MS43 Crystallography for cultural heritage materials

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Metal carboxylates in paintings – the study of their structure and behaviour

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Abstract

Saponification, resulting from pigment-binder interactions is one of the most dangerous degradation phenomena affecting the appearance and stability of paintings. The crystallization of metal carboxylates (soaps) is assumed as a critical point for the development of undesirable changes manifested as protrusions, efflorescence, darkening and etc. However, factors triggering this process are not fully understood, limiting the development of a suitable strategy for conservation and preservation of precious works of art.

Previous research of the portrait miniatures[1] has revealed presence of different types of crystalline metal carboxylates frequently in a conjoined occurrence of lead white ($2PbCO_3 \cdot Pb(OH)_2$) and cinnabar (HgS) pigments in paint layers, exceptionally even without presence of any lead-based pigment (Fig. 1). These findings indicated that HgS assists to the formation of Pb and/or Hg carboxylates. Nevertheless, its role in the reaction mechanism has to be clarified.

The paucity of reliable reference structural data limited the experimental research of HgS effect on the pigment-binder interactions on molecular level. In our previous research[2], the long chain simple and mixed mercury (II) carboxylates in the series $Hg(C16)_x(C18)_{2-x}$ (x= 0.0; 0.2; 0.5; 0.8; 1.0; 1.2; 1.5; 1.8; 2.0) were synthesized in the form of pure polycrystalline powders and characterized by XRPD, ssNMR, FTIR and DSC. The crystal structure of the studied mercury carboxylates was described on the basis of complementary ssNMR and XRPD measurements, Rietveld refinement and DFT calculations. All the subjected compounds crystallize in a monoclinic lattice of the C2/c symmetry. Mercury atoms are arranged in a slightly distorted square antiprismatic geometry and are monodentatically bonded to carboxylate anions. The structural disorder at the aliphatic end of the stearic acid chains was detected in the mixed carboxylates.

The synthesized and characterized metal carboxylates have been applied for the study of formation of metal soaps in model experiments simulating egg and/or oil-based paint systems consisted of lead and/or mercury-based pigments, and furthermore for the study of their crystallization in oil-based polymeric matrix.

References

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2. R. Barannikov, E. Kočí, P. Bezdička, et. al. Dalton Trans., 2022, 51, 4019–4032.

Miniature portrait of Emperor Joseph I of Habsburg