These soaps may form aggregates that can be 100-200 μm in diameter, which swell and protrude through the paint surface, resulting in the degradation of the paint film and damage to the integrity of the artwork. In addition, soap formation has been reported to play a role in the increased transparency of paint films that allows the painting support, the preparatory drawing, and the artists' alterations to become visible to the naked eye. The factors that trigger soap formation and the mechanism(s) of the process are not yet well understood. To elucidate these issues, chemical and structural information are necessary which can be obtained by solid-state ^{207}Pb, ^{119}Sn, and ^{13}C nuclear magnetic resonance (NMR). In the present study, a combination of ^{207}Pb NMR pulse sequences was used to determine accurately the NMR parameters of lead-containing pigments and lead carboxylates known to be involved in soap formation, such as lead palmitate, lead stearate, and lead azelate. These results show that the local coordination environment of lead azelate is different from lead palmitate or lead stearate. In addition, the chemical shifts of the pigments obtained are different from those of the soaps, demonstrating that ^{207}Pb NMR is useful in characterizing the components when present in a mixture, such as a paint film. The NMR methods discussed can also be applied to other Pb-containing cultural heritage materials, electronic and optoelectronic materials, superconducting materials, and environmentally contaminated 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, $2PbCO_3 \cdot Pb(OH)_2$, and lead-tin yellow type I, Pb_2SnO_4, react with fatty acids that result from the hydrolysis of glycerides in the oil binding medium, or from protective coatings [1, 2, 4, 7, 8]. Soaps have been characterized and identified in samples from works of art by microanalytical techniques, such as FTIR, SIMS, GC-MS, DTMS, SEM-EDX, micro-XRF, and Raman spectroscopy, inside aggregates or inclusions that can be as large as 100-200 μm in diameter and may break through the paint surface [1-6]. Soap formation has also been indicated as the cause of the increased transparency of paint films [5, 9-11]. Despite its widespread occurrence, the chemistry of soap formation is not yet fully understood.

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.* [12], Dybowski and Neue [13], and more recently by Dmitrenko *et al*.[14] There is a strong dependence of the chemical-shift parameters on local structure, particularly on the coordination geometry around the lead atom. Hence, principal elements of the ^{207}Pb chemical-shift tensor and the isotropic chemical shifts are indicative of the chemical identity of lead centers and, to the extent that different fatty acids lead to different coordination geometries, can be used to identify reaction pathways. We have previously characterized lead carboxylates known to be involved in soap formation [15]. In this proceeding, we report ^{207}Pb spectra and tensors for lead white and lead-tin yellow and show they can be distinguished from the lead carboxylates.

EXPERIMENTAL DETAILS

Lead palmitate was synthesized from a previously published procedure [15]. Basic lead carbonate (lead white) and lead nitrate was purchased from Sigma-Aldrich and lead-tin yellow type I was purchased from Kremer.

^{207}Pb ssNMR spectra were recorded at 11.75 tesla (104.63 MHz lead-207 frequency) with a standard Bruker 4-mm probe. Approximately 100 mg of sample were packed in a 4-mm rotor. Mixtures of lead carbonate or lead white (95% by weight) and lead nitrate (5%) were prepared. Mixtures of lead palmitate and lead white were also prepared by percent weight of 50:50, 10:90, 1:99. 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 [16]. The spectrum of lead nitrate was recorded at different spinning speeds to compensate for the temperature increase due to spinning.

^{207}Pb WURST-CPMG spectra of the samples were recorded using the parameters of MacGregor *et al*.[17] 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. For lead-tin yellow, 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. For lead white, WURST-CPMG spectra covering the range from 4000 ppm to -5000 ppm were recorded with delays of 7 and 60 seconds. The dip in intensity at the carrier frequency is an artifact of the experimental method.

For lead-tin yellow, ^{207}Pb spectra were acquired using direct excitation with spin-temperature alternation and magic-angle spinning (STA/MAS) at 10, 11, and 12 kHz to obtain the isotropic chemical shift. Spin-temperature alternation was used to minimize the effects of ringdown of the probe circuits [16]. General conditions for these experiments included a π pulse width of 8.5 μs, a delay of 1 ms, and a π/2 pulse width of 4.25 μs.

The analysis of the ^{207}Pb chemical-shift tensors was performed by fitting the WURST-CPMG envelope. The isotropic chemical shift acquired in the MAS experiment was fixed in the fitting procedure, because it could be measured accurately. Fits to the WURST-CPMG envelopes were aided by simulation of the powder pattern with the program WSOLIDS [18].

DISCUSSION

Paintings are multilayered complex systems. In order to study paint samples by NMR, analysis of the individual components needs to be performed. We have studied the spectra of

lead carboxylates known to be involved in soap formation and determined the ^{207}Pb tensors by using both STA/MAS and WURST-CPMG [15] experiments. The tensors reported in Table 1 show that lead palmitate and lead stearate are very similar and indistinguishable by ^{207}Pb NMR spectroscopy. However, the lead NMR parameters of lead palmitate and lead stearate tensors are very different from those of lead azelate, which has a larger span and an isotropic chemical shift of -1188 ppm.

Table 1. The Principal Elements of the ^{207}Pb Chemical-Shift Tensors of Lead Azelate, Lead Stearate, Lead Palmitate and Lead Carbonate.[a]

Compound	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	δ_{iso} (ppm)	Ω (ppm)	κ
Lead Azelate[15]	-160±7	-604±11	-2800±8	-1188±3	2640±11	0.66 ±0.01
Lead Stearate[15]	-1810±3	-2007±6	-2555±3	-2124±4	745±4	0.47±0.03
Lead Palmitate[15]	-1820±3	-2013±5	-2560±3	-2131±3	740±4	0.48±0.02
Lead Carbonate[16]	-2311±2	-2481±2	-3075±8	-2622±3	764±8	0.55±0.03

[a]The fitting procedure used the isotropic shift, as determined from a MAS spectrum 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 $\kappa = 3*(\delta_{iso} - \delta_{22})/\Omega$.

Lead White

The ^{207}Pb spectrum of lead white, basic lead carbonate, was obtained with the WURST-CPMG experiment. (Figure 1) Only one lead species is observed under the current experimental conditions. The crystal structure of lead white shows layers of lead hydroxide and lead carbonate [19]. A fit to the spectrum in Figure 1 is consistent with the tensor of lead carbonate (Table 1) [16], and agrees with previous results by Verhoeven *et al*.[20]

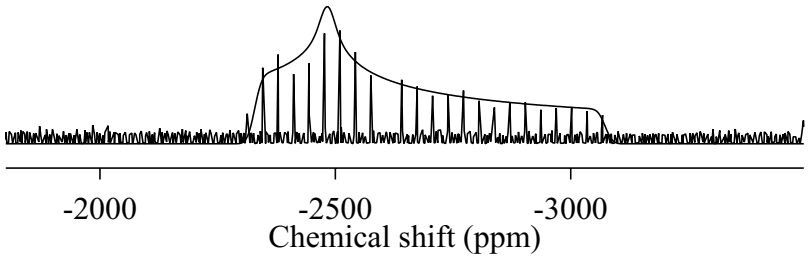

Figure 1. ^{207}Pb WURST-CPMG spectrum of lead white. The spectrum of lead white is overlaid with the tensor of lead carbonate as reported by Neue *et al.* [16]

Depending on how lead white is prepared, there usually is a residual amount of lead carbonate present [21]. To test if the observed signal is from the lead carbonate layers in lead white or a lead carbonate impurity, we mixed a known of amount of lead nitrate (5%) with lead white and with lead carbonate (95%). As shown in Figure 2, using the tensors of lead carbonate and lead nitrate, the fit for the lead white: lead nitrate mixture is 1:1 and lead carbonate: lead nitrate is 95:5. Thus, the lead species observed under our current experimental conditions is a lead carbonate impurity in lead white. The spectra of the lead species in lead white could be very broad, the T_1 could be very long compared to the recycle delay, or T_2 could be very short (which

would interfere with the refocusing of the WURST-CPMG experiment), causing one not to detect the resonance of lead in this phase.

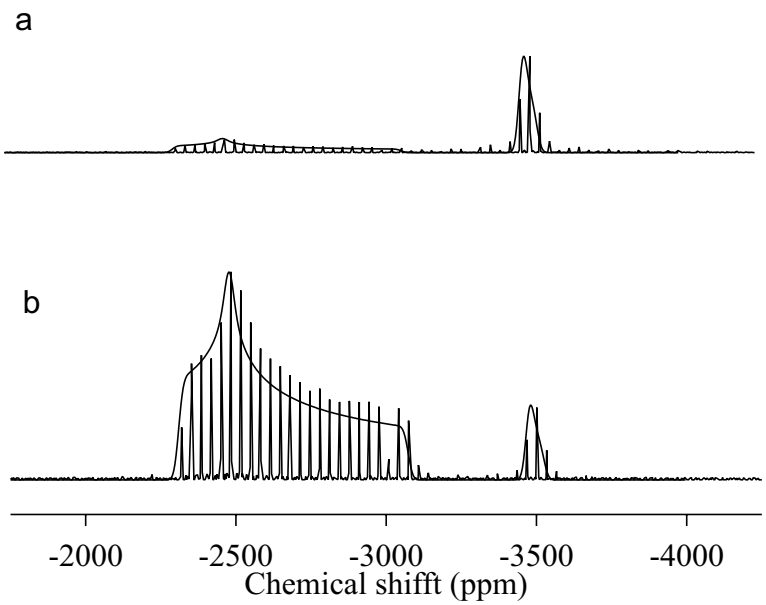

Figure 2. ^{207}Pb WURST-CPMG spectra of 5% lead nitrate in 95% (a) lead white or (b) lead carbonate. The fit of spectrum (a) has an area ratio of 1:1, whereas the fit of spectrum (b) has an area ratio of 95:5. These spectra demonstrate that, in the spectrum of lead white, only the lead carbonate impurity is observed.

Lead-Tin Yellow Type I

The ^{207}Pb spectrum of lead-tin yellow type I obtained with the WURST-CPMG sequence shows three lead species. A preliminary fit is shown in Figure 3. The fit consists of the overlap of the spectra of three lead species, two having similar chemical-shift tensors. The crystal structure [22] shows two lead species with similar coordination environments. The third lead species is a minor impurity. The lead chemical-shift parameters are consistent with the presence of lead titanate, and X-ray fluorescence shows the presence of titanium. Future DFT calculations based on the crystal structure of lead-tin yellow type I will be used to refine the tensor components of the two main species.

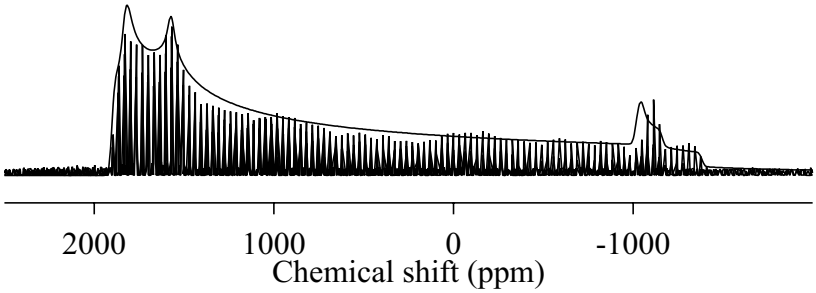

Figure 3. ^{207}Pb WURST-CPMG spectrum of lead-tin yellow type I. The spectrum is an overlay of four subspectra with a preliminary fit of the sum of three tensors.

Mixtures

^{207}Pb spectra of samples containing known amounts of lead white and lead palmitate (Figure 4), verify that one can distinguish these components in a mixture. The fits of the spectra to sums of two species with the known tensors are consistent with the assumption that only the lead carbonate impurity in lead white is detected. As shown in Figure 4c, we can observe 1% lead palmitate in a mixture under our current experimental conditions with a total data acquisition time of 24 hours, which sets the lower detection limit for this experiment. This fact is important when considering smaller sample sizes or more complex mixtures, where there is a smaller percentage of lead palmitate present. Because lead palmitate and lead stearate behave similarly, we expect the same to be true for lead stearate. However, under the same experimental conditions 1% lead azelate is not observed, as the tensor is broader and longer experiment time is needed to obtain an acceptable spectrum.

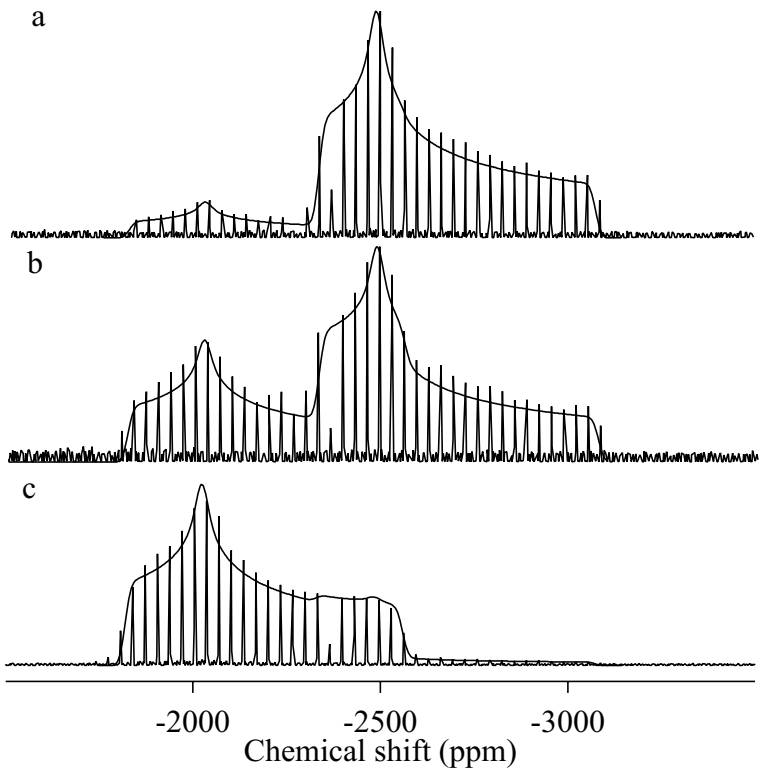

Figure 4. ^{207}Pb WURST-CPMG spectra of mixtures of lead white with lead palmitate; weight ratios of (a) 99:1, (b) 95:5, (c) 50:50. Spectrum (a) shows that 1% lead palmitate is observable under our current experimental conditions. The area ratios in these spectra only reflect the amount of lead palmitate relative to the lead carbonate impurity in lead white.

CONCLUSIONS

NMR chemical-shift tensor analysis of lead-containing pigments and lead carboxylates, known to be involved in soap formation, allows identification and quantification of the lead-containing components of a paint mixture. WURST-CPMG experiments enable shorter total experiment time than STA/MAS experiments, which is helpful when components are present in

low quantities. This study shows the usefulness of ^{207}Pb NMR for characterizing paint samples and other lead-containing materials.

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