Synthesis, Crystal structure and Characterization of a New Oxalate Chromium (III) Complex

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Abstract. A new hybrid salt $(C_5H_9N_2)[Cr(C_2O_4)_2(H_2O)_2].3H_2O$, 3,5-dimethylpyrazole Cis diaquadioxala-tochromate(III) trihydrate, has been prepared by slow evaporation at room temperature and characterized by single crystal X-ray diffraction, IR, UV–visible spectroscopies, PXRD and thermogravimetric analyses. Furthermore, the observed crystal morphology was compared to the simulated one using the Bravais-Friedel, Donnay-Harker model. The structure of the title compound consists of $[Cr(C_2O_4)_2(H_2O)_2]^-$ mononuclear anions, 3,5-dimethylpyrazole cations and three uncoordinated water molecules. The Cr^{3+} ion is six coordinated in a slightly distorted octahedral environment, by two O atoms from two water molecules and four O atoms of two oxalate anions acting as chelating ligands. The cohesion of the structure is established by intermolecular O–H...O, N–H...O hydrogen bonds which connect ionic entities and water molecules and also by $\pi-\pi$ stacking interactions between the rings of 3,5-dimethylpyrazole cations. Hence, both coordinated and uncoordinated water molecules play an important role in the hydrogen-bonding system and stabilize the structure.

Keywords. Chromium (III) complex; crystal structure; spectroscopic studies; thermal behavior.

1. Introduction

Recently, a variety of transition metal ions has been used to construct metal organic frameworks which are now attracting increasing interest not only for their versatile architectures but also for their potential applications in various fields such as catalysis, luminescence, magnetism and even industrial applications.[1,2]

On the other hand, the oxalate group continues to receive considerable attention due to its ability to transmit efficiently magnetic interactions through its bridging mode.[3] Its planar shape, negative charge and good donor ability due to the presence of four oxygens, allow this ligand to act as a remarkably flexible ligand system upon complexation with different metal ions. In fact, this bidentate ligand has the ability to produce an array of new network architectures and to adopt various coordination modes.[4] Moreover, the oxalate bridge can efficiently mediate the exchange interactions between paramagnetic metal ions, leading to interesting magnetic properties.[5]

Up to now, there has been a significant interest in the synthesis and characterization of bis(oxalato) chromium (III) compounds through an impressive synthetic strategy based on supramolecular chemistry and self-assembly processes of two different components. Thus, to investigate new supramolecular architectures containing $[Cr(C_2O_4)_2(H_2O)_2]^-$, we used pyrazole ring as organic cation which is considered as a convenient component for building up supramolecular systems and for participating in hydrogen bonding interactions. Due to the presence of =NN(H) fragment, this component possesses a unique ability to form various complexes with proton donor and proton acceptors.[6,7] Additional stability can also be offered by $\pi-\pi$ stacking interactions of pyrazole rings.[8] Therefore, a variety of complexes containing 3,5-dimethylpyrazole ligands has been synthesized and employed in coordination and organometallic chemistry[9,10]

As a part of our ongoing studies of new oxalate chromium (III) complex of general formula (organic cation) $[Cr(C_2O_4)_2(H_2O)_2].nH_2O$[11] and in order to extend our studies in this field, we describe in the present work the synthesis, structure determination and characterization of a new bis(oxalato)chromate(III) complex.

2. Experimental

2.1 *Materials and Methods*

All reagents and solvents were obtained from commercial sources and used without further purification.

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The infrared spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer as KBr pellets, in 4000–400 cm^{-1} region on a Nicolet 470 FTIR spectrophotometer. The UV–visible absorption spectra were recorded on a 2802 UV/VIS spectrophotometer (UNICO) in the range 250–700 nm. X-ray powder diffraction measurements were performed on a D8 ADVANCE BRUKER diffractometer using Cu $K_{\alpha1/\alpha2}$ radiations and equipped with Lynxeye accelerator. The Thermogravimetric and Differential Scanning Calorimetry (TGA-DSC) were carried out on a Setaram TG-DSC Labsys Evo thermal analyzer, under Ar at a heating rate of 10°C min^{-1}.

2.2 Synthesis of the complex

Aqueous solution of oxalic acid dihydrate (2 mmol, 252.2 mg) and 3,5-dimethylpyrazole (1 mmol, 96.13 mg) was added to Cr(NO$_3$)$_3$.9H$_2$O (1 mmol, 400.15 mg) dissolved in 10 mL of water under continuous stirring at 323 K. Slow evaporation of the resultant solution led to violet single crystals suitable for X-ray diffraction after three weeks. Yield = 49%.

2.3 X-Ray crystallography

A prismatic violet crystal (0.56 × 0.4 × 0.32 mm) was selected for the structural analysis. Diffraction data were collected at 298 K with Enraf–Nonius CAD4 automatic four-circle equipped with graphite monochromator using Mo K_α (λ = 0.71073 Å) radiation and with the ω-2θ scan mode. The structure was solved by Direct method and refined by full-matrix least squares method on F^2 using the SHELX-97 package.[12] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecules were found in a difference Fourier map and refined with restraints: d(O−H) = 0.85(1) Å, d(H...H)= 1.387(2) Å and U_{iso}(H) = 1.5 Ueq(O). H atoms of the 3,5-dimethylpyrazole cation attached to carbon were placed in calculated positions with C–H distance of 0.96 - 0.93 Å while those attached to nitrogen were placed with d(N−H) = 0.86 Å. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

The final cycle of refinement converged to the values of R(F) = 4.6% and wR(F^2) = 12.9%. The molecular plots were drawn with the Diamond 3.0[13] program. Crystal data, experimental details and refinement results of the crystal structure are summarized in table 1.

Table 1. Crystal and structure refinement data for (C$_5$H$_9$N$_2$)[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$].3H$_2$O.

Formula	C$_9$ H$_{19}$ Cr N$_2$ O$_{13}$
Formula weight	415.26
Crystal system	Monoclinic
Space group	P2$_1$/n
Volume (Å^3)	1778.4(7)
Z	4
a (Å)	16.296 (3)
b (Å)	7.103 (2)
c (Å)	17.064 (3)
β(°)	115.79 (2)
ρ (gcm^{-3})	1.551
μ (mm^{-1})	0.71
θ range (°)	2.3 - 26.96
Index ranges	-20 ≤ h ≤ 1, -9≤ k ≤ 1, -19 ≤ l ≤ 21
Total data collected	4655
Independent reflections	3868
Reflections with I > 2σ(I)	3072
R$_{int}$	0.019
Goodness-of-fit on F^2	1.049
R [I > 2σ(I)]^a	0.046
wR [I > 2σ(I)]^b	0.129
Residuals (eÅ^{-3})	0.70 and -0.58

^{a} R = Σ ||F$_o$| −|F$_c$||/Σ|F$_o$|
^{b} wR = { Σ [w(F$_o^2$ −F$_c^2$)^2]/Σ [w(F$_o^2$)^2]} $^{1/2}$

3. Results and Discussion

3.1 Crystal Structure of the complex

The structure of the title compound is formed by one (C$_5$H$_8$N$_2$H)$^+$ cation, one [Cr(ox)$_2$(H$_2$O)$_2$]$^{2-}$ anion, and three water molecules of crystallization (figure 1). The central atom of anion is hexacoordinated by two oxygen atoms from cis water molecules and four carboxylate-oxygen atoms.
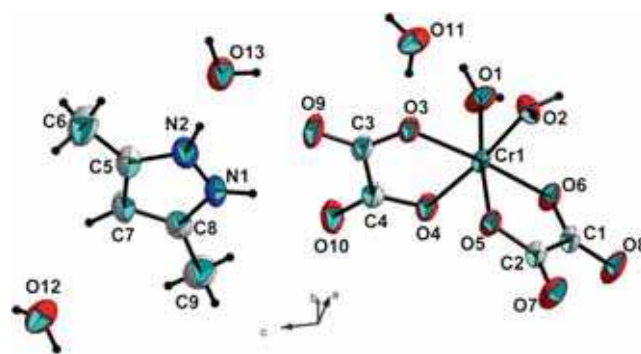
Figure 1. A view of the asymmetric unit with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as spheres of arbitrary radius.

The three diagonal angles of metal polyhedron [173.53(7)° to 175.20(7)°] deviate from linearity, therefore the coordination geometry around Cr(III) atoms is a distorted octahedron built up by two O atoms (O1, O2) from two cis water molecules and four O atoms (O3, O4, O5, O6) from two chelating oxalate dianions.

Because the coordination sphere is not a perfect octahedron, it is appropriate to use Σ parameter, which is the sum of the deviation away from 90° of the twelve possible O-Cr-O bite angles. As such, the value for an ideal octahedron is $\Sigma = 0$, so that higher the value, the greater is the distortion. The formula used for the calculation is the following:[14]

$$\sum = \sum_{i=1}^{12} |90 - \alpha_i|$$

In the case of this compound $\Sigma = 32.52$ indicating a distorted octahedral geometry for the metal coordination sphere. The O–Cr–O bite angles (88.80(7)° to 95.71(7)°) are far from the ideal one range from of 90° because of the usual small bite size of five-membered planar chelate rings formed by the bidentate oxalate ligand.[15,16] Selected bond lengths and angles are gathered in table 2.

The Cr–O(ox) distances are very similar. They are comparable with the values reported for similar compounds containing the $[Cr(C_2O_4)_2(H_2O)_2]^-$ motif, completed with various uncoordinated cations, including quinolinium: $(C_9H_8N) [Cr(C_2O_4)_2(H_2O)_2]$, 4-dimethylaminopyridinium: $(C_7H_{11}N_2)[Cr(C_2O_4)_2(H_2O)_2]$, 4-aminopyridinium: $(C_5H_7N_2) [Cr(C_2O_4)_2(H_2O)_2]$. H_2O, and 1-ethyl-3-methylimidazolium (EMIm)$[Cr(C_2O_4)_2 (H_2O)_2]$.[17–20]

The Cr–O (water) distance of 1.988(2) Å is somewhat longer than the Cr–O(ox) ones, but significantly shorter than those for compounds already mentioned. The oxalate ligands do not show significant deviations from planarity. The dihedral angle between the two chelating oxalate groups is 91.890(8)° and the shortest intermolecular chromium–chromium is 6.644(1) Å.

The C–C bond distances in the oxalate ligand are as expected for single C–C bond [1.556(3) and 1.554(3) Å for C1–C2 and C3–C4, respectively]. The bond length of the peripheral and inner C–O bonds compare well with those reported for other oxalate complexes. The shorter values being due to the greater double bond character of the free C–O bonds.[21]

The 3,5-dimethylpyrazole ligand is planar and the average C–C (1.382(4) Å), C–N (1.337(4) Å) and N–N (1.347(4) Å) bond lengths, and the average angles (108°) within the rings are in a good agreement with those reported in the literature for 3,5-dimethylpyrazole coordinated metal complexes.[22–24] The cation mean deviations are of 0.003 Å from the plane. Both methyl group substituents are almost coplanar with the pyrazole rings.

The structure of the title compound consists of mixed layers of complex anion formed by $[Cr(C_2O_4)_2(H_2O)_2]^-$ and free water molecules parallel to (101) plan intercalated by sheet of organic cations $(C_5H_9N_2)^+$ (figure 2). The cohesion of the structure is ensured by strong O–H...O and N–H...O hydrogen bonds[25,26] and by van der Walls interactions leading to a three-dimensional network.

In this compound $[Cr(C_2O_4)_2(H_2O)_2]$, $(C_5H_9N_2)^+$ cation and uncoordinated water molecules are joined through O–H...O, N–H...O hydrogen bonds [length d(D...A) and angle, (D-H...A) vary from 2.615(3) to 2.988(3) Å and 161 to 174(3)°, respectively] into 3D supramolecular networks (table S1 in Supplementary Information). Hence, the uncoordinated water molecules (O11, O12 and O13) play a role as both acceptors and donors while the coordinated water molecules (O1 and O2) act only as donors, forming an anions-anions interaction type.

For the oxalate groups, the peripheral carboxylate-oxygen atoms O8, O9 and O10 are the only acceptors.

The $[Cr(C_2O_4)_2(H_2O)_2]$ and $(C_5H_9N_2)^+$ are connected via N-H...O hydrogen bonds that link the amino N1-H1 group to the free O10 oxalato O atoms, forming an cations-anions interaction type by connecting the positive and the negative layers (figure 3).

An additional stability of the crystal is afforded by $\pi-\pi$ interactions between the aromatic rings of the cation $(C_5H_9N_2)^+$ to form layers parallel to the bc plane of the unit cell (figure 2). The centroid–centroid distance between two adjacent organic rings of 3,5-dimethylpyrazole, Cg1..Cg1 = 4.826 Å Cg1 is the centroid of the N1-N2-C5-C7-C8 (figure 4).

All these interactions link the layers together forming a three-dimensional network and reinforcing the cohesion of the ionic structure.

Table 2. Selected bond lengths (Å) and angles (°).

Bond lengths

Cr1—O1	1.975 (2)	Cr1—O4	1.971 (2)
Cr1—O2	2.001 (2)	Cr1—O5	1.964 (2)
Cr1—O3	1.972 (2)	Cr1—O6	1.973 (2)

Bond angles

O2—Cr1—O3	90.98 (7)	O6—Cr1—O4	92.81 (7)
O2—Cr1—O1	89.65 (8)	O1—Cr1—O5	173.82 (7)
O3—Cr1—O1	90.29 (7)	O6—Cr1—O5	83.12 (7)
O2—Cr1—O6	93.66 (8)	O2—Cr1—O4	173.53 (7)
O3—Cr1—O6	175.20 (7)	O3—Cr1—O4	82.56 (7)
O1—Cr1—O6	91.01 (7)	O1—Cr1—O4	90.31 (8)
O2—Cr1—O5	88.80 (7)	O5—Cr1—O4	91.89 (7)
O3–Cr1–O5	95.71 (7)		
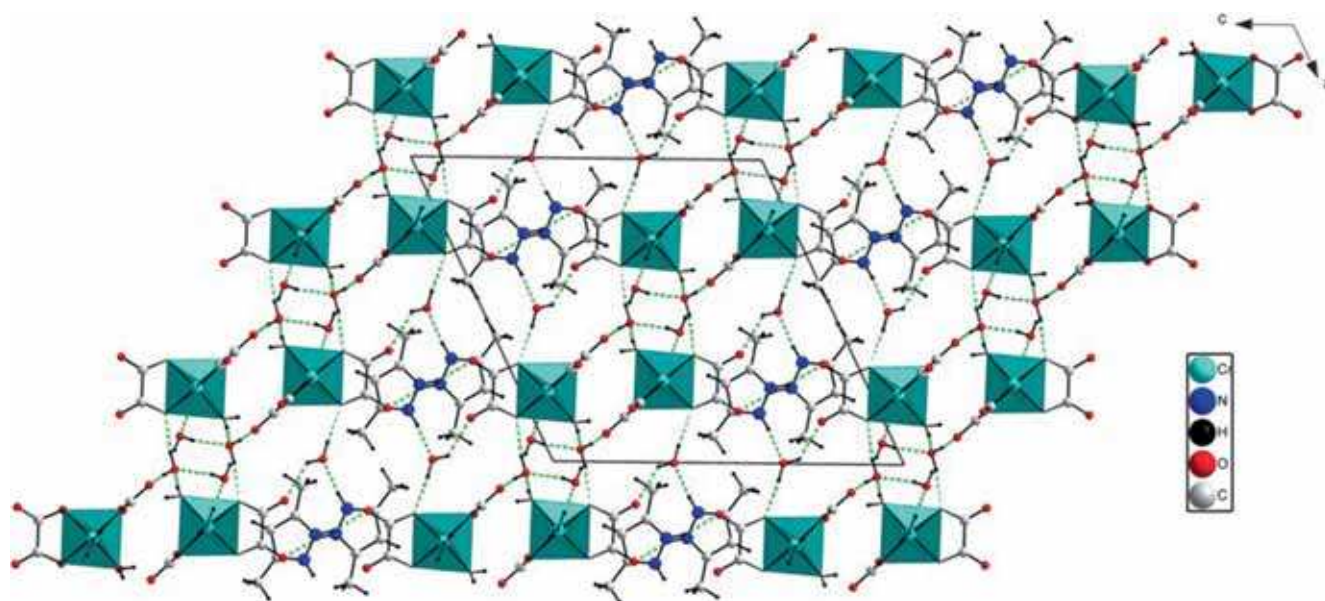
Figure 2. Projection of the $(C_5H_9N_2)[Cr(C_2O_4)_2(H_2O)_2].3H_2O$ structure along the *b* axis showing the hydrogen bonded network.
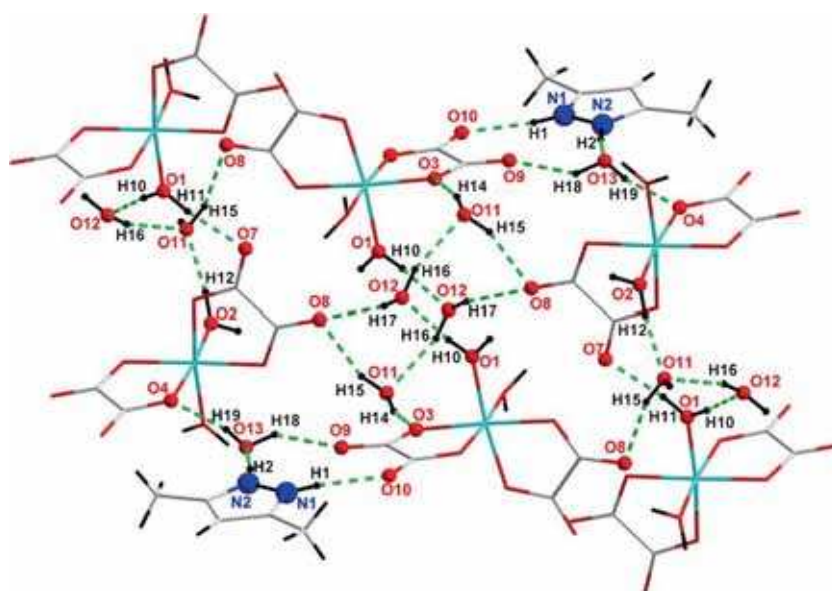
Figure 3. Fragments of the molecular structure of $(C_5H_9N_2)[Cr(C_2O_4)_2 (H_2O)_2].3H_2O$ showing hydrogen bonding interactions.

3.2 *Crystal morphology*

The crystal growth morphology has an enormous impact during the material processing stage. This is why the knowledge of the growth features and morphological properties of the molecular crystals are of crucial importance for understanding and exploiting many of their physico-chemical properties. For this, rationalization of the relationships between crystal morphology and the arrangement of atoms in the bulk crystal lattice is of great interest. Figure S1 shows a good agreement between the observed and predicted morphologies by the Morphology module in Accelrys Materials Studio version 6.0 software.[27] It is predicted that the dominating faces are (-10-1), (-101) as well as (-110) and (01-1).

3.3 *Vibrational spectra*

The infrared spectra of $(C_5H_9N_2)[Cr(C_2O_4)_2(H_2O)_2].3H_2O$ (figure S2) shows the existence of oxalate
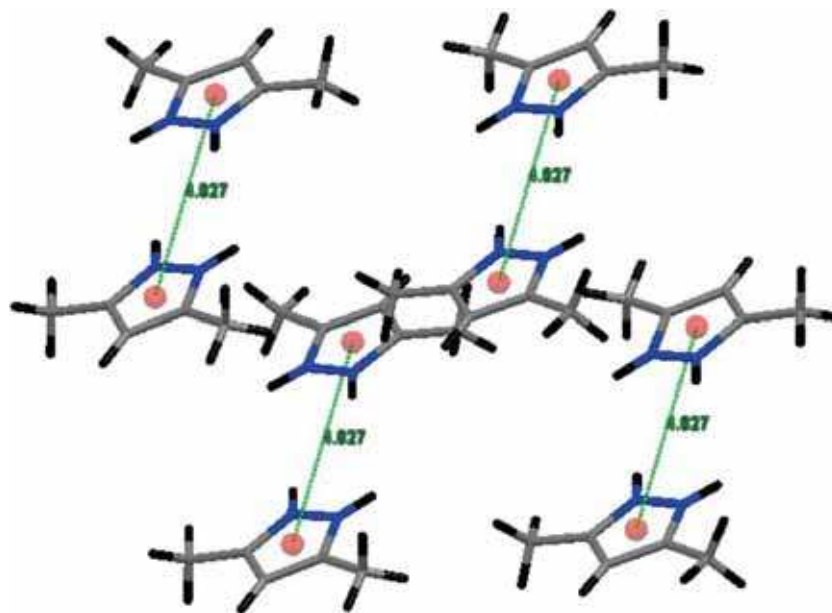
Figure 4. Perspective view of the molecular structure showing $\pi-\pi$ stacking interactions between the neighboring aromatic cations indicated by broken lines.

dianion, 3,5-dimethylpyrazole as well as H_2O. In fact, characteristic bands of the oxalate ligand appear at 1700, 1380 and 801 cm^{-1} for $\nu_{asy}(C=O)$, ν_{sy} (C=O) and δ (C=O), respectively.[28] The region of the $\nu_{asy}(C=O)$ and ν_{sy} (C=O) stretching vibrations of the oxalate group often shows slight differences owing to diverse coordination modes. The split bands are generally characteristic of the bidentate oxalate groups as terminal ligands.[29] The strong and broad absorption band at 3600-3200 cm^{-1} is attributed to the $\nu(OH)$ stretching vibrations of water molecules in the crystal lattice as well as ν (C–H) and ν (N–H).[30] Additionally, the peaks located at 1430, 1276 and 1150 cm^{-1} are assignable to $\nu(C=C)$, $\nu(C–N)$ and $\nu(C–C)$ stretching vibrations of pyrazole groups.[31] Furthermore, the band at about 550 cm^{-1} is characteristic for Cr–O stretching vibration.[32]

3.4 *Electronic spectra*

As shown in figure 5 the electronic spectrum of the title compound recorded in water at room temperature exhibits a strong band in the ultraviolet region, which may be assigned to charge transfer transition, and two bands in the visible, one at 17730 cm^{-1} and the other at 23923 cm^{-1} corresponding to $^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_1) and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (ν_2) transitions, respectively. These results are in good agreement with those mentioned in the literature.[33,34] The very strong absorption in the UV region of the spectra at 280 nm may be assigned to ligand to metal charge transfer.[35]
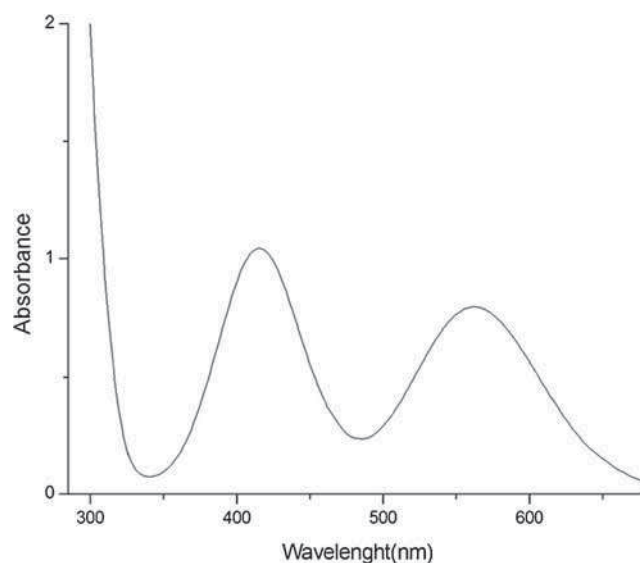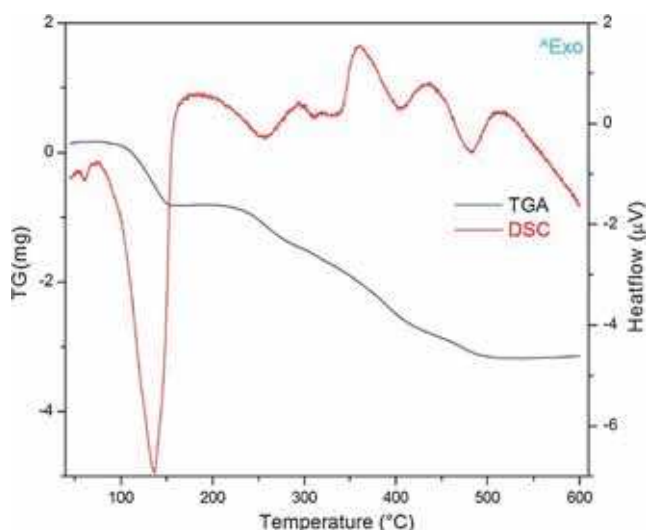

Figure 5. UV-Visible spectrum of $(C_5H_9N_2)[Cr(C_2O_4)_2(H_2O)_2].3H_2O$. Concentration, 6.0×10^{-3} M, path length, 1cm.

The values of Dq and B were found as 1773 cm^{-1} and 546 cm^{-1}, respectively. These parameters were calculated from the values of ν_1 and ν_2 according to the formula of electronic transition energy.[36,37]

$$\nu_1 = 10\,D \tag{1}$$

$$\nu_2 = 7.5\,B + 15\,Dq$$
$$-1/2(225\,B^2 + 100\,Dq^2 - 180\,Dq.B)^{1/2} \tag{2}$$

Figure 6. Thermogravimetric curves (TG and DSC) of $(C_5H_9N_2)[Cr(C_2O_4)_2(H_2O)_2].3H_2O$. Initial weight = 5 mg.

$$\nu_3 = 7.5\,B + 15\,Dq$$
$$+ 1/2(225\,B^2 + 100\,Dq^2 - 180\,Dq.B)^{1/2} \qquad (3)$$

The third spin allowed transition, $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) (ν_3), is predicted to appear at $\nu_3 = 39312$ cm^{-1} (254 nm).

3.5 *X-ray powder diffraction analyses and thermal analyses*

In order to check the purity, X-ray powder diffraction measurement was carried out at room temperature. As shown in figure S3, the similarity of the calculated pattern and the observed one confirms the high purity level of the synthesized phase.

The TG/DSC of the title compund were performed under Ar atmosphere, in the temperature ranging from 40–600°C, with a heating rate of 10°C min^{-1}. The obtained thermograms are shown in (figure 6).

The overall weight loss amounts to 71.04% and is based on the stoichiometry of the starting material $(C_5H_9N_2)[Cr(C_2O_4)_2(H_2O)_2].3H_2O$ (formula weight: 415.26 g.mol^{-1}). In the temperature range 60–150°C, the TG trace shows a 21.44% loss in weight, suggesting that the compound loses five water molecules in one step which is consistent with the calculated weight loss of 21.67%. The result is in agreement with the structure which contains five water molecules. In addition, the salt loses weight between 150–470°C, indicating the decomposition of the oxalate groups and the organic part of the material. But no clear plateaus were reached in these stages and the total weight loss is equal to 49.6%.

4. Conclusions

Single crystals of the new salt $(C_5H_9N_2)[Cr(C_2O_4)_2(H_2O)_2].3H_2O$ were grown from an aqueous solution at ambient temperature. The crystal structure of the title compound has been characterized by single crystal X-ray diffraction and confirmed by XRPD, IR, UV-Visible and TG–DSC techniques. A three-dimensional network was shown to be generated by intermolecular N–H...O and O–H...O hydrogen-bonding interactions involving the cation, the complex anion and the lattice water molecules and by $\pi-\pi$ interactions between the rings of 3,5-dimethylpyrazole. Estimated morphology with the BFDH model is in agreement with the observed crystal shape. IR data and the thermal analysis have allowed to check the number of water molecules as well as the nature of connections to the network of these molecules, confirming the result of the structural study.

Supplementary Information

Crystallographic data and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1005075. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, CAMBRIDGE, CB2 1EZ, UK (fax:+44-1223-336-033; email:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Hydrogen-bonding geometry (table S1), estimated morphology with BFDH model (a), and growth single crystal of the complex (b) (figure S1), infrared spectra of the complex (figure S2) and experimental and simulated PXRD of the complex (figure S3) are available at www.ias.ac.in/chemsci.

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