Solid-State Experimental and Theoretical Investigation of the Ammonium Salt of Croconate Violet, a Pseudo-Oxocarbon Ion

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The present work describes the crystal structure, vibrational spectra, and theoretical calculations of ammonium salts of 3,5-bis-(dicyanomethylene)cyclopentane-1,2,4-trionate, $(NH_4)_2(C_{11}N_4O_3)$ $[(NH_4)_2CV]$, also known as ammonium croconate violet. This compound crystallizes in triclinic $P\bar{1}$ and contains two water molecules per unit formula. The crystal packing is stabilized by hydrogen bonds involving water molecules and ammonium cations, giving rise to a 3D polymeric arrangement. In this structure, a π-stacking interaction is not observed, as the smaller centroid−centroid distance is 4.35 Å. Ab initio electronic structure calculations under periodic boundary conditions were performed to predict vibrational and electronic properties. The vibrational analysis was used to assist the assignments of the Raman and infrared bands. The solid structure was optimized and characterized as a minimum in the potential-energy surface. The stabilizing intermolecular hydrogen bonds in the crystal structure were characterized by difference charge-density analysis. The analysis of the density of states of $(NH_4)_2CV$ gives an energy gap of 1.4 eV with a significant contribution of carbon and nitrogen 2p states for valence and conduction bands.

I. Introduction

Oxocarbon ions are cyclic compounds of general formula $(C_nO_n)^{2-}$, where n varies from 3 (deltate), 4 (squarate), 5 (croconate), to 6 (rhodizonate). The compounds resulting from partial or complete substitution of oxygen atoms by other atoms or groups are known as pseudo-oxocarbons.[1] These molecules are very interesting systems due to their unusual electronic and vibrational properties,[2−4] and also because of their high molecular symmetry (D_{nh}) and degree of electronic delocalization. In particular, the condensation of croconic acid (or croconate ion) with malononitrile ($NCCH_2CN$) forms interesting pseudo-oxocarbons ions denoted as croconate blue [2,4,5-tris(dicyanomethylene)cyclopentane-1,3-dionate][5] and croconate violet [3,5-bis(dicyanomethylene)cyclopentane-1,2,4-trionate] (CV).[1] They present strong absorptions in the UV−vis region, being referred to as croconate dyes. These molecules are very interesting in the area of supramolecular chemistry because of their structural characteristics and simplicity.[6] These molecules can be involved in different types of intermolecular interactions, where their electronic delocalization provides the possibility of a π-stacking interaction between the rings. In addition, these compounds present coordination properties and acceptor sites for hydrogen bonds, which make these systems potentially useful in crystal engineering research.[7] In recent years, our group has been involved in the use of CV and other simple chemical structures such as oxocarbon ions as building blocks in supramolecular chemistry.[8−11]

Some crystallographic and vibrational studies of CV anions are described in literature.[6,12−19] The X-ray structure of potassium (K_2CV),[16] rubidium (Rb_2CV),[17] cesium (Cs_2CV),[18] and tetrabutylammonium ($(NBu_4)_2CV$)[19] salts are reported. The potassium and rubidium salts are dihydrates and the water molecules are involved in medium hydrogen bonds with CV ion. On the other hand, in the solid-phase cesium and tetrabutylammonium CV are anhydrous, suggesting that voluminous cations are able to stabilize the solid state by themselves. The investigation of π-stacking interactions in these salts indicates that this interaction is not as effective as that observed in the similar croconate salts.[20] In the case of tetrabutylammonium croconate violet salt, a π-stacking interaction is not observed in the crystal packing proper due to the great volume of the cation (distance between rings of 12.4 Å). Experimental and theoretical vibrational studies of CV are also described[21,22] and resonance Raman spectra of CV in aqueous solutions[21] indicate a rather small electronic delocalization when compared to croconate ion, which can be interpreted in terms of the two electronic transitions observed in the visible spectrum due to two different chromophoric moieties: one involving the π system of the croconate ring and the other located at the C≡N moieties.

Theoretical investigations in the condensed phase have not been done for such systems, although the importance of the crystal packing in the structure should be taken into account for both geometric and vibrational analysis of the species. Therefore, it is crucial to perform solid-state electronic structure calculations for a better understanding of these systems. In this work, the crystal structure of the ammonium salt of CV is described, together with experimental and theoretical vibrational

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investigations. Our aim is a more complete assignment of the vibrational modes of the anion and a better understanding of the true forces that are important in establishing the solid-state structure, for example π-stacking and hydrogen-bonding interactions.

II. Experimental Section

Synthesis. Potassium bis(dicyanomethylene)croconate [K_2CV] was synthesized by a modification of Fatiadi's method,[1] described by Teles et al.[19] To an aqueous solution of potassium bis(dicyanomethylene)croconate (0.72 mmol) was added ammonium hydroxide solution (1.39 mmol). Dark-gray single crystals of ammonium bis(dicyanomethylene)cyclopentane-1,3-dionate dihydrate salt [$(NH_4)_2$CV] were obtained by slow evaporation at room temperature (yield around 40% for both salts). Elemental analysis of $C_{11}H_{12}N_6O_7$ (318.0 g mol^{-1}): Calcd C 42.86%, N 27.27% and H 3.90%; found C 41.49%, N 27.82% and H 3.55%.

X-ray Diffraction. Single-crystal X-ray data were collected using a Bruker Kappa CCD diffratometer with Mo Kα (λ = 0.71073 Å) at room temperature. Data collection, reduction, and cell refinement were performed by *COLLECT*,[23] *EVAL-CCD*,[24] and *DIRAX*[25] programs, respectively. The structures were solved and refined using *SHELX-97*.[26] An empirical isotropic extinction parameter x was refined, according to the method described by Larson.[27] A multiscan absorption correction was applied.[28] Anisotropic displacement parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were located from Fourier difference maps and isotropic displacement parameters were refined in groups. The structures were drawn by *ORTEP-3 for Windows*[29] and *Mercury*[30] programs. CCDC 705179 contains the supplementary crystallographic data for the $(NH_4)_2$CV compound. This data can be obtained free of charge at www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) 1 44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Vibrational Spectra. Fourier-transform Raman spectroscopy was carried out using a Bruker RFS 100 instrument with Nd^{3+}/YAG laser operating at 1064 nm in the near-infrared and a CCD detector cooled with liquid N_2. Spectra were performed with 256 scans accumulated with a 4 cm^{-1} spectral resolution. Infrared spectra were obtained in a Bomem MB-102 spectrometer fitted with a CsI beam splitter, using KBr disks and a spectral resolution of 4 cm^{-1}. Good signal-to-noise ratio was obtained from the accumulation of 128 scans.

Theoretical Methods. Calculations have been performed by the PWscf code under the generalized gradient approximation (GGA) as implemented in the *Quantum-ESPRESSO* package,[31] using atomic ultrasoft (Vanderbilt) pseudopotential[32] within the density functional theory (DFT)[33,34] using periodic boundary conditions.[35] We adopt the exchange-correlation functional parametrized by Perdew and Wang[36] for GGA approximation. The wave functions of valence electrons are shown by a plane wave basis set with maximum kinetic energy of 20 hartree (40 Ry). For the cell, the lattice parameters a, b, and c and the unit cell angles α, β, and γ were kept constrained during the calculations. Crystallographic positions and parameters of the ammonium salt of croconate violet were used as a starting point for calculations. The nuclei positions were optimized until their Cartesian force components were all less than 0.001 Ry/Bohr. As the unit cell was considered very large, the electronic density was calculated only for the gamma point in the first Brillouin zone. We have also performed phonon calculations to obtain the vibrational structure and confirmed that the analyzed structure is a real minimum in the potential-energy surface (PES). The obtained vibrational frequencies were used to help in the experimental attributions of the bands in infrared spectrum.

TABLE 1: Crystallographic Data for $(NH_4)_2$CV

formula	$C_{11}H_{12}O_5N_6$
fw	308.27 g mol^{-1}
cryst syst	triclinic
space group	$P\bar{1}$
a/Å	8.8372(6)
b/Å	9.3056(9)
c/Å	9.898(1)
α/°	103.578(8)
β/°	106.837(8)
γ/°	101.214(7)
V/Å^3	726.5(1)
Z	2
cryst size/mm	0.18 × 0.07 × 0.05
d_{calcd}/g.cm^{-3}	1.409
μ(Mo Kα)/cm^{-1}	0.144
min/max transmission factors	0.985/0.996
rel. total/unique reflns	24240/4231
R(int)/R(sigma)	0.052/0.051
observed reflns [$F_o^2 > 2s(F_o^2)$]	2556
No. of params refined	201
R	0.049
wR	0.107
S	1.059
rms peak (e$^-$Å^{-3})	0.045

III. Results and Discussion

Crystal data of $(NH_4)_2$CV are listed in Table 1, some of the important geometrical parameters are displayed in Table 2, and the crystal structure can be seen in Figure 1. The ammonium croconate violet salt crystallizes in triclinic space group $P\bar{1}$, similar to the potassium,[16] rubidium,[17] and the anhydrous phase of cesium salts.[18] For each $(NH_4)_2C_{11}N_4O_3$ unit, there are two water molecules, which are involved in medium hydrogen bonds with the CV anion, as well as to the ammonium cations (the average O···O and N···O distances are 2.873(2) and 2.935(2) Å, respectively). Very weak hydrogen bonds between ammonium cations are also observed (the average N···N distance is 3.198(2) Å). These hydrogen bonds give rise to a 3D arrangement, as can be seen in Figure 2. By comparing to the isostructural alkaline salts of CV (e.g., K, Rb, and Cs), it can be noted that the cation size has a great influence over the quantity of water per M_2CV unit, as the increase of the cation size reduces the number of water molecules. In fact, the potassium salt presents two water molecules in the structural unit, whereas the cesium salt does not present any water molecule. However, despite the NH_4^+ size, the crystal structure of $(NH_4)_2$CV shows two water molecules per formula. This fact could be explained by the occurrence of strong hydrogen-bonding interactions between the NH_4^+ ions and the water molecules.

All of the C−C bond lengths within the CV ring are very similar, which strongly suggest electronic delocalization due to the π electrons (the biggest difference between these C−C bonds is 0.04 Å). The average of C−C ring bond lengths is 1.463(2) Å, which is an intermediate value between CC single and double bond (~1.54 and ~1.35 Å, respectively). The CV anions are almost planar, and the dicyanomethylene groups form angles with the oxocarbon ring of 2.81 and 4.11°. The CV anion is an acceptor of medium to weak hydrogen bonds, in which

TABLE 2: Experimental and Selected Geometrical Parameters for $(NH_4)_2CV$

	experimental	theoretical		experimental	theoretical
		Bond/Å			
C1−C2	1.457(2)	1.466	C9−C10	1.433(2)	1.414
C1−C5	1.448(2)	1.450	C9−C11	1.436(2)	1.419
C1−C6	1.390(2)	1.396	C2−O1	1.246(2)	1.248
C2−C3	1.464(2)	1.461	C4−O2	1.245(2)	1.254
C3−C4	1.453(2)	1.447	C5−O3	1.250(2)	1.253
C3−C9	1.391(2)	1.397	C7−N1	1.157(2)	1.169
C4−C5	1.485(2)	1.492	C8−N2	1.148(2)	1.169
C6−C7	1.430(2)	1.420	C10−N3	1.152(2)	1.170
C6−C8	1.436(2)	1.415	C11−N4	1.145(2)	1.170
		Average of Angles/°			
$(C-C-C)_{ring}$	108.0(1)	108.0	C−C−N	176.9(2)	176.9
C−C−C	122.5(1)	120.0	C−C−O	126.0(1)	126.1
		Dihedral/°			
C1−C6−C7−N1	−178.0	−161.8	C3−C9−C10-N3	−158.5	−164.5
C1−C6−C8−N2	127.7	156.6	C3−C9−C11-N4	171.7	99.16
		Hydrogen Bonds			
D···H···A	D−H/Å	H···A/Å	D···A/Å	D−H···A/°	
N7−H1−O2	1.050	1.880	2.914(2)	167.0	
N7−H3−O2[a]	1.040	2.070	2.996(2)	148.0	
N7−H4−O4	1.010	1.990	2.968(2)	161.0	
N8−H5−O4	0.880	1.950	2.804(2)	162.0	
N8−H6−O5	1.020	1.970	2.925(2)	155.0	
N8−H7−O1[b]	0.830	2.760	3.043(2)	102.0	
N8−H8−N3[b]	0.720	2.540	3.034(2)	128.0	
O4−H4A−N4	0.920	2.040	2.890(2)	152.0	
O4−H4B−O3[c]	0.960	1.890	2.845(2)	174.0	
O5−H5A−O1[d]	0.930	1.980	2.900(2)	169.0	
O5−H5B−N1[b]	0.920	2.110	3.029(2)	175.0	

[a] Symmetry codes: *i*: $1 - x$, $2 - y$, $1 - z$. [b] *ii*: $1 + x$, $1 + y$, z. [c] *iii*: x, y, $-1 + z$, [d] *iv*: $1 - x$, $1 - y$, $1 - z$.

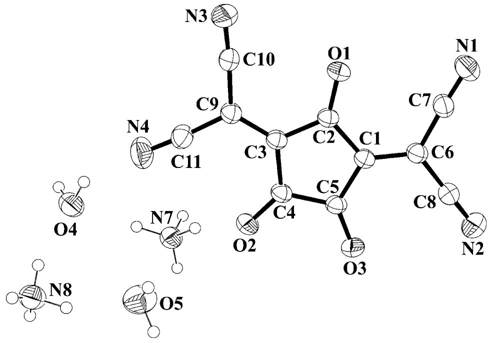

Figure 1. Crystal structure of $(NH_4)_2CV$ and displacement ellipsoids with 50% probability level.

the N3 atom (Figure 1) is involved in a very weak interaction with the ammonium cation (distance $N7^i\cdots N3$ of 3.132(2) Å, symmetry code $i = x$, $y - 1$, z). The CV anions form layers that are separated by the NH_4^+ and the water species. Topological analysis of π-stacking interaction[20] shows that the interplanar distances are 3.38 and 3.44 Å, indicating that the CV layers are very close each other. However the centroid−centroid distances are greater than 4.0 Å (4.35 and 4.73 Å), suggesting a significant horizontal translation (shift) of the pseudo-oxocarbon rings (2.46 and 3.23 Å). Through this interaction is not relevant for the solid-state stabilization, and it has also been observed for the rubidium[17] and tetrabutylammonium[19] salts.

Theoretical calculations of $(NH_4)_2CV$ give centroid−centroid distance equal to 4.41 and 4.74 Å and horizontal shift of rings equal to 2.16 and 3.05 Å. It is possible to observe the interactions between the different species by the calculation of charge-difference analysis. Figure 3 shows the difference charge surfaces obtained by solid-state calculation of $(NH_4)_2CV$. It is worth mentioning that this type of difference map takes into account the influence of the distinct species in the charge density of the individual species that are present in the crystal structure. It must be considered as a representation of the electronic density migration through the solid formation. In this analysis, it must be first considered the total charge density at the equilibrium positions of the solid, and then making the difference between the individual species (CV and ammonium ions and water molecules) at their respective positions in the solid through single point calculations, just to obtain the difference in the charge density. It can be seen in Figure 3 that there are two different types of surfaces, a yellow (positive region) and a blue one (negative region). Yellow surfaces denote where the density has gone after the formation of the solid, and blue surfaces are where the density has come from. In line with experimental evidence, no interaction between the pseudo-oxocarbon rings is observed. On the other hand, it is clear the formation of hydrogen bonds between the water and ammonium cations with the pseudo-oxocarbon species, and transferred charge to the region of intermolecular hydrogen bonds.

As pointed out before, the theoretical calculations using solid state under periodic boundary conditions are very useful to analyze both the structure and the vibrational spectra with a better basis of comparison to experiment. Figure 4 shows Raman and infrared spectra of $(NH_4)_2CV$, and Table 3 lists the main vibrational wavenumbers and their respective assignments. In the infrared spectrum, a very intense absorption band is observed at 2200 cm^{-1}, which is assigned to C≡N stretching mode (ν_{CN}). The theoretical calculation indicates two frequencies related to this mode at 2221 and 2205 cm^{-1}. In the experimental IR, a shoulder is observed around 2216 cm^{-1}, which can be related to the mode calculated at 2221 cm^{-1}. These bands are resolved

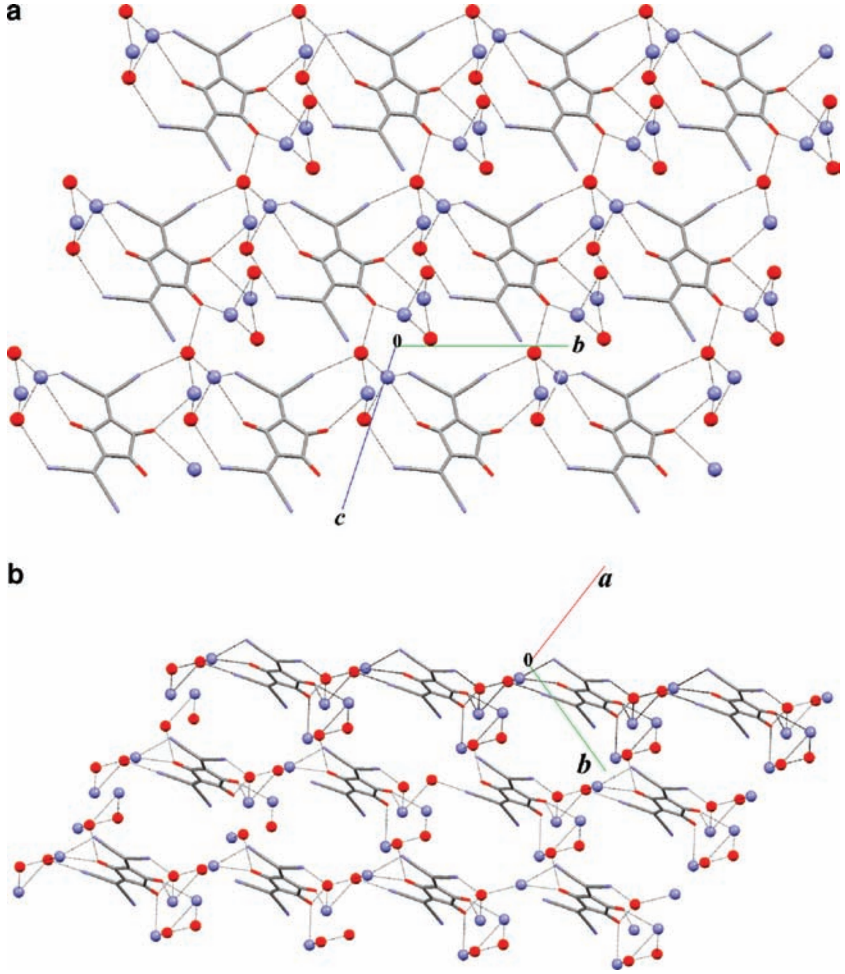

Figure 2. Three dimensional arrangement of the hydrogen bonds' design of $(NH_4)_2CV$: a) view along *a* axis and b) view along *c* axis.

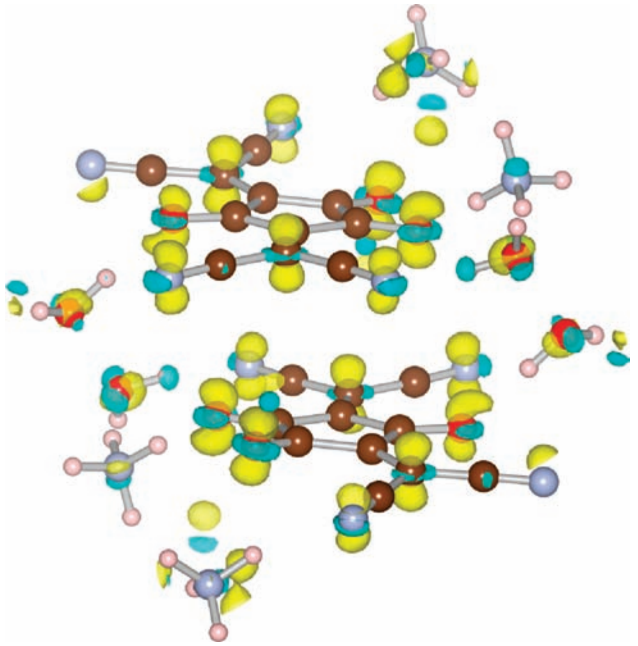

Figure 3. Charge-difference surfaces of $(NH_4)_2CV$. The yellow surfaces are related to positive differences and the blue ones to negative differences.

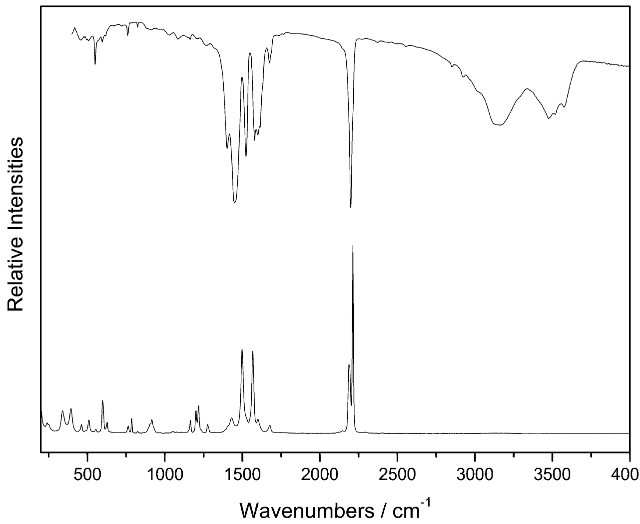

Figure 4. Vibrational spectra of $(NH_4)_2CV$ in the solid state, infrared (up) and FT-Raman (down).

in the Raman spectrum. The calculations indicate that the mode at 2221 cm^{-1} is related to the in-phase C≡N stretching mode, whereas the mode at 2205 cm^{-1} is related to the out-of-phase C≡N stretching mode. At this point, it is important to note that the C≡N stretching mode can be used as a probe for the chemical environment experienced by croconate violet in the solid state. Previous works have demonstrated that the C≡N stretching mode is the main band to analyze this kind of perturbation.[17,18] In the mixed salts of violet croconate containing Rb and K ions,[17] the C≡N stretching bands are quite shifted when compared with the pure salts of Rb[17] and K.[37] The main reason for this behavior is the influence of different possibilities

TABLE 3: Experimental and Theoretical Vibrational Wavenumbers and Assignment of the Most Important Bands Observed in $(NH_4)_2CV$ Spectra

Experimental		Theoretical	Assignment
infrared/cm^{-1}	Raman/cm^{-1}	infrared/cm^{-1}	
	338 m/394 m		ring bending
	462 w	462 w	$\delta(C(CN)_2)$
550 m	510 w, 554 vw	503 w, 541 w	ring bending
596 w	598 m	597 w	$\delta(H_2O) + \delta(C(CN)_2)$
617 vw	627 w	624 w	$\delta(C(CN)_2)$
760 w	762 w	761 w	ring bending
	785 w	768 w	$\delta(H_2O)$
823 w	826 vw	812 w	ring bending
902 vw	905 sh, 916 w	912 w	ring breathing
1090 w	1073 vw	1072 w	$\nu(CC)_{ring}$
1163 w	1165 vw	1151 w	$\nu(CC)_{ring}$
1209 vw	1200 m, 1217 m	1205 w	$\nu(CC)$
1263 vw	1277 w	1265 w	$\nu(CC)$
1400 s		1377 m	$\delta(NH_4^+)$
1450 vs	1431 w	1435	$\nu(CC) + \delta(NH_4^+)$
1524 s	1499 s	1566 s	$\nu(CO) + \nu(CC)$
1580 s	1568 s	1580 s	$\nu(CO) + \nu(CC)$
1600 s	1603 w	1604	$\delta(H_2O)$
1614 s		1627	$\delta(H_2O)$
1676 w	1672 w	1688 w	$\nu_s(CO)$
2201 vs	2187 s,	2205 s	$\nu(CN)$
	2214 vs	2221 s	$\nu(CN)$
2853 vw		2893 m	$\nu(NH)$
2924 vw		2900 w	$\nu(NH)$
3016 sh		3049 s	$\nu(NH)$
3138 s		3113 s	$\nu(NH)$
3477 m		3486 m	$\nu(OH)$
3520 m, 3578 m		3546 s	$\nu(OH)$

of coordination with distinct metallic cations. All of these differences can be seen in the vibrational spectra, more specifically the Raman spectrum: in K_2CV and Rb_2CV spectra these bands are separated by ca. 29 cm^{-1}, whereas for RbKCV they are separated by 22 cm^{-1}. It is also possible to note that the difference between the in-phase and out-of-phase C≡N stretching is smaller in mixed crystals than in pure salts. In the present work, these modes are separated by 27 cm^{-1} in experimental Raman spectra being relative to the different environment of the C≡N groups. So, an interesting conclusion that can be reached with the vibrational data is that the chemical environment experienced by croconate violet in the ammonium salt is similar to that observed in Rb and K salts because the measured separation is similar.

The carbonyl stretching (ν_{CO}) is another important vibrational mode for croconate violet. The calculations indicate that there are three frequencies related to ν_{CO}: one weak band at 1688 cm^{-1}, and two strong bands at 1580 e 1566 cm^{-1}, which are also associated with the ν_{CC} of the pseudo-oxocarbon ring. These bands are also observed in the experimental spectrum at 1676, 1580, and 1524 cm^{-1}. The ν_{CO} band is observed in the Raman spectrum at 1672 cm^{-1}, which does not present a shift in comparison to Rb_2CV and Cs_2CV, where the metal site is coordinated to the CV anion. Other similar wavenumbers are observed for the coupled $\nu_{CC} + \nu_{CO}$ mode: these bands are observed at 1499 and 1568 cm^{-1} in $(NH_4)_2CV$, at 1501 and 1563 cm^{-1} in Rb_2CV, at 1509 and 1588 cm^{-1} for anhydrous Cs_2CV, and at 1504 and 1564 cm^{-1} in K_2CV. However, for hydrated Cs_2CV, these bands are observed at 1540 and 1577 cm^{-1}. This difference is probably due to the fact that NH_4^+, Rb, K, and anhydrous Cs crystallize in the same space group ($P\bar{1}$), which is different for hydrated Cs_2CV ($P2_1/a$).[18]

The bands at 1614 and 1600 cm^{-1} observed in the infrared spectrum are assigned to deformation modes of water molecules according to the calculation (1627 and 1604 cm^{-1}). In Rb[17] and hydrated Cs[18] salts of CV, bands in a similar region have been previously assigned to $\nu_{CC} + \nu_{CO} + \nu_{CN}$, but because these compounds also present water molecules such as $(NH_4)_2CV$, these vibrational modes should be described instead as deformation modes of water molecules. The stretching modes related to C−C (from the dicyanomethylene group) and CC (from the oxocarbon ring) were calculated at 1435 cm^{-1} for C−C, and 1151 and 1072 cm^{-1} for $(CC)_{ring}$, and are in good agreement with experimental infrared data at 1450, 1163, and 1090 cm^{-1}, respectively. In previous works, the band around 1450 cm^{-1} was tentatively assigned as two distinct coupled modes: [$\nu(CO) + \nu(CC) + \nu(CCCN_2)$][38] or [$\nu(CO) + \nu(CC)$].[18] From our calculations, this wavenumber value can be associated at least as a major contribution from the CC stretching mode ($\nu(CC)$), mainly based on the analysis of the displacement vectors displayed at Figure 5.

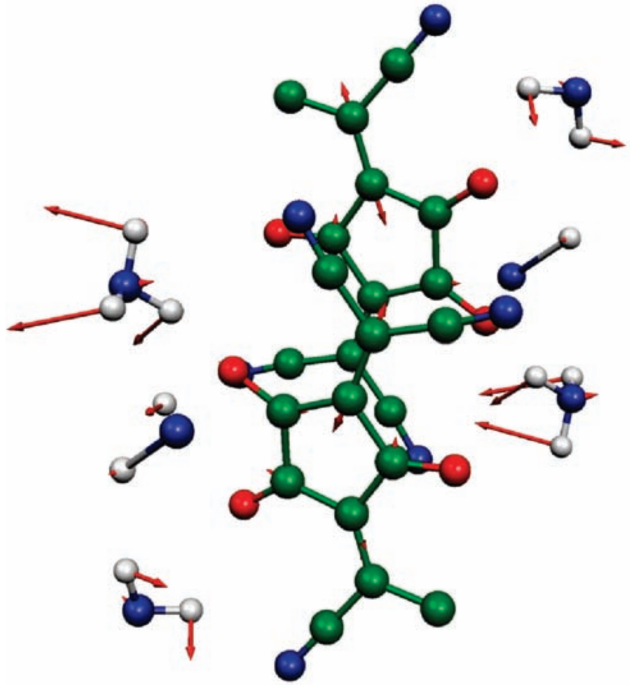

Figure 5. Calculated vibrational modes of CC stretching (the corresponding displacement vectors) in the solid state for $(NH_4)_2CV$.

The crystal structure indicated that the difference in CC bond lengths [Δ(CC)] is 0.040 Å in $(NH_4)_2CV$, which is similar to the Rb salt, suggesting that these salts present similar electronic delocalization. Raman spectra of squarate alkaline salts[39] indicated that the symmetry of the squarate ion in solid state increases with counterion size. This analysis lies on the ν_{CC} bands (1000−1200 cm^{-1}). In the case of the CV anion, such an analysis is not so easy because ν_{CC} is coupled to ν_{CN}. By comparing to calculated frequencies, the weak band at 1165 cm^{-1} and a very weak band at 1073 cm^{-1} are tentatively assigned to ν_{CC}, so that $\Delta(\nu_{CC})$ is 92 cm^{-1}. This value is similar to that observed in Raman spectra of lithium squarate,[38] which presents the smallest symmetric ring in comparition to alkaline squarate salts. However, the molecular symmetry of the CV anion (C_{2v}) is smaller than that of the squarate ring (D_{4h}), which can explain the similarity of $\Delta(\nu_{CC})$ of these compounds and that the electronic delocalization in the squarate ring is more effective than that in the CV ring.

The Raman bands corresponding to ring-breathing (905 cm^{-1}) and ring-bending (394 and 338 cm^{-1}) modes of the pseudo-oxocarbon ring are similar in intensity, with only a small wavenumber shift when compared to rubidium (905, 389, and

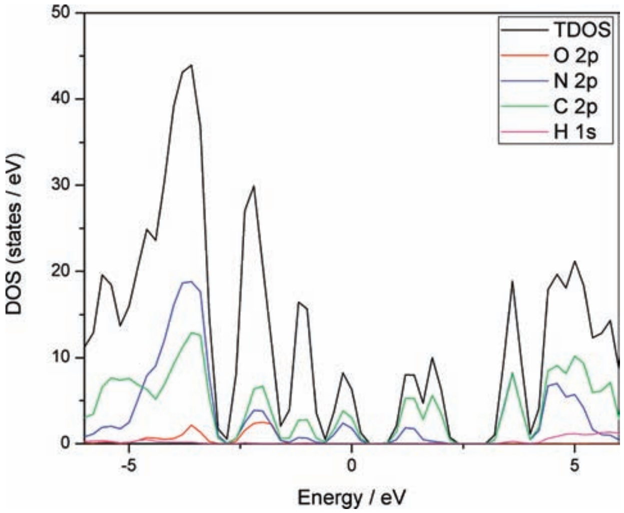

Figure 6. Total and partial density of states for $(NH_4)_2CV$.

334 cm^{-1}) and anhydrous cesium (900, 392, and 333 cm^{-1}) salts. This finding is reasonable on the basis that the CV units in these compounds are almost planar, and the CV units form layers separated by cations and water molecules, which do not affect the CV ring deformations.

Finally, it is interesting to discuss the low-frequency modes, even though they have not been observed experimentally. The periodic boundary condition calculations allow us to perform this kind of analysis because it takes into account the intermolecular interactions, which are predominant for low-frequency modes. The region between 50 and 60 cm^{-1} refers to a slice movement of the pseudo-oxocarbons. At 66 cm^{-1}, an interesting mode appears relative to the out-of-plane deformation of the whole pseudo-oxocarbon. Some specific ranges of frequencies are relative to ammonium and water bending: 74−90, 124−127, 151−165, 173−195, and 263−277 cm^{-1}. The modes at 66, 87, 89, 103−109, and 124−127 cm^{-1} are due to pseudo-oxocarbon torsion. Bending of ammonium ions appears in the 378−399 cm^{-1} range, whereas the out-of-plane deformation modes of the pseudo-oxocarbon are in the 437−450 cm^{-1} range. Unfortunately, it is not possible to confirm these assignments throughout our experimental data; but the present analysis can be very useful to assist in subsequent experimental works.

Figure 6 shows the total density of states (DOS) calculated for $(NH_4)_2CV$, together with the partial DOS for each atom. The Fermi level was shifted to 0 eV on the scale, corresponding to the valence-band edge. It is possible to note that the main contribution for the valence and conduction bands comes from the carbon and nitrogen 2p orbitals. The energy gap between the valence and conduction bands is 1.4 eV, which could characterize $(NH_4)_2CV$ as a low-gap material. It is well-known that the DFT functionals underestimate the energy gap by about 40%.[35] However, our qualitative result indicates that the derivatives of $(NH_4)_2CV$ could be used in band-gap engineering for devices with an energy gap around 2 eV.

All of the data acquired in this investigation point out that croconate violet can be a very powerful building block system to be used in supramolecular chemistry because hydrogen bonds, one of the prominent forces that are important in the solid-state structure, are present in the more simpler units of the salts, as in ammonium croconate violet.[40−42] This fact can be supported by the very different chemical environments that are experienced by the CV ion in the solid state, as we have seen with the vibrational results, mainly the bands due to $C\equiv N$ and $C\equiv O$ stretching modes.

IV. Conclusions

The crystalline structure of $(NH_4)_2CV$ has been determined by X-ray diffraction and the compound has been characterized by infrared and Raman spectroscopy. The CV anions are displayed in layers surrounded by ammonium cations and water molecules. These CV layers distances are close; however, the centroid−centroid distances are bigger than 4.0 Å, suggesting a significant horizontal translation of the pseudo-oxocarbon rings. This finding indicates that no π-stacking interaction is observed in this compound. The crystal packing is stabilized by a 3D hydrogen-bond network between NH_4^+ and water molecules. The assignment of vibrational spectra in the infrared spectrum for ammonium croconate violet has been performed with the support of theoretical calculations in the condensed phase. Some previous literature has described and supported theoretical calculations in the condensed phase. Some previous tentative assignments[17,18] have been corrected here, taking into account the information gained by theoretical calculations. Low-frequency modes were presented as a source for posterior use in experimental assignments. The contribution of the hydrogen bonds for stabilization of the crystal structure is described by a difference of charge-density analysis, which reveals well-localized interactions upon formation of these bonds. The difference in charge-density analysis supports the geometrical data, mainly that no significant π-stacking interaction occurs in $(NH_4)_2CV$. It was also calculated that the energy gap is 1.4 eV, strongly suggesting this compound is a low-gap material.

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