Chemical Science Review and Letters ISSN 2278-6783

Research Article

A Comparative Study on Synthesis, Structural, Thermal and Magnetic Behaviour of $K_{2.72}[Fe(C_2O_4)_3].3H_2O$ and $K_3[Fe(C_2O_4)_3].3H_2O$

M. Narsimhulu* and K.A. Hussain

Department of Physics, Kakatiya University, Warangal, Telangana State, India

Abstract

The synthesis, structural, spectroscopic, thermal and magnetic behaviour of cation deficient (CD) potassium iron(III)oxalate trihydrate {$K_{2.72}[Fe(C_2O_4)_3].3H_2O$} (CDPIOX) compound have been investigated and compared the results with the results of parent potassium iron(III)oxalate trihydrate {$K_3[Fe(C_2O_4)_3].3H_2O$} (PIOX). Single crystal XRD studies revealed the CDPIOX and PIOX belong to the $P2_1/c$ space group of monoclinic crystal system and exhibit 3D chain structures. The Raman spectroscopic studies are used to investigate the vibrational modes of the compound. The thermal studies confirm the CDPIOX compound thermally stable up to 260°C, whereas the thermal stability of parent PIOX is 296°C. The thermal dependence magnetic susceptibility measurements revealed the CDPIOX exhibits strong antiferromagnetic ordering at low temperatures compare to the magnetic behaviour of PIOX.

Keywords: Inorganic materials, Fe(III) complex, structure, Raman spectra, magnetic behaviour

***Correspondence**
Author: M. Narsimhulu
Email: narsimhulu257@gmail.com

Introduction

The metal oxalate complexes are interesting materials, which have potential applications such as precursors to nanocrystalline metallic oxides and to molecular-based magnetic materials [1-7]. Due to the flexible bonding mode of oxalate ion with metal ions, enables to design 2D and 3D multifunctional magnets [8]. The $[Fe(C_2O_4)_3]^{3-}$ anion is an attractive ‘‘building block’’ owing to its magnetic properties and possibility of different dimensional network formations [9]. Blair and Jones reported the synthesis of parent potassium iron(III)oxalate trihydrate {$K_3[Fe(C_2O_4)_3].3H_2O$} (PIOX) for the first time in 1939 [10] and it belongs to $P2_1/c$ space group of monoclinic crystal system [11, 12]. In the recent past, structure, spectroscopic, optical and magnetic properties of this material was investigated owing to its wide applications in sensors, photochemical studies, actinometery, magnetic materials etc [13, 14]. In the past, a few cation deficient (CD) one-dimensional metallic complexes with oxalate ligand were synthesized and reported [15]. Present, the crystals of CDPIOX were synthesized by slightly modifying the procedure adopted by Blair and Jones [10]. Herein, we report the growth, crystal structure, Raman spectroscopic, thermal and magnetic properties of CDPIOX and compared these results with the parent PIOX compound.

Experimental details

Synthesis and crystal growth

All the chemicals were reagent grade and used without further purification. The single crystals of CDPIOX were grown by slow evaporation of a mixture of solutions obtained from adding $K_2C_2O_4.H_2O$, $(NH_4)_2C_2O_4.H_2O$ and $FeSO_4.7H_2O$ in 100 cm^3 distilled water in 1:1:1 molar ratio with constant stirring. This solution was heated for 30 min and filtered at cold condition to remove any unreacted residue. The green colour solution was kept for slow evaporation for crystallization. The as grown crystal is shown in **Figure 1**.

Characterization techniques

Single crystal XRD data was collected on Oxford X Calibur Gemini diffractometer equipped with EOS CCD detector at 293 K. Monochromatic Mo-*Kα* radiation (λ =0.71073Å) was used for the measurements. Data were collected and reduced by using the ‘‘CrysAlispro’’ program [16]. The crystal structure was solved by direct methods using SHELXS-97 [17] and the refinement was carried out against F^2 using SHELXL-97. The Raman spectra were recorded at room temperature using a micro-Raman spectrometer (LABRAM-HR) with a laser excitations of 514.5, 633, 785 nm. The thermal stability of the compound is tested by using TA Q20 differential scanning calorimeter under a nitrogen atmosphere with a heating rate of 10°C/min. Magnetic measurements were performed on polycrystalline samples of the compound with a commercial Quantum Design 9 T PPMS-VSM over the range from 2.5 to 300K.

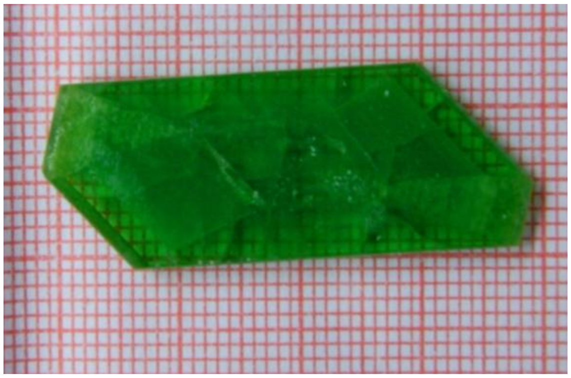

Figure 1 Photograph of CDPIOX crystal.

Results and discussion

We attempted to synthesize potassium ammonium tris(oxalato)ferrate(III) compound, but our attempts were unsuccessful. The Single crystal XRD data revealed the compound is CDPIOX and it belongs to $P2_1/c$ space group of monoclinic crystal system. The crystallographic data and structure determination parameters for the CDPIOX are given in **Table 1** along with the earlier reported structural data of the PIOX. It can be seen that there are small deviations in the values of formula weight, lattice constants and absorption coefficients of two compounds.

Table 1 Crystallographic data and structure refinement for CDPIOX.

Compound	$K_{2.72}[Fe(C_2O_4)_3].3H_2O$	$K_3[Fe(C_2O_4)_3].3H_2O$ [11]
Empirical formula	C_6 Fe $K_{2.72}$ $O_{15.17}$	$C_6H_6FeK_3O_{15}$
Formula weight	477.17	491.26
Temperature	293(2) K	296 K
Wavelength	0.71073 Å	-----
Crystal system	Monoclinic	Monoclinic
Space group	$P\ 2_1/c$	$P\ 2_1/c$
Unit cell dimensions	a=7.7573(4) Å, b=19.8655(8) Å, c=10.3489(6) Å, α=γ=90°, β = 107.946(6)°	a=7.7422(10)Å, b=19.9168(10)Å, c=10.3457(10)Å, α=γ=90°, β=107.946(6)°
Volume	1517.20(13) $Å^3$	1518.5(3)Å3
Z	4	4
Density (calculated)	2.089 Mg/m^3	2.149 g/cm^3
Absorption coefficient	1.822 mm^{-1}	2.149
F(000)	941	-----
Crystal size	0.42 x 0.36 x 0.26 mm^3	-----
Theta range for data collection	2.94 to 26.37°.	-----
Index ranges	-7<=h<=9, -15<=k<=24, -12<=l<=9	-----
Reflections collected	5782	2856
Independent reflection	2652[R(int)=0.066]	-----
Completeness to theta = 26.36°	98.3 %	-----
Absorption correction	Semi-empirical from equivalents	-----
Max. and min. transmission	0.6487 and 0.5149	-----
Refinement method	Full-matrix least-squares on F^2	-----
Data / restraints / parameters	3056 / 0 / 240	-----
Goodness-of-fit on F^2	0.955	-----
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1014	0.0409
R indices (all data)	R1 = 0.0506, wR2 = 0.1103	-----
Largest diff. peak and hole	0.865 and -0.382 e.$Å^{-3}$	-----

The CDPIOX exhibits three dimensional chain structure with consisting $[Fe(C_2O_4)_3]^{3-}$ complex anions, three K^+ cations. The central iron metal having distorted octahedral geometry surrounded by six oxygen atoms from three bidentate oxalate ligands. The K1, K2 ions having nine coordinated oxygen atoms with double trigonal prismatic geometry, while the K3 ion having dodecahedral geometry with eight coordinated oxygens (**Figure 2**).

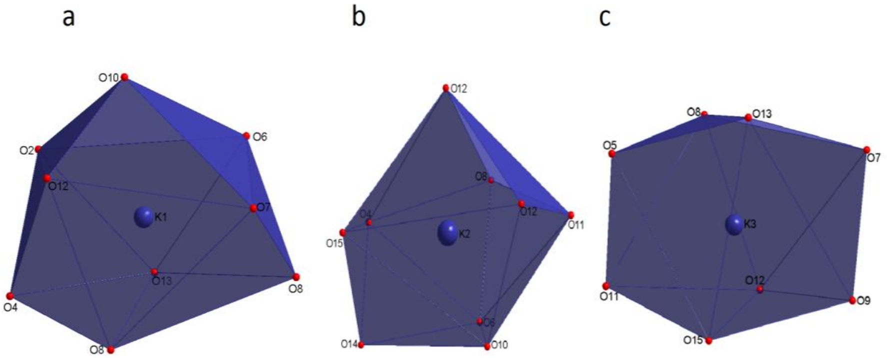

Figure 2 (a, b **)** The double trigonal prismatic geometry about nine-coordinated K(1) & K(2) respectively (c) The dodecahedral geometry about eight-coordinated K(3) in CDPIOX.

Raman Spectroscopy provides superior spatial resolutions of low frequency vibrations. The measurements of IR spectra below approximately 350 cm^{-1} is difficult or impossible due to the absorption of KBr optics [18]. Apart from IR vibrational studies there is no evidence of earlier work on Raman spectroscopy of parent PIOX. In the present study, single crystal Raman spectrum of CDPIOX is recorded at three incident wave lengths 514, 633, 785 nm respectively and shown in **Figure 3**. The intensities of observed peaks are almost same up to wave number 600 cm^{-1} and it can be seen that small variation in intensities of peaks for all three incident wavelenghts above 600 cm^{-1}. The band assignments are made based on earlier Raman studies of similar metal oxalate complexes [19-21]. The ν(Fe-O) vibrational modes were observed at 136, 257, 370 and 558 cm^{-1} respectively. The band at 782 cm^{-1} assigned to δ(O-C-O) mode of oxalate ion. The peak observed at 898 cm^{-1} is attributed to ν(C-C). The bands at 1252, 1451, and 1720 cm^{-1} correspond to stretching modes of oxalate ion.

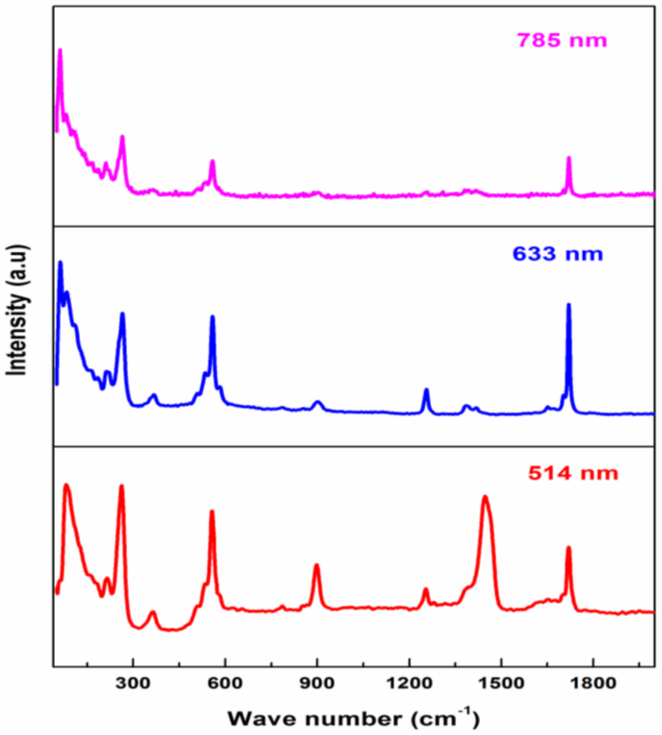

Figure 3 Raman spectrum of CDPIOX.

Figure 4 represents the DSC thermogram of CDPIOX. The endothermic peak around 112°C corresponds to the loss of water molecules in the compound. The second endothermic peak around 260°C corresponds to the docomposition of anhydrous potassium iron oxalate to mixture of potassium oxalate and iron oxide. The third endothermic peak at 417^{o}C attributed to the formation of mixture of iron oxide and potassium carbonate due to the decomposition of potassim oxalate and iron oxide mixture. These peak positions are slightly different from earlier reported DSC thermogram of parent PIOX complex [22], it may be due to the deficiency of cation or partial oxidation of iron in the CDPIOX. It can be seen that, the CDPIOX compound is thermally stable up to 260^{o}C, where as thermal stability of parent PIOX is 296^{o}C.

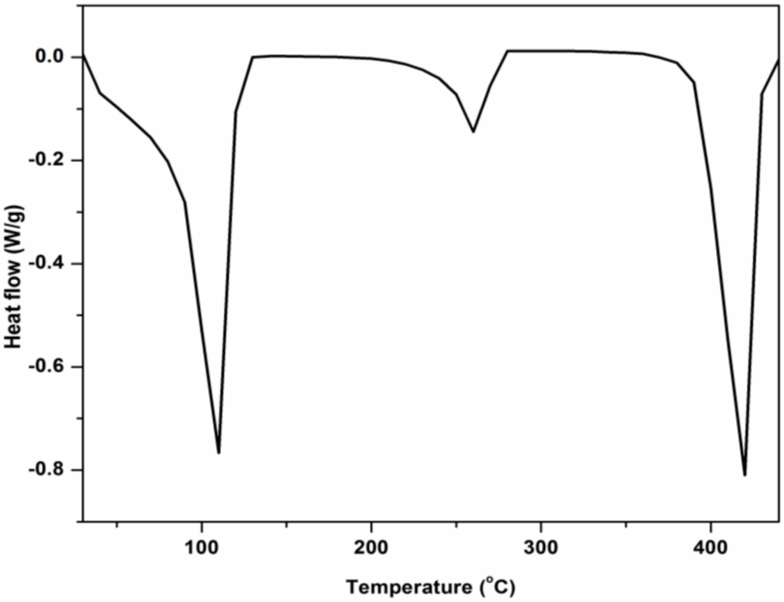

Figure 4 DSC thermogram of CDPIOX.

Figure 5 shows the thermal variation of magnetic susceptibility and inverse magnetic susceptibility for CDPIOX. The results of magnetic susceptibility measurements for CDPIOX are compared with the magnetization results of parent PIOX [12]. In CDPIOX susceptibility values are higher than the earlier reported PIOX, which may be attributed to the non-stoichiometry in the CDPIOX complex or partial oxidation of iron ion. From a good fit of the data to the Curie-Weiss law $\chi = C/(T-\theta)$, gave the Curie constant $C = 0.00918$ (emu K/g) and paramagnetic Curie temperature $\theta = -12$ K, which is greater than the earlier reported θ value {θ= -3.0(1) K} of parent PIOX complex. This large negative θ value indicates very strong antiferromagnetic interactions between the Fe localized magnetic moments in the CDPIOX complex compare to the PIOX.

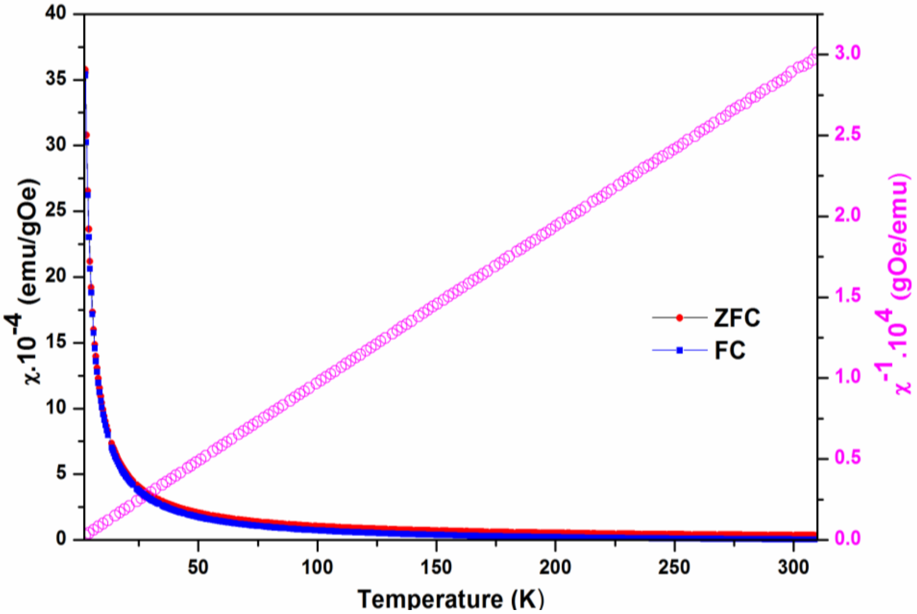

Figure 5 Temperature dependent magnetic susceptibility and inverse magnetic susceptibility for CDPIOX.

Conclusion

In summary, we have synthesized and grown good quality CDPIOX crystals using slow evaporation method and compared the results on structural, spectroscopic, thermal and magnetic behaviour with the results of parent PIOX. The CDPIOX and parent PIOX compounds belong to the monoclinic crystal system with $P2_1/c$ space group. Within the crystal structure of CDPIOX, the central iron possesses distorted octahedral geometry surrounded by six oxygen atoms from three bidentate oxalate ligands. Raman spectroscopic studies confirm the vibrational modes associated with the oxalate ion. The thermal stability of CDPIOX is less compare to the thermal stability of parent PIOX. The magnetic studies revealed the CDPIOX compound exhibits strong antiferromagnetic ordering compare with the parent PIOX.

References

[1] Decurtins S, Schmalle HW, Schneuwly P, Oswald HR, Inorg Chem 199, 32, 1888–1892.
[2] Bataille T, Louer M, Auffredeic JP, Louer D, J Solid State Chem 2000, 150, 81-95.
[3] Mathoniere C, Nutall CJ, Carling SG, Day P, Inorg Chem 1996, 35, 1201-1206.
[4] Louer D, Boultif A, Gotor FJ, Criado JM, Powder diff 1990, 5, 162-164.
[5] Coronado E, Galan-Mascaros JR, Gomez-Garcia CJ, J Chem Soc Dalton Trans 2000, 2, 205-210.
[6] Larionova J, Mombelli B, Sanchez J, Khan O, Inorg Chem 1998, 37, 679-684.
[7] Tamaki H, Zhong ZJ, Matsumoto N, Kida S, Koikawa M, Achiwa N, Hashimoto Y, Okawa H, J A Chem Soc 1992, 114, 6974-6979.
[8] Li YT, Yan CW, Guan HS, Polyhedron, 2003, 22, 3223-3230.
[9] Muziol TM, Wrzeszcz G, Chrzaszcz L, Polyhedron, 2011, 30, 169-177.
[10] Blair JC, Jones EM, Inorg Syn 1939, 1, 35-38.
[11] Junk PC, J Coord Chem 2005, 58, 355-361.
[12] Delgado G, Mora AJ, Sagredo V, Physica B 2002, 320, 410-412.
[13] Spencer HE, Schmidt MW, J Phy Chem 1971, 75, 2986-2990.
[14] Armenatano D, De Munno G, Lloret F, Julve M, Cryst Eng Comm 2005, 7, 57-66.
[15] Underhill AE, Watkins DM, Chem Soc Rev 1980, 9, 429-448.
[16] Oxford Diffraction, CrysAlis PRO, Oxford Diffraction Ltd., Yarnton, England 2009.
[17] Sheldrick GM, Acta Cryst Sec A, 2008, 64, 112-122.
[18] Nakamoto K. Infrared and Raman Spectra of Inorganic and coordination Compounds. Part B.John Wiley & Sons. NewYork 1997.
[19] Edwards HGM, Russell NC, J Mol Stru 1998, 43, 223-231.
[20] D'Antonio MC, Wladimirsky A, Palacios D, Coggiola L, Gonzalez-Baro AC, Baran EJ, Mercader RC, J Braz Chem Soc 2009, 20, 445-450.
[21] Bickley RI, Edwards HGM, Rose SJ, J Mol Struc 1991, 243, 341-350.
[22] Ladriere J, Hyperfine Int 1992, 70, 1095.

Publication History

Received	13th Feb 2018
Revised	10th Mar 2018
Accepted	16th Mar 2018
Online	30th Mar 2018