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## Mixed salts containing croconate violet, lanthanide and potassium ions: Crystal structures and spectroscopic characterization of supramolecular compounds

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### ABSTRACT

The vibrational spectra and crystal structures of four lanthanide and potassium salts of 3,5-bis(dicyanomethylene)cyclopentane-1,2,4-trionate ( $C_1N_4O_3^{2-}$ ), known as croconate violet (CV), are described in this work. All  $LnK_{22}N_8O_6$  ( $Ln = La^{+3}, Nd^{+3}, Gd^{+3}$  and  $Ho^{+3}$ ) compounds are isostructural, crystallizing in the triclinic  $P\bar{1}$  space group. In each compound the lanthanide ion is acting as both monodentate and chelate metal sites, whereas the potassium presents only monodentate coordination. The crystal structure shows the formation of a periodic 2D structure extended by K–N bonds parallel to the crystallographic  $[001]$  direction; these 2D sheets form hydrogen bonds with water molecules giving rise to a 3D extended arrangement. It is not possible to observe any type of  $\pi$ -interaction and the main forces responsible to stabilize the structures are the hydrogen bonds. The vibrational spectra of all the compounds are very similar, and the most important vibrational markers for the croconate violet ion, namely the  $\nu(C\equiv N)$  and  $\nu(C=O)$  modes, behave differently: the  $\nu(C\equiv N)$  modes are not shifted by the presence of the lanthanide ion species, only showing small band intensity differences, whereas the  $\nu(C=O)$  bands are shifted to higher wavenumbers, due to their coordination to the metal sites.

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### 1. Introduction

In the recent years, structural studies involving supramolecular chemistry have been performed trying to understand the role of the interactions which are responsible for the molecular architecture, as for instance hydrogen bonds,  $\pi$  stacking or charge transfer interactions [1–3]. In this sense, several chemicals have appeared as good candidates to generate supramolecules; such chemicals are known as building blocks. Among these building blocks, the so-called oxocarbons and pseudo-oxocarbons [4–11] have been used in the recent years since they present a group of properties which includes the ones described above, such as hydrogen bonds and  $\pi$  stacking.

Oxocarbons are cyclic species of general formula  $(C_nO_n)^{2-}$ , where  $n$  varies from 3 (deltate ion), 4 (sugarate ion), 5 (croconate ion) to 6 (rhodizionate ion) [12]. Their structures are planar, presenting a high molecular symmetry and electronic delocalization over the structures [13–16]. Pseudo-oxocarbons are species derived from the oxocarbon ions where one or more oxygen atoms are replaced by other atoms or groups [13]. In particular, the

reaction between croconate ion and malononitrile ( $NCCH_2CN$ ) gives rise to some pseudo-oxocarbon ions, for example [2,4,5-tris(dicyanomethylene)cyclopentane-1,3-dionate] (known as blue croconate) [17] and [3,5-bis(dicyanomethylene)cyclopentane-1,2,4-trionate] (known as croconate violet or CV) [13]. Specifically the croconate violet ion, due to a very strong electronic absorption in the ultraviolet–visible region of the spectrum, can also be used as a pigment; the vibronic spectrum of the croconate violet ion in aqueous solution has been reported in the literature, as well as some theoretical investigations about the assignments of the electronic transitions for such species [18,19]. The resonance Raman spectra of the CV ion in aqueous solution strongly indicate that the electronic delocalization over the oxocarbon ring is greater than in the analogous croconate ion. Two different electronic transitions can be observed in the optical spectrum due to different chromophoric groups: one from the  $\pi$  system from the oxocarbon ring, and other from the dicyanoethylene groups.

Due to the presence of  $\pi$  electrons in the cyclic ring system, croconate violet ion is a strong candidate for the observation of  $\pi$  stacking interactions. In addition, these ions can also present different geometries of coordination to metal sites: from monodentate geometry using oxygen or nitrogen atoms, to poly-coordination involving both the carbonyl and the cyano groups. In fact,

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several investigations in the literature have explored this capability of the CV ion, which makes this compound a potential ligand for the use in crystallographic engineering [7–11].

Lanthanide ions are well known for their optical properties due to the presence of electrons in *f* orbitals; for this reason they have been used to generate coordination compounds with different oxocarbon ions, such as squarate and croconate ions [15,20–24]. In those investigations the crystalline structures are stabilized by means of hydrogen bond interactions, which are formed by water molecules also coordinated to the rare earth ions. However, in those situations, both oxocarbon ions used in the investigations present only oxygen as the coordination atoms; in the case of croconate violet, besides the oxygen atoms, there are also up to four cyano groups available for coordination, which turns the investigation more exciting with the possibility of other geometries than the observed before.

In this work we describe the supramolecular crystal structures of mixed salts involving lanthanum, neodymium, gadolinium and holmium ions, potassium ion and the pseudo-oxocarbon croconate violet ion. The main purpose of this investigation is to identify the intermolecular interactions which are present in the solid state, as well as to evaluate the effect of the rare earth ions over the crystal packing, to provide a better understanding of the supramolecular chemistry involving the pseudo-oxocarbon croconate violet and lanthanide ions.

## 2. Experimental

Potassium bis(dicyanomethylene)croconate ( $K_2CV$ ) was synthesized as described by Teles et al. [10], which is a modification of the Fatiadi method [13]. Silver violet croconate ( $Ag_2CV$ ) was obtained using a metathesis reaction between aqueous solutions of silver nitrate and potassium violet croconate; the solid  $Ag_2CV$  was employed in another metathesis reaction with solutions of the lanthanide chloride (specifically, lanthanum, neodymium, gadolinium and holmium chlorides). In a few days, suitable crystals were formed in the solution, which were separated by filtration, washed with cold ethanol and dried in vacuum over phosphorus pentoxide.

### 2.1. Lanthanum and potassium 3,5-bis(dicyanomethylene) cyclopentane-1,2,4-trionate ( $LaKCV_2$ )

The compound was characterized as  $LaKC_{22}N_8O_6 \cdot 10H_2O$  (830.41 g mol<sup>-1</sup>); elemental analysis gave the following data: *Anal.* Calc.: C, 31.82; H, 2.43; N, 13.49. Found: C, 32.43; H, 2.37; N, 13.77%.

### 2.2. Neodymium and potassium 3,5-bis(dicyanomethylene) cyclopentane-1,2,4-trionate ( $NdKCV_2$ )

The compound was characterized as  $NdKC_{22}N_8O_6 \cdot 10H_2O$  (835.74 g mol<sup>-1</sup>); elemental analysis gave the following data: *Anal.* Calc.: C, 31.62; H, 2.41; N, 13.41. Found: C, 32.09; H, 2.35; N, 13.58%.

### 2.3. Gadolinium and potassium 3,5-bis(dicyanomethylene) cyclopentane-1,2,4-trionate ( $GdKCV_2$ )

The compound was characterized as  $GdKC_{22}N_8O_6 \cdot 10H_2O$  (848.75 g mol<sup>-1</sup>); elemental analysis gave the following data: *Anal.* Calc.: C, 31.13; H, 2.38; N, 13.20. Found: C, 31.53; H, 2.29; N, 13.20%.

### 2.4. Holmium and potassium 3,5-bis(dicyanomethylene) cyclopentane-1,2,4-trionate ( $HoKCV_2$ )

The compound was characterized as  $HoKC_{22}N_8O_6 \cdot 10H_2O$  (856.43 g mol<sup>-1</sup>); elemental analysis gave the following data: *Anal.*

Calc.: C, 30.85; H, 2.35; N, 13.08. Found: C, 30.85; H, 2.37; N, 12.91%.

Single crystal X-ray data were collected using a Bruker Kappa CCD diffractometer with Mo K $\alpha$  ( $\lambda = 0.71073$  Å) at room temperature. Data collection, reduction and cell refinement were performed by COLLECT [25], EVALCCD [26] and DIRAX [27] programs, respectively. The structures were solved and refined using SHELX-97 [28]. An empirical isotropic extinction parameter *x* was refined, according to the method described by Larson [29]. A multiscan absorption correction was applied [30]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were located from Fourier difference maps and isotropic displacement parameters were refined using the same parameters set. The structures were drawn by ORTEP-3 for Windows [31], POV-ray [32] and MERCURY [33] programs.

The infrared spectra were obtained by using a Bomem MB-102 spectrometer fitted with KBr disks and a spectral resolution of 4 cm<sup>-1</sup>. Good signal-to-noise ratios were obtained from the accumulation of 128 spectral scans. Fourier-transform Raman spectroscopy was carried out using a Bruker RFS 100 instrument with a Nd<sup>3+</sup>/YAG laser operating at 1064 nm in the near infrared and a CCD detector cooled with liquid N<sub>2</sub>. Good signal-to-noise ratios were obtained from 1024 accumulated scans and a spectral resolution of 4 cm<sup>-1</sup>.

Thermogravimetric data were obtained using a SHIMADZU DTG60 thermobalance in which the samples were heated at a rate of 10 °C/min from room temperature to 750 °C in a dynamic air flow. Atomic emission spectroscopic data for potassium ions were obtained using a DIGIMED DM-61 spectrophotometer with standard solutions of potassium salts.

## 3. Results and discussion

In this investigation four new mixed salts of lanthanide (lanthanum, neodymium, gadolinium and holmium) and potassium ions with croconate violet ion were obtained, namely  $LaKCV_2$ ,  $NdKCV_2$ ,  $GdKCV_2$  and  $HoKCV_2$ . Elemental analysis and atomic emission spectroscopy data indicated the presence of potassium ions in each of the compounds. The presence of ten water molecules for all compounds was also determined by means of elemental analysis. However, in the thermogravimetric (TG) analysis (Supplementary material) eight water molecules were found for  $LaKCV_2$  and 11 for  $NdKCV_2$ ,  $GdKCV_2$  and  $HoKCV_2$ . This difference in water content can be attributed to different hygroscopic characteristics of the complexes.

For  $LaKCV_2$  two consecutive steps of weight losses were observed in the temperature range of 50–125 °C, corresponding to the loss of eight water molecules (obsd. 17.72%, calcd. 18.13%). The thermal decomposition of the CV units occurs in the temperature range between 340 and 530 °C, and the final mass residue corresponds to a half mol of La<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O (obsd. 27.96%, calcd. 26.42%). For  $NdKCV_2$ ,  $GdKCV_2$  and  $HoKCV_2$ , the TG curves are very similar and indicate the presence of 11 water molecules (obsd. 22.77%, calcd. 23.19% for  $NdKCV_2$ ; obsd. 23.98%, calcd. 22.84% for  $GdKCV_2$  and obsd. 22.23%, calcd. 22.64% for  $HoKCV_2$ ).

The crystallographic data are listed in Table 1, some important geometrical parameters are displayed in Table 2 and the general crystal structure for the complexes is shown in Fig. 1. The X-ray diffraction analysis indicates that all compounds are isostructural, with  $P\bar{1}$  as the space group, similar to other croconate violet salts described in the literature, such as those of potassium [7], rubidium [8] and cesium [9]. It is interesting to note that from those compounds described hitherto only the cesium salt is anhydrous; all the others contain water molecules in the crystal structure. Analyzing the data displayed in Table 1 it seems clear the existence

**Table 1**Crystal data of LnKCV<sub>2</sub> (Ln = La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup> and Ho<sup>3+</sup>).

Compound	LaKCV <sub>2</sub>	NdKCV <sub>2</sub>	GdKCV <sub>2</sub>	HoKCV <sub>2</sub>
Formula	LaKC <sub>22</sub> H <sub>16</sub> O <sub>14</sub> N <sub>8</sub>	NdKC <sub>22</sub> H <sub>16</sub> O <sub>14</sub> N <sub>8</sub>	GdKC <sub>22</sub> H <sub>16</sub> O <sub>14</sub> N <sub>8</sub>	HoKC <sub>22</sub> H <sub>16</sub> O <sub>14</sub> N <sub>8</sub>
Formula weight (g mol <sup>-1</sup> )	794.44	799.77	812.78	820.46
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.3456(3)	8.3040(5)	8.2826(8)	8.2650(7)
<i>b</i> (Å)	11.9452(11)	11.8877(15)	11.8264(9)	11.8236(12)
<i>c</i> (Å)	16.7931(16)	16.7064(18)	16.6567(16)	16.6590(8)
$\alpha$ (°)	99.133(13)	98.924(9)	98.739(7)	98.488(6)
$\beta$ (°)	90.982(7)	90.951(7)	90.782(9)	90.684(6)
$\gamma$ (°)	106.999(7)	106.966(7)	106.933(8)	106.857(7)
<i>V</i> (Å <sup>3</sup> )	1577.1(2)	1555.0(3)	1539.8(3)	1538.4(2)
<i>Z</i>	2	2	2	2
Crystal size (mm)	0.186 × 0.274 × 0.285	0.301 × 0.165 × 0.207	0.2871 × 0.072 × 0.100	0.428 × 0.265 × 0.538
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.673	1.708	1.753	1.771
$\lambda$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	0.71073	0.71073	0.71073	0.71073
Transmission factors (min/max)	0.495/0.766	0.241/0.6615	0.528/0.873	0.306/0.584
Reflections total/unique reflections	11 718/6296	22 049/6947	26 016/6973	15 509/6825
Observed reflections [ <i>F</i> <sub>o</sub> <sup>2</sup> > 2 <i>s</i> ( <i>F</i> <sub>o</sub> <sup>2</sup> )]	5465	5966	5733	6309
Number of parameters refined	433	431	431	432
<i>R</i>	0.0490	0.0461	0.0628	0.0359
<i>wR</i>	0.1383	0.1375	0.1665	0.1084
<i>S</i>	1.346	1.110	1.104	1.110
RMS peak (e <sup>-</sup> Å <sup>-3</sup> )	0.305	0.166	0.204	0.155

**Table 2**Selected bond distances and bond angles of LnKCV<sub>2</sub> (Ln = La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup> and Ho<sup>3+</sup>).

	LaKCV <sub>2</sub>	NdKCV <sub>2</sub>	GdKCV <sub>2</sub>	HoKCV <sub>2</sub>
<i>Bond</i> (Å)				
C–C <sub>ring</sub>	1.460(8)	1.461(7)	1.462(10)	1.464(7)
C1–O1	1.225(7)	1.222(7)	1.201(9)	1.218(6)
C3–O2	1.273(7)	1.271(7)	1.264(8)	1.255(6)
C4–O3	1.264(7)	1.266(6)	1.260(8)	1.267(5)
C12–O4	1.251(7)	1.263(6)	1.257(8)	1.259(5)
C13–O5	1.266(7)	1.265(6)	1.255(8)	1.264(6)
C15–O6	1.224(7)	1.231(7)	1.231(9)	1.231(6)
C7–N1	1.142(9)	1.147(8)	1.153(11)	1.149(8)
C8–N2	1.146(10)	1.152(10)	1.139(12)	1.134(8)
C10–N3	1.144(10)	1.141(9)	1.146(12)	1.149(8)
C11–N4	1.148(9)	1.147(8)	1.157(10)	1.147(7)
C18–N5	1.157(10)	1.143(9)	1.147(12)	1.142(8)
C19–N6	1.134(9)	1.126(8)	1.117(10)	1.120(7)
C21–N7	1.125(11)	1.132(10)	1.159(12)	1.149(8)
C22–N8	1.132(10)	1.133(9)	1.120(12)	1.134(8)
M–O2	2.609(4)	2.560(4)	2.527(5)	2.513(3)
M–O3	2.577(4)	2.520(4)	2.470(5)	2.430(3)
M–O4	2.593(4)	2.552(4)	2.509(5)	2.497(3)
M–O5	2.588(4)	2.532(4)	2.472(5)	2.436(3)
M–O7	2.542(5)	2.471(4)	2.400(6)	2.363(4)
M–O8	2.574(5)	2.516(5)	2.462(6)	2.436(4)
M–O9	2.606(5)	2.542(4)	2.488(5)	2.445(4)
M–O10	2.545(6)	2.490(5)	2.433(6)	2.391(5)
M–O11	2.547(5)	2.482(5)	2.419(6)	2.377(4)
K1–N2	2.862(10)	2.848(9)	2.825(12)	2.855(8)
K1–N3i	3.245(9)	3.214(8)	3.185(11)	3.197(7)
K1–N4ii	2.998(8)	2.983(7)	2.967(8)	2.995(6)
K1–O12iii	2.915(9)	2.887(8)	2.861(9)	2.886(7)
K1–O12	2.769(8)	2.772(8)	2.805(9)	2.789(7)
K1–O13	2.920(7)	2.910(7)	2.894(9)	2.921(6)
<i>Average of angles</i> (°)				
(C–C–C) <sub>ring</sub>	108.0(5)	108.0(4)	108.0(6)	108.0(4)
C–C–C	120.0(6)	120.0(5)	120.3(7)	120.0(5)
C–C–N	177.0(8)	176.9(7)	177.3(10)	176.8(7)
C–C–O	125.8(5)	125.7(5)	125.7(6)	125.7(4)

Symmetry codes: i(1 – *x*, 1 – *y*, 2 – *z*); ii(–1 + *x*, *y*, *z*) and iii(–*x*, –*y*, 2 – *z*).

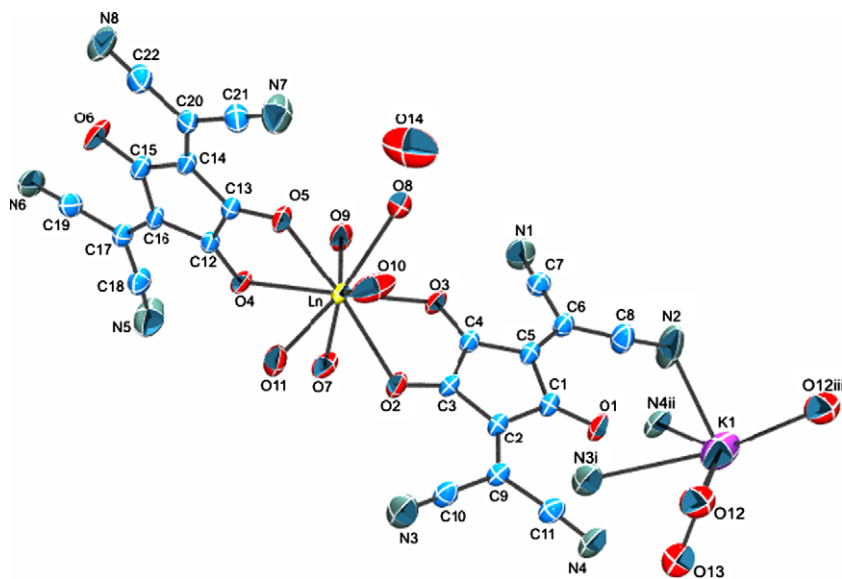
of a relationship between the properties of the complex and the increase in the atomic number of the lanthanide ion; however, these properties are similar since for the investigated compounds the chemical characteristics of the lanthanide ions are also analogous,

due to the small sizes and nuclear charges variation in the series which are caused by the effect of the so-called lanthanide contraction. It is also verified that the axes and angles, the volume and the density of the unit cells for all the complexes are slightly similar, but present a small decrease in values from the lanthanum to the holmium compound. For each LnKC<sub>22</sub>N<sub>8</sub>O<sub>6</sub> (Ln = La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup> and Ho<sup>3+</sup>) unit there are eight water molecules; these data, however, are not in agreement with the thermogravimetric data. This can be attributed to the existence of adsorbed water molecules on the surface of the crystals.

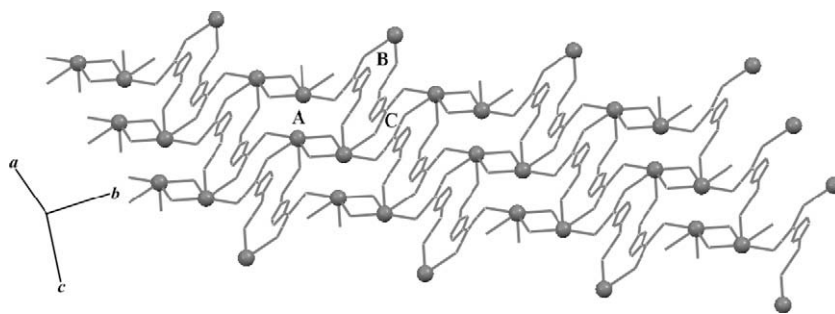
All C–C bond distances in the CV ring are very similar for the compounds studied here, strongly suggesting the presence of an electronic delocalization over the ring caused by the  $\pi$  electrons. The average C–C bond lengths for the CV rings are 1.460(8), 1.461(7), 1.462(10) and 1.464(7) Å for La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup> and Ho<sup>3+</sup> compounds, respectively. These values are intermediate between a single and a double carbon–carbon bond (about 1.54 and 1.35 Å, respectively); once again, these data provide a support for the electronic delocalization over the croconate violet ring.

In all compounds the lanthanide ions are coordinated by two oxygen atoms from two CV anions giving rise to a chelate (the atoms O2–O3 and O4–O5, according to Fig. 1), as well as to five water molecules (O7, O8, O9, O10 and O11, respectively), whereas the potassium atoms appear coordinated by three nitrogen from the CV anions and two water molecules (N2, N3, N4, O12 and O13, respectively); all these distances are displayed in Table 1. Both CV anions are almost planar, and for the CV which is coordinated to both ions (K<sup>+</sup> and lanthanide), the dicyanomethylene groups are more distorted (torsion angles of 5.1 and 10.3 Å) than the CV which is coordinated only to lanthanide ions (torsion angles of 5.3 and 2.3 Å). The angle between the oxocarbon rings of independent CV species (involving the atoms C1–C5 and C12–C16) present values of 83.7(2)°, 84.3(2)°, 84.9(3)° and 85.3(2)° for the lanthanide salts of La<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup> and Ho<sup>3+</sup>, respectively.

The crystal structures show the formation of a periodic 2D structure extended by K–N bonds parallel to the crystallographic [0 0 1] plane, as can be observed in Fig. 2. The interaction between K and CV ions gives rise to three different rings in the 2D sheet, named as A, B and C in Fig. 2. In all rings there are two CV species; however, the rings B and C have two K atoms whereas ring A has four K sites, all of them are five-coordinated; this network has



**Fig. 1.** Crystal structure of  $\text{LnKCV}_2$  ( $\text{Ln} = \text{La}^{+3}, \text{Nd}^{+3}, \text{Gd}^{+3}$  and  $\text{Ho}^{+3}$ ) and displacement with 50% probability level. The symmetry codes identified in atoms are: i( $-x+2, -y+1, -z+1$ ), ii( $x, y+1, z$ ) and iii( $-x+1, -y+1, -z+2$ ).



**Fig. 2.** The 2D sheet design of  $\text{LnKCV}_2$  ( $\text{Ln} = \text{La}^{+3}, \text{Nd}^{+3}, \text{Gd}^{+3}$  and  $\text{Ho}^{+3}$ ), where A, B and C indicate the rings of net  $4^{222}$ .

the Schläfli symbol  $4^{222}$  [34]. These 2D sheets form hydrogen bonds with water molecules, giving rise to a 3D extended arrangement (Fig. 3). The independent CV anions are receptors of four and three hydrogen bonds each; all these interactions are listed in Table 3.

Topological analysis of the  $\pi$  stacking interactions [35] shows that the interplanar distance between CV rings is 3.52 Å for  $\text{LaKCV}_2$  and 3.50 Å for the other salts, suggesting the presence of this type of interaction. However, the centroid–centroid distance (4.08 Å for  $\text{LaKCV}_2$ ,  $\text{NdKCV}_2$  and  $\text{GdKCV}_2$ , and 4.07 Å for  $\text{HoKCV}_2$ ) and the horizontal shift (2.06 Å for  $\text{LaKCV}_2$ , 2.09 Å for  $\text{NdKCV}_2$  and  $\text{GdKCV}_2$ , and 2.08 Å for  $\text{HoKCV}_2$ ) indicate that this interaction is not so efficient to be the appointed as important relations in the crystal structure.

As described before, croconate ion is the precursor for obtaining croconate violet ion, and the crystal structures of the analogous lanthanide croconates have also been reported in the literature [21]. Two coordination modes were observed for those compounds; for Ce, Pr, Nd, Sm, Eu and Gd croconate complexes the metal site is involved in chelate coordination with croconate ion, analogous to that observed in the mixed salts discussed in this work. It is worth noting that the lanthanide compounds form single crystals with croconate ion, but this was not observed for the CV ion complex in our investigation. However, in the literature are listed some crystal structures of mixed compounds involving CV anion and alkaline metals (such as Rb and Cs, among others),

all of them crystallizing with the potassium cation [4,8–11], suggesting that the CV anion forms a very stable interaction with the potassium species that is responsible for stabilizing the crystal packing in such species.

Table 4 presents the main wavenumber values as well as the tentative assignments for the vibrational modes in both infrared and Raman techniques. All the spectra are displayed in Figs. 4 and 5 (infrared) and 5 (Raman) for all the investigated compounds. As the complexes are isostructural, it is expected that the vibrational spectra are similar, with some small band changes arising from different interactions between each one of the lanthanide ions and the croconate violet ion. It is relevant to note here that the only previous vibrational investigation appearing in the literature for these systems is a theoretical calculation for the vibrational assignment for the ammonium croconate violet salt [36]. In this context, the spectrum of the ammonium salt, which does not present any direct interactions between the CV and the cation, is the basis of comparison in this study, being understood as the free CV ligand.

In the  $3500\text{ cm}^{-1}$  region it can be observed the stretching mode arising from the water molecules present in the crystal structures of the compounds, not showed in the infrared spectra (Fig. 4). All the compounds present a very strong absorption band around  $2220\text{ cm}^{-1}$ , which are assigned to the CN bond stretching from the dicyanomethylene groups; these bands are not so affected when compared with the free CV ligand, since the coordination site



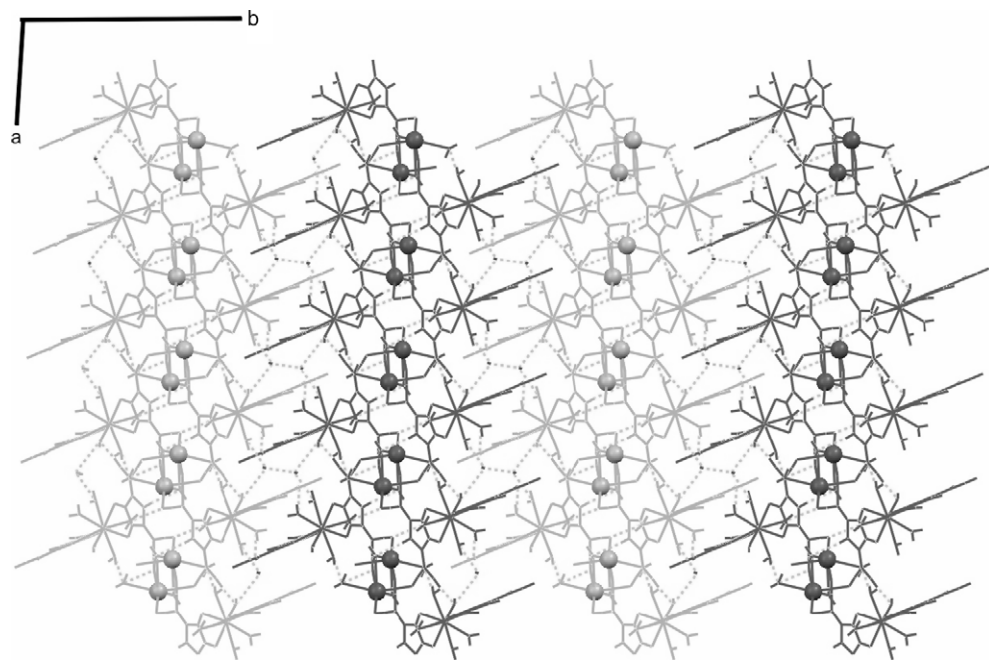


Fig. 3. Hydrogen bonds between 2D sheets of  $\text{LnKCV}_2$  ( $\text{Ln} = \text{La}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Gd}^{+3}$  and  $\text{Ho}^{+3}$ ) view along  $c$  axis.

Table 3

Geometric parameters of hydrogen bonds in  $\text{LnKCV}_2$  ( $\text{Ln} = \text{La}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Gd}^{+3}$  and  $\text{Ho}^{+3}$ ).

D...H...A	$\text{LaKCV}_2$		$\text{NdKCV}_2$		$\text{GdKCV}_2$		$\text{HoKCV}_2$	
	D...A (Å)	D-H...A (°)	D...A (Å)	D-H...A (°)	D...A (Å)	D-H...A (°)	D...A (Å)	D-H...A (°)
O7-H7B-N4i	2.879(10)	158.0	2.867(8)	157.0	2.877(10)	156.0	2.875(6)	155.0
O8-H8A-N7ii	2.943(11)	165.0	2.944(9)	166.0	2.909(12)	168.0	2.933(8)	169.0
O8-H8B-N6iii	2.874(9)	145.0	2.878(8)	145.0	2.887(11)	144.0	2.880(6)	145.0
O9-H9A-O14	2.800(11)	148.0	2.775(11)	150.0	2.752(14)	152.0	2.757(10)	154.0
O9-H9B-O6ii	2.885(7)	151.0	2.881(7)	151.0	2.876(9)	151.0	2.883(6)	151.0
O10-H10A-N1iv	2.842(11)	136.0	2.822(10)	135.0	2.807(12)	133.0	2.820(9)	132.0
O11-H11A-O13i	2.750(9)	171.0	2.744(7)	170.0	2.732(10)	167.0	2.736(7)	167.0
O11-H11B-N8v	2.913(11)	155.0	2.908(9)	155.0	2.915(13)	154.0	2.925(8)	154.0
O12-H12-O7i	3.297(10)	152.0	3.278(9)	153.0	3.276(11)	150.0	3.308(7)	156.0
O13-H13A-N3i	3.008(11)	132.0	3.015(10)	130.0	3.003(13)	130.0	3.009(9)	130.0
O13-H13B-O9vi	3.036(8)	168.0	3.022(7)	166.0	3.044(10)	165.0	3.040(7)	164.0
O14-H14B-O9	2.800(11)	120.0	2.775(11)	122.0	2.752(14)	121.0	3.757(10)	122.0

Symmetry codes: i(1 - x, 1 - y, 2 - z); ii(1 - x, 2 - y, 1 - z); iii(1 - x, 1 - y, 1 - z); iv(1 + x, y, z); v(2 - x, 2 - y, 1 - z) and vi(-x, 1 - y, 2 - z).

is actually the oxygen atoms from the carbonyl groups of the croconate violet structure. Hence, the other key vibrational band, the CO mode, is present in the spectra with both symmetric (in the  $1690\text{ cm}^{-1}$  region) and asymmetric (in the  $1605\text{ cm}^{-1}$  region) components; the wavenumbers for these vibrational modes appear in the high wavenumber region for  $\text{Ho}^{+3}$  in comparison with  $\text{La}^{+3}$ , due to the decrease of the atomic radii for the lanthanide ions along the series in the Periodic Table, giving rise to a more effective interaction for the coordinated bonds between the metal ions and the CO groups.

The spectral region between  $1600\text{ cm}^{-1}$  and  $1400\text{ cm}^{-1}$  comprises several vibrational modes which can be assigned to the stretching of the carbon-carbon bonds from the croconate violet anion, as well as some other vibrational modes attributed to the coupled vibrations of the CC and the CO bonds. For example, in the Raman spectra of the compounds are observed a triplet in the region between  $1450$  and  $1500\text{ cm}^{-1}$ , assigned to the coupled vibration involving  $\nu(\text{CO}) + \nu(\text{CC})$  modes. Two characteristic vibrational modes in the Raman spectra of the croconate violet ion occur in the region below  $1000\text{ cm}^{-1}$ ; one at  $ca. 935$  and  $922\text{ cm}^{-1}$ , as-

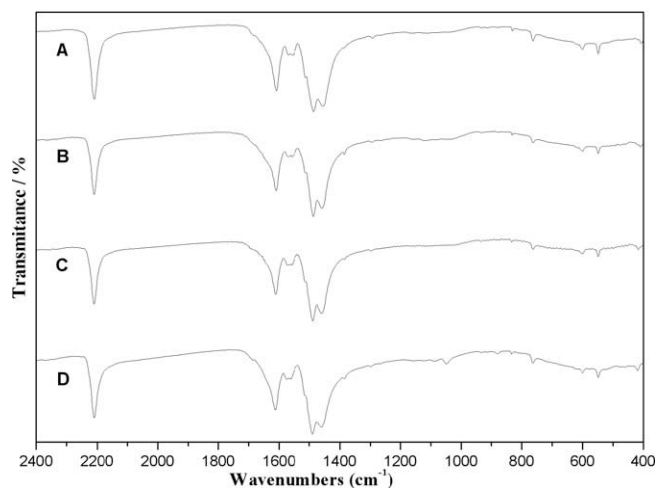
signed to the ring breathing mode, and the other at  $ca. 626\text{ cm}^{-1}$ , assigned to the  $\text{C}(\text{CN})_2$  deformation mode.

Comparison with the previous vibrational data obtained for other croconate violet salts and related coordination compounds shows a remarkable difference, mainly based on the position and intensity of the observed Raman bands. For example, the Raman spectrum of the ammonium croconate violet compound [36] shows bands at  $2200\text{ cm}^{-1}$  resolved for both the symmetric and asymmetric modes (at  $2221$  and  $2205\text{ cm}^{-1}$ , respectively), whereas in the case of the mixed salts involving lanthanide ions these bands are observed at  $2224\text{ cm}^{-1}$  (the symmetric mode) as the strongest band in the spectra, and a not well resolved shoulder at  $ca. 2210\text{ cm}^{-1}$  (the asymmetric mode), with some half of the band intensity. In the case of the mixed salt containing cesium and potassium croconate violet [9], the  $\nu(\text{CN})$  mode is observed at  $2186$  and  $2211$ , the latter as the strongest component; the intensities are also different, with the asymmetric mode being half of that of the symmetric where this band is resolved. This is also the case for the pure cesium croconate violet compound [9]. At first sight, this should be indicative of the coordination site for the ligand,

**Table 4**Vibrational wavenumbers (in  $\text{cm}^{-1}$ ) and tentative assignment of the most important bands observed in the  $\text{LnKCV}_2$  ( $\text{Ln} = \text{La}^{+3}$ ,  $\text{Nd}^{+3}$ ,  $\text{Gd}^{+3}$  and  $\text{Ho}^{+3}$ ) spectra.

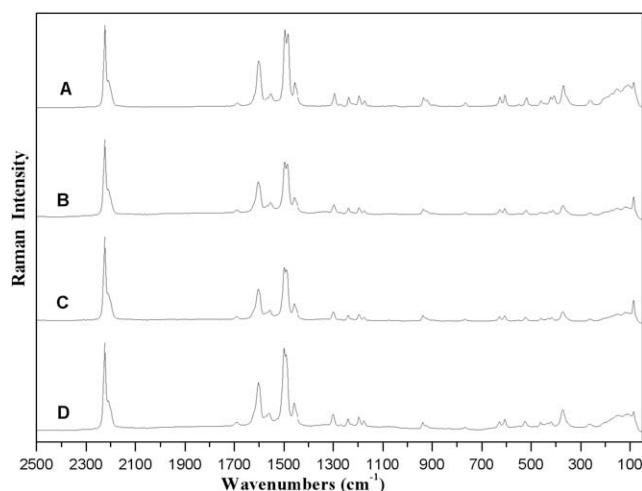
$\text{LaKCV}_2$		$\text{NdKCV}_2$		$\text{GdKCV}_2$		$\text{HoKCV}_2$		Tentative assignment
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	
	370 w		372 w		372 w		373 w	ring bending
	407 w		411 w		417 w		419 w	ring bending
	421 w		426 w		432 w		434 w	ring bending
	461 w		461 w		461 w		461 w	$\delta(\text{C}(\text{CN})_2)$
519 w	519 w	417 w	521 w	416 w	523 w	418 w	524 w	ring bending
540 w	551 w	540 w	552 w	540 w	552 w	540 w	551 w	ring bending
600 w	605 w	600 w	606 w	599 w	606 w	599 w	606 w	$\delta(\text{C}(\text{CN})_2) + \delta(\text{H}_2\text{O})$
	625 w		626 w		627 w		628 w	$\delta(\text{C}(\text{CN})_2)$
763 w	766 w	763 w	767 w	763 w	767 w	763 w	767 w	ring bending
	778 w		778 w		778 w		778 w	ring bending
830 w	831 w	831 w	833 w	833 w	834 w	833 w	835 w	ring bending
	921 w		921 w		922 w		922 w	ring breathing
933 w	934 w	934 w	936 w	934 w	937 w	935 w	937 w	ring breathing
	1174 w		1175 w		1176 w		1176 w	$\nu(\text{CC})_{\text{anel}}$
	1196 w		1196 w		1197 w		1197 w	$\nu(\text{CC})_{\text{anel}}$
	1237 w		1238 w		1240 w		1240 w	$\nu(\text{CC})$
1293 w	1295 w	1295 w	1298 w	1297 w	1300 w	1298 w	1301 w	$\nu(\text{CC})$
1455 s	1456 m	1458 s	1457 m	1459 s	1458 m	1460 s	1458 m	$\nu(\text{CO}) + \nu(\text{CC})$
1486 s	1484 s	1487 s	1486 s	1488 s	1489 s	1489 s	1491 s	$\nu(\text{CO}) + \nu(\text{CC})$
	1496 s		1497 s		1499 s		1500 s	$\nu(\text{CO}) + \nu(\text{CC})$
1556 w		1557 w		1558 w		1561 w		$\nu(\text{CC})$
1569 w	1553 w	1569 w	1554 w	1573 w	1557 w	1575 w	1560 w	$\nu(\text{CC})$
1609 m	1601 m	1610 m	1603 m	1611 m	1603 m	1613 m	1602 m	$\nu_{\text{ass}}(\text{CO})$
	1688 w		1689 w		1690 w		1690 w	$\nu_s(\text{CO})$
2209 s	2209 m	2209 s	2210 m	2209 s	2210 m	2209 s	2210 m	$\nu(\text{CN})$
	2224 s		2224 s		2224 s		2224 s	$\nu(\text{CN})$
3500 s		3500 s		3500 s		3500 s		$\nu(\text{OH})$

Abbreviations: w – weak; m – medium and s – strong.

**Fig. 4.** Infrared spectra of  $\text{LaKCV}_2$  (A),  $\text{NdKCV}_2$  (B),  $\text{GdKCV}_2$  (C) and  $\text{HoKCV}_2$  (D).

since there is a significant change in the spectrum when comparing the wavenumbers and intensities for symmetric and asymmetric modes for the  $\text{C}\equiv\text{N}$  bond in coordinated species; however, the delocalized character of the  $\pi$  electrons over the pseudo-oxocarbon ring, as well as over the dicyanomethylene groups, promotes the perturbation of very different chemical environments for this anion, as it can be seen when comparing the vibrational spectra of salts containing distinct cations such as potassium, cesium and the lanthanide.

On the other hand, the analysis of the carbonyl stretching mode is very interesting, since the coordination occurs via the oxygen atoms to the metal sites, as can be noticed from Fig. 1. This type of interaction has also been viewed in the structures of potassium [7], rubidium [8] and cesium [9] salts of croconate violet, but not in the case of the ammonium salt [36], where the CV species is not di-

**Fig. 5.** Fourier-transform Raman spectra of  $\text{LaKCV}_2$  (A),  $\text{NdKCV}_2$  (B),  $\text{GdKCV}_2$  (C) and  $\text{HoKCV}_2$  (D).

rectly bonded to the anion. In all cases, the  $\nu(\text{C}=\text{O})$  appears in the spectra as a weak band at  $1670\text{--}1685\text{ cm}^{-1}$  region, depending on the nature of the cation. For example, in  $\text{CsKCV}$ , another mixed salt [9], this band can be observed at  $1683\text{ cm}^{-1}$ , whereas for the pure  $\text{Cs}_2\text{CV}$  (which has two different crystalline forms) shows up at  $1686$  for  $\text{Cs}_2\text{CV-1}$  (triclinic) and at  $1681\text{ cm}^{-1}$  for the triclinic structure of  $\text{Cs}_2\text{CV-2}$ . In the case of the ammonium salt, where the croconate violet ion is not directly bonded to the cation, this band is observed at  $1672\text{ cm}^{-1}$  in the Raman spectrum and in Table 4 this band is tentatively assigned to the ones at  $1688\text{--}1690\text{ cm}^{-1}$  region, depending on the lanthanide ion. This implies that the interaction with the metal site is not as strong as in the case of alkaline ions, since the vibrational mode has been observed in the high wavenumber region. It is worth noting that in the Raman spectrum of

the supramolecular complex  $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$  [10], where the  $CV^{-2}$  anion is directly coordinated to the zinc(II) metal ion by the oxygen atoms, the  $\nu(C=O)$  band can not be observed in the region between 1650 and 1700  $cm^{-1}$ , and the authors claim this band disappears due to the coordination to the metal [10].

Other vibrational bands can also be assigned, according to Table 4. One of the most important vibrational modes for oxocarbon ions, the one related to the ring vibration, which can be seen at ca. 1220  $cm^{-1}$  in the case of croconate violet ion, can be affected by the chemical environment. In the case studied here, this mode is assigned to the bands at 1176  $cm^{-1}$  for all the complexes, with no wavenumber shift observed for the cation; this band can be observed at 1164 for  $K_2CV$ , 1162 for  $Rb_2CV$ , 1168 for  $CsKCV$  and 1164  $cm^{-1}$  for  $Cs_2CV-2$ , which is an indicative that this vibrational mode is not so sensitive to different chemical environments. On the other hand, the vibrational mode assigned to the  $\nu(C-C)$  from the dicyanomethylene species occurs in the 1200–1220  $cm^{-1}$  region; for example, in ammonium croconate violet this mode shows up as a doublet of medium intensity at 1200 and 1217  $cm^{-1}$  in the near infrared Raman spectrum. For other compounds this band shows up also as a doublet, as for instance for potassium (1204 and 1217  $cm^{-1}$ ), rubidium (1200 and 1215  $cm^{-1}$ ), cesium (1202 and 1212  $cm^{-1}$ ) and for the mixed  $CsKCV$  (at 1197 and 1220  $cm^{-1}$ ), or sometimes as a single band, as in the case of the other mixed salt  $RbKCV$  (1204  $cm^{-1}$ ). However, these bands show intensities which can vary from very weak to medium intensity, what sometimes become difficult its use in a vibrational analysis. For the compounds investigated in this work, these bands can be seen at 1197 and 1240  $cm^{-1}$ , respectively; these deviations can be understood in terms of the very different chemical environment the croconate violet is experiencing in the solid state structure containing the lanthanide ions, which implies that a weak chemical interaction occurs between the CV anion and the metal sites.

As a concluding remark, the vibrational spectra of these compounds are very similar, with some minor differences when compared to other related compounds; this can be ascribed to the weak interactions between the ligand and the lanthanide ions being not as strong as that observed for other transition metal ions, such as the metal ions from the first transition series of the Periodic Table.

#### 4. Conclusions

The crystalline structure of the  $LaKCV_2$ ,  $NdKCV_2$ ,  $GdKCV_2$  and  $HoKCV_2$  salts were characterized by means of X-ray diffraction, thermogravimetric analysis and vibrational spectroscopy (infrared and Raman). All synthesized compounds are isostructural, mainly due to the similarity of the lanthanide ion sizes. The  $\pi$  stacking geometrical parameters indicate these complexes do not possess an effective interaction of this nature, which means the crystal packing is generated mainly by the cationic and anionic interactions, supported by the hydrogen bonds. There are eight water molecules for each  $LnKCV_2$  unit ( $Ln = La^{+3}$ ,  $Nd^{+3}$ ,  $Gd^{+3}$  and  $Ho^{+3}$ ), comprising five water molecules which are coordinated to the metal sites, two coordinated to the potassium ion and one of hydration. All water molecules are involved in weak hydrogen bonds and are responsible for the extension of the structure along the *b* axis. The lanthanide ion is coordinated to the oxygen atoms of two CV anions, giving rise to a chelate (O2–O3 and O4–O5), and also to five water molecules (O7, O8, O9, O10 and O11), whereas the potassium ion shows a monodentate coordination with two nitrogen atoms from the CV anion and with two water molecules (N2, N4, O12 and O13). It is straightforward to note that all attempts to synthesize the pure lanthanide complexes were in vain; this fact addresses that the usual synthesis involving the mixture

of solutions containing lanthanide ions and croconate violet, at room temperature and pressure, only leads to the obtaining of mixed compounds, where the potassium ions are also acting as space filler. The vibrational spectra of all the compounds are very similar, with only minor deviations of the CV anion vibrations previously reported for other compounds; these small deviations are due to the lanthanide ions sizes used in this investigation. The most important vibrational markers for croconate violet ion, the  $\nu(C\equiv N)$  and  $\nu(C=O)$  modes, present significantly different spectroscopic behavior: the  $\nu(C\equiv N)$  modes are not shifted by the modification of the lanthanide species, only presenting small differences in terms of intensity, and the  $\nu(C=O)$  are shifted to higher wavenumbers, due to the coordination to the metal sites.

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#### Appendix A. Supplementary material

CCDC 734232, 734233, 734234 and 734235 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2009.09.050](https://doi.org/10.1016/j.ica.2009.09.050).

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