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Vibrational spectroscopy and aromaticity investigation of squarate salts: A theoretical and experimental approach

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Abstract

Experimental and theoretical investigations of squarate salts $[M_2(C_4O_4)]$ (M=Li, Na, K and Rb) were performed aiming to correlate the structures, vibrational analysis and aromaticity. Powder X-ray diffraction data show that these compounds are not isostructural, indicating that the metal-squarate and hydrogen bonds to water molecules interactions play a significant role on the the crystal packing. The infrared and Raman assignents suggest an equalization of the C–C bond lengths with the increasing of the counter-ion size. This result is interpreted as an enhancement in the electronic delocalization and consequently in the degree of aromaticity for salts with larger ions. Quantum mechanical calculations for structures, vibrational spectra and aromaticity index are in agreement with experimental finding, giving insights at molecular level for the role played by distinct complexation modes to the observed properties. Comparison between our results and literature, regarding molecular dynamics in different chemical environments, shows that aromaticity and hydrogen bonds are the most important forces driving the interactions in the solid structures of squarate ion.

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1. Introduction

Oxocarbon dianions $[(C_nO_n)^{2^-}$, where n=3, deltate; n=4, squarate; n=5, croconate and n=6, rhodizonate] (Fig. 1) were recognized by West [1] in the 1960 as a new group of organic compounds. These ions in aqueous solution present D_{nh} symmetry and high degree of electronic delocalization, which have been subject of several studies, mainly concerning structural [2–6] and spectroscopic investigations [7–10], in addition to some theoretical works [11–16]. Most studies of oxocarbons involve squarate and croconate ions. The crystal structures of croconate salts [17] show that Li⁺, Na⁺ and K⁺ complexes present two water molecules bonded per M₂C₅O₅ unit, although Rb⁺ and Cs⁺ salts are anhydrous. Unit cell and crystal structure of Na⁺, Rb⁺, K⁺ and Cs⁺ squarate salts were previously described [18]. Na⁺ and K⁺ squarate salts present different numbers of water molecules: three molecules for Na₂C₄O₄, which present two different crystalline phases [19,20], and only one in K₂C₄O₄ salt [21]. Another major difference is observed in the crystalline system of these salts, one phase of Na⁺ salt crystallizes in a triclinic system and space group $P\bar{1}$ [19] and another in a monoclinic space group C2/c [20], and K⁺ salt in monoclinic space group C2/c [21]. These differences in the crystalline system show that the change of cation in squarate salts can be responsible for some significant modifications in the crystal packing.

Ito and West [22] have investigated Raman and infrared spectroscopy of such a family, initially identifying that croconate ion $[(C_5O_5)^{2^-}]$ in aqueous solution presents D_{5h} symmetry, which is stabilized by resonance. This outcome was also reached from infrared spectra of potassium croconate, where the band around 1700 cm⁻¹ assigned to the stretching of isolated CO groups [ν (CO)] was not observed. Instead, a broad band was just found at lower wavenumbers, which is an indicative of resonance in the croconate ring. Similar

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Fig. 1. The main cyclic oxocarbon ions: (a) deltate; (b) squarate; (c) croconate and (d) rhodizonate.

observation was done for squarate ion $[(C_4O_4)^{2^-}]$, which also showed a symmetric planar structure stabilized by resonance. From the normal coordinate analysis of these dianions, it was found that the CC bond order increases and the CO bond decreases for larger rings whereas the force constants of k_{CC} decreases and the k_{CO} increases from $(C_4O_4)^{2-}$ to $(C_5O_5)^{2-}$. The average force constant $k_{\rm CC}$ for oxocarbons $(\sim 4 \text{ mdynes } \text{\AA}^{-1})$ is smaller than that for benzene $(\sim 6 \text{ mdynes } \text{\AA}^{-1})$, but is larger than those observed for a single C-C bond (~2 mdynes Å⁻¹). This comparative analysis was very important to West and co-workers establish the croconate and squarate ions as aromatic species. There have been some works [23,24] in the literature regarding to electron delocalization in oxocarbons raising many discussions about the aromaticity of these compounds. In 1981, Aihara [23] used MO calculations of diamagnetic susceptibility of dianions and neutral oxocarbons, concluding that only deltate ion presents high degree of aromaticity, and the other oxocarbon dianions were considered not aromatic. However, in 1983, Herndon [24] used valence bond theory (VB) to analyze the stabilization aspects, as for instance resonance energy, charge distribution and bond order quantities. All of the dianions were considered stabilized by resonance and were assigned as aromatic, whereas the neutral oxocarbon species were also considered to be stabilized by resonance, but not aromatics. Recently, Schleyer and co-workers [25] have adopted, as an aromatic criterion, a method based on the negative chemical shift of the center of the rings and at 1 Å above, in a methodology known as nucleus-independent chemical shifts (NICS). This method gives results in good agreement with energetic (energy of aromatic stabilization), geometric (bond order) and magnetic (diamagnetic susceptibility) criteria. Negative values of NICS indicate aromaticity (diamagnetic or diatropic current are

dominant in the ring), whereas positive values indicate antiaromaticity (paramagnetic or paratropic current dominates in the ring). This metodology has been used to calculated the NICS value of oxocarbons at 1 Å above the ring plane [26] and found values of -11 to deltate ion, -8.6 to squarate ion, -5.8to croconate ion and -4.4 to rodizonate ion. For comparison purposes, the NICS value calculated for benzene was -10, and the authors have concluded that deltate ion is actually the most aromatic of the oxocarbons ions, and the aromaticity degree decreases with the ring size in the oxocarbon series. The aromaticity of oxocarbons is still not completely defined so far and several works have been done in this attempt [9,23,26,27]. The aromaticity concept can be defined in several ways. Nowadays, it is known that the planarity of conjugated systems is not enough for a molecule to be aromatic, and a complete analysis must be done including geometric, energetic and magnetic parameters [28]. The vibrational spectroscopic studies of aromaticity is concentrated at the 800–1680 cm^{-1} region, where it is observed the CC bond stretching $[\nu(CC)]$ $(800-1200 \text{ and } 1640-1680 \text{ cm}^{-1})$ and CC aromatic stretching $[\nu(CC)_{ar}]$ (1200–1640 cm⁻¹). In this work, the experimental and theoretical spectroscopy and structural properties are obtained and aromaticity investigations of squarate salts $[M_2(C_4O_4)]$ (where M=Li⁺, Na⁺, K⁺ and Rb⁺) carried out with all data correlated to the structural features, trying to bring some light in the discussion of the aromatic properties of oxocarbon ions and their relations with the vibrational spectrum.

2. Methodology and experimental section

2.1. Calculation methods

Geometries and Raman and infrared vibrational frequencies and intensities were obtained at B3LYP/6-311+G(d) level of theory to the squarate salts $[M_2(C_4O_4)]$ (were M=Li⁺, Na⁺ and K⁺) and at B3LYP/6-311+G(d)/LANL2DZ level for RbC₄O₄ with the effective core potential (ECP) LANL2DZ used for the Rb atom. Aromaticity indexes were obtained by NICS method (nucleus-independent chemical shifts) at Hartree-Fock level and 6-31+G(d) basis set. All calculations were carried out using the GAUSSIAN 03 program [29].

2.2. Syntheses

The syntheses of the compounds were done by neutralization reaction of squaric acid $(H_2C_4O_4)$ to lithium, sodium and potassium hydroxide. Rubidium squarate was obtained by reaction of lithium squarate and rubidium chlorate. All the reactions were done in aqueous solutions, and crystals were obtained by slow evaporation at room temperature. X-ray crystal structure of sodium [19,20] and potassium [21] salts are described in literature, but unfortunately, attempts to obtain single crystals suitable to X-ray diffraction analysis of lithium and rubidium squarates were unfruitful.

2.2.1. Lithium squarate

An aqueous solution containing 8.3 mmol of LiOH were added to aqueous solution of $H_2C_4O_4$ (4.2 mmol), obtaining 3.9 mmol of the salt (yield: 93.8%). Thermogravimetric analysis: mass loss at 100 °C of 20%, showing the presence of two water molecules. Li₂C₄O₄·2H₂O (161.95 g mol⁻¹), calculated C 29.7 and H 2.5%; found C 32.16 and H 2.39%.

2.2.2. Sodium squarate

An aqueous solution containing 2.5 mmol of NaOH were added to aqueous solution of $H_2C_4O_4$ (5.0 mmol), obtaining 2.3 mmol of the salt (yield: 92.7%). Thermogravimetric analysis: mass loss at 100 °C of 25%, showing the presence of three water molecules. Na₂C₄O₄·3H₂O (212.07 g mol⁻¹), calculated C 22.7 and H 2.8%; found C 22.90 and H 2.39%.

2.2.3. Potassium squarate

An aqueous solution containing 7.2 mmol of KOH were added to aqueous solution of $H_2C_4O_4$ (3.6 mmol), obtaining 3.2 mmol of the salt (yield: 88.9%). Thermogravimetric analysis: mass loss at 100 °C of 10%, showing the presence of one water molecules. $K_2C_4O_4 \cdot H_2O$ (208.25 g mol⁻¹), calculated C 23.1 and H 0.96%; found C 22.94 and H 0.72%.

2.2.4. Rubidium squarate

An aqueous solution containing 3.2 mmol of RbCl were added to aqueous solution of $Li_2C_4O_4$ (1.6 mmol), obtaining 1.6 mmol of the salt (yield: 37.4%). Thermogravimetric analysis: mass loss at 100 °C of 10%, showing the presence of two water molecules. $Rb_2C_4O_4 \cdot 2H_2O$ (319.01 g mol⁻¹), calculated C 15.1 and H 1.25%; found C 11.14 and H 1.38%.

2.3. Vibrational spectroscopy

Infrared spectra were obtained in Bomem MB-102 spectrometer with CsI beam spplitter, using CsI disks, spectral resolution of 4 cm^{-1} and 128 scans were accumulated to improve the signal-to-noise ratio. Fourier-transform Raman spectroscopy was carried out using a Bruker RFS 100 instrument and a Nd³⁺/YAG laser operating at 1064 nm in the near infrared and CCD detector cooled with liquid N₂. To improve the signal-to-noise ratio, 500–1000 scans were accumulated over a period of about 30 min, using 4 cm⁻¹ as spectral resolution. All spectra were obtained more than two times to show reproducibility, and no changes in band positions and intensities were observed.

2.4. X-ray diffaction

Powder X-ray diffraction were carried out using RIGAKU GEIGERFLEX 2037 with graphite monocromator [0002] and 2d=6.708 Å, NaI sinthilator detector and Co K α radiation (λ =1.789 Å), except to rubidium salt that was used Cu K α (λ =1.541 Å) and scans of 0.1 ° min⁻¹.

2.5. Thermogravimetric measurements

The thermogravimetric data were obtained in a Mettler STARe TG50 thermobalance, the samples were heated at 10 °C/min from ambient temperature to 800 °C in atmospheric air flow. Thermogravimetric curves are deposited as Supplementary materials.

3. Results and discussion

3.1. Structural analysis

From the thermogravimetric analysis of the squarate compounds associated to elemental analysis and previous crystal structure investigations, it can be concluded that lithium, sodium, potassium and rubidium salts present water molecules in the crystal packing. This water content is related to two main features: the specific crystal packing of each compound and the hydrogen bonds formed between these water molecules and the ions present in the structure. Thermogravimetric analysis of squarate salts $M_2C_4O_4$ (M= Li^+ , Na^+ , K^+ and Rb^+) indicates the existence of a correlation between cation size and quantities of water molecules in the structures. In the Li⁺ and Rb⁺ salts, there are two water molecules for each $M_2C_4O_4$ unit, three in Na⁺ salt and only one in K⁺. These results suggest that not only cation size is important in crystal packing, since intermolecular interactions also demand a strong influence in the supramolecular structure. Another important discussion can be done on the thermal degradation profile of each squarate compound, since after water loss the anhydrous salts $(M_2C_4O_4)$ of sodium and rubidium are more thermal stable than lithium and potassium salts. Qualitative analysis of TG curves suggests that the squarate salts decomposition yields a carbonate and then decomposes in oxide after water loss. The complete decomposition was observed for potassium squarate and partially for lithium squarate. Sodium carbonate is very stable with decomposition occurring around 1000 °C, and sodium oxide was not observed in this TG curve obtained up to 800 °C. Similar result was obtained for rubidium squarate.

In a recent investigation by Braga and co-workers [17], the crystal structures of Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ croconate compounds show that most of salts crystallizes in monoclinic system and C2/c space group, with exception made to potassium salt which crystallizes in orthorrombic system and Pbcn space group. These results indicate the crystal system is not significantly affected by the cation size, whereas it has a significant influence in the amount of water molecules in the crystals. On the other hand, similar results were not observed for squarate compounds. X-ray crystal structures of Na⁺ and K⁺ [19–21] show that these salts do not present the same number of water molecules; for instance, Na⁺ salt present three water molecules per M₂C₄O₄ unit and only one in K⁺ salts.

The obtained crystals of lithium and rubidium squarate do not present adequate quality to be analyzed by single crystal X-ray diffraction. For this reason, the powder diffraction



Fig. 2. X-ray diffraction pattern of $(Li_2C_4O_4)$, $(Na_2C_4O_4)$, $(K_2C_4O_4)$ and $(Rb_2C_4O_4)$.

patterns of squarate salts were obtained, indicating that these salts present different solid states structures, as can be observed in Fig. 2. Experimental diffraction pattern of sodium squarate is similar to the one simulated for triclinic phase [19], thus suggesting that this phase was obtained. Diffraction pattern of potassium salt is similar to the one simulated from the crystal structure described by Macintyre and Werkema [21]. Experimental and simulated powder diffraction patterns of sodium and potassium squarate salts are deposited as Supplementary materials.

The analysis of interplanar distances is very important to define the π -stacking interaction between oxocarbon rings in the solid state structure. Although the cations are monovalent ions M⁺, the diffraction pattern shows that the cation size plays a significant role on crystal packing. Table 1 shows the diffraction angles and the respective interplanar distances (d_{hkl}) for the most intense peaks observed in the powder diffraction. The interplanar distance ranged from 3.14 Å (Li⁺ salt) to 2.84 Å (K⁺ salt), whereas Rb⁺ salt presents the largest value of d_{hkl} (3.30 Å). Comparing these data to crystal structure of croconate salts [17] it is possible to infer that the distance between the squarate ions planes in crystal packing are

Table 1

Diffraction angles $(2\theta_{hkl})$ and respective interplanar distances (d_{hkl}) for the most intense peaks $(I_{\text{relative}} (\%))$ of Li₂C₄O₄, Na₂C₄O₄, K₂C₄O₄ and Rb₂C₄O₄

Compound	I _{relative} (%)	$2\theta_{hkl}$ (°)	$d_{hkl}\left(m{\AA} ight)^{a}$
Li ₂ C ₄ O ₄	100	33.2	3.14
	63	35.3	2.95
	58	37.6	2.78
Na ₂ C ₄ O ₄	100	35.5	2.94
	77	40.3	2.60
	90	32.0	3.25
$K_2C_4O_4$	78	33.6	3.10
	100	36.7	2.84
	61	38.5	2.72
$Rb_2C_4O_4$	100	27.0	3.30
- · ·	32	38.6	2.33

^a Values obtained using Co K α (λ =1.791 Å), except to Rb₂C₄O₄ where was used Cu K α (λ =1.542 Å).



Fig. 3. Structure of $[M_2(C_4O_4)]$ complexes in (a) cis and (b) trans geometries.

becoming smaller with the increasing of cation size, except for Rb⁺ salt, which presents the largest d_{hkl} value. Squarate ions in Rb⁺ salt are probably arranged horizontally translated in despite of vertical translation, justifying the interplanar distance observed. Analyzing the croconate salts [17] it can be observed that the cation size is not directly related to the interplanar distances. This parameter presents the same value in Li⁺, K⁺ and Rb⁺ salts (3.30 Å), with the smallest value observed in Na⁺ salt (3.12 Å) and the largest in Cs⁺ salt (3.42 Å). Although sodium croconate presents the smallest interplanar distance, the rings are horizontally translated around 3.0 Å, which is the biggest translation for these salts. Similar translation was observed for Rb⁺ and Cs⁺ croconate salts (1.92 and 2.11 Å).

Structural and spectroscopic theoretical studies were performed for $[M_2C_4O_4]$ compounds with M=Li⁺, Na⁺, K⁺ and Rb⁺ in cis e trans arrangements and for squaric acid [H₂C₄O₄]. As it can be seen in Fig. 3, the counter-ions can interact with $(C_4O_4)^{2-}$ ring structure in two different ways. In the first, named cis-[M₂C₄O₄], the squarate anion acts as a bisbidentated ligand, with the counter-ions sharing a common oxygen atom of the ring. In the other geometrical form, trans-[M₂C₄O₄], the squarate also act as a bis-bidentated ligand, but with the counter-ions lying on opposite sides of the ring. Analyzing the structural results obtained for the cis structure, given in Table 2, it is observed a systematic increasing in the M–O bond length with of the counter-ion size (Li^+ , Na^+ , K^+ and Rb⁺). The O-M-O bond angles show a remarkable decreasing from 106.7° (Li⁺) to 70.5° (Rb⁺). On the other hand, C(1)-O(7) and C(2)-O(5) bond length present a small variation (~ 0.02 Å) from Li⁺ to Rb⁺. Analyzing the C–C bond lengths, the C(2)–C(3) bond decreases by about 0.03 Å and the C(1)-C(2) was found to be slightly longer with the cation size. These results are in agreement with a recent theoretical investigation [14] carried out at MP2/6-31+G(d)

Table 2 Geometric parameters obtained for the cis and trans-[$M_2(C_4O_4)$] complexes

	Li ^{+a}	Na ^{+a,b}	$K^{+a,c}$	$Rb^{+a,d}$
$cis-[M_2(C_4O_4)]$				
M-O(7)	1.946	2.258(2.419)	2.586(2.860)	2.843
M-O(5)	1.904	2.222(2.419)	2.508(2.860)	2.754
C(1)–O(7)	1.316	1.309(1.260)	1.304(1.260)	1.297
C(2)–O(5)	1.259	1.256(1.260)	1.255(1.260)	1.254
C(3)–O(10)	1.202	1.209(1.260)	1.214(1.260)	1.219
C(1)-C(2)	1.421	1.439(1.471)	1.449(1.457)	1.457
C(2)–C(3)	1.535	1.520(1.471)	1.511(1.457)	1.506
O-M-O	106.7	90.1	78.1	70.5
trans- $[M_2(C_4O_4)]$	1			
M–O	1.897	2.234(2.419)	2.544(2.860)	2.795
C–O	1.258	1.256(1.260)	1.256(1.260)	1.254
C(3)–C(4)	1.469	1.478(1.471)	1.480(1.457)	1.484
C(2)–C(3)	1.467	1.469(1.471)	1.471(1.457)	1.473
O-M-O	102.5	87.7	76.4	69.5

Values in parenthesis are the average parameter obtained from X-ray diffraction data.

^b Experimental data from Ref. [19].

^c Experimental data from Ref. [21].

^d The ECP LANL2DZ was used for Rb atom.

level, where the structural and spectroscopic aspects of free squarate ion $[(C_4O_4)^{2^-}]$ and in its cis salts with Li⁺, Na⁺ and K^+) were studied. Analyzing the results for the trans isomers reported in Table 2, it can be seen an enlargement of M-O bond $(\sim 0.8 \text{ Å})$ with the cation size, similar to the cis form and a small effect in the C-C and C-O bonds. The O-M-O bond angles are smaller for bigger cations. Experimental structural parameters obtained from X-ray diffraction of Na⁺[19] and $K^{+}[21]$ salts show that the M–O bond length increases from Na^+ to K^+ (Table 2). The average M–O bond lengths are 2.419 and 2.860 Å for Na⁺ and K⁺ salts, respectively. The greatest difference between C-C bonds is 0.024 Å for both salts, even though the average C-C bond is slightly smaller in K^+ salt (1.457 Å) than in Na⁺ salt (1.471 Å). As can observed in the cis compounds, the average C-O bond lengths present similar values for both salts (1.260 Å), although the difference between the largest and the shortest bonds for K^+ salt is 0.004 and 0.018 Å for Na⁺. The cis/trans relative energy and the dipole moment for the complexes are given in Table 3. For all investigated species the trans form is found to be favorable in gas phase with lower values found for heavier alkaline metals. However, it is important to note that the dipole moments of the

Table 3

Gas phase relative energy values (ΔE and ΔE^{ZPE} in kcal/mol) and dipole moments (μ in Debye) for the *cis* and *trans*-[M₂(C₄O₄)] isomers calculated at B3LYP/6-311+G(d) level of theory

	μ		$\Delta E_{cis-trans}$	$\Delta E_{cis-trans} +$ ZPE	
	cis	trans			
Li	10.2	0.0	8.8	8.4	
Na	13.9	0.0	6.4	6.2	
Κ	16.5	0.0	5.9	5.8	
Rb ^a	19.5	0.0	6.0	6.2	

^a The ECP LANL2DZ was used for Rb atom

Table 4

NICS values for cis and trans-[M2C4O4] compounds and H2C4O4 obtained at 0.6 Å above ring center

$[M_2C_4O_4]$	Li ⁺	Na ⁺	K^+	Rb^{+a}	$H_2C_4O_4$
cis	-9.8	-10.0	-10.1	-10.3	-8.3
trans	-11.0	-11.0	-11.0	-11.0	-

^a For Rb the ECP LANL2DZ was used.

cis forms are larger than those calculated for the trans isomers, which might favor the cis forms in solution due to electrostatic interactions.

Despite the presence of the same oxocarbon structure in all compounds, the significant change observed for the interplanar distances as function of the cation size can affect the electrostatic interactions and lead to variations in electronic delocalization that can be related to aromaticity of squarate ions in the solid structures. In order to quantify the degree of aromaticity, values of NICS were obtained by calculating the absolute shielding constant at 0.6 Å above the ring center in order to reduce the local shielding of nearby σ -bond [30] for $M_2C_4O_4$ (M=Li⁺, Na⁺, K⁺ and Rb⁺) in the cis and trans forms (Fig. 3). The results are reported in Table 4. According to the values of calculated NICS at HF/6-31 + G(d)//B3LYP/6-311+G(d) level for the cis compounds an increasing of the aromaticity is obtained with the size of the counter-ion, with a constant value equal to -11 found for the trans isomers. Additionally, it is worth mentioning that all NICS values of the salts are greater than those for the squaric acid (-8.3), showing that the complexes must be more aromatic than the respective acid form.

3.2. Vibrational spectroscopy

The spectroscopic analysis was done for squaric acid and squarate complexes with Li^+ , Na^+ , K^+ and Rb^+ counterions. The experimental results are shown in Table 5, and the vibrational spectra are depicted in Fig. 4 (infrared) and Fig. 5 (Raman). As in this investigation, the main goal is the discussion of the aromaticity of squarate salts, the most important vibrational modes related to the electronic delocalization are the stretching modes of CC and CO bonds, which can be observed in the 1700–1500 and 1200–1000 cm⁻¹ region, respectively.

Ito and West [22], in the pioneer investigation of the vibrational spectra of squarate ion in aqueous solution have assigned the D_{4h} symmetry to this ion and then, seven bands are expected in the Raman spectrum, and the normal coordinate analysis pointed out two CO stretching (ν_1 , A_{1g} and ν_9 , B_{2g}), one CC stretching (ν_5 , B_{1g}), one ring breathing (ν_2 , A_{1g}), two CO bending (ν_{11} , E_g and ν_6 , B_{1g}) and one ring bending mode (ν_{10} , B_{2g}). Crystal structure of sodium [19] and potassium salts [21] show that in solid state the symmetry is reduced; the factor group analysis indicate C_i^1 and C_{2h}^6 symmetries for potassium and sodium salts, respectively. In addition, vibrational spectra (Raman or infrared) obtained in the solid state present more bands than the observed in aqueous solution spectra [31].

^a Geometry was optimized at B3LYP/6-311+G(d) level of theory.

Table 5

$H_2C_4O_4$		$Li_2C_4O_4$		Na ₂ C ₄ O ₄		$K_2C_4O_4$		$Rb_2C_4O_4$		Tentative assign- ment
IR	R	IR	R	IR	R	IR	R	IR	R	-
1813m	1823w	1810w	1810w	1780w	1798w	1711m	1802w	1749w	1802w	ν(C=O)
1646m	1617w	1640s	1650s	1649m	1686m		1611m	1653w	1615m	$\nu(C=C)$
1508s	1515w	1551s	1592w	1592m	1596m	1528s	1524w	1524s		v(C=C) + v(C=O)
1317s		1462w								ν (C–C)
	1295w	1271w								ν (C–C)
1166w	1172m	1128w	1161s	1128w	1165m	1100m	1127s		1126s	$\nu(C-C)$
1050w	1048w	1068m	1075m	1088m	1113s	1088m	1091w	1098m		ν (C–C)
928w										$\nu(C-C)$
850w		864w		821m						ν (C–C)
721w	726s	721w	722s		718s	745m	726s		726s	Ring breathing
632m	635s	607m	649s	594m	641s	683m	651s	685w	651s	δring
383m	380s	374w	326m	363m	304m	343m	319m	347w	317m	$\delta(CO)$

Experimental vibrational bands of squaric acid and squarate salts with respective tentative assignment

Initially analyzing the IR spectra, an intense band is observed between 1510 and 1550 cm^{-1} assigned to a $\nu(CC) + \nu(CO)$ mode. From the analysis of the 800- 1680 cm^{-1} region, it can be observed seven vibrational bands for the $H_2C_4O_4$, seven for $Li_2C_4O_4$, five for $Na_2C_4O_4$, three for $K_2C_4O_4$ and $Rb_2C_4O_4$. The vibrational bands related to the CC bonds close to 1600 cm^{-1} were not observed for the $K_2C_4O_4$ and also a smaller number of bands assigned to $\nu(CC)$ single and $\nu(CC)$ aromatic was found. Analyzing the Raman spectra, the overall trend is the same as for the IR. An important aspect in the Raman analysis is that a smaller number of bands for the squarate salts is observed when the size of the counterion increases, which can be related to the higher symmetry, when comparing squarate structure in all compounds. In other words, it seems that the squarate ion is less disturbed by electrostatic forces when the counter-ion is very large in volume, as the case of rubidium ion. An important region for analysis in the Raman spectrum is located close to 1200-1000 cm⁻¹, involving the $\nu(CC)$ modes. The squaric acid presents a band of medium intensity at 1171 cm⁻¹ and another band of low intensity at 1047 cm^{-1} , shifted from each other by



Fig. 4. Infrared spectra of squaric acid $(H_2C_4O_4)$ and $Li_2C_4O_4,\,Na_2C_4O_4,\,K_2C_4O_4$ and $Rb_2C_4O_4$ salts.

 124 cm^{-1} . The Li₂C₄O₄ spectrum shows bands at 1161 and 1075 cm^{-1} , separated by 86 cm⁻¹. In the Na₂C₄O₄ spectrum, three bands were observed in this region, a band of low intensity at 1165 cm^{-1} , a band of medium intensity at 1113 cm^{-1} and a band of low intensity at 1063 cm⁻¹, with a difference of 50 cm⁻¹ between two consecutive bands. For the $K_2C_4O_4$ complex two bands are observed at 1127 cm⁻¹ of medium intensity and at 1090 cm^{-1} of low intensity, with the separation between them equal to 37 cm⁻¹. The Rb₂C₄O₄ salt presents only one strong band at 1126 cm^{-1} . The important outcome from the previous analysis is that the difference between these bands becomes smaller from Li⁺ to K⁺, and for Rb⁺ salt only one band was observed. These facts strongly suggest equalization in the CC bonds lengths, and then an increasing in the symmetry of the squarate ion in solid state when bigger counter-ions are present. These results are in agreement with X-ray crystal structure of Na⁺ and K⁺ salts, which shows that potassium salt (C_{2h}^6) is more symmetric than sodium salt (C_i^1) in solid state.

The theoretical vibrational spectra were calculated for *cis* and *trans*- $[M_2C_4O_4]$ complexes, $(M = Li^+, Na^+K^+ and Rb^+)$,



Fig. 5. Raman spectra of squaric acid $(H_2C_4O_4)$ and $Li_2C_4O_4,\ Na_2C_4O_4,\ K_2C_4O_4$ and $Rb_2C_4O_4$ salts.



Fig. 6. Correlations between experimental and theoretical vibrational frequencies of $H_2C_4O_4$, $Li_2C_4O_4$, $Na_2C_4O_4$ and $K_2C_4O_4$ molecules. Infrared (a) cis and (b) trans and Raman (c) cis and (d) trans geometries.

and also for the squaric acid [H₂C₄O₄] for comparison purposes (the calculated frequencies and intensities are available as Supplementary material). Theoretical results are in good agreement with the experiment regarding to the values of the vibrational frequencies, intensities and assignments of the vibrational modes. In Fig. 6, the calculated vibrational wavenumber are plotted against the experimental data; the correlations are fairly good with r > 0.99. These results indicate a good agreement between experimental and theoretical frequencies, and then no scale factor was used. For all the investigated compounds it is calculated a vibrational frequency around 1500 cm⁻¹, very intense in IR, assigned as $\nu(CC)$ + ν (CO). The important aspects observed experimentally in the Raman spectrum are also verified theoretically for the bands in the 1200–1000 cm⁻¹ region, relative to the ν (CC) mode. In this region, the difference between the vibrational frequencies with highest and lowest Raman activity decreases, in the sequence: $[Li_2C_4O_4]$ (1267, 1089 cm⁻¹, $\Delta = 178$ cm⁻¹); $[Na_2C_4O_4]$ (1199, 1080 cm⁻¹, $\Delta = 119$ cm⁻¹) and $[K_2C_4O_4]$ (1162, 1077 cm⁻¹, $\Delta = 85$ cm⁻¹). These results are in agreement with the experimental data, and support the trend of the C-C bond lengths equalization, suggesting an increasing in the symmetry of the squarate ion throughout the series analyzed.

Ribeiro and co-workers [32], investigating the molecular dynamics of squarate anion in acetronitrile solution, have shown that there is a blue shift of the Raman wavenumbers of the carbonyl stretching and ring breathing modes, when compared with the aqueous solution results [33]. In a very recent work, Cavalcante and Ribeiro [34] have shown, by vibrational dephazing analysis, that croconate ion when submitted to very different chemical environments such as water and acetonitrile solutions and also the ionic liquid croconate tetrabuthylammonium, the carbonyl stretching and ring breathing modes are shifted. The authors claim this behavior is due to very strong hydrogen bond interactions acting on the dephasing dynamics of $C_5 O_5^{2-}$ ion, and it can be seeing a similar behavior in the present investigation with squarate salts in the solid state, which could support the conclusions obtained by those authors. If one compares the Raman wavenumbers for both vibrational modes (carbonyl stretching and ring breathing) in the series going from rubidium to lithium salts, which can be seen in Table 5, almost the same trend is observed with a blue shift from lithium to rubidium salt, and in these structures there are also water molecules involved in intermolecular hydrogen bonds. Summing up, aromaticity is one of the most important interactions acting in the crystalline structure of the squarate salts, and together with hydrogen bonds plays an important role in the analysis of the vibrational spectra of oxocarbon ions.

4. Conclusions

In the present work, the investigation of the experimental and theoretical aspects of the structure and spectroscopic properties of several squarate salts was carried out. From the analysis of these parameters it could be concluded that the molecular symmetry and consequently the electronic delocalization are higher for the salts with bigger counter-ions. Powder diffraction data showed that the salts analyzed present distinct solid states structures. In the solid state, the cation size affects the distance between parallel planes of squarate ions and the cation-anion bond length, playing an important role in the interatomic and intermolecular interactions in solid state. The difference in these interactions can modify the electronic delocalization of squarate ions, and the compounds can present different degrees of aromaticity. Vibrational spectra of Li⁺, Na⁺, K⁺ and Rb⁺ salts showed a decreasing in the number of bands and coincident bands at IR and Raman spectra with the enlargement of the cation size. This result indicates a higher symmetry of these compounds, and might be evidence that the degree of aromaticity is also increasing throughout the series. Considering only geometric parameters, the increasing of aromaticity is observed from the equalization of C-C and C-O bond lengths, which also can be used to explain the observed decreasing of the number of vibrational bands and coincident bands in the IR-Raman spectra. Theoretical results were in good agreement to the experimental data regarding to structure, vibrational spectrum and aromaticity trend. According to NICS calculation in the ring center of the compounds cis: -9.8 $[Li_2C_4O_4]$, -10.0 $[Na_2C_4O_4]$, -10.1 $[K_2C_4O_4]$, and -10.3 $[Rb_2C_4O_4]$ it could be observed the increasing of aromaticity degree with the cation size, supporting the experimental proposal.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2006.01. 035.

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