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# Crystal structure and vibrational spectra of cesium salts of bis(dicyanomethylene)croconate (croconate violet) ion

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## Abstract

The vibrational spectra and crystal structures of cesium salts of 3,5-bis(dicyanomethylene)cyclopentane-1,2,4-trionate ( $C_{11}N_4O_3^{2-}$ ), known as croconate violet, are described in this work: 1-cesium and potassium croconate violet ( $CsKCV$ ), 2-cesium croconate violet ( $Cs_2CV-1$ ), and 3-cesium croconate violet hydrate ( $Cs_2CV-2$ ). Only  $CsKCV$  and  $Cs_2CV-2$  presented single crystals suitable for X-ray diffraction analysis; these compounds crystallize in triclinic  $P\bar{1}$  and monoclinic  $P2_1/a$  space group, respectively. The stoichiometries of the salts show one water molecule to each  $M_2C_{11}N_4O_3$  unit, which are involved in hydrogen bonds forming dimers in  $CsKCV$  and an extended structure with one-dimensional arrangement (1D) in  $Cs_2CV-2$ . Two types of coordination modes are observed in both salts: monodentate and chelate. Powder diffraction data show that  $Cs_2CV-1$  is isostructural to potassium and rubidium croconate violet salts. Vibrational spectra of cesium salts are almost similar, and the biggest differences can be observed in CV ring stretching modes ( $1600\text{--}1400\text{ cm}^{-1}$ ), probably due to small changes in electronic delocalization over pseudo-oxocarbon ring. In despite of different crystal packing in these salts, the CV units are almost planar and are displayed in layers, which are separated by cations and water molecules in  $CsKCV$  and  $Cs_2CV-2$  crystal structures.

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**Keywords:** Croconate violet ion; Crystal structure; Vibrational spectroscopy; Pseudo-oxocarbon

## 1. Introduction

Croconate violet dianion [3,5-bis(dicyanomethylene)cyclopentane-1,2,4-trionate] (CV) is one of cyclic derivatives of oxocarbon family which is obtained by condensation of croconic acid (or croconate ion) with malononitrile ( $NCCH_2CN$ ) [1]. These molecules are very interesting due to their unusual electronic and vibrational properties [2–7], their high molecular symmetry and electronic delocalization degree. They present strong absorp-

tions in the UV–visible region, being referred as croconate dyes. These dyes display reversible electrochemical behaviour [8,9] as well as some typical semiconductor properties [9,10]. They also present reversible oxidation steps, which can be investigated by photophysical studies [11,12]. Moreover, these molecules have been currently applied in supramolecular chemistry that can be defined as the chemistry beyond the molecules [13]. In this sense, oxocarbon systems are very interesting due to their structural characteristics and simplicity. Oxocarbon and pseudo-oxocarbon molecules can be involved in different types of intermolecular interactions, where their electronic delocalization provides the possibility of  $\pi$ -stacking interaction between the rings. Besides, these molecules present

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coordination properties and acceptor sites of hydrogen bonds, which make these systems potentially useful in crystal engineering research.

Few crystallographic and vibrational studies of CV anions are described in literature [14–21]; concerning the X-ray structures of alkaline salts of CV, potassium ( $K_2CV$ ) [19] and rubidium ( $Rb_2CV$ ) [21] and also tetrabutylammonium ( $(NBu_4)_2CV$ ) [20] have been reported. Potassium and rubidium salts are dihydrate and the water molecules are involved in medium hydrogen bonds with CV ion. The investigation of  $\pi$ -stacking interaction in these salts indicates that this interaction is not effective as that observed in croconate salts [13]. Tetrabutylammonium salt is anhydrous and due to the great volume of the cation,  $\pi$ -stacking interaction is not observed in the crystal packing (distance between rings of 12.4 Å). Experimental and theoretical vibrational studies of CV are also described [22,23], and resonance Raman spectra of CV in aqueous solutions [22] indicate a rather small electronic delocalization when compared to croconate ion, which can be discussed in terms of the two electronic transitions observed in the visible spectrum due to two different chromophoric moieties, one involving the  $\pi$  system of the croconate ring and the other located at  $C\equiv N$  moieties.

In this work we are describing the crystal structures and vibrational spectra of cesium salts of CV. We have synthesized the mixed cesium potassium croconate violet ( $CsKCV$ ), and also two phases of cesium croconate violet, an anhydrous blue ( $Cs_2CV$ -1) and a hydrate green ( $Cs_2CV$ -2) compounds. The main purpose of this investigation is to identify the intermolecular interactions present in the solid state and their influences in the crystal packing.

## 2. Experimental

### 2.1. Synthesis

Potassium bis(dicyanomethylene)croconate ( $K_2CV$ ) was synthesized as a modification of Fatiadi method [1], described by Teles et al. [20]. To an aqueous solution of potassium bis(dicyanomethylene)croconate (0.72 mmol) a cesium iodide aqueous solution was added (1.39 mmol). Deep blue single crystals were obtained by slow evaporation at room temperature, and were identified as a mixed salt, cesium potassium bis(dicyanomethylene)cyclopentane-1,3-dionate hydrate salt ( $CsKCV$ ) (yield 40%). Elemental analysis of  $CsKC_{11}N_4O_3 \cdot H_2O$  (426.2 g mol<sup>-1</sup>): calc. C 30.98%, N 13.14% and H 0.47%; found C 31.22%, N 13.24% and H 0.55%.

The mixed salt was re-crystallized in cesium chloride solution and deep blue crystals were obtained and identified as cesium bis(dicyanomethylene)-cyclopentane-1,3-dionate salt ( $Cs_2CV$ -1). The  $Cs_2CV$ -1 salt was re-crystallized in aqueous solution and few deep green single crystals were obtained and identified as cesium bis(dicyanomethylene)-cyclopentane-1,3-dionate hydrate

salt ( $Cs_2CV$ -2). Elemental analysis:  $Cs_2CV$ -1 [ $Cs_2C_{11}N_4O_3$  (501.95 g mol<sup>-1</sup>); calc. C 26.32%, N 11.16% and H 0.00%; found C 26.92%, N 12.65% and H 0.22%;  $Cs_2CV$ -2 [ $Cs_2C_{11}H_2N_4O_4$  (519.97 g mol<sup>-1</sup>); calc. C 25.42%, N 10.78% and H 0.39%; found C 23.47%, N 16.00% and H 0.28%.

### 2.2. X-ray diffraction

Single crystal X-ray data were collected in a Nonius Kappa CCD diffractometer with MoK $\alpha$  ( $\lambda = 0.71073$  Å) at room temperature. Data collection and reduction, and cell refinement were performed by DENZO and SCALE-PAK programs [24]. The structure was solved and refined using SHELXL-97 [25]. CCDC 600033 and 600034 contain the supplementary crystallographic data for both compounds. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223/336 033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

### 2.3. Raman spectra

Fourier-transform Raman spectroscopy was carried out using a Bruker RFS 100 instrument, Nd<sup>3+</sup>/YAG laser operating at 1064 nm in the near infrared and CCD detector cooled with liquid nitrogen. Good signal-to-noise ratios were obtained from 2000 scans accumulated over a period of about 30 min, using 4 cm<sup>-1</sup> as spectral resolution.

### 2.4. Infrared spectra

Infrared spectra were obtained in a Bomem MB-102 spectrometer fitted with CsI beam splitter, using KBr disks and spectral resolution of 4 cm<sup>-1</sup>. Good signal-to-noise ratio was obtained from the accumulation of 128 scans.

### 2.5. Thermogravimetric analysis

Thermogravimetric data for  $CsKCV$  and  $Cs_2CV$ -1 were obtained in a Mettler STARE TG50 thermobalance; the samples were heated at 10 °C/min from room temperature to 800 °C in dynamic air flow.

## 3. Results and discussion

In this work three cesium salts of CV were obtained: a mixed salt of potassium and cesium [ $CsKCV$ ] and two phases of cesium salts, one blue ( $Cs_2CV$ -1) and another green ( $Cs_2CV$ -2). Thermogravimetric analysis of  $CsKCV$  shows a mass loss of 4% at 100 °C, indicating the presence of one water molecule. The thermogravimetric curve of  $Cs_2CV$ -1 indicates that this compound is anhydrous, since any loss of mass was observed until 335 °C. Thermogravimetric curves are deposited as [Supplementary materials](#).

Cs<sub>2</sub>CV-1 salt does not present single crystals suitable to X-ray diffraction analysis; due to this fact, this salt was analysed by X-ray powder diffraction. As it can be seen in [Supplementary materials](#), the diffraction pattern of Cs<sub>2</sub>CV-1 is very similar to Rb<sub>2</sub>CV [21] salt and different from CsKCV. These results indicate that Cs<sub>2</sub>CV-1 is isostructural to Rb<sub>2</sub>CV salt [21], which crystallizes in triclinic space group  $P\bar{1}$  being isostructural to potassium croconate violet [19]. Crystal structure of Rb<sub>2</sub>CV was used to simulate the diffraction pattern and also to identify some reflections in the experimental data of Rb<sub>2</sub>CV and Cs<sub>2</sub>CV-1. The interplanar distances  $d_{hkl}$  of (100), (010) and (001) reflections are related to *a*, *b* and *c* unit cell parameters, respectively. In the experimental diffraction pattern of Cs<sub>2</sub>CV-1 the (001) and (010) reflections are identified, and the calculations of  $d_{hkl}$  to these peaks are shown in [Table 1](#). The peak (100) is not observed in experimental data, although a peak related to (300) reflection is identified and has been used to correlate to *a* crystal axis. As can be observed in [Table 1](#), Rb<sub>2</sub>CV presents smaller values for  $d_{hkl}$  than Cs<sub>2</sub>CV-1, indicating that in cesium salt the unit cell is bigger than in rubidium salt. This effect is observed in the crystal structure of K<sub>2</sub>CV, Rb<sub>2</sub>CV and (NBu<sub>4</sub>)<sub>2</sub>CV [20], where *a*, *b* and *c* cell parameters increase with counter-ion size increasing.

Crystal data of CsKCV and Cs<sub>2</sub>CV-2 are listed in [Table 2](#) and some geometrical parameters in [Table 3](#), and the crystal structures can be seen in [Fig. 1](#). The mixed salt crystallizes in triclinic space group  $P\bar{1}$ , similar to rubidium salt and to Cs<sub>2</sub>CV-1. On the other hand, the unit cell of Cs<sub>2</sub>CV-2 is monoclinic and crystallizes in  $P2_1/a$  space group. Both salts contain one water molecule for each M<sub>2</sub>C<sub>11</sub>N<sub>4</sub>O<sub>3</sub> unit. The amount of water molecules seems to be affected by both cation size and crystal packing, since in the triclinic salts (K<sub>2</sub>CV, CsKCV and Cs<sub>2</sub>CV-1) the number of water molecules decreases due to the cation size: K<sub>2</sub>CV has two water molecules, the mixed salt (CsKCV) has only one water molecule, and Cs<sub>2</sub>CV-1 is anhydrous. The Cs<sub>2</sub>CV-2 crystallizes in a different system with a unit cell volume ( $V = 1393.8(2) \text{ \AA}^3$ ) bigger than the other salts (around  $680 \text{ \AA}^3$ ), which allows the inclusion of one water molecule in the asymmetric unit. Similar results are not observed in mixed potassium–rubidium (RbKCV) and rubidium (Rb<sub>2</sub>CV) salts, where the cation exchange (by changing potassium for

Table 2

Crystal data of CsKCV and Cs<sub>2</sub>CV-2

Compound	CsKCV	Cs <sub>2</sub> CV
Formula	CsKC <sub>11</sub> N <sub>4</sub> O <sub>3</sub> ·H <sub>2</sub> O	Cs <sub>2</sub> C <sub>11</sub> N <sub>4</sub> O <sub>3</sub> ·H <sub>2</sub> O
Formula weight	426.20	519.97
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/a$
<i>a</i> (Å)	8.3731(3)	15.2077(13)
<i>b</i> (Å)	9.2900(5)	5.0460(3)
<i>c</i> (Å)	10.5696(4)	18.4875(16)
$\alpha$ (°)	104.731(2)	90.00
$\beta$ (°)	112.068(2)	100.754(3)
$\gamma$ (°)	105.111(2)	90.00
<i>V</i> (Å <sup>3</sup> )	676.19(5)	1393.78(19)
<i>Z</i>	2	4
Crystal size (mm)	0.03 × 0.11 × 0.15	0.02 × 0.02 × 0.24
<i>d</i> <sub>calc</sub> (g cm <sup>−3</sup> )	2.093	2.478
$\mu$ (MoK $\alpha$ ) (cm <sup>−1</sup> )	3.060	5.241
Min./max. transmission factors	0.5994/0.9138	0.5583/0.9238
Unique reflections	3005	3151
Observed reflections [ $F_o^2 > 2s(F_o^2)$ ]	2558	1871
No. of parameters refined	192	211
<i>R</i>	0.0454	0.0863
w <i>R</i>	0.0862	0.1397
<i>S</i>	1.074	1.082
RMS peak (e <sup>−</sup> Å <sup>−3</sup> )	0.098	0.162

rubidium ion) does not modify the quantity of water molecules and the crystal packing [21].

In both cesium salts the metal ions are forming interactions to both nitrogen and oxygen atoms of CV and also to water molecules, as it can be seen in [Fig. 2](#). In CsKCV, potassium atom is coordinated to CV in two different types: chelate (O2–O3) and monodentate (O2, N1, N2 and N3). The averages of K–O chelate and K–N monodentate bond distances are respectively 2.811(3) and 2.891(4) Å, and the K–O2 distance is 2.708(3) Å. The cesium atom presents the same two coordination modes to CV, chelate (N2–O3) and monodentate (N1 and N3), and the averages of Cs–N and Cs–O bond distances are 3.417(4) and 3.242(4) Å, respectively, whereas the average of Cs–N bond distances of the monodentate coordination is 3.328(4) Å. The water molecule is coordinated to both metals, and K–O4 and Cs–O4 bond distances are 2.871(4) and 3.188(4) Å, respectively. All these selected bond distances are displayed in [Table 3](#).

In Cs<sub>2</sub>CV-2 structure two crystallographic independent metal sites (Cs1 and Cs2) are observed, and both of them are disordered. These disorders have been identified since after location of all atoms in asymmetric unit, a significant positive residual electron densities remain in the fourier difference density maps close to the cesium sites. Similar results were also observed by Thomas and Womersley in the crystal structure of Cs<sub>x</sub>Rb<sub>1−x</sub>TiOAsO<sub>4</sub>[27], suggesting a partial occupancy of Cs atom in two sites. In this sense, the occupational factor of Cs<sub>1</sub> and Cs<sub>2</sub> in the Cs<sub>2</sub>CV-2 structure were refined individually and similar values were obtained in both sites

Table 1

Diffraction angles ( $2\theta_{hkl}$ ) and respective interplanar distances ( $d_{hkl}$ ) for some peaks of Rb<sub>2</sub>CV and Cs<sub>2</sub>CV-1

Compound	Peak	$2\theta_{hkl}$ (°)	<i>I</i> <sub>relative</sub> (%)	$d_{hkl}$ (Å)
Rb <sub>2</sub> CV	001	9.70	17.0	9.11
	010	10.2	9.6	8.66
	300	33.3	2.3	2.69
Cs <sub>2</sub> CV-1	001	8.10	4.9	10.9
	010	9.70	6.7	9.10
	300	33.0	5.9	2.71

Table 3  
Select bond distances (Å) and bond angles (°) of CsKCV and Cs<sub>2</sub>CV-2

<i>CsKCV</i>					
K—O2	2.708(3)	K—O2 <sup>vi</sup>	2.767(3)	Cs—O3 <sup>iv</sup>	3.156(3)
K—O4	2.871(4)	K—O3 <sup>vi</sup>	2.855(3)	Cs—O4 <sup>vii</sup>	3.188(4)
K—N2 <sup>i</sup>	2.803(4)	Cs—N1	3.238(4)	Cs—O3 <sup>viii</sup>	3.328(4)
K—N3 <sup>ii</sup>	3.010(4)	Cs—N3 <sup>iii</sup>	3.513(4)	Cs—N2 <sup>viii</sup>	3.500(4)
K—N1 <sup>v</sup>	2.861(4)	Cs—N2 <sup>iv</sup>	3.333(4)	Cs—N3 <sup>ix</sup>	3.232(4)
<i>Cs<sub>2</sub>CV-2</i>					
Cs1—O1	3.573(8)	Cs1—N4 <sup>vii</sup>	3.649(12)	Cs2—N2 <sup>v</sup>	3.289(10)
Cs1—N1	3.198(9)	Cs1—N3 <sup>viii</sup>	3.477(11)	Cs2—O3 <sup>v</sup>	3.106(7)
Cs1—O4	3.380(11)	Cs2—O2	3.502(7)	Cs2—O2 <sup>vi</sup>	3.288(8)
Cs1—N1 <sup>ii</sup>	3.066(10)	Cs2—O3	3.578(8)	Cs2—O3 <sup>vi</sup>	3.302(8)
Cs1—O4 <sup>iii</sup>	3.287(9)	Cs2—O2 <sup>i</sup>	3.099(7)	Cs2—N2 <sup>ix</sup>	3.216(10)
Cs1—N3 <sup>iv</sup>	3.207(10)	Cs2—N4 <sup>i</sup>	3.352(11)	Cs2—N2 <sup>x</sup>	3.381(11)
Cs1—N3 <sup>vii</sup>	3.345(10)				
<i>Angle(°)</i>					
C—C—C <sub>ring</sub>	108.0(3)	111.6(9)	C—C—N	176.5(5)	174.8(12)
C—C—C	120.0(3)	120.0(9)	C—C—O	126.2(3)	126.9(10)
<i>Diedro(°)</i>					
C1—C6—C7—N1	−172.3	−175.2	C3—C9—C10—N3	147.1	132.6
C1—C6—C8—N2	174.1	148.5	C3—C9—C11—N4	−159.3	156.2
<i>Hydrogen bonds (Å)</i>					
D ... H ... A	D— (Å)	H ... A (Å)	D ... A (Å)	D—H ... A (°)	
<i>CsKCV</i>					
O4—H4A—O1 <sup>x</sup>	0.83	2.55	3.244(5)	141	
O4—H4B—O1 <sup>vii</sup>	1.22	1.73	2.948(5)	177	
<i>Cs<sub>2</sub>CV-2</i>					
O4—H4A—O4 <sup>iv</sup>	1.10	1.85	2.941(11)	178	
O4—H4B—O1	1.06	1.75	2.802(11)	178	

Symmetry code as shown in Fig. 1.

[0.76(4)]. The total occupancy of Cs sites could be completed using the additional sites obtained by difference density maps. Similar to the Cs<sub>x</sub>Rb<sub>1-x</sub>TiOAsO<sub>4</sub> structure, the extinction parameter was refined to zero, suggesting that the additional sites might in some way be compensating the effects of extinction. The average distance Cs—Cs in this disordered structure is 0.472(3) Å, which is similar to that observed in Cs<sub>x</sub>Rb<sub>1-x</sub>TiOAsO<sub>4</sub> [27] (average of 0.413 Å).

Cs1 is coordinated to one water molecule, and the average of Cs1—O4 bond distance is 3.333(10) Å. In both metal sites, chelate (O1—N1 and N3—N4 for Cs1 and O2—O3; O3—N2 and O2—N4 for Cs2) and monodentate (N1 and N3 for Cs1 and O2, O3, N2 for Cs2) coordination modes are observed, similarly to CsKCV. The averages of Cs—N and Cs—O bond distances in the chelate coordination are 3.359(11) and 3.443(8) Å respectively, and for Cs—N of the monodentate coordination is 3.275(11) Å. The bond distances of CV anion are deposited as [Supplementary materials in Table S1](#). The CV anions are almost planar and the dicyanomethylene groups form angles with oxocarbon ring of 3.52 and 7.83° for CsKCV, and 0.40 and 2.20° for Cs<sub>2</sub>CV-2. The CV anions in CsKCV structure display a layer design, although in Cs<sub>2</sub>CV-2 they form a wave design

with planar angle of 80.9° (Fig. 3). The CC and CO bond distances are almost similar in both salts, suggesting a degree of electronic delocalization in the pseudo-oxocarbon ring. The biggest differences in CC and CO bonds are smaller in CsKCV (0.035 and 0.011 Å) than in Cs<sub>2</sub>CV-2 (0.107 and 0.016 Å), suggesting a more effective delocalization in the mixed salt. In both compounds the CV is involved in hydrogen bonds with water molecules.

In CsKCV the CV anion is acceptor of two weak hydrogen bonds and the average of O...O distance is 3.096(5) Å. In this salt two water molecules link two CV species forming a dimeric structure bridged by water molecules, as can be seen in Fig. 4a. In Cs<sub>2</sub>CV-2 two medium hydrogen bond interactions are observed, where CV anion is acceptor of one and the other occurs between the water molecules. The average of O...O distance is 2.872(11) Å, and these interactions link the planes of CV anions (Fig. 4b). Topological parameters of  $\pi$ -stacking interaction [13], which are listed in Table 4, strongly suggesting that this interaction is not effective in cesium salts. The interplanar distance indicates that the CV layers are close to each other, however the centroid-centroid distance is bigger than 4.0 Å, suggesting a horizontal translation (shift) of pseudo-oxocarbon



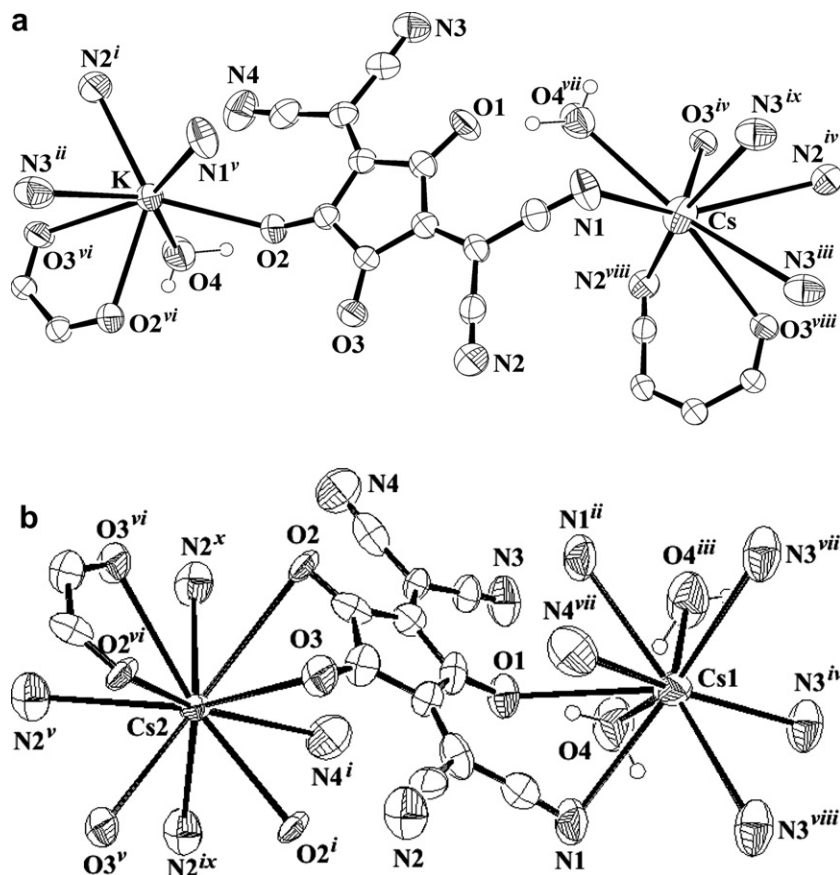


Fig. 1. ORTEP [26] view of crystal structures of (a) CsKCV and (b) Cs<sub>2</sub>CV-2. The symmetry code identified in atoms are: (a) i (x, y, 1 + z); ii (x, y - 1, z); iii (x, y, z - 1); iv (x, y + 1, z); v (2 - x, -y, 2 - z); vi (1 - x, -1 - y, 2 - z); vii (1 - x, -y, 2 - z); viii (1 - x, -y, 1 - z); ix (2 - x, 1 - y, 2 - z); x (x - 1, y - 1, z); (b) i (x, 1 + y, z); ii (x, y - 1, z); iii (1/2 - x, y - 1/2, -z); iv (1/2 - x, y + 1/2, -z); v (1 - x, 1 - y, 1 - z); vi (1 - x, -y, 1 - z); vii (x - 1/2, -y - 1/2, z); viii (x - 1/2, 1/2 - y, z); ix (x - 1/2, 1 + 1/2 - y, z); x (x - 1/2, 1/2 - y, z).

rings. This effect was also observed in rubidium [21] and tetrabutylammonium [20] salts. Despite different crystal packing of these salts, the CV units are almost planar and are displayed in layers separated by cations and water molecules (except to Cs<sub>2</sub>CV-1).

Table 5 shows the main vibrational wavenumbers and a tentative assignment of the cesium salts; it is worth of mention there is no normal mode calculations for the croconate violet in literature. Infrared and Raman spectra of these compounds are displayed in Figs. 5 and 6, respectively. In the infrared spectra of all cesium salts (Fig. 5) can be observed a very intense absorption around 2200 cm<sup>-1</sup>, assigned to C≡N stretching mode. Comparison of the spectral region of pseudo-oxocarbon ring stretching (1800–1400 cm<sup>-1</sup>) shows significant differences in wavenumber and band shapes. In mixed salt, the bands are broader than the ones of both crystallographic phases of Cs<sub>2</sub>CV, being interpreted by the presence of different cation–anion interactions. The ν(CO) is assigned to a band around 1680 cm<sup>-1</sup> in all salts and does not present wavenumber shift due to the cation change. Comparing the spectra of the two phases of cesium salts, it can be observed broader bands in the ring stretching modes of CV (1650–1400 cm<sup>-1</sup>) for Cs<sub>2</sub>CV-2. In this salt,

crystal data show that the difference in CC bond distances (Δ(CC)) of CV ring is 0.107 Å, suggesting a small electronic delocalization, which can be responsible for the spectral differences. On the other hand, Cs<sub>2</sub>CV-1 is isostructural to Rb<sub>2</sub>CV [21], which presents Δ(CC) equal to 0.039 Å, and this result indicates that electronic delocalization of CV anion in Cs<sub>2</sub>CV-1 is more effective than in Cs<sub>2</sub>CV-2. Bands in the region 1420–1580 cm<sup>-1</sup> are tentatively assigned to a mode containing both CO and CC stretching contributions; however, only a refined normal coordinate analysis could be precise enough to guarantee the assignment.

Similar to rubidium salts [21], in the Raman spectra of cesium salts (Fig. 6) two bands around 2200 cm<sup>-1</sup> are observed, assigned to stretching mode of C≡N [ν(C≡N)]. The difference between these bands can be related to crystal packing; the biggest differences in C≡N bond distances of CsKCV and Cs<sub>2</sub>CV-2 are 0.011 and 0.045 Å, respectively, and this effect can be seen in the Raman spectra, where the difference in ν(C≡N) bands is smaller in CsKCV (25 cm<sup>-1</sup>) than in Cs<sub>2</sub>CV-2 (33 cm<sup>-1</sup>). This difference in Cs<sub>2</sub>CV-1 is almost equal to the CsKCV (27 cm<sup>-1</sup>), and probably in Cs<sub>2</sub>CV-1 salt the C≡N bond distance is similar to CsKCV. On the other hand, the spec-

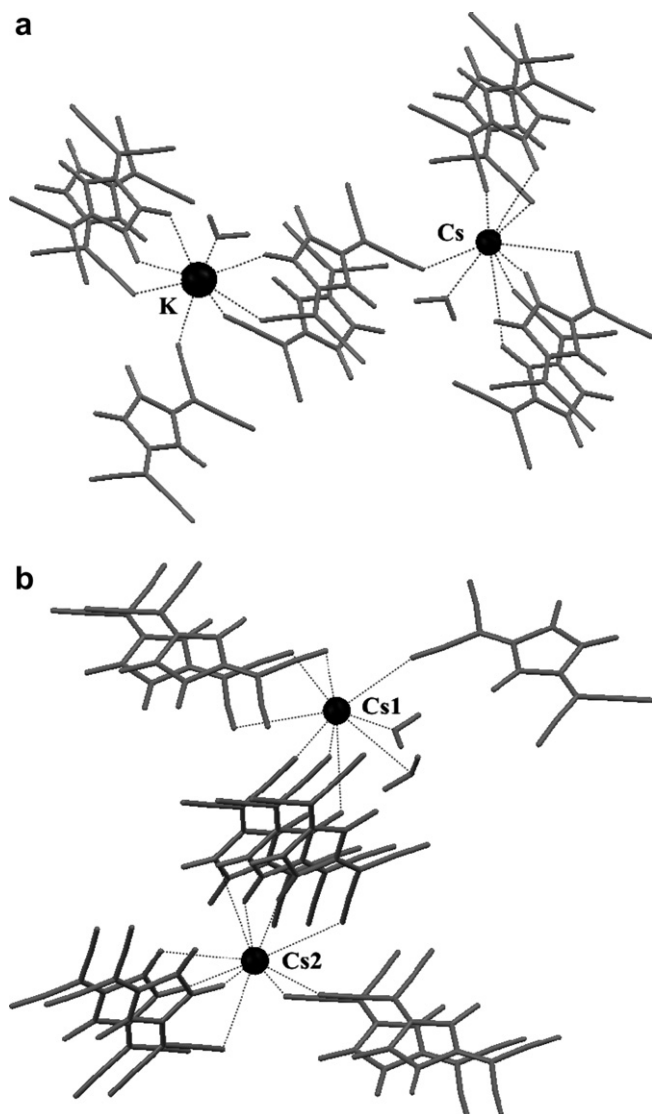


Fig. 2. Metal sites interactions in (a) CsKCV and (b) Cs<sub>2</sub>CV-2.

tral region of CV ring stretching modes ( $1600\text{--}1400\text{ cm}^{-1}$ , which contains vibrational modes who have the contributions of both  $\nu(\text{CO})$  and  $\nu(\text{CC})$ ) is different for cesium salts, but similar to the observed in the infrared spectra. In the mixed salt two intense bands are observed, although in Cs<sub>2</sub>CV only one intense band can be seen. Comparing

the crystal packing of these salts, the spectral differences could be attributed to changes in the electronic delocalization in the CV ring, and also to the presence of two different cations in the mixed salt (Cs<sup>+</sup> and K<sup>+</sup>). However, the two CO stretching modes, assigned to symmetric and asymmetric stretching modes, observed in all salts, do not present significant changes in intensity or wavenumber. The bending modes of pseudo-oxocarbon ring are also very similar in intensity and present a small wavenumber shift when compared to cesium salts.

#### 4. Conclusion

X-ray crystal structures of CsKCV and Cs<sub>2</sub>CV-2 show that these salts present different crystal packing, and powder diffraction pattern of Cs<sub>2</sub>CV-1 indicates that this compound is isostructural to Rb<sub>2</sub>CV salt [21]. The geometric parameters of  $\pi$ -stacking indicate that these compounds do not present this type of interaction and the crystal packing is influenced by cation–anion interaction and hydrogen bonding design. There is one water molecule in the M<sub>2</sub>CV unit in the both mixed salt and Cs<sub>2</sub>CV-2, whereas Cs<sub>2</sub>CV-1 is anhydrous. This water molecule is involved in medium and weak different hydrogen bonds to CV anion and to another water molecule in Cs<sub>2</sub>CV-2. In the mixed salt this interaction forms a dimeric structure, whereas in Cs<sub>2</sub>CV-2 it gives rise to a polymeric structure with one-dimensional arrangement (1D). In both salts the CV anion presents two coordination modes: monodentate and chelate. In the mixed salt only Cs<sup>+</sup> forms interaction with water molecule and in the Cs<sub>2</sub>CV-2 this interaction is observed only with one metal site. Vibrational spectra of cesium salts are almost similar, the major differences can be observed in the CV ring stretching modes ( $1600\text{--}1400\text{ cm}^{-1}$ ), probably due to the difference in the electronic delocalization of the pseudo-oxocarbon ring, which is less effective in Cs<sub>2</sub>CV-2. In the Raman spectra are observed two bands in the C $\equiv$ N stretching region; the difference between these bands is similar in both CsKCV and Cs<sub>2</sub>CV-1 (around  $26\text{ cm}^{-1}$ ) and for Cs<sub>2</sub>CV-2 ( $33\text{ cm}^{-1}$ ). This result is in agreement with X-ray diffraction, which shows bigger differences in C $\equiv$ N bond distances for Cs<sub>2</sub>CV-2 than for CsKCV. This fact suggests that C $\equiv$ N bond distance

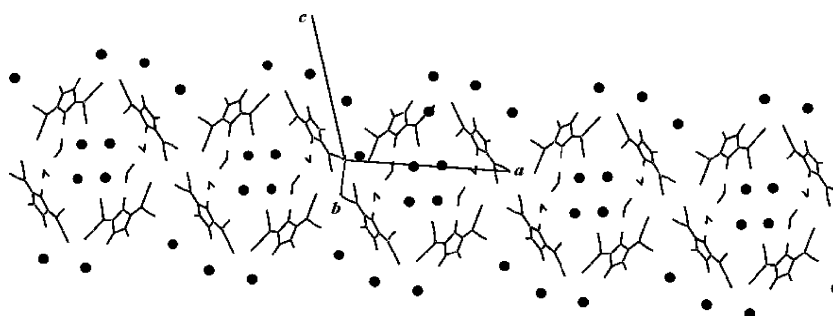
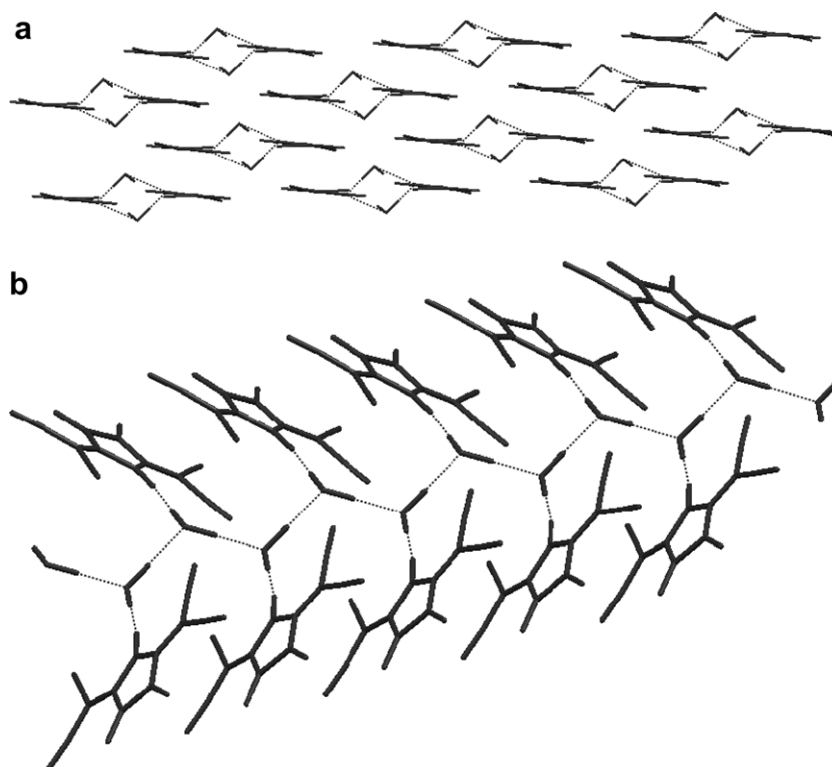


Fig. 3. Crystal packing of croconate violet anion in Cs<sub>2</sub>CV-2.

Fig. 4. Hydrogen bonding design observed in (a) CsKCV and (b) Cs<sub>2</sub>CV-2 crystal structure.Table 4  
Geometrical parameters of  $\pi$ -stacking interaction for CsKCV and Cs<sub>2</sub>CV-2

	CsKCV	Cs <sub>2</sub> CV-2
Interplanar distance (Å)	3.38	3.25
Distance between centroids (Å)	4.02	5.05
Shift between centroids (Å)	1.83	3.77

in Cs<sub>2</sub>CV-1 is similar to that observed in CsKCV. Vibrational bands assigned to symmetric and asymmetric  $\nu(\text{C}=\text{O})$  and ring bending modes do not present significant wavenumber shift due to the cation exchange in vibrational spectra. The bending modes of pseudo-oxo-carbon ring are very similar in intensity and present a small wavenumber shift; this can be explained by the fact

Table 5  
Vibrational wavenumbers (in  $\text{cm}^{-1}$ ) and tentative assignment of the most important bands observed in CsKCV and Cs<sub>2</sub>CV vibrational spectra

CsKCV		Cs <sub>2</sub> CV-1		Cs <sub>2</sub> CV-2		Tentative assignment
Infrared	Raman	Infrared	Raman	Infrared	Raman	
	336 m		333 m		329 m	Ring bending
	389 m		392 m		387 m	
548 m	553 vw	552 w	553 vw	552 w	551 vw	CCN+CCCN bend
597 w	597 m		599 w	594 w	603 w	
621 w	628 w		626 w		634 w	
824 w	763 w		761 w	824 vw	763 w	$\nu(\text{CCCN})+\nu(\text{CC})$
	907 vw		900 vw		905 w	Ring breathing
1167 w	1168 vw	1163 vw	1152 vw	1163 vw	1164 vw	$\nu(\text{CC})$
	1197 w		1202 w		1202 vw	$\nu(\text{CC})$
	1220 w		1212 w		1212 w	$\nu(\text{CC})$
	1276 w		1273 vw		1272 w	$\nu(\text{CC})$
1456 vs	1420 w	1450 vs	1415 w	1427 s	1420 w	$\nu(\text{CO})+\nu(\text{CC})$
1528 s	1505 s	1524 s	1509 m	1466 vs	1540 vs	$\nu(\text{CO})+\nu(\text{CC})$
1580 s	1567 s	1572 s	1588 w	1525 s	1577 w	$\nu(\text{CO})+\nu(\text{CC})$
1618 s	1620 w	1616 s	1609 w	1601 s	1611 w	$\nu_{\text{ass}}(\text{CO})$
1674 m	1683 w	1676 m	1686 w	1682 w	1681 w	$\nu_{\text{s}}(\text{CO})$
2197 vs	2186 m	2199 vs	2182 m	2195 s	2176 w	$\nu(\text{CN})$
	2211 vs		2209 vs		2209 vs	$\nu(\text{CN})$
3605 m		3574 m				$\nu(\text{OH})$
3497 m		3520 m				$\nu(\text{OH})$



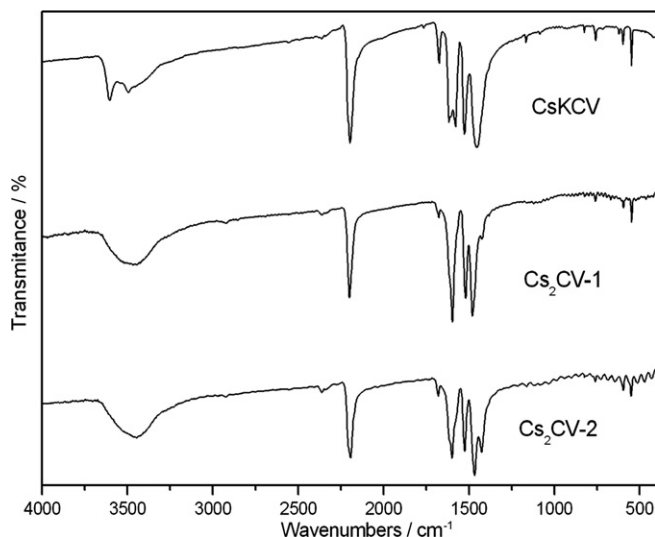


Fig. 5. Infrared spectra of cesium salts of croconate violet in KBr pellets.

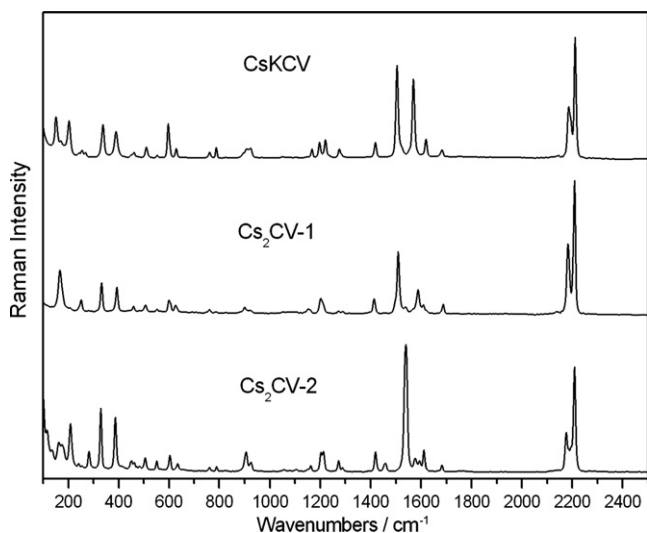


Fig. 6. Fourier transform Raman spectra of cesium salts of croconate violet.

that the CV units are almost planar and are displayed in layers separated by cations and water molecules (except to  $\text{Cs}_2\text{CV-1}$ ) in these salts.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2007.06.001](https://doi.org/10.1016/j.molstruc.2007.06.001).

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