



## Spectroscopic and structural investigation of oxocarbon salts with tetraalkylammonium ions



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### ABSTRACT

In this study the synthesis, vibrational spectra (infrared and Raman) and crystal structures of three oxocarbon compounds with tetra-alkyl ammonium counter cations, namely  $[\text{N}(\text{C}_3\text{H}_7)_4](\text{HC}_4\text{O}_4)$  (**1**),  $[\text{N}(\text{C}_4\text{H}_9)_4]_2[(\text{C}_4\text{O}_4)(\text{H}_2\text{C}_4\text{O}_4)_2]$  (**2**) and  $[\text{N}(\text{C}_2\text{H}_5)_4]_2(\text{C}_5\text{O}_5) \cdot 5\text{H}_2\text{O}$  (**3**), have been reported. The supramolecular arrangement for all compounds as shown by x-ray diffraction indicate that strong donor (D)–acceptor (A) hydrogen bonds  $\text{D} \cdots \text{H} \cdots \text{A}$  are present in the dimer formation with monohydrogen squarate anion  $\text{HC}_4\text{O}_4^{2-}$  (2.503 Å) and for the trimer with two squaric acid moieties ( $\text{H}_2\text{C}_4\text{O}_4$ ) and the squarate dianion  $\text{C}_4\text{O}_4^{2-}$  (2.500 Å), for compounds **1** and **2**, respectively. In contrast, compound **3** was stabilized through only averagely strong hydrogen bonds (2.735 Å) between all five oxygen atoms of the croconate dianion with different water molecules of crystallization of the supramolecular system. The presence of bands in the Raman spectrum at 1793 and 1670  $\text{cm}^{-1}$  for compounds **1** and **2** have been assigned to the  $\nu(\text{C}=\text{O})$ ,  $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{O})$  modes, thus confirming the oxocarbon presence in the solid structure, as well as the bands at 1716 and 1601  $\text{cm}^{-1}$  for compound **3**, assigned to the  $\nu(\text{C}=\text{O})$  and  $\nu(\text{CO}) + \nu(\text{CC}) + \delta(\text{CCC}) + \delta(\text{CO})$  coupled modes of the associated croconate dianion ( $\text{C}_5\text{O}_5^{2-}$ ). An important Raman signal observed for all structures can be seen at ca. 2950  $\text{cm}^{-1}$  which is associated with the  $\nu(\text{CH}_2)$  and  $\nu(\text{CH}_3)$  stretching modes from the tetraalkylammonium cations.

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### 1. Introduction

Studies of noncovalent interactions, which include hydrogen bonding,  $\pi$ -stacking and electrostatic interactions has been an interesting focus at many frontiers in modern chemistry [1,2]. Among these, hydrogen bonding has attracted much attention because of its importance for the solid state structures adopted by many well-known chemical and biological systems [3,4].

In supramolecular chemistry, the understanding of such weak interactions plays a fundamental role in the construction of complicated extended arrays of structural self-organized systems. Supramolecular studies of the intermolecular interactions resulting from the association of different chemical entities which give rise to compounds with a wide range of catalytic, magnetic, optic, biological, microporous and electronic applications [5–7] are vital for

the understanding of these properties. In this context, there has been interest in the recent literature in the study of different supramolecular building blocks that can provide these physical characteristics; among the candidates oxocarbons and pseudo-oxocarbons are ideal building blocks for the construction of ordered organic intermolecular structures based on hydrogen bond and  $\pi$ -stacking networks [8,9].

Dianionic oxocarbons are cyclic building blocks of the general formula  $(\text{C}_n\text{O}_n)^{2-}$ , where  $n = 3, 4, 5$  and 6 for deltate, squarate, croconate and rhodizonate, respectively. This class of compounds has received much attention from the spectroscopic point of view because of their high electronic delocalization and molecular planarity from which some intriguing supramolecular structural arrangements have been observed [10–13]. In the field of materials chemistry an example is provided by the work of Kikuchi et al. [14], who studied anodic porous alumina using different acid solutions of oxocarbons for applications in memory devices, diodes, sensors and nanocontainers.

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Extensive synthetic work has been carried out hitherto in our group involving oxocarbon and pseudo-oxocarbon ions with tetraalkylammonium counter cations, for example the study of Ribeiro and coworkers [15] on the spectroscopic properties of tetrabutylammonium croconate and squarate compounds in the low frequency region associated with their high viscosity/temperature dependence and glass transition temperature to evaluate the molecular dynamics in such systems. Teles and coworkers [16] have more recently investigated the solid state properties (structural and vibrational) of tetrabutylammonium 3,5-bis (dicyanomethylene) cyclopentane-1,2,4-trionate (containing the croconate violet anion); these authors have called attention to the observed vibrational characteristics of different croconate violet salts, with potassium and tetrabutylammonium counter ions, based upon the lowering of the electrostatic interaction between the pseudo-oxocarbon ion and the counter cations. In another investigation, the same conclusions were achieved by de Oliveira and coworkers [17] who investigated the formation and bonding of tetrabutylammonium cations with the pseudo-oxocarbon bis(dicyanomethylene) squarate ion in the *cis* and *trans* forms using vibrational spectroscopic data. In these studies, the wavenumber shift of the  $\nu(\text{CN})$  stretching mode in several alkaline and tetrabutylammonium salts was seen to be indicative of the strong interaction between the cations and anions. In a more recent study involving these species performed by Pigot and coworkers [18] a secondary product of the synthesis was identified as a crystalline material containing the tetrabutylammonium cation and squaric acid in both anionic and acid forms, leading to the formation of a supramolecular trimer where hydrogen bonds between two squaric acid and one squarate anion species can be identified.

This investigation presents the synthesis, spectroscopic and structural characterization of the organic crystalline arrays obtained from the interaction between squarate and croconate oxocarbon ions with tetrabutylammonium, tetrapropylammonium and tetraethylammonium cations which are all bulky ions involved in studies where there the cations are required to possess a large volume [17]. The ideal structural arrangement in the solid state for cyclic species with delocalized electrons is defined by the stacking of the oxocarbon moieties [20]. In contrast, the large volume of the counter cationic species can promote a weaker electrostatic interaction between the anionic species. It is well known that the weak electrostatic interaction of the tetraalkylammonium cations makes these salts appropriate for investigating anions in different systems [21–27]; in this sense, because of the weak electrostatic interaction of the tetraalkylammonium cation with the anion the vibrational information of the anions in the solid state facilitates a comparison with the spectra of the anions in several different solutions. With support of single crystal diffraction data for the identification of the molecular species present in tetraalkylammonium salts the characteristic vibrational spectra of the anionic species in the tetraalkylammonium salts can be used to monitor the presence of the particular anionic species which occur in different solutions.

Furthermore, the importance of the particular investigation described here consists in the provision of a formal explanation of the stability of these crystalline arrays formed through weak supramolecular interactions which are mainly based on hydrogen bonds as well as determining the electrostatic interactions. Another important focus of this work is centred on the fact that solving the crystalline structure of the tetraalkylammonium salts by X ray diffraction supports the interpretation and understanding of the infrared and Raman spectra of the oxocarbon anions. The chemical environment experienced by the oxocarbon moieties involving very large cations in such crystalline systems is mainly due to the lower electrostatic interactions (when compared with crystalline systems involving smaller cations) and is very close to the

molecular and ionic environments experienced in solutions. This scenario can be confirmed when the infrared and Raman spectra of the anions from tetraalkylammonium salts are obtained and a comparison made with the analogous spectra of the “free” oxocarbon ions in dilute aqueous solution, which is essential for understanding the interactions occurring in different chemical environments [15,16]. Hence the behaviour of the anionic oxocarbon species when structural modifications are occurring as, for example, in the electrostatic interaction between oxocarbon anions and porous alumina [14] and their electrical conductivity in solution [17]. The possibility to obtain this information rapidly and in real time makes vibrational spectroscopy one of the few techniques capable of identifying the presence of different species qualitatively and quantitatively and to monitor the interactions between different chemical species in several systems.

## 2. Experimental section

### 2.1. Chemicals and reagents

All chemicals used in this study were used as purchased without further purification from SIGMA ALDRICH: squaric acid ( $\text{H}_2\text{C}_4\text{O}_4$ , 99.5%), potassium rhodizonate ( $\text{K}_2\text{C}_6\text{O}_6$ , 97.0%), potassium hydroxide (KOH, 85%), silver nitrate ( $\text{AgNO}_3$ , 99.0%), tetraethylammonium chloride ( $\text{C}_8\text{H}_{20}\text{ClN}$ , 98%), tetrapropylammonium chloride ( $\text{C}_{12}\text{H}_{28}\text{ClN}$ , 98%) and tetrabutylammonium chloride ( $\text{C}_{16}\text{H}_{36}\text{ClN}$ , 97%).

### 2.2. Synthesis

The compounds  $[\text{N}(\text{C}_3\text{H}_7)_4](\text{HC}_4\text{O}_4)$  (**1**) and  $[\text{N}(\text{C}_4\text{H}_9)_4]_2[(\text{C}_4\text{O}_4)(\text{H}_2\text{C}_4\text{O}_4)_2]$  (**2**) were synthesized using similar methods as follows. Firstly, 20 mL of an ethanolic solution containing 280 mg (2.45 mmol) of squaric acid was mixed with 10 mL of a solution containing 832 mg (4.90 mmol) of  $\text{AgNO}_3$ , resulting in the formation stoichiometrically of a precipitate of 804 mg (2.45 mmol)  $\text{Ag}_2(\text{C}_4\text{O}_4)$ . To this precipitate was added in complete darkness 20 mL of a solution containing 1088 mg (4.90 mmol) of  $[\text{N}(\text{C}_3\text{H}_7)_4]\text{Cl}$ ; the white precipitate of  $\text{AgCl}$  formed was filtered and discarded leaving a solution containing 1188 mg (2.45 mmol) of  $[\text{N}(\text{C}_3\text{H}_7)_4]_2(\text{C}_4\text{O}_4)$ , the product of interest. After approximately 30 days with the slow evaporation of the solvent, the  $[\text{N}(\text{C}_3\text{H}_7)_4]_2(\text{C}_4\text{O}_4)$  was obtained as a very viscous liquid as previously observed for the croconate of tetrabutylammonium [15]. Finally, to obtain a crystalline product a third stage was necessary in which 10 mL of a 50% (ethanol/water) solution containing 280 mg (2.45 mmol) of squaric acid was added to the product obtained in the above process. After approximately 25 days with complete evaporation of the solvent the formation of a colourless crystalline material was observed with an overall yield of 42% in relation to the tetrapropylammonium cation. Elemental analysis for  $[\text{N}(\text{C}_3\text{H}_7)_4](\text{HC}_4\text{O}_4)$  (**1**) gave: Calc: C, 64.18%; H, 9.76%; N, 4.68%; Found: C, 65.13%; H, 10.02%; N, 4.52%. For the synthesis of compound **2**, 20 mL of a solution containing 1360 mg (4.90 mmol) of  $[\text{N}(\text{C}_4\text{H}_9)_4]\text{Cl}$  was added in the second stage with the resultant formation of a material of high viscosity termed  $[\text{N}(\text{C}_4\text{H}_9)_4]_2\text{Sq}$ . After evaporation of the solvent in the third step, 10 mL of a 50% solution of ethanol/water containing 280 mg (2.45 mmol) of squaric acid was added. Following the slow evaporation of all solvent after 20 days the formation of a colourless crystalline material was observed. The yield was 38% in relation to the tetrabutylammonium cation. Elemental analysis of  $[\text{N}(\text{C}_4\text{H}_9)_4]_2[(\text{C}_4\text{O}_4)(\text{H}_2\text{C}_4\text{O}_4)_2]$  gave (**2**): Calc: C, 64.05%; H, 9.28%; N, 3.40%; Found: C, 66.13%; H, 9.53; N, 3.51%.

For the synthesis of  $[\text{N}(\text{C}_2\text{H}_5)_4]_2(\text{C}_5\text{O}_5) \cdot 5\text{H}_2\text{O}$  (**3**), potassium

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