Characterization of metal carboxylates relevant for degradation of oil paintings by complementary XRPD and ssNMR

Ruslan Barannikov[1,2], Silvie Švarcová[1], Eva Kočí[1], Petr Bezdička[1], Libor Kobera[3], Jan Rohlíček[4], Jiří Plocek[1]

[1]Institute of Inorganic Chemistry of the Czech Academy of Sciences, ALMA Laboratory, Husinec-Řež 1001, 250 68 Husinec-Řež, Czech Republic,
[2]Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030/8, 128 43 Prague 2, Czech Republic,
[3]Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovského nám. 2, 162 06 Praha 6, Czech Republic,
[4]Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 182 21 Praha 8, Czech Republic.

ruslan-kz94@mail.ru

Saponification occurring in paint layers represents a serious degradation process affecting the appearance and stability of paintings, leading for example to protrusions, efflorescence, darkening, delamination, exudates etc. A substantial part of saponification is formation of metal carboxylates, resulting from the interaction between metal cations (e.g., Pb^{2+}, Zn^{2+}) released from pigment particles (e.g., lead white, red lead, zinc white) with fatty acids (usually palmitic and/or stearic) released from triglycerides making-up oil-based binders. Metal carboxylates can adopt variable structures from ionomers to amorphous complexes to crystalline phases, and up to now the mechanism of their crystallization is not elucidated. Moreover, crystal structures of most metal carboxylates are not determined. This paucity complicates the study of the degradation process and clarifying of factors promoting or inhibiting the saponification. However, without knowledge of degradation mechanism it is impossible to find a suitable strategy to prevent it.

Within the study of miniature paintings by combination of non-destructive spectroscopic and diffraction techniques (X-ray fluorescence, infrared spectroscopy and X-ray powder diffraction), unusual patterns of crystalline metal carboxylates together with the red pigment cinnabar (HgS) were detected Fig.1 [1], indicating the possible effect of the cinnabar on the formation of these carboxylates.

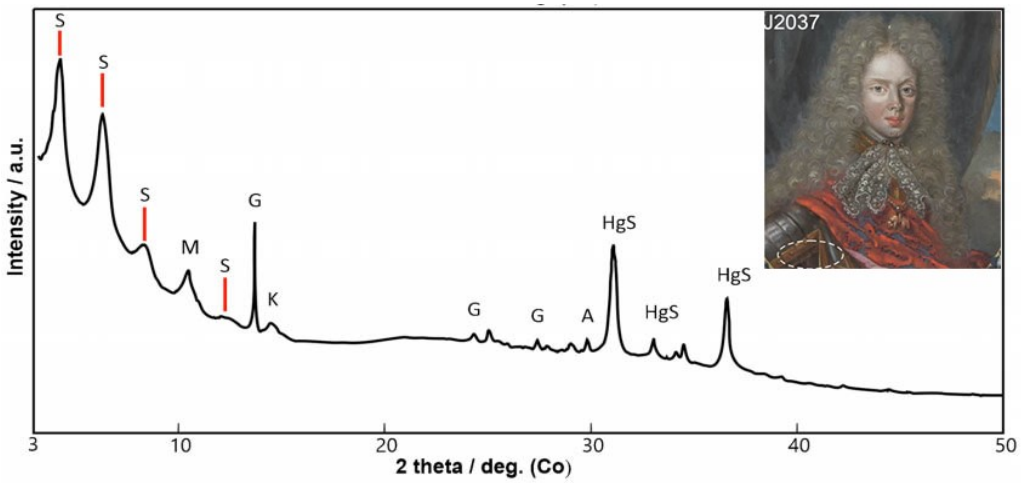

Figure 1. Part of diffraction patterns of the miniature portrait J2037 with the best evidence of all important lines of metal soaps in low angle region (S lead soaps, H hydrocerussite, K kaolinite, HgS cinnabar, G gypsum, M mica, A anhydrite)

The necessity to identify metal soaps found in the paintings and to understand their formation, the synthesis of mixed mercury carboxylates was carried out. The composition of the mercury carboxylates corresponds to the formula $Hg(C16)_x(C18)_{2-x}$ (where C16 is a palmitic acid and C18 is a stearic acid, x from 0 to 2,0 with 0,1 increments). The synthesized compounds serve as reference materials for the study of the degradation processes performed on model the paint layers. The synthesized carboxylates of the formula were investigated by X-Ray powder diffraction (XPRD), Fourier-transform infrared spectroscopy (FTIR) and ultra-wideline solid state nuclear magnetic resonance spectroscopy (ssNMR).

The structural model of selected prepared mercury carboxylates was described from the refinement of the obtained XRPD data complemented by DFT calculations from obtained ssNMR spectra. Previously reported data for lead palmitate-stearate was used as a

reference [2]. We revealed that both hexadecanoate (C16) and octadecanoate (C18) chains are present in one crystal structure, creating the statistical disorder at the ethyl end of the chains.

[1] Garrappa, S., Hradil, D., Hradilová, J. et al. Non-invasive identification of lead soaps in painted miniatures. Anal Bioanal Chem 413, 263–278 (2021). https://doi.org/10.1007/s00216-020-02998-7

[2] Kočí E, Rohlíček J, Kobera L. et al. Mixed lead carboxylates relevant to soap formation in oil and tempera paintings: the study of the crystal structure by complementary XRPD and ssNMR. Dalt Trans. 2019; 48:12531–40. https://doi.org/10.1039/C9DT02040C

Keywords: mercury carboxylates; lead carboxylates; metal soaps; saponification; XRPD; ssNMR; FTIR

The study was supported by the Czech Academy of Sciences in the frame of the programme Strategy AV21 no. 23 - City as a Laboratory of Change; Historical Heritage and Place for Safe and Quality Life