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Crystal structure of two new carboxylamidophosphates
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In recent years, carboxylamidophosphates with the C(O)NHP(O) skeleton have attracted much attention due to their properties as prodrugs [1,2], ureas inhibitors [3], and efficient ligands in coordination chemistry either as O-donor or O,O’-donor ligand [4,5]. In earlier works we considered the structural properties of some of these molecules with formula C(H)CONHP(O)R. To further investigate this area, here we have synthesized two new compounds with general formula C(H)CONHP(O)R. R= 2-CICH2CH(NH)H (1) and C6H5(NH)2 (2) and present their X-ray crystal structures.

Colorless crystals of 1 and 2 were obtained from a concentrated chloroform solution at room temperature. The compounds 1 and 2 crystallize in the triclinic and Orthorhombic space groups P-1 and Pn21 respectively. In the structure of compounds 1 and 2, as in the most carboxylamidophosphates [6], the carbonyl and phosphonyl groups are in anti-positions to each other, and the bond lengths (1.226(2) and 1.4797(13) Å in 1; 1.219(5) and 1.478(3) Å in 2 respectively) fall within the norms for these linkages. The dihedral angles between the PO double bond and the N–C amidic bond are -166.04(15) and 180° in 1 and 2 respectively. The phosphorus atoms have a slightly distorted tetrahedral configuration with angles in the range of 101.18(10)–119.75(8)° in 1 and 102.50(16)–119.75(8)° in 2. As expected, the P–Namide bond length (namide) the nitrogen atom of P(O)N(H)(C=O) moiety is longer than the P–Namide distances (Namide the nitrogen atom of P(O)NH2 moiety) and the C–Namide bond is shorter than the C–Namide bond lengths (1.374(2) Å for C–Namide versus 1.453(2) and 1.469(2) Å for C–Namide bonds in 1). All of the P–N bonds in 1 and 2 are shorter than the typical P–N single bond length (1.77 Å) [7]. This is likely due to the electrostatic effects which overlap with P–N bond.

The two molecules in the unit cell of 1 are coupled into centro symmetric dimers by two H-bonds between the phosphate oxygen atoms and the hydrogen atoms of the amidic groups forming an eight-membered cycle. The observed hydrogen bonding pattern is due to the overlap of P–N σ bond.

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X-ray fluorescence imaging of ancient artifacts
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Synchrotron-based X-ray fluorescence imaging (XRFI) is a powerful tool for examining archeological artifacts. Many artifacts have been damaged by weathering and other processes, often to the point where letters or figures have become difficult or impossible to see by visual or topographic inspection. XRFI allows imaging of elemental concentrations, and can detect minute remaining traces of elements arising from paints, pigments and tool wear associated with the original pattern. Since X-rays penetrate a significant distance beneath the surface, XRFI can see through overlayers of paint and debris and can detect elements that have soaked or diffused into stone substrates.

We have imaged a large number of ancient Greek and Roman inscriptions on stone [1] and a variety of Mayan artifacts. Element maps have revealed significant new information, including letters outlined by traces of iron from tools and lead from pigments, and painted designs which were previously invisible due to overpainted layers. They have also proved useful in establishing inscription provenance [2]. Opportunities and challenges in applying XRFI to ancient artifacts will be discussed.

Keywords: crystal structure, carboxylamidophosphate, hydrogen bond

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Opacity in mosaic glass: crystals make technological history
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Opaque glass represents the first record of glass production at the end of the second millennium AD in Mesopotamian region. The opacity of glass, in most of the cases, is given by the presence of crystalline phases dispersed in the glass matrix. The crystal phases used as opacifiers changed across the centuries and different compounds were used to obtain the opaque effect and the desired nuances. Antimony-based opacifiers (lead antimonate yellow and calcium antimonate white)
were used from the beginnings of glass production through into the Roman period for the opacification of green, blue and white samples. Subsequently, they started to be replaced by tin-based opacifiers during the fourth century AD in glass produced from the eastern Mediterranean through into northern Europe. For the production of red and orange samples, it seems that across the centuries only Cu-based opacifiers were used.

In this work, the opacifiers identified in a series of mosaic tesserae coming from Mediterranean region and dated from the 6th to the 11th century are compared and employed to sketch the glass technology evolution on a chronological and geographical base. The coupling of the chemical data with the SEM-EDS and XRD investigations allows the identification of the opacifiers employed in the glass production.

In particular, the data relative to San Severo Basilica (VI century AD, Classe– Ravenna–Italy), represent an useful tool to understand the shift from Sb to Sn bearing opacifiers. The sample set coming from this site presents a peculiar characteristic: all the blue samples, colored mainly with copper, are lead and tin free and are opacified with calcium antimonates, on the contrary all the green samples are antimony-free and contain high levels of lead and rather high levels of tin.

On the whole, San Severo samples fit with the chemical composition of the coeval mosaic tesserae. The co-presence of Sb-based opacifiers and of tin bearing samples in the sample set, represent a rather peculiar trait, but, it is well known that in Italy, the tin based opacifiers have been found from the fifth century AD onwards, but at the same time, antimony-based opacifiers continued to be used, or reused, until the 13th century AD.

The simplified pattern of Sb and Sn bearing opacifiers is then complicated in some areas of the Mediterranean glass production by the occurrence of quartz crystals dispersed in the glass matrix. The study of the opacifiers could be an indirect method for dating and provenancing the mosaic glass.

Keywords: Sb based opacifiers, Sn based opacifiers, mosaic tesserae

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Spectroscopic study of chromophores in ancient HIMT glass
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We have studied a series of Late Roman glass fragments belonging to the peculiar group called HIMT (High Iron Magnesium Titanium glass), characterized by different color nuances, and previously chemically characterized [1-3]. XANES, UV-VIS and luminescence spectroscopies [4-6] are exploited for determining the distribution of the oxidation states of the two chromophores Fe and Mn in the ancient finds and in two synthetic glass specifically prepared with selected chemically compositions.

Fe and Mn K-edge XANES spectra were collected in fluorescence mode at the GILDA-CRG beamline (ESRF, Grenoble, France). A dynamically and sagittally focussing monochromator with Si (311) crystals was used. Energy calibrations were achieved using Fe and Mn foils as references and the position of the first inflection point was taken at 7112.0 and 6538.0 eV respectively. The pre-edge region was extracted from the normalized spectra and analysed by least-square fitting of pseudo-Voigt functions of equal width to the pre-edge spectral envelope. For each sample, the pre-edge centroid was calculated from the average position of the pseudo-Voigt functions, weighted by their respective integrated areas. UV-VIS absorption spectra were measured on a Varian Cary 100 double-beam spectrophotometer operated between 900 and 200 nm. Luminescence emission and excitation spectra were collected in a Spex Jobin-Yvon Fluoromax3 spectrophotometer.

On the basis of both XANES and UV-VIS results, in all the ancient glass samples Fe results to be mostly in its oxidate state 3+. XANES data indicate that the prevalent Mn oxidation state is 2+, however the presence of minor amounts of Mn3+ has been proved by UV-VIS and luminescence spectroscopy. The different spectroscopic techniques, used in a combined approach, are able to interpret the apparent anomalous colour of some of the ancient glass samples.

Keywords: μ-XRF, ancient Thai pottery, Au Thong

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μ-XRF study on unearthed ancient pottery at Au Thong, Thailand
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Pottery has been produced in Thailand for thousands of years. In this work, unearthed potsherds examined come from the Au Thong prehistorical site, Suphan Buri Province, Central Thailand. A multi-analytical approach was carried out on the same sample to reduce the sampling, including petrographic, mineralogical and chemical investigations by mean of micro-beam X-ray fluorescence (μ-XRF), optical microscope, scanning electron microscope coupled with energy dispersive X-ray fluorescence spectroscopy (SEM-EDS) and Particle induced X-ray emission spectroscopy (PIXE). X-ray diffractometry (XRD) analysis was also performed to confirm the presence of clay minerals. The composition analysis showed the heterogeneous matrices which were commonly associated with high concentrations of elements such as Ca, Fe, Al or Ti that used to be the pottery characterization.

Keywords: μ-XRF, ancient Thai pottery, Au Thong