New Insight on the Investigation of the Role of Water in the Solid-State Structures of Potassium Croconate, $K_2C_5O_5{\cdot}2H_2O$, and Its Anhydrate

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This work presents a comparative study of dihydrated and anhydrous forms of potassium croconate crystals by vibrational spectroscopy, X-ray powder diffraction, and thermogravimetry. These compounds have different colors (dihydrated is orange, and dehydrated is yellow) due to the presence of coordinated water molecules. X-ray diffraction patterns show that the unit cell of the yellow compound is smaller than that of the orange analogue, suggesting that the croconate ion layers are more closely bonded in this salt. The loss of water is reversible due to the potassium cation size which is intermediate between small (Li^+ and Na^+) and large (Rb^+ and Cs^+) alkaline metal ions. However, the hydrated compound (orange) is more stable, and with a small quantity of water the yellow compound is quickly converted to the orange compound. A diagnostic feature of the Raman spectrum for the orange (hydrated) and yellow (anhydrous) analogues is the singlet at 1240 cm^{-1} in the former, assigned to a $\nu(CC) + \delta(CCC) + \nu(CO) + \beta(CO)$ mode of E'_2 symmetry, which splits in the yellow form to a doublet at 1256 and 1232 cm^{-1}.

Introduction

The bottom-up building in a supramolecular chemistry view has provided new interest in some old issues of structural chemistry, since the interactions between molecules and ions are responsible for molecular assembly behavior, connectivity, cohesion, and stability in the solid state, mainly in crystal phases where the higher organization causes the lowering of entropy. Therefore, these interactions have an important role in the collective properties, and they cannot be neglected. In the literature it has been argued that ion interactions are the result of the compromise between the need to achieve maximum packing density and the preservation of weak intermolecular interactions.[1,2] The presence of small molecules able to realize intermolecular interactions is very important for crystal packing and solid designing. Besides the contribution to the stabilization of the crystal structure, they can act to attenuate the Coulombic repulsion strength in systems composed of charged species, which make possible other interactions as, for example, π-stacking. These interactions also allow the building of two- and three-dimensional extended structures, being enabled to give rise to highly compact structures. Likewise, the intermolecular interactions, the presence of solvent molecules linked in the structure, cannot be undervalued since these species are also responsible for filling the crystal arrangement when only the Coulombic strength is not enough to generate stable structures.

The croconate ion ($C_5O_5{}^{-2}$) belongs to the cyclic oxocarbon family with a planar geometry, high molecular symmetry, and an appreciable degree of electronic delocalization; these properties offer considerable potential for applications of croconates as new materials.[3,4] Recently, the potential use as building blocks in crystal engineering of oxocarbon species, in particular, squarate and croconate ions, has been demonstrated and ascribed to several different kinds of chemical and physical interactions possessed by these ions in the solid state, for example, hydrogen bonding and π-stacking, depending on the nature of the other chemical species present in the structure.[5] For example, in the crystal structures of the alkaline croconates described by Braga and co-workers,[6] π-stacking interactions are observed between the oxocarbon rings stabilizing the crystal structures. Additionally, for smaller cations (Li^+, Na^+, and K^+), two water molecules are observed in their structures, and the crystal packing is additionally stabilized by hydrogen bonds between the croconate ions and water molecules.

In recent years we have probed the chemical environments of oxocarbon species through the analysis of their Raman spectra,[7−10] since such species have a small number of vibrational bands which are dependent on the chemical nature of the other species present in the structure. The analysis of the Raman spectra, in conjunction with solid-state crystalline structural information, gives rise to a set of properties that are important in understanding the role of oxocarbons in supramolecular chemistry, as well in the design of novel materials with specific solid-state properties.

In the specific case of potassium croconate, the dihydrate salt was first synthesized as a crystalline orange material by Gmelin in 1825.[11] The crystal structure of $K_2C_5O_5{\cdot}2H_2O$ (see Figure 1) has been determined by Dunitz et al.,[12] who observed strong

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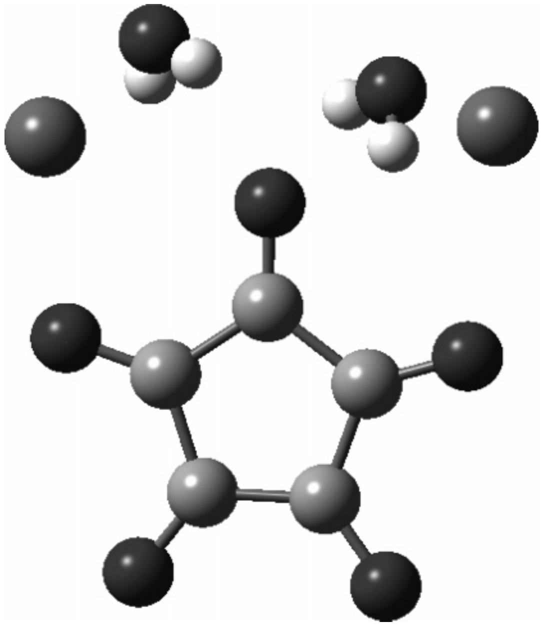

Figure 1. Molecular structure of dihydrated potassium croconate obtained from reference 12.

π-stacking interaction between the anions. The centroid−centroid distance of the π-stacked layers is about 3.34 Å and the croconate ions in adjacent layers are not superimposed, presenting a rotation with respect to each other of about 36°. Each potassium ion interacts with eight oxygen atoms from four different croconate ligands belonging to two separate layers and two water molecules. Each water molecule is hydrogen-bonded to two croconate species in different layers, which generates a strongly anisotropic environment around the potassium ions. However, it is observed that at elevated temperatures or in conditions of low humidity the color of the crystals changes reversibly from orange to yellow; no explanation has been proposed for this phenomenon. In this work, we present a comparative study of both yellow and orange potassium croconate crystals by means of vibrational spectroscopy, X-ray powder diffraction, and thermogravimetry to correlate the observed color changes with structural and molecular interactions. Despite potassium croconate being known since the early 19th century, there has been no investigation of this problem hitherto.

Experimental Section

Potassium croconate dihydrate, $K_2C_5O_5 \cdot 2H_2O$, was synthesized according to the general method described in the literature.[6] The anhydrous compound was obtained by keeping the potassium croconate dihydrate under low pressure and also by warming at 120 °C in atmospheric pressure. The deuterated compound was obtained by successive recrystallizations of the anhydrous sample in D_2O.

Fourier-transform Raman spectroscopy was carried out using a Bruker RFS 100 instrument, an Nd^{3+}/YAG laser operating at 1064 nm in the near-infrared, and a CCD detector cooled with liquid N_2. For the orange sample, a good signal-to-noise ratio was obtained from 512 scans accumulated over a period of about 30 min and 20 mW of laser power, with 1 cm^{-1} as an operating spectral resolution. In the case of yellow croconate, the sample was exchanged after 64 scans; eight spectra were obtained and the average was applied to obtain a better noise-to-signal rate. All spectra were recorded several times to demonstrate reproducibility, and no changes in band positions and relative intensities were observed. Infrared spectra were obtained with a Bomem MB-102 spectrometer fitted with CsI beam splitter, using mineral oil to generate a suspension that was kept between KRS-5 plates, and spectral resolution of 4 cm^{-1} in the 4000−1350 cm^{-1} region. Good signal-to-noise ratios were obtained from an accumulation of 128 spectral scans.

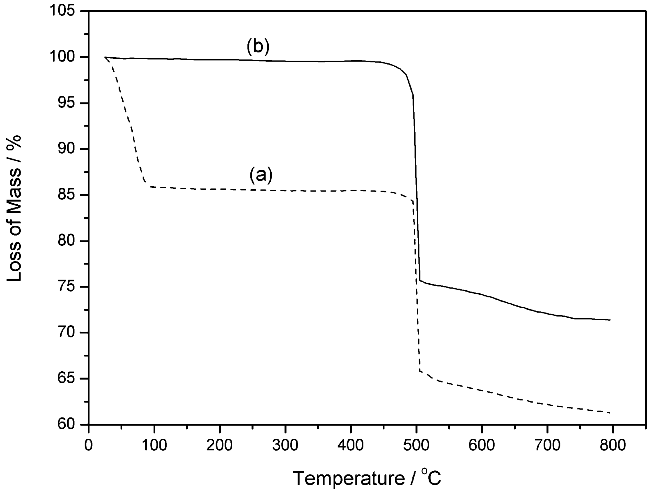

Figure 2. Thermogravimetric curves of (a) orange and (b) yellow compounds.

Powder X-ray diffraction measurements were carried out using a RIGAKU GEIGERFLEX 2037 with a graphite monochromator [0002] and $2d = 6.708$ Å, a NaI scintillation detector, using Cu Kα radiation ($\lambda = 1.541$ Å), and a scan rate of 0.05° s^{-1}.

Thermogravimetric analyses (TG) were obtained on a TG-50 Mettler STARe using a synthetic air atmosphere, a flow rate of 200 mL/min, and a heating rate of 10 °C/min from room temperature to 800 °C.

Results and Discussion

The thermogravimetric experiment (Figure 2) indicates that for the orange compound, $K_2C_5O_5 \cdot 2H_2O$, a continuous mass loss occurs from 25 up to 110 °C, which corresponds to a 14.2% total mass loss consistent with the loss of two molecules of water per formula unit. In contrast, the yellow crystals do not present any mass loss over the same temperature range. From 110 °C the thermal behavior is identical for both compounds, and at 500 °C an abrupt weight loss is observed which corresponds to about 25% of the initial mass of both compounds; this step can be related to the formation of potassium oxalate. Above 500 °C, a gradual weight loss occurs and the final residue (61.3% and 71.5% to hydrated and anhydrous compound, respectively) closes to the presence of potassium carbonate. This result indicates that the difference in thermal behavior between the two compounds is related to the water molecules in the orange material.

The infrared spectra of the two compounds, displayed in Figure 3, are essentially similar except for a broad band centered at 3392 cm^{-1} (two shoulders are also observed at 3527 and 3290 cm^{-1}) assignable to OH stretching modes from the coordinated water in the orange compound. However, the spectral data suggest that infrared spectroscopy is not an appropriate technique for the discrimination between the two compound structures since the molecular vibrational modes of the croconate ligands are too diffuse for analysis. However, in contrast, the Raman spectra of the oxocarbons generally offer well-defined bands which are much more effective for the molecular characterization.[7−9]

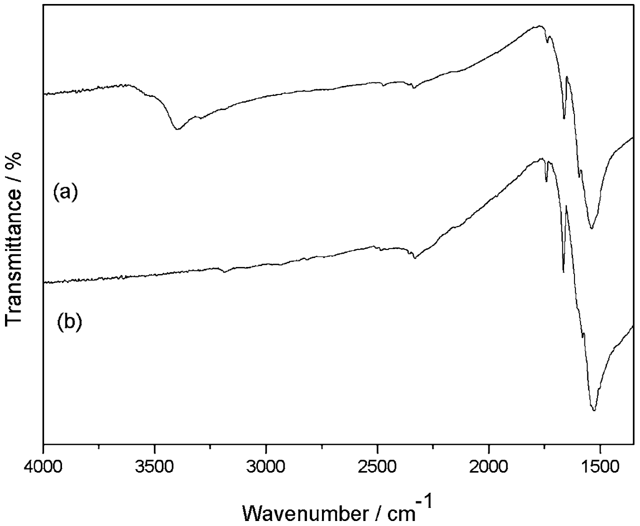

Figure 3. Infrared spectra of (a) orange and (b) yellow compounds.

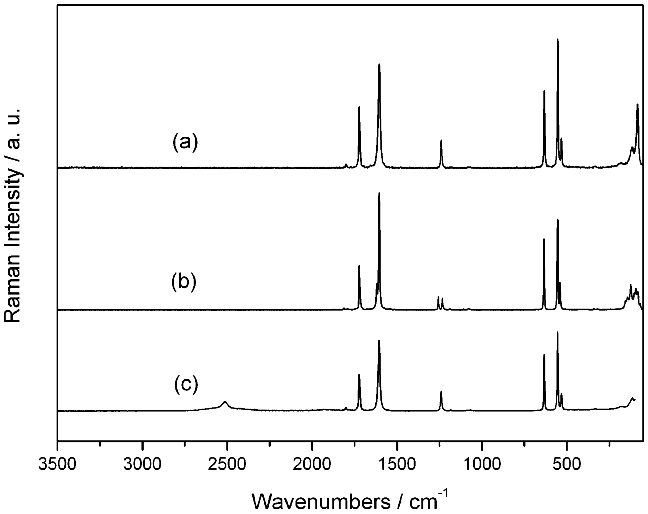

Figure 4. Raman spectra of (a) orange, (b) yellow, and (c) deuterated analogue of orange compounds.

The normal modes calculation for $C_5O_5^{2-}$ dianion in D_{5h} molecular symmetry predicts seven active Raman bands, of which six of them were observed in an aqueous solution of cronocate ion,[13] and the seventh was assigned later in studying the solid-state spectrum of sodium croconate salt.[4] In the particular case of the two croconate species being studied here, the Raman spectra (Figure 4) show eight and thirteen for orange and yellow compounds, respectively, in the spectral molecular vibrational range. The assignment of these bands has already been described in the literature,[13−17] and the most prominent Raman bands are listed in Table 1. Figure 4 shows that both the orange and yellow crystals have similar spectra, as expected, with the exception of the feature at 1240 cm^{-1} in the spectrum of the orange compound, which becomes a doublet at 1256 and 1232 cm^{-1} in the spectrum of the yellow compound (Figure 5). The other bands have very similar wavenumbers for the two compounds but changes in relative band intensities are observed, for example, the bands at 1606, 633, and 555 cm^{-1}. Following the thermal treatment as described above, the yellow compound presents the main characteristic bands of orange croconate and of the aqueous solution,[13] which suggests there is no decomposition of the oxocarbon moiety.

Ribeiro and co-workers,[18] investigating the molecular dynamics of squarate anion in acetonitrile solution, have shown that there is a blue-shift of the Raman wavenumbers of the CO stretching and ring-breathing modes, when compared with the aqueous solution results.[19] Recent work has shown[20] by means of vibrational dephasing analysis that croconate ion when submitted to different chemical environments such as water and acetonitrile solutions as well as the pure croconate tetrabutylammonium ionic liquid demonstrate carbonyl stretching and ring modes are also shifted in a way similar to that observed here. The authors have attributed this fact to the very strong hydrogen-bond interactions acting on the dephasing dynamics of the anion. Georgopoulos et al.[21] have shown a similar behavior for squarate alkaline salts in the solid state, where different hydrogen bonds are generated by exchanging the counterions. Therefore the CO stretching and the breathing modes are very sensitive to the environment and are excellent probes with which to investigate hydrogen bonds in oxocarbons. A more detailed analysis of the Raman spectra shows that the carbonyl stretching mode appears as a doublet at 1723 and 1718 cm^{-1} in the Raman spectra of the yellow (anhydrous) and orange compounds (Figure 5). This feature is different when compared to the Raman spectrum of aqueous solution, where only one band is observed at 1718 cm^{-1}.[13] In the aqueous solution environment, the CO bonds have homogeneous values of the force constant, as suggested by the appearance of only one band. However, in the solid state this vibrational mode occurs as a doublet, indicating an inhomogeneous force constant as a result of the anisotropic environment around the CO bond in the crystal packing. On the other hand, the νCO spectral range is unchanged after removing the water molecules, which indicates that this effect does not promote significant changes in the moiety, since the water molecules interact very weakly with the croconate anion. This is in agreement with the crystallographic data,[12] where the hydrogen-bond distances are 2.783 and 2.877 Å. According to the geometrical criteria for classifying hydrogen bonds proposed in literature,[22,23] the ones observed in the potassium croconate investigated here are weak.

All the results discussed above lead to the question about the role of water molecules in the solid structure of potassium croconate, and what is the other intermolecular strength which can be responsible for the spectroscopic changes observed in the spectrum of the anhydrous compound. To answer these questions, a more detailed analysis of the vibrational spectra of both compounds has to be done.

For the breathing mode (for which wavenumbers can be seen in Table 1), no splitting is observed for either the orange or the yellow compounds. For the free croconate anion in aqueous solution, this mode has been assigned to a Raman feature at 637 cm^{-1}. The comparison between the wavenumber values of this mode and the ones for hydrated and anhydrous compounds follow the same trend as that discussed above for the CO stretching mode, and they present a small shift in wavenumber when compared to the wavenumber obtained for croconate ion in solution.

Clearly, the key vibrational feature for the structural discrimination between the two croconates is the singlet/doublet in the region of 1230−1260 cm^{-1} (Figure 5B). Earlier Raman spectroscopic studies from our laboratory on alkaline metal squarates, based on the ligand $C_4O_4^{2-}$, have established a relationship between the νCC modes and the electronic delocalization degree.[21] Through correlation between the NICS index (related to aromaticity degree) and crystallographic data with the observed wavenumbers of these modes, the authors have shown that the decrease of the wavenumber difference between the splitting of the ν_5 mode (B_{1g}) is the result of the CC length bond equalization. Therefore, this is an indication of a more

TABLE 1: Raman Wavenumbers and Tentative Assignment of Potassium Croconate in the Anhydrous and Hydrated Forms[a]

$K_2C_5O_5.2H_2O$ (orange)	$K_2C_5O_5$ (yellow)	symmetry species[b]	assignment[b]
56 vw	68 vw		lattice mode
84 m	84 w		lattice mode
	94 w		lattice mode
	103 vw		lattice mode
114 w	125 w		lattice mode
	143 vw		lattice mode
	155 vw		lattice mode
183 vw	187 vw		lattice mode
	321 vw	ν_{12} (E′$_2$)	β(CO) + ν(CO) + ν(CC) + δ(CCC)
	341 vw	ν_7 (E′$_1$)	Δ(ring) + β(CO)
532 w	540 w	ν_8 (E″$_1$)	Ω(ring)
555 vs	555 s	ν_{11} (E′$_2$)	δ(CCC) + ν(CC) + ν(CO) + β(CO)
	558 ms	ν_{11} (E′$_2$)	δ(CCC) + ν(CC) + ν(CO) + β(CO)
633 ms	635 ms	ν_2 (A′$_2$)	ring breathing
	1078 vw		2 ν_8
1240 w	1232 vw	ν_{10} (E′$_2$)	ν(CC) + δ(CCC) + ν(CO) + β(CO)
	1256 vw	ν_{10} (E′$_2$)	ν(CC) + δ(CCC) + ν(CO) + β(CO)
1606 ms	1606 vs	ν_9 (E′$_2$)	ν(CO) + ν(CC) + δ(CCC) + β(CO)
	1620 w	ν_9 (E′$_2$)	ν(CO) + ν(CC) + δ(CCC) + β(CO)
1718 w	1718 w	ν_1 (A′$_1$)	ν(CO)
1723 m	1723 m	ν_1 (A′$_1$)	ν(CO)
1801 vw	1794 vw		$\nu_1 + \nu_{10}$
	1813 vw		$\nu_1 + \nu_{10}$

[a] Abbreviations: vw, w, m, ms, s, vs are, respectively, related to very weak, weak, medium, medium-to-strong, strong, and very strong; ν, β, ω, Δ, Ω, and δ represent stretch, in-plane deformation, out-of-plane deformation, ring deformation, idem, and dihedral angle deformation. [b] Mode numbering, symmetry species, activity, and description for the croconate anion normal modes.[14]

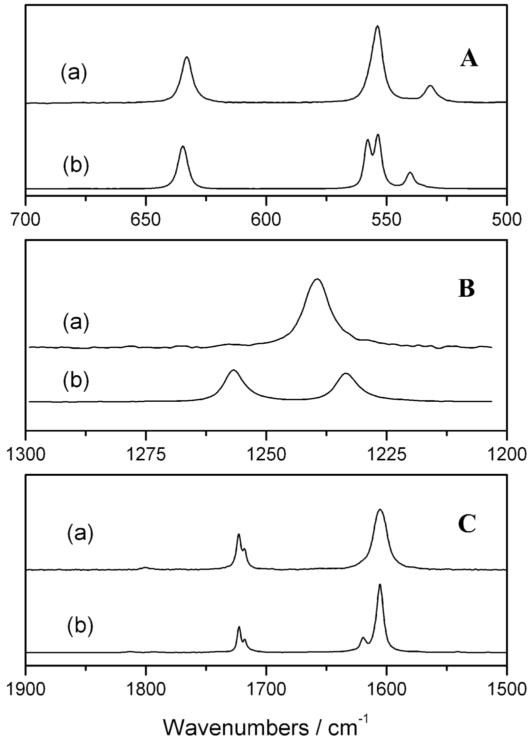

Figure 5. Expanded regions of the Raman spectra of (a) orange and (b) yellow croconates.

effective resonance effect in the oxocarbon ring. Here, we infer that the band splitting of the ring vibrations in the yellow croconate can be ascribed to a similar effect, namely, that the removal of the water molecules could permit a stronger interaction between the stacked layers in the crystal structure. In this range of the Raman spectrum, the orange potassium croconate is very similar to the anion in aqueous solution. In both, only one band assigned to νCC is observed which indicates that the croconate anion is less affected by solid-state interactions than the yellow compound. Additionally, the structure obtained by X-ray diffraction of the hydrated croconate[12] shows that the water molecules are located between the stacked layers formed by the anions, connecting the croconate anions of adjacent layers acting as "pincers" toward the dianions. It has a short interplanar separation (3.30 Å) and a short shift between the ring centroids of stacked layers (1.10 Å).[6] Therefore, the removal of waters causes a more effective interaction between the layers, which are responsible for a more effective perturbation in the molecular structure of the yellow compound.

Moreover, the ν_8 mode (assigned as out-of-plane ring deformation) presents remarkable modifications after the dehydration process. In the Raman spectrum of the orange compound this mode appears at 532 cm^{-1}, whereas for the yellow compound it can be seen at 540 cm^{-1} (Figure 5A). Another affected mode is the ν_{11}, assigned as a mode containing the contribution of four oscillators [δ(CCC) + ν(CC) + ν(CO) + β(CO)], which can be observed as a doublet at 554 and 558 cm^{-1} for the anhydrous croconate and as a singlet at 554 cm^{-1} for the hydrated compound (Figure 5A). Another difference is the splitting of the ν(CO) + ν(CC) + δ(CCC) + β(CO) mode which has been assigned as a strong band at 1606 cm^{-1}; in the Raman spectrum of yellow croconate this mode occurs as a splitting band at 1606 and 1620 cm^{-1} (Figure 5C). This band is the most intense one in the Raman spectrum of the anhydrous compound, whereas for the dihydrated compound the most intense band appears at 555 cm^{-1}.

From the analysis of the lattice modes region, it is easy to realize that the yellow compound presents more bands than the orange compound, similarly to the molecular vibrations region. All the observed differences can be attributed to the strong interactions between the stacked layers in the yellow compound, which are attenuated by the presence of water molecules in the orange structure. It is worthy of mention that the investigation of the thermal and spectroscopic properties of lithium croconate dihydrate has been carried out by Santos and Goncalves.[14] In that paper, the authors refer to a significant change in the vibrational spectra (Raman and infrared) mainly in the low-wavenumber region, which is related to the crystal lattice modes,

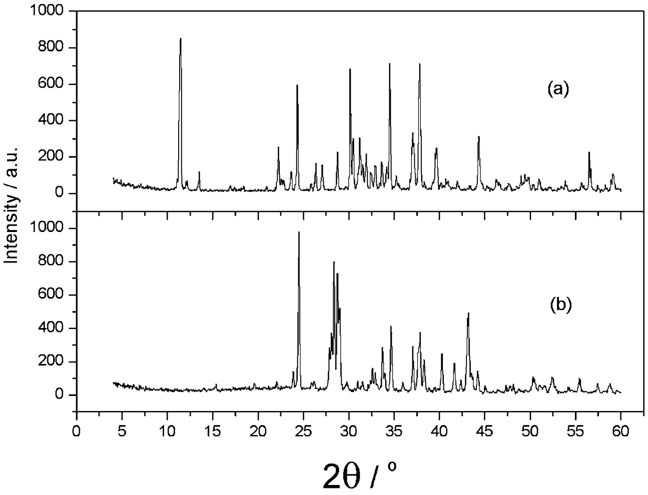

Figure 6. Powder X-ray diffraction patterns of the orange and yellow compounds.

when water is removed from the structure, accompanied by changes in band intensity. However, the most remarkable changes in the vibrational spectra are related to the ν(OH) modes. In contrast, in the 1230−1260 cm^{-1} region, the bands assigned to a ν(CC) + ν(CO) + δ(CCC) + β(CO) mode description appear as a doublet in the spectra of both the hydrated and dehydrated species of lithium croconate; in the present work, the same spectral feature is observed here only for the anhydrous potassium croconate and this collapses to a singlet for the hydrated form. This feature can be explained by the more symmetrical unit cell of $K_2C_5O_5{\cdot}2H_2O$ which presents a D_{2h} point group, whereas that obtained for $Li_2C_5O_5{\cdot}2H_2O$ is C_{2h}.[24] Another remarkable behavior is the similarity between the Raman spectrum of the croconate aqueous solution and the orange croconate; the same behavior can be seen in the lithium croconate dihydrate and anhydrous potassium croconate.

To confirm the hypothesis that water removal is responsible for the structural changes described above, we prepared an orange material containing D_2O; the Raman spectrum of this deuterated material can be seen in Figure 4, for which the wavenumbers of the skeletal croconate bands are seen to be identical with those of the hydrate. The band at 2500 cm^{-1} for the deuterated compound in Figure 4 is assignable to the OD symmetric and asymmetric stretching modes.

The removal of water molecules has also been investigated by means of X-ray powder diffractometry, and the data are displayed in Figure 6. The diffraction patterns of both the orange and yellow compounds are quite different, indicating that the loss of water strongly modifies the crystal packing of potassium croconate. Comparing the peaks of these two diffraction patterns, it can be seen that the hydrated compound (orange) has a higher crystalline degree in relation to the anhydrous (yellow) compound, mainly in the 2θ region between 25 and 30°, where the yellow compound presents broader peaks, in contrast to those of the orange compound, which presents sharper peaks. This result suggests that the water loss not only modifies the crystal packing but also reduces the degree of crystallinity of the potassium croconate structure. The influence of water molecules in the crystal packing of alkaline croconate crystals has been described by Braga and co-workers;[6] for small cations (Li^+, Na^+, and K^+), the solids normally possess two hydrated water molecules; on the other hand, for the larger cations (Rb^+ and Cs^+) the salts are anhydrous. In contrast to the observation for K^+ salts, in the Li^+ and Na^+ salts the loss of water is not reversible and the anhydrous compounds are not crystalline. The reversible loss of water observed in the K^+ salts could be explained by the size of the potassium cation, which is intermediate between the small (Li^+ and Na^+) and large (Rb^+ and Cs^+) alkaline metal ions. Hence, the croconate ion is able to efficiently complete the spherical coordination of K, and the formation of the yellow compound is possible. However, the hydrated compound (orange) is more stable, and with only a small quantity of water (even in an atmospheric environment with a low humidity) the yellow compound is converted into the orange.

TABLE 2: Interplanar Distances (d_{hkl}) of Major Peaks of the Orange and Yellow Compounds

compound	I_{rel}/%	$2\theta_{hkl}$/°	d_{hkl}/Å
orange	100	11.45	7.72
	70	24.30	3.63
	80	30.15	2.96
	84	34.50	2.60
	84	37.80	2.38
yellow	100	24.50	3.63
	82	28.35	3.15
	74	28.75	3.10
	53	29.00	3.07
	50	43.15	2.09

In the diffraction pattern of the hydrated (orange) compound strong peaks are observed between 10 and 20° in 2θ, whereas in the diffraction pattern of the yellow anhydrous material the most intense peaks are located at higher diffraction scattering angles (∼25°), strongly suggesting that the yellow compound has a unit cell which is smaller in comparison with the orange compound; probably, the distances between croconate ions are also smaller in the yellow compound. The main diffraction peaks of the two compounds are listed in Table 2. The major peaks at $2\theta = 11.45$ and 24.5° for the orange and yellow compounds represent the d_{hkl} values of 7.72 and 3.63 Å, respectively. These values indicate that the interplanar distance of the most important diffraction peak for the orange compound is larger than that of the yellow analogue. This evidence confirms the conclusions derived from the Raman spectra concerning the decrease in interactions between the stacked layers on going from the yellow to the orange species, and can be ascribed to the influence of the water molecules present in the unit cell.

Conclusions

The experimental data from thermogravimetry and vibrational spectroscopy, mainly Raman spectroscopy, have shown that the color difference between the two potassium croconate compounds considered here is due to the presence of coordinated water molecules. The results indicate that the removal of the water molecules produces a decrease in the size of the unit cell; a diagnostic feature of the Raman spectrum for the orange (hydrated) and yellow (anhydrous) analogues is the singlet at 1240 cm^{-1} in the former which splits in the yellow form to a doublet at 1256 and 1232 cm^{-1}. X-ray diffraction patterns show that the unit cell of the yellow compound is smaller than that of the orange analogue, suggesting that the croconate ion layers are more closely bonded in this salt. However, the degree of crystallinity of the yellow compound is smaller, which confers difficulty in the crystal structure determination, confirming this proposition. The reversible loss of water observed in the K^+ salts could be explained due to the potassium cation size being intermediate between small (Li^+ and Na^+) and large (Rb^+ and Cs^+) alkaline metal ions. Due to this fact, the croconate ion can effectively undertake the spherical coordination of K^+ and the formation of the yellow compound is possible. However, the hydrated compound (orange) is more stable, and with a small quantity of water the yellow compound is quickly converted to the orange compound. This experimental evidence, together with the comparison with lithium croconate literature data, clearly shows that the chemical and physical properties of each alkaline salt of the croconate ion present distinctive behavior, and they cannot be taken as general features for this family of compounds.

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