Chromium(III) Complex Obtained from Dipicolinic Acid: Synthesis, Characterization, X-Ray Crystal Structure and Electrochemical Studies

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The synthesis, X-ray crystallography, spectroscopic (IR, UV-vis), and electrochemical properties of the title compound, $[H_3O][Cr(dipic)_2]$ $[H_3O^+.Cl^-]$ (1), (H_2dipic = 2,6-pyridinedicarboxylic acid), are reported. This complex crystallizes in the monoclinic space group Cc with a = 14.9006(10) Å, b = 12.2114(8) Å, c = 8.6337(6) Å, α = 90.00°, β = 92.7460(10)°, γ = 90.00°, and V = 1569.16(18) Å^3 with Z = 4. The hydrogen bonding and noncovalent interactions play roles in the stabilization of the structure. In order to gain a better understanding of the most important geometrical parameters in the structure of the complex, atoms in molecules (AIM) method at B3LYP/6-31G level of theory has been employed.

Introduction

Among the dicarboxylic acids, dipicolinic acid (H_2dipic, 2,6-pyridinedicarboxylic acid) is a relevant N–O chelating agent, present in many natural compounds that shows various biological functions and potential pharmacological activities. It can coordinate the metal center through dianionic ($dipic^{2-}$),[1-3] monoanionic ($Hdipic^-$)[4,5] or neutral (H_2dipic) forms, acting as a tridentate ligand and the carboxylate groups sometimes can bridge two metal atoms.[6]

Chromium is known to activate enzymes, maintain protein stability and enhance carbohydrate metabolism. Organic chromium(III) sources have been shown to enhance the availability of chromium.[7] Accordingly, a number of Cr(dipic) complexes have been prepared during the recent decades. Complex anion $[Cr(dipic)_2]^-$ is rather frequent in the literature and the corresponding cations can be either organic, inorganic or complex.[8-14] The first $[Cr(dipic)_2]^-$ complex containing inorganic cationic counter ion, has been $NH_4[Cr(dipic)_2]$.[15] Preparations with potassium[16] and sodium[17] cations subsequently followed. The first crystal structure containing $[Cr(dipic)_2]^-$ has been $Rb[Cr(dipic)_2]$.[18] According to the Cambridge Structural Database, organic ligands found as cations in complexes with $[Cr(dipic)_2]^-$ are 2,6-diaminopyridinium,[8] creatinium,[9] 4-(4-pyridyl) pyridinium,[10] [(2-pyridyl)(1-hydro-2-pyridinium) amine][19] and 2,9-dimethyl-1,10-phenanthroline.[20]

In this work, we report the synthesis and crystal structure of a complex anion $[Cr(dipic)_2]^-$ containing the hydroxonium chloride and hydroxonium as cation namely $[H_3O][Cr(dipic)_2]$ $[H_3O^+.Cl^-]$.

Experimental

Metformin (Met) was purchased from TSA, International (Indian company), 2,6-pyridinedicarboxylic acid (H_2dipic) and $CrCl_3\cdot6H_2O$ were obtained from Merk. Elemental analyses were performed by using a Leco, CHNS-932 elemental analyzer. Fourier transform infrared spectra were recorded on a FT-IR JASCO 680-PLUS spectrometer in the region of 4000-400 cm^{-1} using KBr pellets. Cyclic voltammograms were recorded with a SAMA Research Analyzer M-500. Three electrodes were utilized in this system, a glassy carbon (GC) disk working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode. Cyclic voltammetry measurements of a DMF solution of the complex were performed at 25 ºC with a 0.1 M solution of tetrabutyl-ammonium hexafluorophosphate (TBAH) as a supporting electrolyte. Electronic spectra were obtained using a UV-JASCO-570 spectrometer. Quantum mechanical calculation has been performed by Gaussian98 program and using the AIM2000 program packages. The structure was optimized at B3LYP/6-31G level of theory by Gaussian98 package program.[21]

Synthesis of Complex $[H_3O][Cr(dipic)_2]$ $[H_3O^+.Cl^-]$ (1). Dipicolinic acid (H_2dipic, 0.167 g, 1.0 mmol) and NaOH (0.080 g, 2.0.mmol) were dissolved in the mixture of ethanol/water (20 mL) and dropwise added, under continuous stirring, to an aqueous solution (5 mL) of $CrCl_3\cdot6H_2O$ (0.988 g, 0.50 mmol). Then metformin hydrochloride (0.057 g, 0.50 mmol) was added to the resulting mixture and was refluxed for 12 h, filtered off and then left to evaporate in a beaker in air at the ambient temperature. In an attempt to prepare the

complex [MetH][Cr(dipic)$_2$], after 5 day, dark purple crystals suitable for X-ray structural analysis from the title complex, (1), were obtained. The yield was 65%. Anal. Calc. for C$_{14}$H$_{12}$ClCrN$_2$O$_{10}$: C, 36.90; H, 2.65; N, 6.15. Found: C, 36.7; H, 2.80; N, 5.9%. IR (KBr) (ν, cm^{-1}): 3599 (w), 3558 (m), 3474 (m), 3423 (m), 3078 (m), 3049 (m), 2923 (w), 1673 (s), 1598 (w), 1479 (w), 1428 (m), 1332 (s), 1261 (w), 1169 (s), 1090 (s), 1036 (w), 1010 (w), 920 (s), 854 (w), 779(s), 750(s), 682 (s), 593 (w), 541 (w), 452 (s). UV–vis (aqueous solution) (ν, nm): 260, 267, 301, 352, 551.

Crystal Structure Determination. The crystal structure of [H$_3$O][Cr(dipic)$_2$] [H$_3$O$^+$.Cl$^-$] was obtained by the single-crystal X-ray diffraction technique. Data for the complex were collected on a Bruker APEX II area-detector diffracto-meter using graphite monochromated Mo Kα radiation, λ = 0.71073 Å at 100(2) K. Data was analyzed with APEX2 software, reduced using SAINT program and the empirical absorption corrections were applied using the SADABS program.[22] The structure was solved by direct methods and refined with the full-matrix least-squares technique on F^2 using SHELXTL program packages.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the oxygen atoms were located from a difference Fourier map and the remaining H atoms were placed in calculated position (C–H = 0.95 Å). All the hydrogen atoms were refined using a riding model with U$_{iso}$(H) = 1.2U$_{eq}$(C) and 1.5$_{eq}$(O).

Full crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 935120. These data can be obtained free of charge *via www.ccdc.cam.ac.uk* or from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2, 1EZ, UK; fax +44 (0)1223-336-033 or email: *deposit @ccdc.cam.ac.uk*.

Results and Discussion

Vibrational Spectra. The patterns of IR spectrum show two sets of vibrations due to the aqua and dipicolinate ligands. The ν(O–H) vibrations belonging to the (H$_3$O)$^+$ fragments are observed as four bands in the 3599, 3558, 3474 and 3423 cm^{-1} and the stretching frequencies due to the aromatic rings at 2923, 3049 and 3078 cm^{-1}. In the IR spectrum of complex, all the bands involving O–H vibrations of the carboxylate group are absent, namely the O–H stretch-ing of the COOH groups, the C–OH in-plane bending and out-of-plane O–H deformation modes, hence showing de-protonation of the –COOH group and coordination to the metal,[24] as disclosed by the X-ray structure. The ν_{asym} (COO$^-$) and ν_{sym} (COO$^-$) of the carboxylato group in the complex show the separation value ($\Delta\nu$) greater than 200 cm^{-1}. This indicates monodentate binding of the carboxylato group to the metal ion.[25] The absorption bands at 541 and 452 cm^{-1} correspond to Cr–O and Cr–N vibrations of the complex.

The Electronic Spectra. The electronic spectra of complex **1** (Figure 1) is in agreement with the spectrum of complex reported Na[Cr(dipic)$_2$]·2H$_2$O.[26] For the hexa-coordinated Cr(III) complex, there are three spin allowed transitions, *i.e.*,
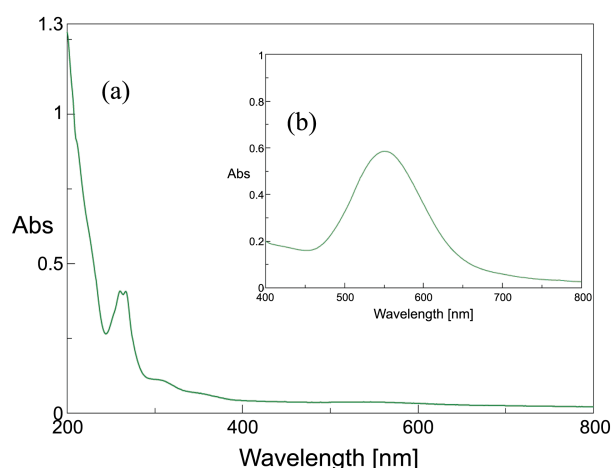

Figure 1. Electronic spectra of complex in aqueous solution. (a) 3.3×10^{-5} M; (b) 1.6×10^{-3} M, in a restricted wavelength range.

ν_1: ^{4}A$_{2g} \rightarrow$ ^{4}T$_{2g}$(F), ν_2: ^{4}A$_{2g} \rightarrow$ ^{4}T$_{1g}$(F), and ν_3: ^{4}A$_{2g} \rightarrow$ ^{4}T$_{1g}$(P).[27] These transitions are not seen in the experimental spectrum. It can be assumed to be hidden by the more intense charge-transfer bands. The broad band with a maximum at 551 nm for complex (**1**) can be assigned to Cr $\rightarrow$ dipic charge-transfer transitions, mainly involving ligand rings. The strong absorp-tion at the short wavelength end of the spectrum presents two shoulders, located at 352 nm and 301 nm. The first one can be considered as a combination of intraligand and dipic $\rightarrow$ Cr charge-transfer transitions, involving the oxygen atoms of the ligands. The shoulder at higher energy can be mainly attributed to dipic $\rightarrow$ Cr charge-transfer transitions, from the oxygen atoms.[26] Two strong absorption bands with equal intensity at 267 and 260 nm are assigned to n $\rightarrow$ π^* and $\pi \rightarrow$ π^* transitions of the dipic ligand.

Electrochemistry. The electrochemical behavior of the Cr(III) complex which were carried out at varying scan rates in the range 100-500 mVs^{-1}, revealed two one-electron quasi reversible redox processes due to the chromium metal center.

The cyclic voltammogram of the complex, at a scan rate of 100 mVs^{-1} (Figure 2), shows the Cr$^{III/II}$ reduction at a catho-
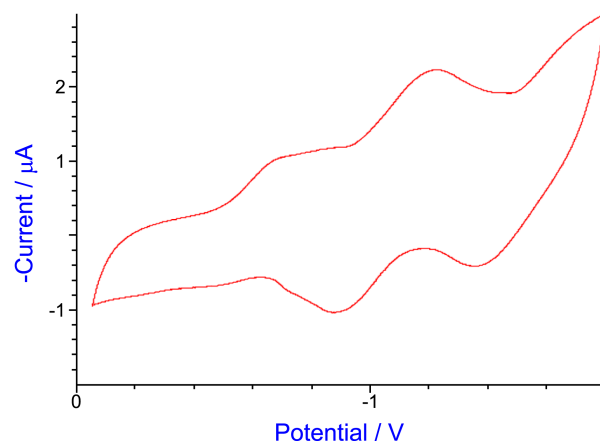

Figure 2. Cyclic voltammogram of complex in DMF. Supporting electrolyte: TBAH; scan rate: 100 mV s^{-1}; reference and working electrodes are Ag/AgCl and GC disk respectively.

Table 1. Crystal data and details of the structure determination for complex **1**

Empirical formula	$C_{14} H_{12} Cl Cr N_2 O_{10}$
Formula weight	455.71
Temperature (K)	100(2)
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	14.9006(10)
b (Å)	12.2114(8)
c (Å)	8.6337(6)
α (°)	90.00
β (°)	92.7460(10)
γ (°)	90.00
Volume (Å^3)	1569.16(18)
Z	4
D_{calc} (Mg/m^3)	1.9290(2)
Crystal size (mm)	0.11 × 0.19 × 0.31
Absorption coefficient (mm^{-1})	0.966
F(000)	924
Theta range for data collection	2.74 to 32.64°
Index range	$-22 \leq h \leq 22$
	$-18 \leq k \leq 18$
	$-12 \leq l \leq 12$
Goodness-of-fit on F^2	1.067
Total data	10930
Unique data	4932
R(int)	0.017
Observed data [I > 2.0 sigma(I)]	4799
R_1	0.0338
wR_2	0.1016

dic peak potential, E_{pc1}, of −0.73 V, and the reoxidation of the Cr^{II} species at −0.87 V. The Cr$^{II/I}$ reduction is seen at E_{pc2} = −1.23 V with the reoxidation occurring at −1.35 V.

The Crystal Structure. Crystal data and refinement results for complex (**1**) are summarized in Table 1. Experimental bond distances and angles around Cr(III) ion are presented in Table 2. The asymmetric unit of (1) is shown in Figure 3. It consists of a complex anion, two hydroxonium cations and a chloride anion.

Table 2. The bond distances (Å) and angles (°) around chromium for complex (**1**)

Cr1–N1	1.9792(16)	Cr1–O1	1.9973(16)
Cr1–N2	1.9826(15)	Cr1–O2	2.0015(14)
Cr1–O3	1.9906(16)	Cr1–O4	2.0023(14)
N1–Cr1–N2	172.36(7)	O3–Cr1–O2	90.32(6)
N1–Cr1–O3	94.24(6)	O1–Cr1–O2	157.13(5)
N2–Cr1–O3	78.88(6)	N1–Cr1–O4	108.19(6)
N1–Cr1–O1	78.67(6)	N2–Cr1–O4	78.67(6)
N2–Cr1–O1	98.40(6)	O3–Cr1–O4	157.55(5)
O3–Cr1–O1	94.51(7)	O1–Cr1–O4	89.18(7)
N1–Cr1–O2	78.69(6)	O2–Cr1–O4	94.83(6)
N2–Cr1–O2	104.46(6)		
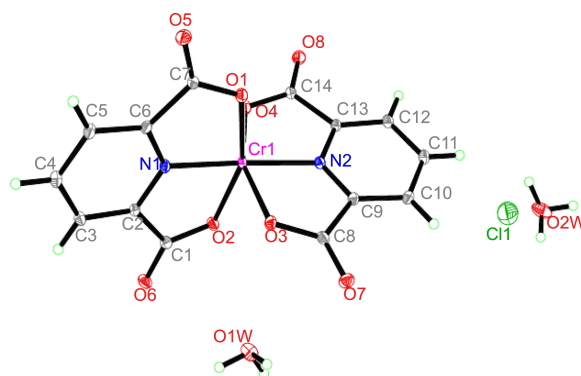
Figure 3. ORTEP view of complex [H$_3$O][Cr(dipic)$_2$] [H$_3$O$^+$.Cl$^-$].

Although we have used metformin as starting material, it has not incorporated in the structure. In the complex anion, the chromium(III) ion is octahedrally coordinated by two perpendicular O, N, O-tridentate dipicolinate ligands (bound *via* pyridine N and two carboxylate O atoms), each forming two five-membered chelate ring [Cr–O distances within the range from 1.9906(16) to 2.0023(14)Å and d(Cr–N1) = 1.9792(16) and d(Cr–N2) = 1.9826(15) Å]. Coordinated pyridine N atoms are situated in trans position [N1–Cr1–N2, 172.36(7)°]. The intermolecular forces in this complex consist of hydrogen bonding as type O–H···O, C–H···O and O–H···Cl and ion pairing. The hydrogen bonding is summarized in Table 3.

Hydrogen bonding is an interesting feature of the structure of Cr(III) complex. The hydrogen bonding O1W–H3W1···Cl1 distance is much less than the value previously reported for such hydrogen bonding.[28] Another noncovalent interactions are C–H···π and C–O···π stacking between the CH groups and C–O groups with the benzene rings of the (dipic)$^{2-}$ fragments due to the short distances of about 3.5 Å (Figure 4).

Theoretical Investigation. AIM method at B3LYP/6-31G level of theory has been employed in order to gain a better understanding of the most geometrical parameters in the structure of complex. The numbers of critical points and

Table 3. Hydrogen bond details, distances (Å) and angles (°) for complex

D–H···A	D–H	H···A	D···A	D–H···A
O1W–H1W1···O8 (*v*)	0.850	2.470	2.983	119.00
O1W–H2W1···O5 (*vi*)	0.850	2.450	2.885	113.00
O1W–H3W1···Cl1 (*i*)	0.960	1.640	2.3252	124.00
O1W–H3W1···O (*vii*)	0.960	2.600	3.294)	130.00
O2W–H1W2···O6 (*i*)	0.850	2.390	2.794	110.00
O2W–H2W2···O (*iv*)	0.850	2.320	3.144	161.00
C3–H3A···O3 (*ii*)	0.950	2.550	3.427	153.00
C5–H5A···O7 (*iii*)	0.950	2.240	3.069	145.00
C10–H10A···O5 (*iv*)	0.950	2.340	3.260	164.00

Symmetry Codes: (i) x, 1−y, −1/2+z (ii) x, 2−y, 1/2+z (iii) −1/2+x, 1/2+y, z (iv) 1/2+x, −1/2+y, z (v) 1/2+x, 1/2+y, z (vi) 1/2+x, 3/2−y, 1/2+z (vii) 1/2+x, 3/2−y, −1/2+z.
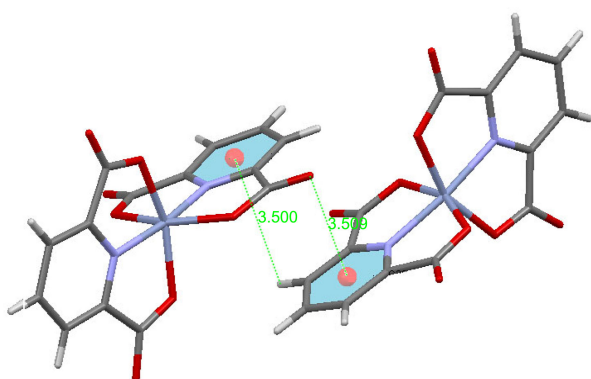
Figure 4. The C-H⋯π and C-O⋯π stacking representation in complex.

intramolecular interactions have been recognized. Further investigation was undertaken in order to determine intramolecular interactions of the complex, on the basis of AIM calculations[29] at B3LYP/6-31G level of theory by the AIM2000 program package.[30] In recent years, AIM theory has often applied in the analysis of H-bonds and intramolecular interactions. In this theory, the topological properties of the electron density distribution are derived from the gradient vector field of the electron density $\rho(r)$ and on the Laplacian of the electron density $\nabla^2\rho(r)$. The Laplacian of the electron density, $\nabla^2\rho(r)$, identifies regions of space wherein the electronic charge is locally depleted [$\nabla^2\rho(r) > 0$] or built up [$\nabla^2\rho(r) < 0$].[29] Two interacting atoms in a molecule (AIM) form a critical point in the electron density, where $\nabla\rho(r) = 0$, called the bond critical point (BCP). The values of the charge density and its Laplacian at these critical points give useful information regarding the strength of the H-bonds.[27] The ranges of $\rho(r)$ and Laplacian of electron density [$-1/4\nabla^2\rho(r)$] is (0.002-0.035 e/a_0^3) and (0.024-0.139 e/a_0^5), respectively, if H-bonds exist.[31] The AIM calculation indicates intramolecular interactions and critical points (H-BCP) for the complex. Intramolecular H-BCPs with a part of molecular graphs for the structure is shown in Figure 5.

Most important structural parameters involving some H-bonds and intramolecular interactions (bond lengths and their relevant bond angles) are reported in Table 4. The electron density $\rho(r)$ and Laplacian of electron density [$-1/4\nabla^2\rho(r)$] are also reported in Table 5.
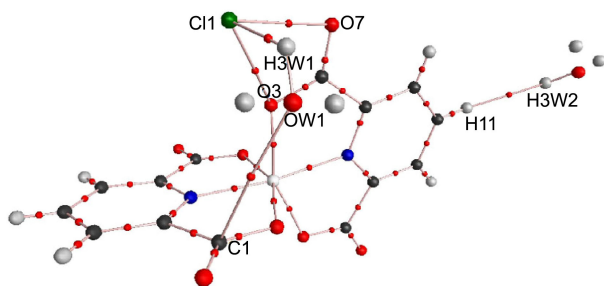

Figure 5. A part of molecular graphs, including intermolecular hydrogen bond at critical points (BCPs) for the complex [H₃O]-[Cr(dipic)₂] [H₃O⁺.Cl⁻].

Table 4. Most important geometrical parameters corresponding to H-bonds and intramolecular interactions for complex

	Bond lengths (Å)	bond angles (°)
C1⋯OW1	3.42	124.53
H11⋯H3W2	2.12	157.51
H3W1⋯Cl1	1.6406	124.50
O7⋯Cl1	2.47	
O3⋯Cl1	2.62	

Table 5. The values of $\rho \times 10^3$ and Laplacian of electron density [$-1/4\nabla^2\rho(r)$] for complex calculated at the critical points. All quantities are in atomic units

	$\rho \times 10^3$	Laplacian of electron density [$-1/4\nabla^2\rho(r)$] $\times 10^3$
C1⋯OW1	1.25	11.04
H11⋯H3W2	5.77	28.52
H3W1⋯Cl1	101.12	141.42
O7⋯Cl1	32.21	222.04
O3⋯Cl1	21.95	148.92

The value of $\rho(r)$ and Laplacian of electron density [$-1/4\nabla^2\rho(r)$] for the H⋯Cl is 0.101 e/a_0^3 and 0.141 e/a_0^5 respectively (See Table 5). These HBs show Laplacian of electron density > 0 for the H⋯Cl interaction, which according to classification of Rozas *et al.*[32] are not a medium or strength hydrogen bond. This interaction may be stronger than hydrogen bond.

Conclusion

In an attempt to prepare the complex [MetH][Cr(dipic)₂], the title complex [H₃O][Cr(dipic)₂] [H₃O⁺.Cl⁻] was obtained and structurally characterized by some spectroscopic methods. In this product, H₃O⁺, acts as a cation to stabilize the [Cr(dipic)₂]⁻ anion, forming a salt. Based upon the X-ray crystallography results, we can conclude that C–H⋯π and C–O⋯π stacking, ion pairing, and hydrogen bond interactions in the crystal structure play an important role in the stabilization of the title crystalline compound.

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