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Research paper

A new bis(oxalato)chromate(III) salt: synthesis, crystal structure, thermal behavior and magnetic properties of $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$

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ABSTRACT

A new chromium(III) salt $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$, trans-diaquabis(oxalato) chromate(III) imidazolium dihydrate, has been synthesized and characterized by single crystal X-ray diffraction. This compound crystallizes in the monoclinic system, C2/c space group with $a = 10.836(1)$Å, $b = 7.541(1)$Å, $c = 16.349(3)$Å and $\beta = 93.52(1)°$. The structure of the title compound consists of $[Cr(C_2O_4)_2(H_2O)_2]^-$ mononuclear anions, imidazolium cations and uncoordinated water molecules. The crystal structure data indicates that the Cr^{+III} ion is six coordinated in a distorted octahedral geometry, with four equatorial O atoms of two oxalate anions acting as chelating ligands and two axial O atoms from two water molecules. Structural cohesion is established by intermolecular O—H…O hydrogen bonds connecting the ionic entities and water molecules. In fact, both coordinated and uncoordinated water molecules play an important role in the hydrogen-bonded system, stabilizing the structure. Magnetic susceptibility measurements of the title compound in the range 2-300K exhibit paramagnetic behavior at high temperature. However, at low temperature, the magnetic data show the occurrence of weak antiferromagnetic intermolecular interactions between the local spin.

Keywords: chromium(III) complexes, crystal structure, thermal properties, visible and ultraviolet spectrometers, magnetic properties

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1. INTRODUCTION

In recent years the area of inorganic crystal engineering[1−3] has become one of intense research activity due to the growing need for novel solid-state architectures with potential applications as functional materials in fields such as catalysis, conductivity and magnetism.[4,5]

The coordination chemistry of the oxalate dianion has been subject of thorough investigation.[6−8] Its planar shape, negative charge and good donor ability due to the presence of four oxygen donors, make this ligand very appropriate to build coordination polymers in its interaction with metal ions. The versatility of the oxalate as a ligand is well illustrated by the variety of coordination modes that it can exhibit in its metal complexes.[9−11]

In this context, the design of chromium(III) complexes containing oxalate anion is attracting much attention.[12,13] This chemistry has been stimulated mainly by the increasing interest in the search for new molecule-based magnets[14] and the fascinating structural topologies offered by the different coordination modes of the oxalate anion.[15] In fact, previous studies have demonstrated that the $C_2O_4^{2-}$ ion is a powerful candidate able, by its exceptional versatility, to yield supramolecular architectures with interesting magnetic properties.[16,17] Furthermore, such compounds have proven to be suitable starting materials for the preparation of homo-and heteropolynuclear systems.[18,19]

In this direction, our investigation has thus been focused on the synthesis and characterization of new bis(oxalato)chromate(III) species of general formula (organic cation) $[Cr(C_2O_4)_2(H_2O)_2].nH_2O$. By using imidazolium as organic cation, we have isolated a new salt: $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$ and we report in this contribution its synthesis and structural characterization as well as its spectroscopic, thermal and magnetic properties.

2. METHODS

2.1. Materials and physical measurements

All chemicals were commercially available and were used without further purification. The X-ray data was collected on an Enraf-Nonius CAD-4 diffractometer. TG/DTA 92 SETARAM thermal analyzer was employed for the investigation of the thermal behavior in Ar atmosphere from 50 to 600°C, and UV-Vis spectrum was recorded on a Perkin Elmer UV/Vis spectrometer Lambda 20, in the range 250−800 nm.

Magnetic susceptibility measurements of a polycrystalline sample were carried out using a quantum design (superconducting quantum interference device SQUID) magnetometer in the temperature range 2-300K, at a magnetic field of 0.1 T.

Table 1. Crystal data and structure refinement parameters.

Formula	$C_7H_{13}CrN_2O_{12}$
Formula weight	369.2
Crystal system	monoclinic
Space group	C2/c
a (Å)	10.836(1)
b (Å)	7.541(1)
c (Å)	16.349(3)
β (°)	93.52(1)
Volume (Å^3)	1333.4(3)
Z	4
T (K)	298(2)
μ (mm^{-1})	0.929
θ Range (°)	2.50−26.97
hkl ranges	$-13 \leq h \leq 13$
	$-1 \leq k \leq 9$
	$-20 \leq l \leq 1$
Total data collected	1848
Independent reflections	1452
R_{int}	0.0109
Goodness-of-fit on F^2	1.116
R indices [$I > 2\sigma(I)$]	R = 0.0294[a]
	wR = 0.0845[b]
Largest difference peak and hole (e Å^{-3})	0.55 and − 0.38

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{1/2}$.

2.2. Synthesis

A mixture of imidazole (1 mmol), oxalic acid dihydrate (2 mmol) and $Cr(NO_3)_3.9H_2O$ (1 mmol) was dissolved in 40 mL of water. The resulting solution was then stirred for 2 h and allowed to evaporate at room temperature. After two months, violet prism-shaped crystals suitable for X-ray analysis were obtained.

2.3. X-ray structure determination

A single crystal, of dimensions 0.6 × 0.4 × 0.3 mm, was used for data collection, and single crystal X-ray diffraction measurements were carried out at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromator, using Mo K_α ($\lambda = 0.71073$ Å) radiation.

The structure was solved by direct methods and then refined on F^2 by a full-matrix least-squares procedure (SHELXL 97)[20] using anisotropic displacement parameters for non-H atoms. After several cycles of refinement, the hydrogen atoms were found in a difference Fourier map and the H(7) was placed in calculated position with C—H distance of 0.93 Å and constrained to ride on his parent atom [C(3)] with $U_{iso}(H) = 1.2\ U_{eq}(C)$. The final cycle of refinement converged at the values of R(F) = 2.94% and $wR(F^2) = 8.45\%$. Details of the crystal structure determinations are summarized in Table 1.

3. RESULTS AND DISCUSSION

3.1. Crystal structure description

In the title compound $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$, the asymmetric unit is formed by one-half cation, one half anion and one water molecule of crystallization (Figure 1). The Cr^{+III} ion lies on an inversion center and the C and H atoms of C(4)—H(6) groups lie on twofold rotation axis.

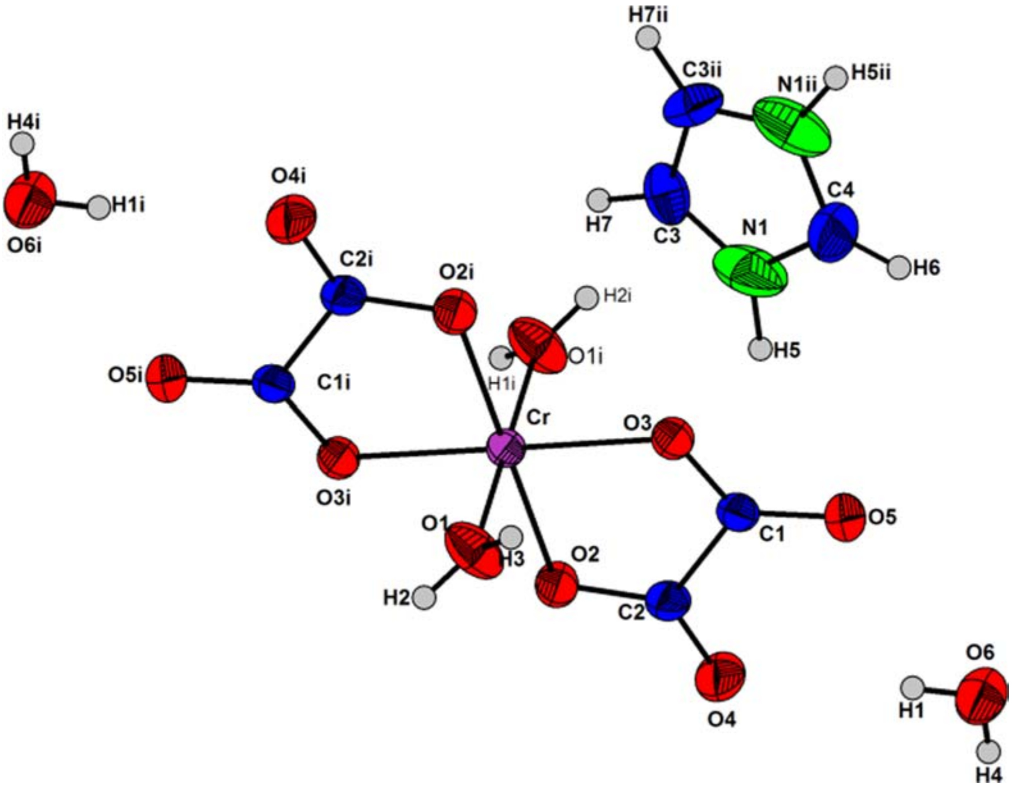

Figure 1. A view of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as spheres of arbitrary radius. (i = $-x+3/2, -y+1/2, -z+1$; ii = $-x+2, y, -z+3/2$).

In the anionic complex, the coordination environment of Cr^{+III} ion involves six oxygen atoms (two from *trans* water molecules and four from two chelating oxalate dianion) in a slightly distorted octahedral geometry. The main distortion of the CrO_6 octahedron is associated with the reduction from the ideal 90° value of some bond angles [83.11(5)° for O(3)—Cr—O(2) and $O(3)^i$—Cr—$O(2)^i$], i.e. each

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

Bond lengths			
Cr — O(3)^{I}	1.963(1)	O(2)— C(2)	1.284(2)
Cr — O(3)	1.963(1)	O(3)— C(1)	1.286(2)
Cr — O(2)	1.966(1)	O(4)— C(2)	1.224(2)
Cr — O(2)^{I}	1.966(1)	C(1) — O(5)	1.223(2)
Cr — O(1)^{I}	1.979(2)	C(1)— C(2)	1.560(2)
Cr — O(1)	1.979(2)	C(3)— N(1)	1.295(3)
		C(3)— C(3)^{ii}	1.315(4)
		N(1)— C(4)	1.363(3)
Bond angles			
O(3)^{i}—Cr—O(3)	180.00(7)	C(2)—O(2)—Cr	114.2(1)
O(3)^{i} — Cr—O(2)	96.89(5)	C(1)— O(3)—Cr	114.4(1)
O(3) —Cr—O(2)	83.11(5)	O(5)—C(1)—O(3)	126.1(2)
O(3)^{i} —Cr—O(2)^{I}	83.11(5)	O(5)—C(1)—C(2)	120.0(2)
O(3) —Cr—O(2)^{I}	96.89(5)	O(3)—C(1)—C(2)	113.8(1)
O(2) —Cr—O(2)^{I}	180.00(1)	O(4)—C(2)—O(2)	125.8(2)
O(3)^{i} — Cr—O(1)^{I}	91.78(7)	O(4)—C(2)—C(1)	119.9(2)
O(3) — Cr—O(1)^{I}	88.22(7)	O(2)— C(2)—C(1)	114.2(1)
O(2) — Cr—O(1)^{I}	89.52(7)	N(1)—C(3)—C(3)^{ii}	109.0(1)
O(2)^{i}—Cr—O(1)^{I}	90.48(7)	C(3)—N(1)—C(4)	108.7(2)
O(3)^{i}—Cr—O(1)	88.22(7)	N(1)^{ii}- C(4)— N(1)	104.7(3)
O(3)—Cr—O(1)	91.78(7)		
O(2)—Cr—O(1)	90.48(7)		
O(2)^{i}—Cr—O(1)	89.52(7)		
O(1)^{i}—Cr—O(1)	180.00(5)		

Symmetry transformations used to generate equivalent atoms: i = −x + 3/2, − y + 1/2, − z + 1;ii = −x + 2,y, − z + 3/2.

oxalate ion is coordinated by only two oxygen atoms to the Cr^{+III} ion, in this structure the $C_2O_4^{2-}$ is more a bridge between the metal sites. While imadazolium cations are not bound to the central atom.

The equatorial Cr—O(ox) distances are very similar, 1.963(1)Å [Cr—O(3), Cr—O(3)^{i}] and 1.966(1)Å [Cr—O(2), Cr—O(2)^{i}], and 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: $(C_9H_8N)[Cr(H_2O)_2(C_2O_4)_2]$,[21] 4-dimethylaminopyridinium: $(C_7H_{11}N_2)$ $[Cr(C_2O_4)_2(H_2O)_2]$,[22] 4-aminopyridinium: $(C_5H_7N_2)[Cr(C_2O_4)_2(H_2O)_2].H_2O$[23] and 1-ethyl-3-methylimidazolium: $(EMIm)[Cr(C_2O_4)_2(H_2O)_2]$.[24]

The axial Cr—O(water) distances of 1.979(2)Å are 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 96.87(4)°. The shortest intermolecular chromium–chromium is 6.601(1) Å.

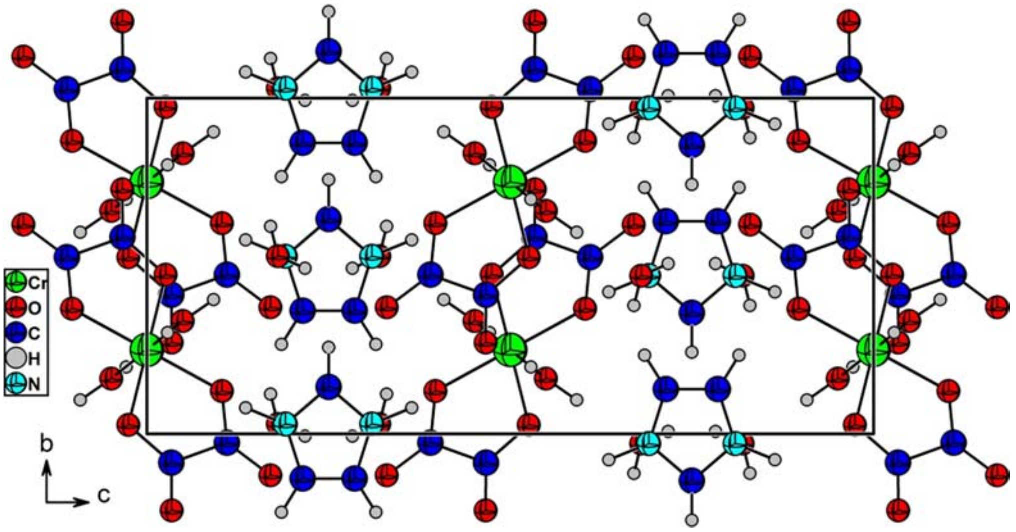

Figure 2. A view of the supramolecular anionic chains resulted from hydrogen bond interactions between the $[Cr(C_2O_4)_2(H_2O)_2]$ units (hydrogen bonds are shown as dashed lines) 110.

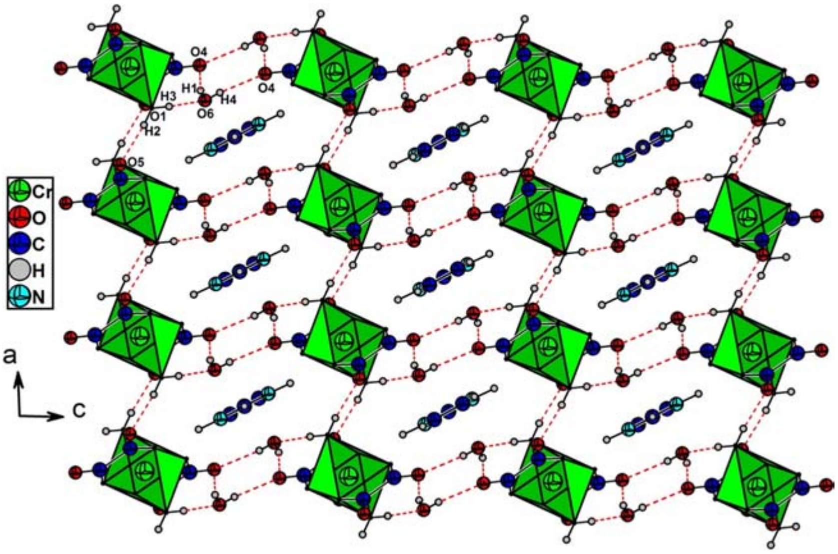

Figure 3. A view of the packing of $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$ showing the hydrogen-bonded network leading to the formation of supramolecular cavities where imidazolium cations are located (hydrogen bonds are shown as dashed lines).

The C—C bond distance in the oxalate ligands is as expected for a single C—C bond [1.560(2)Å for C(1)—C(2) and $C(1)^i$—$C(2)^i$]. The bond length values 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.[19] Selected bond lengths and angles are gathered in Table 2.

Within the crystal structure, there are strong intermolecular O—H . . . O hydrogen bonds between water molecules and oxalate anions. In fact, the coordinated water molecules of the $[Cr(C_2O_4)_2(H_2O)_2]^-$ units are hydrogen-bonded to the peripheral oxalate-oxygens [O(5)] from adjacent chromium complexes forming anionic chains 110 (Figure 2). The supramolecular chains are further connected by O—H . . . O hydrogen bonds involving both coordinated and uncoordinated water molecules and generating cavities where the imidazolium cations are located (Figure. 3). As a consequence, the overall hydrogen-bonded length d(D . . . A) and angle <(D—H . . . A) vary from 2.601(2) to 2.984(2) Å and 168(3)−176(3)°, respectively. This scheme can be described as a three-dimensional network. The data of the hydrogen bonds are listed in Table 3.

Table 3. Hydrogen-bond geometry (Å, °).

D	H	A	D—H	H . . . A	D . . . A	D—H . . . A
O6	H1	O4	0.80(3)	2.20(3)	2.984(2)	168(3)
O6	H4	$O4^i$	0.73(4)	2.16(3)	2.878(2)	174(4)
O1	H2	$O5^{ii}$	0.79(4)	1.93(3)	2.717(2)	173(3)
O1	H3	$O6^{iii}$	0.85(3)	1.75(3)	2.601(2)	176(3)

Symmetry codes: $i = -x + 3/2, y - 1/2, -z + 1/2$; $ii = x - 1/2, y + 1/2, z$; $iii = -x + 3/2, -y - 1/2, -z + 1$.

As far as the imidazolium cations are concerned, the C—N [1.363(3)Å for N(1)—C(4) and $N(1)^{ii}$—C(4), 1.295(3)Å for N(1)—C(3) and $N(1)^{ii}$—$C(3)^{ii}$] and C—C bond lengths of 1.315(4)Å for C(3)—$C(3)^{ii}$, agree with those reported for similar compounds.[25,26]

3.2. Electronic spectrum

Figure 4 shows the electronic spectrum of the title compound. It exhibits a strong band in the ultraviolet area, which may be assigned to charge transfer transition, and two bands in the visible area, one at 574 nm (ν_1) and the other at 430 nm (ν_2) corresponding to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions, respectively. These results agree with those in the literature.[27,28]

Very strong absorption (with ε too elevated) in the UV region of the spectra (at ca. 300 and ca. 340 nm) originates from charge-transfer metal-to-ligand transitions.[29−31]

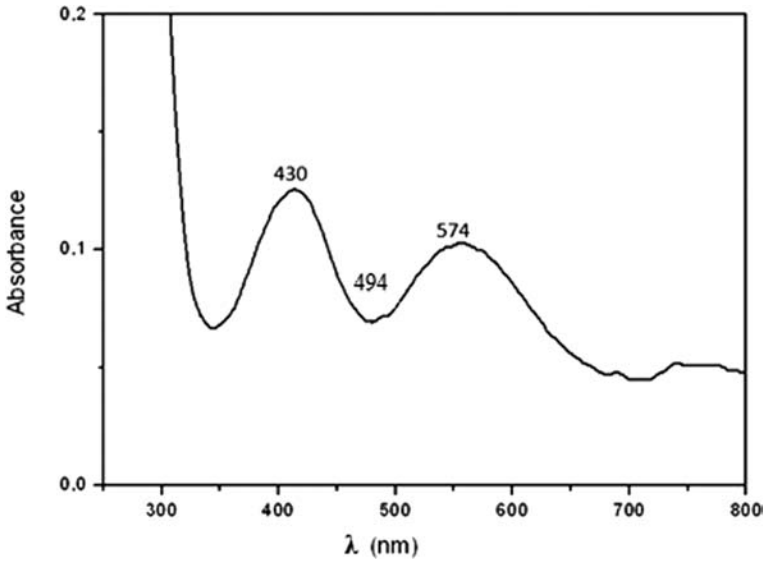

Figure 4. UV-Visible spectrum in the range 250–800 nm.

The values of Dq and B were found as 1792.1 cm^{-1} and 592.5 cm^{-1}, respectively. These parameters were calculated from the values of ν_1 and ν_2 according to the formula of electronic transition energy[32,33]:

$$\nu_1 = 10\text{Dq}$$

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

Thus, the transition at 493 nm, can be readily ascribed to the spin Laporte-forbidden transitions of Cr(III) in an octahedral field.[34,35]

3.3. Thermal analysis

Thermal stability of the title compound was studied by differential thermal analysis (DTA) and thermogravimetry (TG) from 50 to 600°C, as shown in Figure 5. Within this interval, several degradation steps were observed. The overall weight loss amounts to 85.74% and is based on the stoichiometry of the starting material $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$ (formula weight: 369.2 g.mol^{-1}).

The DTA trace shows an endothermic peak at 145°C. The loss in weight (20.41%) suggests that the compound losses four water molecules in two consecutive steps as shown in the TG trace; the first loss corresponds to the weakly coordinated water molecules [O(6)], and the second loss to the coordinated ones O(1) (theoretical mass loss 19.5%).

This result is in agreement with the structure characterization, which reveals that the synthesized compound contains four water molecules of two types, guest and coordinated water molecules. Then, the salt loses weight sharply between 176 and 600°C (65.33%) suggesting the decomposition of the organic part.

3.4. Magnetic measurements

The observed temperature dependence of the magnetic susceptibility is depicted in Figure 6. The least square fit to the Curie–Weiss law shows paramagnetic interaction in the prepared sample.

The temperature dependence of $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2]._2H_2O\chi M$ is the magnetic susceptibility per mol of chromium(III) in the temperature range 1.9–300 K, shown in Figure 7. At room temperature, the value of χ_M(ca. 1.87 $\text{cm}^3\,\text{mol}^{-1}\,\text{K}$) is as expected for a magnetically isolated spin quartet. This value remains constant when cooling and it decreases smoothly in the lower temperature, attaining values of 0.8 (1) $\text{cm}^3\,\text{mol}^{-1}\,\text{K}$ at 1.9 K. No susceptibility maximum was observed in the temperature range explored. This decrease $\chi_M T$ at lower temperatures may be attributed to the zero field splitting (D) of the chromium(III) or to weak antiferromagnetic intermolecular interactions (θ) between the local spin quartets, or to both factors simultaneously.

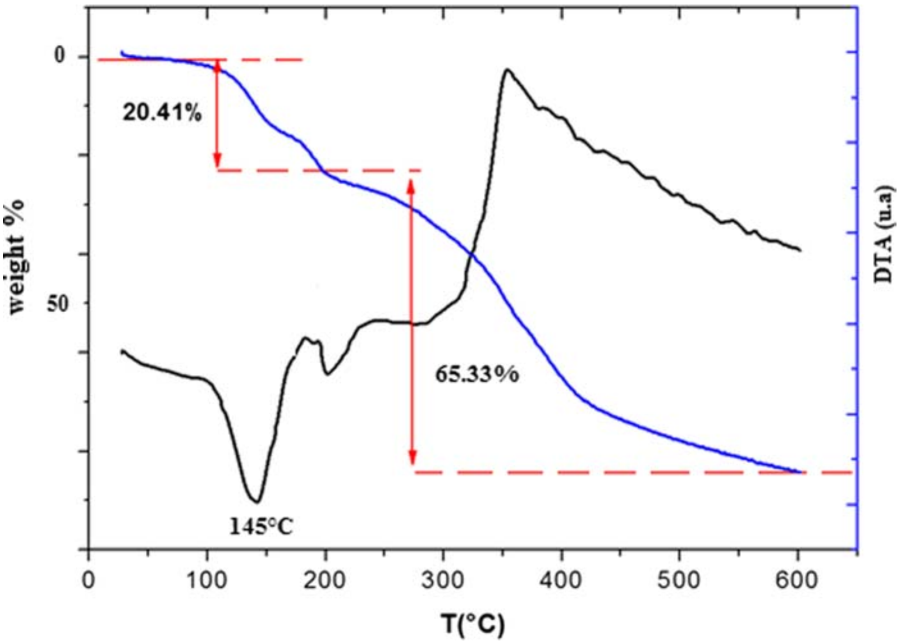

Figure 5. TG/DTA thermogram of $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$ from room temperature to 600°C.

As far as the values of the intermolecular interactions are concerned, they are antiferromagnetic and weak. The small magnitude of the magnetic coupling in $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$ is in agreement with its structure. In fact, the hydrogen-bonds linking the chromium(III) mononuclear units in the sample provide the exchange pathway. In this respect, the somewhat larger antiferromagnetic coupling in $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$, when compared with that of $PPh_4[Cr(bpym)(ox)_2].H_2O$,[36]

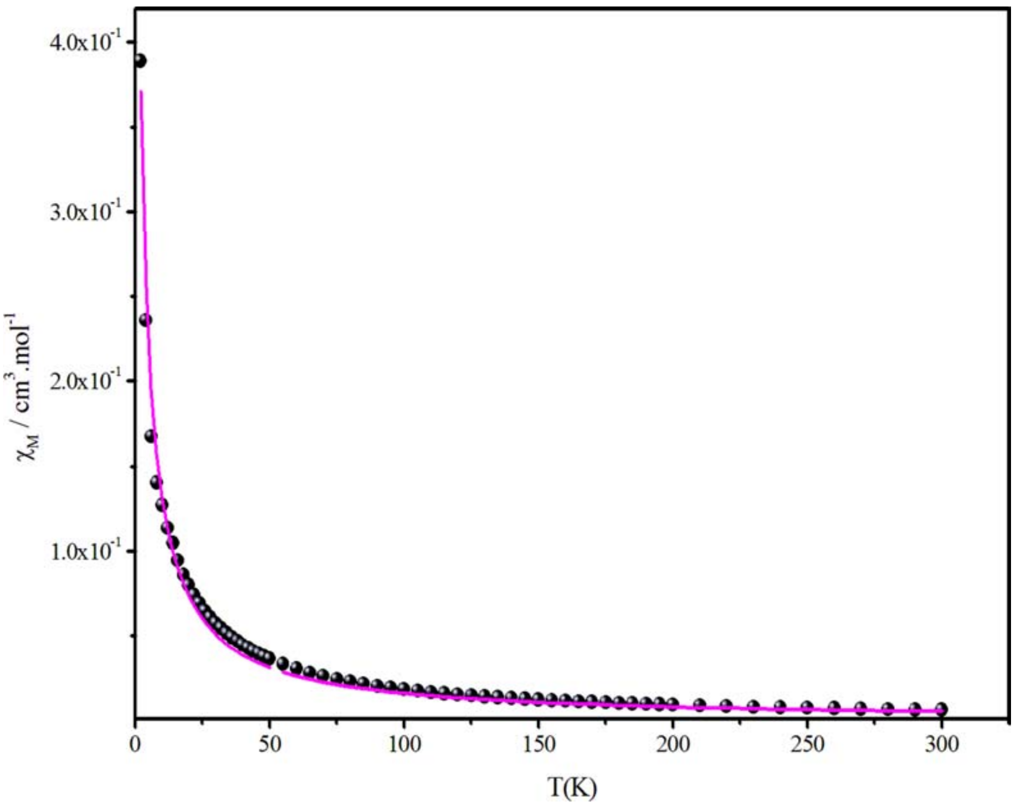

Figure 6. Plot of the temperature dependence of χ_M.

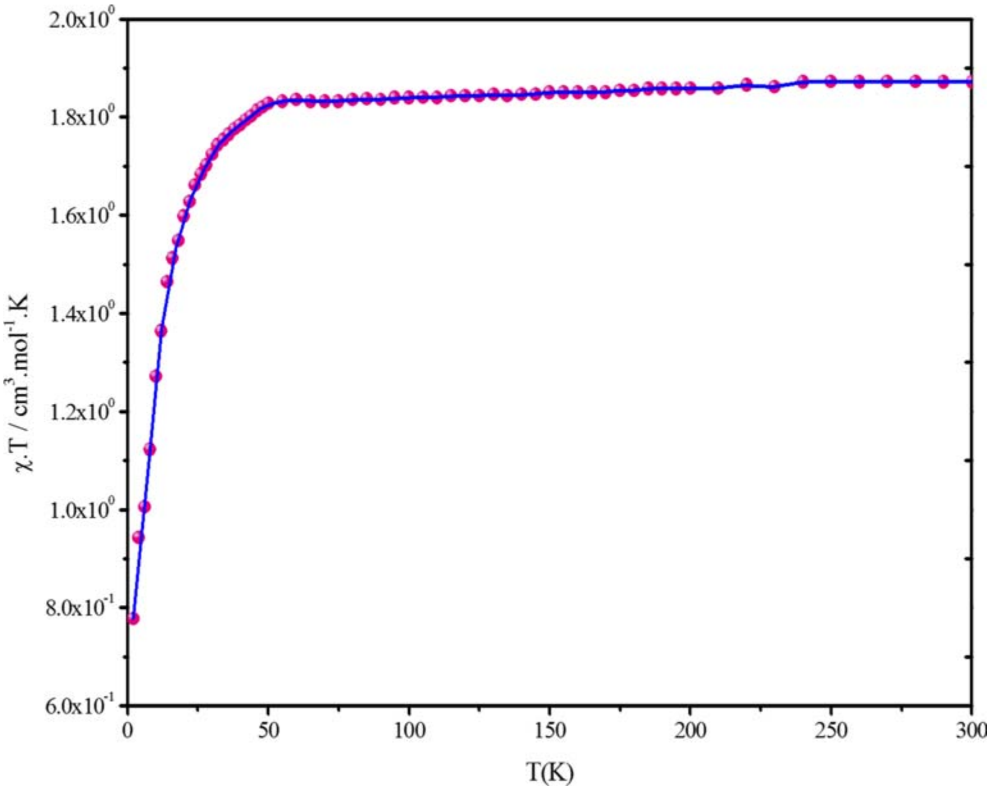

Figure 7. Thermal dependence of χ_MT.

can be understood by an inspection of their networks. One can see that for compound $PPh_4[Cr(bpym)(ox)_2].H_2O$, the uncoordinated water molecule is hydrogen-bonded to two peripheral oxalate-oxygens from two $[Cr(bpym)(ox)_2]$- units (the chromium-chromium separation being 7.242(2) A°).[37] Whereas, in the case of $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$, the coordinated water--molecules of a $[Cr(ox)_2(H_2O)_2]$- unit are hydrogen-bonded to the peripheral oxalate-oxygens from adjacent chromium units (the chromium-chromium distance being 6.601(1) A°). The hydrogen-bonding pattern in 1 is therefore more efficient than that of $PPh_4[Cr(bpym)(ox)_2].H_2O$ (Figure 8).

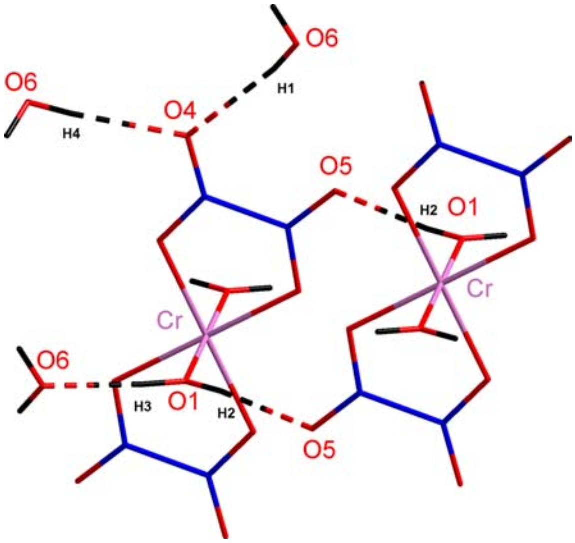

Figure 8. A part of the structure showing the hydrogen bonds between the oxalate oxygen and the water molecules.

4. CONCLUSION

The new salt $(C_3H_5N_2)[Cr(C_2O_4)_2(H_2O)_2].2H_2O$ has been synthesized via slow solvent evaporation technique at room temperature. It has been fully characterized by single crystal X-ray diffraction, UV-Vis spectroscopy and thermal analysis. Magnetic studies show the occurrence of weak antiferromagnetic intermolecular interactions between the local spin.

Supplementary material

Crystallographic data and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 802679. 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; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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