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$K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$: The first Zn(II) complex structurally characterized containing the pseudo-oxocarbon Croconate Violet (CV^{2-})

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Note

$K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$: The first Zn(II) complex structurally characterized containing the pseudo-oxocarbon Croconate Violet (CV^{2-})[☆]

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Abstract

The synthesis, thermal behavior, spectroscopic characterization and crystal and molecular structure of a Zn(II) complex containing the pseudo-oxocarbon Croconate Violet (CV^{2-}) dianion, namely $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$ are reported. Thermal analysis has shown that the complex structure presents coordination and lattice water molecules. According to vibrational spectroscopy the Croconate Violet dianion is coordinated to Zn(II) center through the vicinal oxygen atoms in a chelating fashion with no involvement of CN moieties. The complex structure has been confirmed by single crystal X-ray diffraction analysis. The dianionic units $[Zn(CV)_2(H_2O)_2]^{2-}$ adopt an slight distorted octahedral geometry in which the metallic center is surrounded by six oxygen atoms. These discrete dianionic units are connected through intermolecular hydrogen bonding giving rise to a supramolecular array extended along the crystallographic *a* axis. © 2006 Elsevier B.V. All rights reserved.

Keywords: Croconate Violet; Zn(II) complex; Building block subunit

1. Introduction

Oxocarbons, organic cyclic dianions of general formula $(C_nO_n)^{2-}$, where $n = 3, 4, 5$ and 6 , present high symmetry (D_{nh}) and intriguing spectroscopic properties [1–6]. Partial or complete replacement of carbonyl oxygen atoms by sulfur, selenium or dicyanomethylene groups leads to the formation of derivatives so-called pseudo-oxocarbons [5,7–9]. In special, the disubstituted product 3,5-bis(dicyanomethylene)cyclopentane-1,2,4-trionate dianion, namely Croconate Violet (CV^{2-}) shows extended π electron delocalization, strong absorption in the visible region, reversible electrochemical behavior as well as electrical conductivity typical

of semiconductors materials [10–12]. Surprisingly, few works concerning to the coordination chemistry of this interesting pseudo-oxocarbon are reported. It has been recently observed that CV^{2-} dianion is a versatile ligand exhibiting several coordination modes; for instance through the vicinal oxygen atoms in a chelating fashion [13–15] or through the nitrogen atoms of dicyanomethylene groups in a bridging mode [16]. Despite these investigations, studies on Croconate Violet coordination chemistry remain insipient.

In this context, the present work reports the synthesis, physical chemical and spectroscopic studies of the zinc complex containing the CV^{2-} dianion namely $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$ as well as its crystal and molecular structure. Following our studies on searching for novel molecular building blocks [17] and coordination polymers construction [18], the replacement of the coordinated water

[☆] To the memory of Dr. Wagner Magno Teles.

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molecules by an appropriate bifunctional spacer ligand can give rise to coordination polymers containing the interesting core $[\text{Zn}(\text{CV})_2]^{2-}$ that can be used as a novel building block subunit.

2. Experimental

2.1. Materials and physical measurements

All solvents and chemicals were reagent grade and used as received without further purification. $\text{K}_2\text{CV} \cdot 2.5\text{H}_2\text{O}$ was synthesized according to the published method [15].

Elemental analyses for C, H and N were carried out on a Perkin–Elmer 2400 analyzer whereas zinc was measured with an atomic absorption spectrophotometer Hitachi Z-8200. IR spectra were recorded on a Bomem Michelson 102 FTIR spectrophotometer using KBr pellets in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ with an average of 128 scans and 4 cm^{-1} of spectral resolution. Raman spectra were obtained in the solid state in a Bruker RFS 100 instrument equipped with Nd^{3+} /YAG laser operating at 1064 nm in the near infrared and CCD detector cooled with liquid N_2 with an average of 1000 scans and 4 cm^{-1} of spectral resolution. Electronic spectra were measured on a Shimadzu UV-1601 PC spectrophotometer in different solvents. Thermogravimetric analyses (TG/DTG) data were collected on a TG-50 Mettler STARE using 6.0 mg packed in alumina crucible. Samples were heated at $10^\circ\text{C}/\text{min}$ from room temperature to 800°C in a dynamic nitrogen atmosphere (flow rate = $200\text{ mL}/\text{min}$). Differential scanning calorimetry (DSC) measurements were carried out on a Shimadzu DSC50, using 1.0 mg samples packed in aluminum crucible, with a heating rate of $10^\circ\text{C}/\text{min}$ in the range of $25\text{--}480^\circ\text{C}$. Dynamic nitrogen atmosphere (flow rate = $50\text{ mL}/\text{min}$) was used.

X-ray data collection was performed on an automated SIEMENS P4 diffractometer at room temperature with a graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) using XSCANS software [19]. The structure was solved by direct methods using SHELX97 program [20]. Table 1 summarizes the crystal data and structure refinement parameters.

2.2. Synthesis of $\text{K}_2[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

To 10 mL of an aqueous solution at 65°C containing 50 mg (0.37 mmol) of ZnCl_2 , 265 mg (0.73 mmol) of $\text{K}_2\text{CV} \cdot 2.5\text{H}_2\text{O}$ dissolved in 25 mL of water were slowly added. This mixture was kept at 65°C for 2 h. The resulting solution was set aside and after a week metallic dark single crystals suitable for X-ray diffraction analysis were recovered by filtration. Yield: 100 mg (40%). Anal. Calc. for $\text{C}_{22}\text{H}_8\text{N}_8\text{O}_{10}\text{K}_2\text{Zn}$: C, 38.41; H, 1.17; 16.29; Zn, 9.51. Found: C, 38.56; H, 1.21; 16.74; Zn, 9.91%. IR (KBr, cm^{-1}): $\nu(\text{OH})$, 3611 (m), 3484 (m), 3427 (m); $\nu(\text{CN})$, 2223 (m), 2210 (s); $\nu(\text{C}=\text{O} + \text{C}=\text{C} + \text{CC}(\text{CN}))$, 1613 (s), 1567 (s), 1467 (s). Raman (1064 nm, cm^{-1}): $\nu(\text{CN})$, 2222 (s),

Table 1

Crystal data and structure refinement parameters for $\text{K}_2[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

Empirical formula	$\text{C}_{22}\text{H}_8\text{N}_8\text{O}_{10}\text{Zn}$
Formula weight	683.93
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	
<i>a</i> (\AA)	10.471(2)
<i>b</i> (\AA)	10.885(3)
<i>c</i> (\AA)	11.840(3)
α ($^\circ$)	90
β ($^\circ$)	108.460(10)
γ ($^\circ$)	90
Volume (\AA^3)	1280.0(5)
<i>Z</i>	2
<i>D</i> _{calc} (g cm^{-3})	1.785
Absorption coefficient (mm^{-1})	1.359
<i>F</i> (000)	688
Crystal size (mm)	$0.20 \times 0.18 \times 0.16$
θ Range for data collection ($^\circ$)	$2.27\text{--}26.29$
Index ranges	$0 \leq h \leq 12$, $0 \leq k \leq 12$, $-14 \leq l \leq 13$
Reflections collected/unique/parameters	2376/2246/208
Refinement method	full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.172
Final <i>R</i> indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0442$, $wR_2 = 0.1281$
<i>R</i> indices (all data) ^{a,b}	$R_1 = 0.0517$, $wR_2 = 0.1437$
Largest difference in peak and hole (e \AA^{-3})	0.678 and -0.643

^a $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

^b $R_w = \{ \Sigma [w(F_o^2 - F_c^2)]^2 / \Sigma w(F_o^2)^2 \}^{1/2}$; where $w = [\sigma^2(F_o^2) + (aP)^2]^{-1}$, $a = 1 \times 10^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$.

2212 (sh); $\nu(\text{C}=\text{O} + \text{C}=\text{C} + \text{CC}(\text{CN}))$, 1613 (s), 1550 (s), 1495 (s), 1477 (w), 1441 (w). Electronic spectra/VIS (H_2O , λ/nm): 534 ($\epsilon = 150\,000\text{ mol}^{-1}\text{ L cm}^{-1}$); 450 ($\epsilon = 21\,000\text{ mol}^{-1}\text{ L cm}^{-1}$).

3. Results and discussion

3.1. Synthesis and general characterization

Metallic dark single crystals of the title complex were obtained from the reaction between ZnCl_2 and $\text{K}_2\text{CV} \cdot 2.5\text{H}_2\text{O}$ in aqueous media. The analytical data are consistent with the formation of a monometallic complex of (1:2)/(Zn(II):CV²⁻) stoichiometric ratio.

Thermogravimetric curve of $\text{K}_2[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, presented in Fig. 1A, shows two weight losses in $58\text{--}160^\circ\text{C}$ and $200\text{--}265^\circ\text{C}$ temperature ranges, corresponding to four water molecules. These results suggest the presence of coordination and lattice water molecules in the zinc complex structure. The DSC curve, shown in Fig. 1B, corroborates these results. It can be observed an endothermic event around 100°C and another one at 260°C attributed to the complex dehydration. It must be pointed out that the second step of dehydration process occurs at a high temperature and it can be inferred that

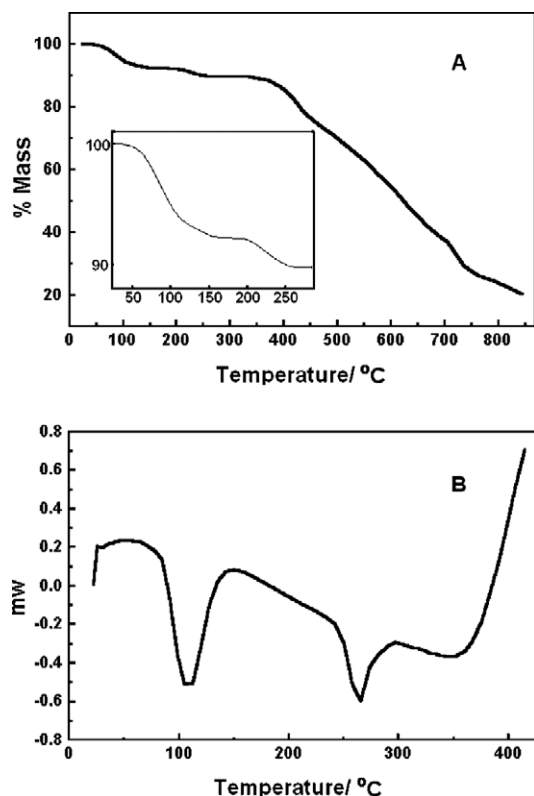


Fig. 1. Thermal analysis of $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$ in N_2 atmosphere: (A) TG curve, (B) DSC curve.

these water molecules are retained in the crystalline lattice and probably involved in hydrogen bonding.

Electronic spectrum of $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$ in water solution presents the same strong absorption bands observed for the precursor Croconate Violet potassium salt [21], at 534 nm ($\epsilon = 150\,000\text{ L mol}^{-1}\text{ cm}^{-1}$) and 450 nm ($\epsilon = 21\,000\text{ L mol}^{-1}\text{ cm}^{-1}$), assigned to $\pi \rightarrow \pi^*$ transition involving molecular orbitals delocalized over the pseudo-oxocarbon ring and to the one mostly localized on CN moieties, respectively, indicating that the coordination does not affect significantly the π electronic density localized over the pentacyclic ring.

The IR spectrum of $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$ (Fig. 2A) shows three well resolved absorption bands in the 3611–3427 cm^{-1} wavenumber range attributed to $\nu(\text{OH})$, confirming the presence of coordination and lattice water molecules involved in hydrogen bondings. In addition, the most important aspect in the complex spectrum is the absence of bands assigned to $\nu(\text{CO})$ originally at 1675 and 1630 cm^{-1} in the free CV^{2-} spectrum. This fact strongly suggests the Croconate Violet dianion coordination in a chelating fashion, through the vicinal oxygen atoms toward the Zn(II) center. On the other hand, the $\nu(\text{CN})$ stretching bands are not affected, indicating that the nitrile groups are not involved in the complex formation. Similar spectral behaviors have been observed to the analogous $K_2[M(\text{CV})_2(H_2O)_2] \cdot 2H_2O$ ($M = \text{Co(II)}, \text{Cu(II)}$) described in the literature [13,14], in which the coordination mode observed is O,O-bonding.

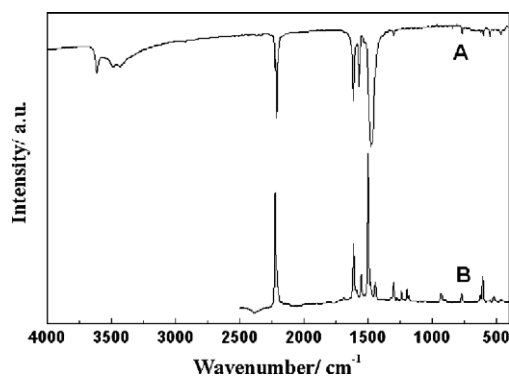


Fig. 2. Infrared (A) and Raman (B) spectra of $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$.

The Raman spectrum of $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$ (Fig. 2B), obtained with 1064 nm excitation, also shows the same pattern described in the infrared spectrum. It can be seen a medium intensity band at 2222 cm^{-1} with a shoulder at 2212 cm^{-1} assigned to CN stretching mode, which reveals the small perturbation over the dicyanomethylene groups with the complex formation, according to the proposition that these groups do not participate in the coordination. The bands at 1500–1600 cm^{-1} assigned to CO + CC + CC(CN) coupled modes are almost at the same positions and intensities in both infrared and Raman spectra, and there is no sign of the pure C=O stretching modes observed in the free ligand at 1675 cm^{-1} . All these facts reinforce the coordination by the oxygen atoms to the metallic center with no involvement of the CN groups.

3.2. Crystal structure of $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$

The molecular structure of the complex confirmed by single crystal X-ray diffraction analysis is shown in Fig. 3 and Table 2 presents selected bond distances and angles.

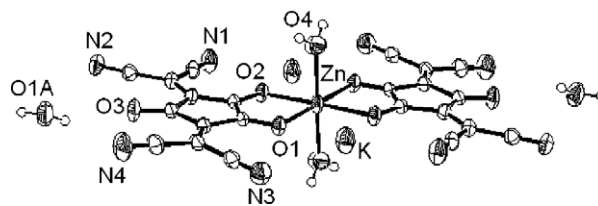


Fig. 3. Molecular structure and atom labeling scheme for $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$.

Table 2
Selected bond distances (\AA) and angles ($^\circ$) for $K_2[Zn(CV)_2(H_2O)_2] \cdot 2H_2O$

Zn–O1	2.085(2)	C1–C2	1.460(4)
Zn–O2	2.146(2)	C2–C3	1.443(4)
Zn–O4	2.093(2)	C3–C4	1.473(4)
C1–O1	1.267(4)	C4–C5	1.476(4)
C2–O2	1.267(4)	C5–C1	1.442(4)
C4–O3	1.234(4)		
O1–Zn–O2	82.86(8)	O1–Zn–O2'	97.14(8)
O4–Zn–O1	89.46(11)	O4–Zn–O1'	90.54(10)
O4–Zn–O2	90.10(11)	O4–Zn–O2'	89.90(11)

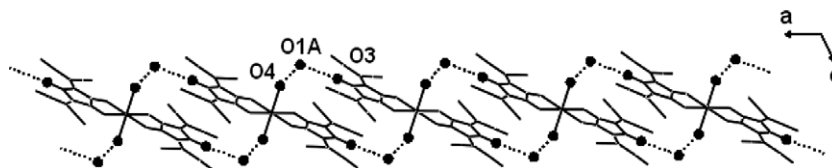


Fig. 4. Supramolecular array of $\text{K}_2[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ extended through hydrogen bonding along crystallographic a axis. The oxygen atoms involved in the hydrogen bonding are represented as spheres.

The complex structure contains discrete dianionic mononuclear centrosymmetrical entities of $[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2]^{2-}$, in which the metallic cation is placed on an inversion center and is surrounded by six oxygen atoms, adopting a slightly distorted octahedral geometry. Two CV^{2-} dianions are coordinated to Zn(II) centers in an asymmetrical bidentate fashion through the vicinal oxygen atoms O1 and O2 with Zn–O1 and Zn–O2 bond distances of 2.085(2) and 2.146(2) Å, respectively. This asymmetrical coordination mode has already been observed in the case of Co(II) and Cu(II) analogous described in the literature [13,14]. For Co(II) complex the Co–O bond distances are 2.122(3) and 2.109(3) Å and in particular for Cu(II) complex the difference between these bond distances is more pronounced (Cu–O, 1.967(2) and 2.332(2) Å) due to the Jahn–Teller effect. Actually, comparing the Co(II) and Cu(II) complexes crystallographic parameters [13,14] with those obtained to Zn(II) complex reported hereon, it can be noticed that all three compounds are isostructural. The angles formed between the Zn(II) center and the oxygen atoms are close to the ideal value of 90° for a perfect octahedron, except for O1–Zn–O2 ($82.86(8)^\circ$) and O1–Zn–O2' ($97.14(8)^\circ$). The mean C–C bond length of 1.4588(13) Å in the zinc complex is close to that observed for the precursor potassium salt (1.450(8) Å) described in the literature [7], indicating that the complexation does not affect the carbon pentacyclic ring very much. However, observing the three C–O bond lengths, it is noteworthy that C1–O1 and C2–O2 bond distances (1.267(4) Å), which oxygen atoms are involved in the coordination toward the metal center, are longer than the C4–O3 one (1.234(4) Å). In fact, C4–O3 bond acquires a greater carbonyl character upon complexation, suggesting that there is a partial localization of the π electrons in the solid state. Additionally, the five ring atoms lie in the same plane but the dianion is not quite planar. The dicyanomethylene groups are twisted out of the plane defined by the ring atoms by $5.03(26)^\circ$ and $7.28(18)^\circ$. Similar situations have been observed for the free ligand in the salts $\text{K}_2\text{CV} \cdot 2\text{H}_2\text{O}$ (3.36° and 6.30°) [7], $(\text{NBu}_4)_2\text{CV}$ (4.08° and 9.77°) [15], $\text{RbKCV} \cdot 2\text{H}_2\text{O}$ (4.44° and 6.07°) and $\text{Rb}_2\text{CV} \cdot 2\text{H}_2\text{O}$ (4.19° and 5.66°) [22]; and for the isostructural complexes $\text{K}_2[\text{Co}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (4.7° and 5.2°) [13] and $\text{K}_2[\text{Cu}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (5.29° and 7.22°) [14].

It is interesting to note that the discrete dianionic units $[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2]^{2-}$ are connected through intermolecular hydrogen bonding, leading to a supramolecular array extended along the crystallographic a axis, as can be seen in Fig. 4. These hydrogen bonds involve the O4 and O1A

oxygen atoms of coordination and lattice water molecules and Croconate Violet non-coordinated oxygen atom O3. The O4...O1A and O3...O1A distances are 2.823 and 2.860 Å, respectively, indicating medium hydrogen bonds [23].

4. Conclusions

In summary, the synthesis, thermal behavior, spectroscopic characterization and crystal and molecular structure of $\text{K}_2[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ are reported. Thermal analysis showed that the Zn(II) complex structure presents coordination and lattice water molecules. According to vibrational spectroscopic data, the Croconate Violet dianion is coordinated to Zn(II) center through the vicinal oxygen atoms O1 and O2 in a chelating fashion with no involvement of CN moieties. All these facts were confirmed by single crystal X-ray diffraction analysis. The dianionic units $[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2]^{2-}$ adopt an slightly distorted octahedral geometry in which the metallic center is surrounded by six oxygen atoms. These discrete dianionic units are connected through intermolecular hydrogen bonding giving rise to a supramolecular array extended along the crystallographic a axis.

The coordination polymers construction using the core $[\text{Zn}(\text{CV})_2]^{2-}$ as a building block subunit and bifunctional spacer nitrogen ligands is under investigation in our laboratory and will be presented in subsequent papers.

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Appendix A. Supplementary data

Crystallographic data for the $\text{K}_2[\text{Zn}(\text{CV})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ structure reported in this communication have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 293115. This information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2006.04.005](https://doi.org/10.1016/j.ica.2006.04.005).

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