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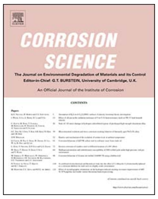

Characterization of a new efflorescence salt on calcareous historic objects stored in wood cabinets: $Ca_2(CH_3COO)(HCOO)(NO_3)_2{\cdot}4H_2O$

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ABSTRACT

White efflorescence crystals grown on the surfaces of a bronze bowl, classical ceramic and ancient wine jugs were investigated. X-ray powder diffraction (XRPD) revealed that in each case an identical, hitherto unknown phase was formed. The crystal structure was solved from high resolution XRPD measurements and revealed a phase composition of $Ca_2(CH_3COO)(HCOO)(NO_3)_2{\cdot}4H_2O$, which is in accordance with the complementary analysis. The overall structural motif of $Ca_2(CH_3COO)(HCOO)(NO_3)_2{\cdot}4H_2O$, one dimensional calcium carboxylate zig zag chains in which acetate and formate ions are arranged in an alternating fashion, is closely related to other naturally occurring or artificial efflorescence salts like thecotrichite or calclacite.

1. Introduction

Wood, especially oak, emits some formic and acetic acid the latter being ester bound in the wood polyoses ("hemicellulose"). In situations with limited air exchange as in cupboards or drawers, typically hundred to thousand ppb can be measured [1]. These pollutants may cause damage on sensitive artefacts stored for long time in them under such conditions. Acetate containing efflorescence on calcareous natural history specimen like shells ("Byne's disease") has already been reported end of the 19th century [2]. Calcium acetates, often exhibiting needle like shape, have also been detected occurring on ceramics. During soil logging, calcareous accretions may be deposited on ceramics. Whether calcium from the ceramic body itself can also be mobilized to form calcium acetates has not been thoroughly studied yet, at least some clays are rich in calcium and are used for yellow wares. On fossils and limestone stored in wooden museum cases, on pottery sherds [3] including classical ceramics from the Agora of Athens stored in oak drawers and cabinets [4], calcium acetate hemihydrate and calclacite ($Ca(CH_3COO)Cl{\cdot}5H_2O$) have been detected in efflorescence. The pattern of calclacite could be indexed with a monoclinic unit cell [3],[5] and it's crystal structure was already solved in 1972 [6]. The chloride was attributed to the former practice of cleaning the ceramic sherds from the calcareous accretions with hydrochloric acid and directly drying them without prior soaking with water. This must have left considerable amounts of calcium chloride in the porous ceramic body. Especially on tiles which can take up migrating soluble salts from walls thecotrichite, a compound also containing nitrate, was detected [7]. Its exact formula, $Ca_3(CH_3COO)_3Cl(NO_3)_2{\cdot}6H_2O$, and its crystal structure have recently been determined [8].

The chemistry and the crystallography of calcium acetate and formate salts are rather complex, as for anhydrous calcium formate four distinct polymorphs [19],10] and for anhydrous calcium acetate three distinct polymorphs [11] are known. Crystal structures of calcium acetate formates are unknown so far although they are reported from molluscs in oak cabinets [12]. A pronounced polymorphism was also observed for calcium acetate monohydrate. Different polymorphs can be obtained when the phase is crystallized in pure water [13], water ethanol mixtures [14] or in presence of organic admixtures [15]. Calcium acetate hemihydrate ($Ca(CH_3COO)_2{\cdot}0{\cdot}5H_2O$) was identified as an efflorescence product as well [4] but it's crystal structure remains still unknown. This phase occurs as an intermediary product of the thermal decomposition of calcium acetate monohydrate [16]. In aqueous solution the monohydrate phase was found to be thermodynamically stable [17]. The occurrence of the hemihydrate phase as an efflorescence product can be understood from the relative humidity (rH)-temperature diagram for the calcium acetate phases [4]. At room temperature, the monohydrate transforms to the hemihydrate below 71% rH. The systems $Ca(CH_3COO)_2$-$CaCl_2$-H_2O and $Ca(CH_3COO)$-$Ca(NO_3)_2$-H_2O have been studied systematically in order to find a thermodynamic explanation for the formation of calclacite and thecotrichte [14],18]. At 25 °C calclacite was found to crystallize in (3–7) m $CaCl_2$ solutions with a calcium acetate concentration from 0.1 to 1.4 mol/ kg (H_2O). The investigation on the system $Ca(CH_3COO)_2$-$Ca(NO_3)$-H_2O resulted in the discovery and characterization of an additional, artificial efflorescence

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Table 1
Overview on investigated corrosion samples.

Sample notation	Sample Description	Source
Sample 52273	white efflorescence crystals grown on an Anatolian copper alloy bowl	Rautenstrauch-Joest-Museum Cologne
Sample SH-1413	white efflorescence crystals grown on a black figured Attic amphora, bought in 1831 by Ludwig I. of Bavaria from the Candelori collection	Antikensammlung Munich
Sample PC25	white efflorescence crystals grown on black-figured Attic wine jugs (*oinochoai*), ca. 500 BCEE	Prince of Canino Collection, in the National Museum of Antiquities Leiden (NL)
Sample PC26		

salt $Ca_2(CH_3COO)_3NO_3{\cdot}2H_2O$ [19]. Despite their occurrence as efflorescence, the system calcium acetate-calcium formate lacks a systematic study.

As needle like, white efflorescence crystals can be visually easily mistaken for thecotrichite or calclacite, calcareous efflorescence were sampled in natural history and historic collections in the framework of the RaCoPhInO ("Rare Corrosion Phenomena of Inorganic Objects") research in the Objects' Conservation program of the State Academy of Art and Design Stuttgart. In four cases the same unknown compound was detected by X-ray powder diffraction (XRPD). One of the samples was evaluated to contain the new efflorescence phase without any impurities and used for a detailed characterization. As no suitable crystal for single crystal diffraction was found, the crystal structure was solved from XRPD measurements.

2. Materials and methods

2.1. Sample collection

Four samples of white efflorescence crystal were collected from four different objects, which were stored in three different museums (Table 1) under different conditions (relative humidity, temperature, furniture, etc.). The first object investigated here is an Anatolian copper alloy bowl from the Rautenstrauch-Joest-Museum Cologne bought from an antiquities trader in the bazaar of Istanbul and a few hundred years old. On the surface of the bowl turquoise coloured sections attributed to corrosion of the bronze material can be found besides white efflorescence crystals having a needle like shape (Fig. 1). Needle like white efflorescence crystals were found on the inner and outer side of an Attic black figured amphora depicting a bridal and a warrior procession of the Antikensammlung Munich (Fig. 2), excavated near Vulci (Italy) and bought in 1831 on behalf of Ludwig I. of Bavaria from the Candelori Collection. Two black figured Attic wine jugs [20], ca. 500 BCE (Fig. 3) from the National Museum of Antiquities Leiden also exhibit white efflorescence crystals.

Fig. 1. Anatolian copper alloy bowl (Rautenstrauch-Joest-Museum Cologne) with white efflorescence crystals (magenta highlighted areas). ©Anke Freud.

2.2. Phase characterization

2.2.1. SEM-EDX analysis

The white efflorescence crystals of samples 52273 and SH-1413 (Table 1) were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) using a Zeiss EVO 60 microprobe and an accelerating Voltage of 20 kV. For the micrographs, the samples have been sputtered with carbon.

2.2.2. Ion chromatography

The sample 52273 (Table 1) was analysed using a protocol developed for the analysis of soluble salts occurring on the surface of historic glasses, for experimental details see [21].

2.2.3. Raman-spectroscopy

μ-Raman spectroscopy of samples 52773 and SH-1413 (Table 1) was conducted using a Renishaw inVia Raman spectrometer with a Leica DMLM microscope and a RenCam CCD detector. The spectrometer was equipped with a He-Ne laser operating at 632.8 nm, with power kept below 400 μW on the sample surface.

2.2.4. Thermal analysis

Thermal analysis was carried out on sample SH-1413 (Table 1) using a STA 449 F5-Jupiter (Netzsch) device for TG-measurements. 2.3 mg of the sample were placed in an Al_2O_3 crucible and heated up from 30 °C to 1000 °C with a heating rate of 2 K/min in a 50 mL/min Ar-stream. An empty Al_2O_3 crucible was used as reference material. After cooling down to room temperature in an Ar-stream, the residue of the thermal decomposition was immediately transferred into a capillary, that was sealed and analysed by ex-situ X-ray powder diffraction (see below).

2.2.5. Laboratory X-ray powder diffraction

The XRPD patterns of all solids used for quantitative phase analysis and crystal structure solution were collected at room temperature on a laboratory powder diffractometer in Debye-Scherrer geometry (Stadi P-Diffraktometer (Stoe), Cu-Kα1 radiation from primary Ge(111)-Johann-type monochromator, Mythen 1 K detector (Dectris)). The samples were sealed in 0.3 mm diameter borosilicate glass capillaries (Hilgenberg glass No. 14), which were spun during the measurements. Each pattern was measured in a 2 θ range from 5.0° to 90.5° applying a total scan time of 14 h and 17 min.

2.2.6. In- and ex-situ X-ray powder diffraction

Temperature dependent *in situ* XRPD measurements were carried out on a laboratory powder diffractometer in Debye-Scherrer geometry (Stadi P-Diffraktometer (Stoe), Mo-Kα1 radiation from primary Ge (111)-Johann-type monochromator, array of 3 Mythen 2 K detectors (Dectris)) using sample SH-1413 (Table 1). The sample was sealed in a 0.3 mm diameter borosilicate glass capillary (Hilgenberg glass No. 14), which was spun during the measurements. The patterns were measured in a 2 θ range from 2.0° to 115.0° applying a total scan time of 30 min per measurement. The temperature was adjusted using an Oxford Cryostream device (Oxford Cryostream 500, Oxford Cryosystems). The sample was heated form 30 °C to 220 °C in steps of 5 K. During each step